High-valent Cu^{II}Cu^{III} Species in Action: Demonstration of Aliphatic C–H Bond Activation at Room Temperature

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1-General

All starting materials were commercially available and used as purchased, unless stated otherwise. Solvents were purified by standard methods before use. Electrospray mass spectra were recorded on an ESI Ion Trap mass spectrometer (BRUKER Daltonics Esquire 3000 plus). The oxidized sample were analysed by GC-MS (Agilent 7890B/5977A GC/MSD). The mass spectrometer was operated in the Electron Impact (EI) mode with electron energy of 70 eV coupled to a gas phase chromatograph using the software Agilent MassHunter. A Bruker AVANCE III 500 MHz spectrometer was used for collection of ¹H NMR. Room temperature electrochemical studies of the copper complex were performed in a glovebox (Jacomex) ($O_2 < 1$ ppm, $H_2O < 1$ ppm) with a home-designed 3-electrodes cell (WE: glassy carbon (GC) or boron doped diamond (BDD), RE: Pt wire in a Fc^{+}/Fc solution or a Ag wire in a 0.01 M AgNO₃ solution, CE: Pt or graphite rod). Similar voltammetric behaviors were obtained with BDD and GC working electrodes as shown for example in Fig. 3 and S9. BDD electodes were used for better analysis of the electrocatalytic reaction (lower capacitive current than with GC). Ferrocene was added at the end of the experiments to determine redox potential values. The potential of the cell was controlled by an AUTOLAB PGSTAT 100 (Metrohm) potentiostat monitored by the NOVA software. HPLC-grade acetonitrile was degased under argon and stored in the glovebox. Voltammetric simulation was carried out by using the DigiElch software.¹

2-Synthetic details of $[Cu^{II}_2(L)(\mu-OH)_2](ClO_4)_2 \cdot 6H_2O$

Safety Note. Although no problems were encountered during the preparation of perchlorate salts, suitable care should be taken when handling such potentially hazardous compounds.

15 mg complex **1** $[Cu^{II}_{2}(L)(\mu-OH)_{2}(OTf)](OTf)^{2}$ as crystals were dissolved in a solution of NBu₄ClO₄ in water. The solution was then placed at room temperature for slow evaporation. Blue crystals suitable for XRD analysis were obtained after one week. The crystals (10 mg) were collected from the batch by filtration and washed with THF. Anal. Calcd. For C32H28N6O10Cu2Cl2·5.33H2O: C,40.43; H,4.10; N,8.84. Found C, 40.28, H, 4.12; N, 9.22. ESI-MS (CH₃CN), m/z: z = 1, 753 = (M – ClO₄⁻), z = 2, 327 = (M – 2ClO₄⁻).

¹ www.ElchSoft.com

² Isaac, J. A.; Gennarini, F.; Lopez, I.; Thibon-Pourret, A.; David, R.; Gellon, G.; Gennaro, B.; Philouze, C.; Meyer, F.; Demeshko, S.; Le Mest, Y.; Réglier, M.; Jamet, H.; Le Poul, N.; Belle, C. *Inorg. Chem.* **2016**, *55*, 8263.



Figure S1. Experimental and theoretical isotopic patterns of (A) $[Cu_2(C_{32}H_{28}O_2N_6)(ClO_4)]^+$ ion and (B) $[Cu_2(C_{32}H_{28}O_2N_6)]^{2+}$ in acetonitrile.

3-X-ray structure determination of copper(II) complex [Cu^{II}₂(L)(µ-OH)₂](ClO₄)₂·6H₂O

Measurements were made on a Bruker AXS-Enraf Nonius-Kappa APEX II diffractometer equipped with an Incoatec high brilliance microsource with multilayers mirrors monochromated Mo(K α) radiation (λ = 0.71073Å) and an Oxford cryosystem cryostream cooler.

Crystal data and refinement for $[Cu_2(C_{32}H_{28}O_2N_6)(ClO_4)_2]\cdot 6(H_2O)$, Mw =962.68: crystal dimensions (mm): 0.41 × 0.40 × 0.37, crystal system: monoclinic, space group : *C*2/*c*, unit-cell dimensions and volume: a = 26.151(5) Å, b = 10.682(2) Å, c = 14.443(3) Å, $\alpha = 90^\circ$, $\beta = 107.88(3)^\circ$, $\gamma = 90^\circ$, $V = 3839.9(15) Å^3$, no. of formula units in the unit cell *Z* = 4, calculated density $\rho_{calcd} = 1.665$ g cm⁻³, linear absorption coefficient μ : 1.328 mm⁻¹, temperature of measurement: *T* = 200 K, $2\theta_{max} = 55^\circ$. The complex possesses a two-fold axis going through C4 and C5 atoms and only half of the molecule unit is crystallographically defined. No. of measured and independent reflections: 15115 and 4370, no. of reflections with *F*>2 σ , 3885, no. of parameters and restraints: 327 and 298, Rint = 0.0241, R1 = 0.0252, wR2 = 0.0647, residual electron density: 0.431, Goodness of fit *S* = 1.074. Final refinement is based on

w =
$$1/[\sigma^2(F_o^2) + (0.0253p)^2 + 6.5625p]$$
 where $p = (F_o^2 + 2F_c^2)/3$.

Data were collected using phi and omega scans. Data reduction, cell determination and refinement were performed using EvalCCD.³ Data were corrected for absorption using SADABS-2004/1 (Bruker, 2004). The structure was solved using SHELXS⁴ and refined using SHELXL³, run under Olex2i. C, N, O, Cl and Cu atoms were refined anisotropically by the full matrix least-squares method. H atoms were set geometrically and constrained to their bearing atoms. The CIF file with data for $[Cu_2(C_{32}H_{28}O_2N_6)(ClO_4)_2]\cdot 6(H_2O)$, has been deposited at the Cambridge Crystallographic Data Centre, CCDC1449816. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK. Fax (+44) 1223-336-033

³ Duisenberg, A. J. M.; Kroon-Batenburg , L. M. J.; Schreurs, A. M. M. J. Appl. Cryst, **2003**, 36, 220.

⁴ Sheldrick, G. M. Acta Cryst., **2008**, A64, 112.

Table	S1 :	Comparison	of	selected	bond	distances	[Å]	and	angles	[°]	for
[Cu ₂ (C ₃₂	2H28O2N	₆)(ClO ₄) ₂]·6H ₂ O	(2 ·6H ₂	O) and [C	u₂(L)(µ-Oŀ	H) ₂ (OTf)](OTf)·1.8C⊦	l₃CN (1 ·	1.8CH₃CN)	with	two
indeper	ndent m	olecules (1A an	nd 1B r	espectively) inside th	ne asymmetri	ic unit (Referer	nce ii).		

Г

Selected bond distances [Å]						
1A	1B	[Cu ₂ (C ₃₂ H ₂₈ O ₂ N ₆)(ClO ₄) ₂]·6(H ₂ O)				
<i>Cu1ACu2A</i> = 2.7511(12)	Cu1BCu2B = 2.7514(12)	Cu1Cu1' = 2.7934(8)				
<i>Cu1A-O1A = 1.936(3)</i>	<i>Cu1B-O1B = 1.940(3)</i>	Cu1-O1 = 1.9609(13)				
Cu1A-O2A = 1.925(3)	<i>Cu1B-O2B</i> = 1.930(3)	Cu1-O1' = 1.9520(12)				
Cu1A-N1A = 2.276(3)	Cu1B-N1B = 2.284(3)	Cu1-N1 = 2.2883(15)				
Cu1A-N3A = 1.989(3)	Cu1B-N3B = 1.987(3)	Cu1-N3 = 1.9840(16)				
Cu1A-N4A = 1.987(3)	Cu1B-N4B = 2.002(3)	Cu1-N4 = 1.9959(16)				
Cu2A-O1A = 1.942(3)	<i>Cu2B-O1B</i> = 1.948(3)	Cu1'-O1 = 1.9609(13)				
Cu2A-O2A = 1.946(3)	Cu2B-O2B = 1.938(3)	Cu1'-O1' = 1.9520(12)				
<i>Cu2A-O3A</i> = 2.615	<i>Cu2B-O3B</i> = 2.615	-				
Cu2A-N2A = 2.352(3)	Cu2B-N2B = 2.337(3)	Cu1'-N1' = 2.2883(15)				
Cu2A-N5A = 1.995(3)	Cu2B-N5B = 1.982(3)	Cu1'-N4' = 1.9959(16)				
Cu2A-N6A = 1.978(3)	Cu2B-N6B = 2.003(3)	Cu1'-N3' = 1.9840(16)				
Selected angles [°]						
<i>Cu1A-O1A-Cu2A = 90.38(12)</i>	<i>Cu1B-O1B-Cu2B</i> = 90.11(12)	Cu1-O1-Cu1' = 91.10(5)				
<i>Cu1A-O2A-Cu2A = 90.58(12)</i>	<i>Cu1B-O2B-Cu2B</i> = 90.67(12)	Cu1-O1'-Cu1' = 91.10(5)				
<i>O2A-Cu1A-O1A = 82.11(12)</i>	O2B-Cu1B-O1B = 82.83(12)	01-Cu1-O1' = 80.05(6)				
<i>O1A-Cu2A-O2A = 82.41 (12)</i>	O1B-Cu2B-O2B = 82.41 (12)	01-Cu1'-O1' = 80.05(6)				
<i>O1A-Cu1A-N3A = 93.45(13)</i>	O1B-Cu1B-N1B= 104.11(12)	01-Cu1-N3 = 94.48(6)				
<i>O1A-Cu1A-N4A = 169.75(13)</i>	O1B-Cu1B-N3B = 167.66(13)	01-Cu1-N4 = 171.69(6)				
N1A-Cu1A-N4A = 88.14(13)	N1B-Cu1B-N4B = 83.76(12)	N1-Cu1-N4 = 85.88(6)				
N1A-Cu1A-N3A = 88.21(14)	N1B-Cu1B-N3B = 88.19(13)	N1-Cu1-N3 = 86.15(6)				
N1A-Cu1A-O1A = 103.08(12)	N1B-Cu1B-O1B = 104.11(12)	N1-Cu1-O1 = 101.66(5)				
N1A-Cu1A-O2A = 100.72(12)	N1B-Cu1B-O2B = 98.60(12)	N1-Cu1-O1' = 102.12(5)				
N5A-Cu2A-N6A = 88.77(14)	N5B-Cu2B-N6B = 88.51(14)	N3'-Cu1'-N4' = 89.45(6)				
N2A-Cu2A-O2A = 98.31(12)	N2B-Cu2B-O2B = 97.93(12)	N1'-Cu1'-O1' = 101.66(5)				
N2A-Cu2A-O1A = 98.97(11)	N2B-Cu2B-O1B = 100.94(12)	N1'-Cu1'-O1' = 102.12(5)				
N2A-Cu2A-N5A = 84.40(13)	N2B-Cu2B-N5B = 85.85(13)	N1'-Cu1'-N4' = 85.88(6)				
N2A-Cu2A-N6A = 85.69(13).	N2B-Cu2B-N6B = 83.80(13).	N1'-Cu1'-N3' = 86.15(6)				

4- Experiments in presence of toluene and absence of base

4.1: Simulations of CVs in presence of toluene and absence of base

Voltammetric simulation was carried out to quantify the effect of toluene-H8 or toluene-D8 on the voltammetric signature of the $1\rightarrow 1^+$ process. The mechanism is described in Scheme 1: it includes three different steps E, C₁ and C₂, where E depicts the electrochemical reaction, C₁ is the reaction between the oxidized complex 1^+ and the solvent (CH₃CN), and C₂ is the reaction of 1^+ with toluene. X and Y are undefined species.

Scheme S1. Proposed mechanism modelling the CV in oxidation displayed by **1** in the presence of toluene.

Parameters used:

- The diffusion coefficient (D) of **1** was determined by DOSY experiments to be 0.9×10^{-5} cm²·s^{-1.1}
- k⁰ (heterogeneous standard rate constant for electron transfer was defined as 1 cm.s⁻¹ to fit the experimental peak to peak separation.
- $E^0 = 1.12$ V (oxidation potential extracted from the experimental CV).
- α = 0.5 (denotes the transfer coefficient, symmetry of the oxidation and reduction waves)
- Concentrations: [1] = 1.2 mM; $[CH_3CN] = 19 \text{ M}$; [Toluene]: 0 mM, 135 mM, 270 mM and 540 mM.
- Diffusion coefficients: **1** ($0.9 \times 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$); **1**⁺ ($0.9 \times 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$), toluene ($4.0 \times 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$), species X ($1 \times 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$), Y ($1 \times 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$), CH₃CN ($4.0 \times 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$).

Parameters determined:

For **C**₁: $K_1 = 0.15$ M⁻¹, $k_{f1}=0.02$ M⁻¹·s⁻¹; For **C**₂ with Toluene-H8: $K_2 = 30$ M⁻¹, $k_{f2}= 1.1$ M⁻¹·s⁻¹; For **C**₂ with Toluene-D8: $K_2 = 30$ M⁻¹, $k_{f2}= 0.5$ M⁻¹·s⁻¹ giving a KIE value of $k_{f2H}/k_{f2D} = 2.2$.



Figure S2. Experimental (**A** and **C**) and simulated (**B** and **D**) CVs of **1** at two different scan rates (v = 0.02 V.s⁻¹ (Panels A and B) and v = 0.2 V.s⁻¹ (Panels C and D)) with either no toluene (black), toluene-H8 (pink) or toluene-D8 (orange). Simulated CVs were generated according to the parameters defined in Scheme S1. Experimental curves: [**1**] = 1.2 mM; [Toluene] = 0 or 540 mM; Area of electrode = 0.07 cm².



Figure S3. Experimental (**A** and **C**) and simulated (**B** and **D**) CVs of **1** at v = 0.2 V.s⁻¹ for different concentrations of toluene-H8 (Panels A and B) or toluene-D8 (Panels C and D). Simulated CVs were generated according to the parameters defined in Scheme S1. Experimental curves: [**1**] = 1.2 mM; [Toluene] = 0 mM (black), 135 mM (red), 270 mM (green), 540 mM (blue); T = 293 K, Area of electrode = 0.07 cm²·s⁻¹.

4.2: Plots of $i_{pa}(1)$ vs. $v^{1/2}$ for 0 and 540 mM of Toluene



Figure S4. Plots of $i_{pa}(1) vs. v^{1/2}$ in the 20-500 mV/s scan rate range from CVs at a glassy carbon electrode of complex **1** (*C* = 1.20 mM) in CH₃CN / NBu₄ClO₄ 0.1 M at 20°C.

From the CVs, plots of $i_{pa}(1) vs. v^{1/2}$ are similar for 0 and 540 mM of Toluene H8, leading to a linear variation. It suggests that it is a simple EC mechanism (stoichiometric) for toluene oxidation without base, within this scan rate range (20-500 mV/s). So this is different from the reaction of the complex at very low scan rate (<10 mV/s) as previously published² for which an ECE or ECcat mechanism occurs in CH₃CN alone. This is in accordance with a competitive reaction of the **1**⁺ species during electrolysis, between CH₃CN and toluene oxidation.

4.3: Determination of the oxidation products

Bulk electrolysis was performed on the complex **1** (1 mM) in a 0.1 M solution of NBu₄ClO₄/CH₃CN to a potential of 1.3 V *vs.* Fc⁺/Fc in the presence of 490 equivalents of toluene-H8 at 20° C. Due to no differences in the response inside and outside the glovebox for the reactivity of the Cu^{III}Cu^{III} species with toluene followed by CV, the electrolysis was performed outside the glovebox.

After exhaustive electrolysis the solution was concentrated, the large excess of NBu₄ClO₄ precipitated with diethyl ether and filtered, concentrated and precipitated a second time and the

remaining diethyl ether solution was analysed by GC-MS (see Figure S5, top) where the MS was operated in EI mode (70eV).

A blank electrolysis was also completed as a control experiment – an electrochemical cell was set up in the same conditions but with no complex, and set at 1.3 V vs. Fc^+/Fc for the same amount of time (Figure S5, bottom). This was to ensure that no oxidation of toluene occurred at the electrode just because of the potential applied.

The GC-MS trace presented in Figure S5 shows several peaks of which only the peaks at 3.9 min (toluene) and 11.8 (butylated hydroxytoluene, present in the diethyl ether) were observed after the electrolysis without the complex. The remaining products (determined by GC-MS analysis of commercially available reference products or synthesised using literature procedures)⁵ correspond to benzaldehyde, benzyl alcohol, benzylacetamide, 2-(methylphenyl)-toluene, and 4-(methylphenyl)-toluene were formed because of the presence of the Cu^{II}Cu^{III} species generated by bulk oxidation of the complex **1**. Oxidation of toluene to benzoic acid was not observed.

5

Li, J.-H.; Liu, W.-J.; Yin, D.-L. Synth. Commun. **2004**, 34 (17), 3161.



Figure S5. Top: GC-MS trace of the residue after bulk electrolysis of **1** in the presence of toluene followed by treatment with diethyl ether. Stared peak: present in the diethyl ether. Bottom: GC-MS trace of the blank electrolysis followed by treatment with diethyl ether.

4.4: Oxidation products in presence of H₂¹⁸O

An exhaustive electrolysis of the complex **1** (1mM) in the presence of 50 equivalents of $H_2^{18}O$ in a glove box using a 0.1 M solution of NBu₄ClO₄/CH₃CN dried over 3Å molecular sieves was performed. The

same procedure was used as that reported by Williams *et al.*⁶ who determined a water content of less than 4 ppm. After electrolysis the solution was purified as previously described (precipitation of the NBu₄ClO₄ salt with diethyl ether) and analysed by GC-MS (Figure S6). Retention times, m/z and the assignment of peaks observed are displayed in Table S2.



Figure S6. El spectra from the GC-MS of the purified residue after the electrolysis of **1** in the presence of toluene and H_2^{18} O. El spectra from retention times: Top: 8.03-8.06 min, middle 7.24-26 min, bottom 11.23-11.26 min.

⁶ Williams, D. B. G.; Lawton, M. J. Org. Chem. 2010, 75 (24), 8351.

Table S2: Retention time, m/z and assignment of peaks observed by GC-MS after electrolysis of **1** in the presence of toluene and $H_2^{18}O$.

Retention time / min	EI-MS /(m/z)	Assignment
8.03-8.06	108 and 110	PhCH ₂ ¹⁶ OH and PhCH ₂ ¹⁸ OH
7.24-7.26	106 and 108	PhCH ¹⁶ O and PhCH ¹⁸ O
11.23-11.26	149 and 151	PhCH ₂ NHC ¹⁶ OCH ₃ and PhCH ₂ NHC ¹⁸ OCH ₃
11.87-11.90 and 11.93-11.95	182	2-(methylphenyl)-toluene and 4-
		(methylphenyl)-toluene

5-Molecular electrochemical catalysis conditions

5.1: Determination of oxidation products (without toluene)

Bulk electrolysis in a 0.1 M solution CH_3CN/NBu_4ClO_4 of **1** (1 mM) in the presence of 8 equivalents of 2,6-Lutidine was completed until a total of eight electrons.mol⁻¹ of catalyst had been passed (4 Coulombs). The ¹H-NMR of the resulting residue is shown in Figure S7.



Figure S7. ¹H-NMR spectra in CD₃CN of the aromatic regions of 2,6-lutidine (blue), 2,6-lutidine after electrolysis in the presence of **1** (red) and 6-methyl-2-pyridinemethanol (green).

5.2: Addition of water

The electrochemical solution (0.1 M NBu₄ClO₄/CH₃CN) was prepared by drying over 3 Å molecular sieves,⁵ and the CV of **1** (1 mM) in the presence of 1 eq of 2,6-lutidine (Lut) was investigated upon addition of water (0-50 eq). The CVs of 2,6-lutidine (1 mM) and different quantities of water were

subtracted from the CVs of the complex with 2,6-lutidine and the respective amount of water, so that any changes to the current are not due to the oxidation of water (or 2,6-lutidine) at the electrode.



Figure S8. A : CVs of the addition of water to **1** in the presence of 1 eq of 2,6-lutidine (Lut). The CV curves of 2,6-lutidine and water were subtracted from the respective CVs of **1**, 2,6-lutidine and water. Dotted line: 0 eq 2,6-lutidine, 0 eq H₂O. Coloured lines: 1 eq 2,6-lutidine, 0-50 eq H₂O. Parameters: v = 20 mV/s; NBu₄ClO₄ in CH₃CN (0.1 M); concentration of **1** = 1 mM; concentration of 2,6-lutidine = 0 or 1 mM; boron doped diamond (BDD) used as the working electrode; inert atmosphere. **B**: maximum current of each of the CV curves of **1** with 1 eq 2,6-Lutidine upon addition of water (0-50 eq).

5.3: Analysis of the CVs for the total catalysis case



Figure S9. CVs of complex **1** (1.0 mM) in absence and presence of 2,6-lutidine in 0.1 M CH_3CN/NBu_4ClO_4 , glassy carbon electrode, scan rate = 0.02 V.s⁻¹ at 20 °C.



Figure S10. A: Anodic peak current $i_{pa}(2)$ against the concentration of 2,6-lutidine added from CVs (Figure 3) of the addition of different concentrations of 2,6-lutidine to the complex **1**. Parameters: solvent: 0.1 M NBu₄ClO₄ in CH₃CN, dried over molecular sieves; concentration of complex: 0.8 mM; concentration of 2,6-lutidine: 0.3, 0.6, 1.2 and 2.4 mM; scan rate: 0.02 V.s⁻¹, working electrode: BDD; *T* = 293 K; under Ar; **B**: Plot of the peak current $i_{pa}(2)$ as a function of $v^{1/2}$ from CVs of **1** with 0.6 mM of 2,6-lutidine at different scan rates (Figure 4). Parameters: solvent: 0.1 M NBu₄ClO₄/CH₃CN dried over molecular sieves; concentration of 2,6-lutidine: 0.6 mM; working electrode: BDD at 20°C under Ar.

5.4: Determination of the number of electrons and kinetics of the catalytic reaction

The equation E1 gives the relationship between the anodic peak current, $i_{pa}(2)$, of the pre-peak detected by CVs (Figure 4) as a function of the scan rate (v) and number of electrons (n) involved. This equation is valid for monoelectronic and bielectronic processes, considering that the substrate (acetonitrile) is in a large excess of the co-substrate (2,6-lutidine) and catalyst precursor (complex 1).^{7,8}

Equation E1:

$$i_{\rm pa}(2) = 0.609 n FAC_{\rm lut}^0 \sqrt{D_{\rm lut} \frac{Fv}{RT}}$$

where

 C_{lut}^0 : Bulk concentration of 2,6-lutidine / M

 $D_{\text{lut}} = 4.4 \times 10^{-5} \text{ cm}^2.\text{s}^{-1}$ (Diffusion coefficient of 2,6-lutidine / cm².s⁻¹) measured by DOSY NMR in a 0.1 M solution of KPF₆ in CD₃CN

 $A = 0.07 \text{ cm}^2$ (area of the electrode)

The plot of the peak current against the square root of the scan rate shown in Figure 5 gives n=0.9, consistent with a one-electron mechanism.

Given the monoelectronic process, in the case of total catalysis, the kinetics of the reaction can be extracted from the variation of the potential of the pre-peak, $E_{pa}(2)$, with v^{-1} (equation E2).

Equation E2:

$$E_{\rm pa}(2) = E^0(1) - 0.409 \frac{RT}{F} + \frac{RT}{2F} ln \left(\frac{RT}{F} \frac{k_{\rm obs} D_{\rm Cu_2^{\rm II}} (C_{\rm Cu_2^{\rm II}}^0)^2}{v D_{\rm lut} (C_{\rm lut}^0)} \right)$$

 $E^{0}(1)$: Standard potential of **1⁺/1** (1.12 V vs. Fc⁺/Fc)

 D_{Cull} : Diffusion coefficient of **1** (0.9 x 10⁻⁵ cm².s⁻¹)¹

 $D_{\rm lut}$: Diffusion coefficient of 2,6-lutidine (4.4 x 10⁻⁵ cm².s⁻¹)

⁷ Savéant J.-M., In *Elements of molecular and biomolecular electrochemistry: an electrochemical approach in electron transfer chemistry*, Wiley: Hoboken NJ . 2006.

⁸ Costentin, C.; Nocera, D. G.; Brodsky, C. N., *Proc. Natl. Acad. Sci.* **2017,** *114* (43), 11303-11308

 $C_{Cu_2}^0$: Bulk concentration of **1** (0.8 mM) C_{lut}^0 : Bulk concentration of **2**,6-lutidine (0.6 mM)

A plot of $\exp \frac{2F}{RT} \left(E_{pa}(2) - E^0(1) + 0.409 \frac{RT}{F} \right)$ against v^{-1} is displayed in Figure S11, according to the CVs shown in Figure 4. A gradient of 0.381 V.s⁻¹ was obtained leading to the second order rate constant k_{obs} determined to be 6 x 10⁴ M⁻¹.s⁻¹.



Figure S11. Plot of $\exp(\frac{2F}{RT})\left(E_{pa}(2) - E^{0}(1) + 0.409\frac{RT}{F}\right)$ against v^{-1} corresponding to the data from CVs displayed in Figure 4 for determining the rate constant k_{obs} .

5.5: Voltammetric simulations

The cyclic voltammetry of the addition of sub-stoichiometric amounts of 2,6-lutidine is shown in Figure S12 (top). 2,6-lutidine (0 to 0.4 eq) was added sequentially to **1** (0.8 mM) in a 0.1 M solution of NBu₄ClO₄/CH₃CN (dried over 3 Å molecular sieves) in a glove box. Voltammetric simulations using a $EC_1C_2C_3C_4$ mechanism (Scheme 1) are displayed in Figure S12 (bottom).



Figure S12. Experimental (**A**) and simulated (**B**) CVs of complex **1** (0.8 mM) upon addition of substoichiometric amounts of 2,6-lutidine. v = 10 mV/s; NBu₄ClO₄ in CH₃CN (0.1 M) dried over 3 Å molecular sieves; working electrode: BDD at 20°C under argon. For simulation parameters: see text below and Scheme 1.

Mechanism of the electrocatalysis by complex 1 used for simulating the CV curves:

A EC₁C₂C₃C₄ mechanism was used for simulating the electrocatalysis by the complex **1** as shown in Schema 1 (main text). This is for two reasons: *i*) the CV of **1** with no base is not fully reversible ($i_{pa} \neq i_{pc}$, indicating that **1**⁺ also has side reactions without the presence of 2,6-lutidine (an EC mechanism) and *ii*) there is a complete loss of reversibility wave assigned as the oxidation of $\mathbf{1}$ to $\mathbf{1}^{+}$ upon the addition of only 0.4 equivalents of 2,6-lutidine. This is unusual for the case of "total catalysis" as generally the reversible system of the catalyst is observable after the catalytic.

In terms of the parameters, values chosen were as close to the experimental values as possible (concentration and E^0 of the catalyst, concentration of the 2,6-lutidine). The concentration of the solvent SH was calculated from its density to give a value of 19 M. The measured value of the diffusion of the catalyst was used for all oxidation/protonation states of the catalyst. The measured diffusion coefficient of the 2,6-lutidine (4.4 x 10^{-5} cm².s⁻¹) was also used for other small molecules (the solvent SH, the oxidised solvent S[•] and the protonated 2,6-lutidine (Lut-H)). Rate constants and equilibrium constants were then changed until the simulated values of the catalytic peak current and potential fitted the experimental CVs.

Parameters used: Concentration: [1] = 0.8 mM, [SH] = 20 M, [2,6-lutidine] = 0, 0.1 mM, 0.2 mM, 0.3 mM, 0.4 mM. Diffusion coefficients: $D([1]^{n+}) = 0.9 \times 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$; D(SH), $D(S^{\bullet})$, D(Lut) and $D(Lut-H) = 4.4 \times 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$; D(A) and $D(B) = 1 \times 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$. v = 10 mV/s, $\alpha = 0.5$, $E^{\circ} = 1.12 \text{ V vs. Fc}^+/\text{Fc}$

Parameters obtained from simulation: C_1 : $[k_{f_1} = 1 \times 10^{-3} \text{ M}^{-1} \cdot \text{s}^{-1}, K_1 = 1 \times 10 \text{ M}^{-1}]; C_2$: $[k_{f_2} = 7 \times 10^5 \text{ M}^{-1} \cdot \text{s}^{-1}, K_2 = 1 \times 10^7 \text{ M}^{-1}]; C_3$: $[k_{f_3} = 1 \times 10^6 \text{ M}^{-1} \cdot \text{s}^{-1}, K_3 = 1 \times 10^7 \text{ M}^{-1}]; C_4$: $[k_{f_4} = 5 \times 10^3 \text{ M}^{-1} \cdot \text{s}^{-1}, K_4 = 1 \times 10^6 \text{ M}^{-1}].$

5.6: Bulk electrolysis experiments of complex 1 for aliphatic C-H oxidation of toluene or ethyl benzene

Typical bulk electrolysis of the complex **1** were performed in the presence of 8 equivalents of 2,6-lutidine and 490 equivalents of toluene (or ethylbenzene) using 0.8 mM of the complex **1** in a solution of 0.1 M NBu₄ClO₄/CH₃CN (6 mL) to a potential of 1.3 V *vs.* Ag/AgNO₃ under an atmosphere of air at RT. A blank electrolysis in the same conditions (the same potential for the same amount of time) but without the complex was also completed for each experiment. The residue was concentrated until 1 mL, purified by precipitation with diethylether (25 mL), filtered to remove the NBu₄ClO₄ salt, and precipitated a second time. After filtration, the remaining diethyl ether solution was concentrated again then analysed by GC (Figures S13 and S14). Oxidation products analysis has been performed by gas chromatography (Agilent 7890B GC System-5977A MSD, with HP-5MS 5% Phenyl Methyl Silox column). The temperature sequence used for the gas chromatograph was as follows: the temperature was held at 40°C for 4 min then increased at 20°C/min to a temperature of 280°C, for which the temperature was held for 4 min. Oxidation products were confirmed by comparison to commercially available pure oxidized species standards and specifically with benzaldehyde and benzylic alcohol for toluene. For ethyl benzene, the pure oxidized standards used are: acetophenone, 1- and 2-phenylethanol, 2-hydroxyacetophenone, 2-phenyl acetaldehyde, 2-hydroxyphenylaldehyde, and 1-phenyl-1,2-ethanediol. The yields of the corresponding product signals were calculated on the basis of comparisons to a calibration curve; externally added nitrobenzene was used as an internal standard.

Bulk electrolysis experiments of complex 1 in presence of toluene



Figure S13. Top: GC trace of the solution after bulk electrolysis of **1** (1 equiv.) in $CH_3CN/TBAP 0.1M$ solution at RT in the presence of 2,6-lutidine (8 equiv.) and toluene (490 equiv.) that has been taken up in diethyl ether after workup. Bottom: GC trace of the blank electrolysis performed under the same conditions (same electrolysis potential for the same amount of time but with no complex). The stared peak is present in the diethyl ether used.

The GC trace shown in Figure S13 reveals several peaks of which only the peaks at RT of 3.6 min (toluene), 5.8 min (2,6-lutidine), nitrobenzene (8.4 min) and 12 min (butylated hydroxytoluene, present in the diethyl ether) were observed after the electrolysis without the complex. The yield of oxidized products is around 0.1% yield, ratio benzaldehyde:benzyl alcohol of 2.8 : 1, with benzylacetamide only as trace.



Bulk electrolysis experiments of complex 1 in presence of ethylbenzene

Figure S14. Top: GC trace of the solution after bulk electrolysis of **1** (1 equiv.) in $CH_3CN/TBAP 0.1M$ solution at RT in the presence of 2,6-lutidine (8 equiv.) and ethylbenzene (490 equiv.) that has been taken up in diethyl ether after workup. Bottom: GC-MS trace of the blank electrolysis performed under the same conditions (same electrolysis potential with the same amount of time but with no complex). The stared peak is present in the diethyl ether used.

The controlled potential electrolysis in the absence of complex **1** (Figure S14 bottom) using the same experimental procedure (same electrolysis potential for the same amount of time) generates acetophenone (RT of 8.1 min) and 1-phenylethanol (RT of 8.2 min) evidencing that at the potential used the more oxidizable α -hydrogen aliphatic C-H bond is oxidized in part at the electrode. Electrolysis in presence of complex **1** generates exclusively acetophenone and 1-phenylethanol (1.5:1 ratio, yield 0.3%) as oxidized products (Figure S14, top) but with an improvement of ~20% of the yield compared to the blank, arising exclusively from reaction at the benzylic position, no tertiary C-H oxidation product was detected.