Supporting Information

For

Hydrogen Atom Abstraction from Hydrocarbons by a Copper(III)-Hydroxide Complex

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Figure S1. Representative experimental and simulated UV-vis spectra depicting deconvolution (program Fityk 0.9.8) into mixtures of 4 and 2 at different titration points in the titration of 4 with H₂O. The black dashed trace represents the observed experimental spectrum, the green trace represents the simulated spectrum for 4, the red trace represents the simulated spectrum for 2, and the blue trace represents the overall simulated spectrum.

Figure S2. Linearized titration plot for conversion of 4 to 2 (monitored by UV-vis using simulations to determine concentrations of 4 and 2), where the slope of the line \(R^2 = 0.9682\) represents the value of \(K_2\) \((440 \pm 20)\).
**Figure S3.** Experimental (black) and simulated (red) EPR spectra of (left) 4 in pure THF (right) 4 in H$_2$O-saturated THF. Conditions: 9.3863 GHz, 125 K. Parameters derived from simulations:

| sample | g(x) | g(y) | g(z) | A(Cu) (x 10$^{-4}$ cm$^{-1}$) | A(N$_{Pyridine}$) (x 10$^{-4}$ cm$^{-1}$) | A(N$_{Amide}$) (x 10$^{-4}$ cm$^{-1}$) |
|--------|------|------|------|-----------------|------------------|------------------|
| 4 pure THF | 2.048 | 2.052 | 2.190 | 197 | 15 | 17 |
| 4 in H$_2$O-saturated THF | 2.020 | 2.056 | 2.215 | 195 | 13 | 17 |

**Simulation of Cyclic Voltammograms to obtain equilibrium constant between 4 and 2:** The experimental voltammograms were simulated using DigiSim 3.03b with the overall chemical model depicted below.

\[
\begin{align*}
[\text{LCu(THF)}]^+ & \rightleftharpoons \text{LCu(THF)} + \text{e}^- \\
[\text{LCu(OH}_2)]^+ & \rightleftharpoons \text{LCu(OH}_2) + \text{e}^- \\
[\text{LCu(THF)}] + \text{H}_2\text{O} & \rightleftharpoons K \rightarrow \text{LCu(OH}_2) + \text{THF}
\end{align*}
\]

In order to initially obtain reasonably optimized chemical parameters for the chemical reaction involving equilibrium between 4 and 2, the transfer coefficient (\(\alpha\)) and heterogeneous electron transfer rate constant (\(k_s\)) for all electrochemical reactions were fixed at 0.5 and 0.02 cm/s, while the diffusion coefficient of all involved species were taken to be 10$^{-5}$ cm$^2$/s. Following this, all parameters were allowed to refine freely, except for \(\alpha\) (restrained between 0.3 and 0.7) until the fitting converged. Finally, the capacitance and resistance were manually varied until a

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(1) (a) Wiedner, E. S.; Roberts, J. A.; Dougherty, W. G.; Kassel, W. S.; Dubois, D. L.; Bullock, R. M. *Inorg. Chem.* 2013, 52, 9975-9988. (b) Baron, R.; Kershaw, N. M.; Donohue, T. J.; Compton, R. G. *J. Phys. Org. Chem.* 2009, 22, 247-253. (c) Baron, R.; Kershaw, N. M.; Donohue, T. J.; Compton, R. G. *J. Phys. Org. Chem.* 2009, 22, 1136-1141.
satisfactory visual fit was obtained between the simulated and the experimental voltammograms. In particular, the value of the resistance was found to be 50 Ω while that for the capacitance was found to be $3 \times 10^{-6}$ F, which is in close agreement with previously reported values. In general, a semi-infinite diffusion model at a planar electrode geometry having a surface area of 0.07 cm$^2$ (for glassy-carbon electrode) was employed for the simulations.

| Eq. of water added | $K$ |
|--------------------|-----|
| 90                 | 384 |
| 150                | 405 |
| 210                | 412 |
| 300                | 428 |
| 360                | 397 |
| 450                | 405 |
| 540                | 422 |
| **Avg.**           | **408 ± 15** |

**Figure S4.** Experimental (black) and simulated (red) cyclic voltammograms of 4 in THF with increasing equivalents of water.
**Figure S5.** The observed progressive changes in the UV-vis spectrum of a solution of $1^-$ in THF (1 mM) upon the addition of [Et$_3$NH]OTf in 0.125 equivalent increments. The absorption maxima shifts from 597 nm to 577 nm consistent with the formation of $4$. There are only dilution effects and no shifts beyond the addition of 1.25 equivalents of acid (data not shown).

**Figure S6.** The experimental and simulated (Fityk 0.9.8) UV-vis spectra for $1^-$ (left) and $4$ (right) in THF. The black dashed trace represents the observed experimental spectrum and the red trace represents the simulation. These simulated spectra were used to fit the titration spectra in Figure S7.
Figure S7. Representative experimental and simulated UV-vis spectra depicting deconvolution (program Fityk 0.9.8) into mixtures of 4 and 1 at different titration points in the titration of 1 with [Et₃NH]OTf. The black dashed trace represents the observed experimental spectrum, the blue trace represents the simulated spectrum for 1, the green trace represents the simulated spectrum for 4, and the red trace represents the overall simulated spectrum.

Figure S8. Linearized titration plot for conversion of 1 to 4 (monitored by UV-vis using simulations to determine concentrations of 1 and 4; all data from multiple titrations shown), where the slope of the line ($R^2 = 0.8975$) represents the value of $K_3 = 17 \pm 1$.

Figure S9. Scan rate normalized cyclic voltammograms of 1 in THF at different scan rates depicting only the 1/1 couple. Conditions: 1 mM analyte, 0.2 M TBAPF₆, 20 °C. Parameters estimated from the data are listed as follows:
Simulation of Cyclic Voltammograms of $1^-$ in THF and THF-$d_8$. The experimental voltammograms of $1^-$ in both solvents (across scan rates ranging from 50 to 1000 mV/s) were simulated using DigiSim 3.03b with an ECE mechanism as shown below.

\[
\begin{align*}
[\text{LCuOH}]^- - e & \rightleftharpoons \text{LCuOH} \\
\text{LCuOH} + \text{THF}/\text{THF-}d_8 & \rightleftharpoons \text{LCu(OH}_2) \\
\text{LCu(OH}_2) - e & \rightleftharpoons [\text{LCu(OH}_2])^+ 
\end{align*}
\]

In order to initially obtain reasonably optimized chemical parameters for the chemical reaction involving $1$ and the solvent, the transfer coefficient ($\alpha$) and heterogeneous electron transfer rate constant ($k_s$) for all electrochemical reactions were fixed at 0.5 and 0.02 cm/s, while the diffusion coefficient of all involved species were taken to be $10^{-5}$ cm$^2$/s. In addition, recognizing that the chemical reaction is essentially irreversible, the equilibrium constant for the same was fixed to be $10^5$. Following this, all parameters were allowed to refine freely, except for $\alpha$ (restrained between 0.3 and 0.7) until the fitting converged. Finally, the capacitance and resistance were manually varied until a satisfactory visual fit was obtained between the simulated and the experimental voltammograms. In particular, the value of the resistance was found to be 50 $\Omega$ while that for the capacitance was found to be $3 \times 10^{-6}$ F, which is in close agreement with previously reported values. In general, a semi-infinite diffusion model at a planar electrode geometry having a surface area of 0.02 cm$^2$ (for platinum electrode) was employed for the simulations.
Figure S10. Representative experimental (black) and simulated (red) cyclic voltammograms of 1− in THF (top) at two different scan rates of 100 mV/s (left) and 500 mV/s (right), and in THF-d₈ (bottom) at two different scan rates of 100 mV/s (left) and 300 mV/s (right). Conditions: 1 mM analyte, 0.2 M TBAPF₆, 20 °C. The simulated rate constants according to an ECE mechanism are as follows:

| Scan Rate (mV/s) | $k_H$ (M⁻¹ s⁻¹) | $k_D$ (M⁻¹ s⁻¹) |
|-----------------|-----------------|-----------------|
| 50              | 0.11229         | 0.01195         |
| 100             | 0.11330         | 0.01191         |
| 200             | 0.11195         | 0.01185         |
| 300             | 0.11084         | 0.01248         |
| 500             | 0.10963         | 0.01249         |
| 700             | 0.11903         | 0.01185         |
| 1000            | 0.11951         | 0.01154         |
| **avg**         | **0.114 ± 0.004** | **0.0112 ± 0.0003** |
Figure S11. Scan rate normalized cyclic voltammograms of 1 in 1,2-difluorobenzene (DFB) at different scan rates. Conditions: 1 mM analyte, 0.1 M TBAPF$_6$, 20 °C). Parameters estimated from the data are as follows:

| Scan rate (mV/s) | $E_{pa}$ (V vs Fc/Fc) | $E_{pc}$ (V vs Fc/Fc) | $E_{1/2}$ (V vs Fc/Fc) | $\Delta E$ (mV) | $i_{pc}/i_{pa}$ |
|------------------|-----------------------|------------------------|------------------------|-----------------|-----------------|
| 10               | -0.054                | -0.125                 | -0.090                 | 71              | 0.54            |
| 20               | -0.045                | -0.134                 | -0.090                 | 89              | 0.65            |
| 50               | -0.027                | -0.121                 | -0.074                 | 94              | 0.70            |
| 100              | -0.009                | -0.129                 | -0.070                 | 120             | 0.80            |
| 200              | -0.001                | -0.157                 | -0.079                 | 156             | 0.91            |
| 300              | 0.006                 | -0.162                 | -0.078                 | 168             | 0.99            |
| 500              | 0.026                 | -0.179                 | -0.077                 | 205             | 0.99            |
Figure S12. Plots of $k_{\text{obs}}$ vs [substrate] for the reactions of 1 with the substrates in DFB at -25 °C. The second order rate constants $k_2$ were determined from the slopes of the indicated linear fits ($R^2 = 0.9016$, 0.9821, 0.9625, 0.9602, 0.9773, and 0.9871, respectively). The second order rate constants and BDE values used to construct Figure 7 are as follows:

| Substrate      | $k$ (M$^{-1}$ s$^{-1}$) at -25 °C | BDE (kcal mol$^{-1}$) |
|----------------|----------------------------------|-----------------------|
| DHA            | 0.50$^a$                         | 76.3$^b$              |
| Cyclohexene    | 0.157                            | 81                    |
| Fluorene       | 0.634                            | 82                    |
| Diphenylmethane| 0.0400                           | 84.5                  |
| Toluene        | 0.0042                           | 88.5                  |
| THF            | 0.00625                          | 92.1                  |
| Cyclohexane    | 2.64 x 10$^{-5}$                 | 99.8                  |

$^a$This rate constant is slightly different from the previously reported value of 150 M$^{-1}$ s$^{-1}$ (Tehranchi, J.; Donoghue, P. J.; Cramer, C. J.; Tolman, W. B. Eur. J. Inorg. Chem. 2013, 2013, 4077-4084). We note that in this study we used Fc[BAr$_F^4$] (for better solubility) as the oxidant, whereas FePF$_6$ was used in the previous work. $^b$The reported BDE values of DHA range from 76-83 kcal/mol depending on the method used. For consistency, the recommended BDE value in the following source is used: Handbook of Bond Dissociation Energies in Organic compounds; Luo, Y., Ed.; CRC Press: New York, USA, 2002, pp. 11-93.

| THF conc (M) | Rate of reaction (M/s) | Error bar (M/s) |
|--------------|------------------------|-----------------|
| 0.0123       | 4.42E-08               | 1.17E-09        |
| 0.221        | 2.67E-07               | 6.68E-09        |
| 0.616        | 4.01E-07               | 9.62E-09        |
| 1.23         | 6.46E-07               | 1.69E-08        |
| 3.08         | 1.23E-06               | 2.13E-08        |
| 6.16         | 1.85E-06               | 2.68E-08        |
| 9.25         | 2.30E-06               | 7.30E-08        |

Figure S13. Table of rate constants and error bars for the reaction of 1 with THF in DFB.
Figure S14. Plots of $\log k$ vs. redox potential (left) or $pK_a$ (right) of substrates, illustrating much poorer linear correlations than that shown for $\log k$ vs. BDE in Figure 7.

Figure S15. Representative time courses for the reactions of the indicated substrates with 1 in DFB at -25 °C. Note that pseudo-first order rate constants were not derived from fits to these data, and instead were determined from initial rate measurements as described in the text.