

Supporting Information for
Reduction of dioxygen to water by a Co(N₂O₂) complex with a 2,2'-bipyridine backbone

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Experimental and Methods

General. All chemicals and solvents (ACS or HPLC grade) were commercially available and used as received unless otherwise indicated; Co(salen) was obtained from TCI America (>95.0%). For all air-sensitive reactions and electrochemical experiments, HPLC-grade solvents were obtained as anhydrous and air-free from a PPT Glass Contour Solvent Purification System, with the exception of methanol. Gas cylinders were obtained from Praxair (Ar as 5.0; O₂ as 4.0) and passed through activated molecular sieves prior to use. Gas mixing for variable concentration experiments was accomplished using a gas proportioning rotameter from Omega Engineering. UV-vis absorbance spectra were obtained on a Cary 60 from Agilent. HRMS and elemental analyses were performed at the University of Virginia utilizing an Agilent 6545B QTOF and PerkinElmer 2400 Series II CHNS/O Analyser instruments. An Anton-Parr Multiwave Pro SOLV, NXF-8 microwave reactor was used for microwave syntheses.

Electrochemistry. All electroanalytical experiments were performed using a Metrohm Autolab PGSTAT302N potentiostat. Glassy carbon working ($\varnothing = 3$ mm) and non-aqueous silver/silver chloride pseudoreference electrodes behind CoralPor frits were obtained from CH Instruments. The pseudoreference electrodes were obtained by depositing chloride on bare silver wire in 10% HCl at oxidizing potentials and stored under light-free conditions in 0.1 M tetrabutylammonium hexafluorophosphate/acetonitrile solution prior to use. The counter electrode was a glassy carbon rod ($\varnothing = 3$ mm). All CV experiments were performed in a modified scintillation vial (20 mL volume) as a single-chamber cell with a cap modified with ports for all electrodes and a sparging needle. Tetrabutylammonium hexafluorophosphate (TBAPF₆) was purified by recrystallization from ethanol and dried in a vacuum oven before being stored in a desiccator. All data were referenced to an internal ferrocene standard (ferricenium/ferrocene reduction potential under stated conditions) unless otherwise specified. All voltammograms were corrected for internal resistance.

Synthesis of ^{tbu}dhbpy[H]₂

^{tbu}dhbpy was synthesized according to our previously reported procedures.¹⁻²

Synthesis of [Co(^{tbu}dhbpy)(py)₂][PF₆] (1)

A two-necked round-bottom flask (100 mL) was charged with a stir bar, ^{tbu}dhbpy (0.150 g, 0.266 mmol), and methanol (25 mL). The suspension was capped with a septum and a condenser was attached before it was brought to reflux (65 °C) under aerobic conditions. Co(OAc)₂•4H₂O (0.066 g, 0.27 mmol) was dissolved in minimal MeOH (~5 mL) and added to the suspension via syringe. A color change from yellow (ligand) to black was observed. After 3 h, excess pyridine (1.0 mL, 13 mmol) and NH₄PF₆ (0.216 g, 1.33 mmol) were added. Color change from black to red was observed following this addition. The suspension was allowed to reflux for an additional 10 m, then allowed to cool to room temperature. The suspension was filtered to remove excess ligand, solvent was removed under reduced pressure, and the isolated solid was recrystallized from minimal hot methanol. After 48 h in the freezer, 92 mg (44% yield) was recovered via vacuum filtration. Elemental Analysis for CoC₄₈H₅₆F₆N₄O₂P Calc'd: C 62.33 H 6.10 N 6.06; Found: C 61.98 H 6.05 N 5.94. ESI-MS: Calc'd (M-2py⁺): 621.289 Found: 621.2887 ¹H NMR (600 MHz): δ 8.26 (dd, 2H), 8.21 (t, 2H), 8.15 (dd, 2H), 7.67 (dd, 4H) 7.57 (t, 2H), 7.50 (2H, d), 7.44 (2H, d), 6.99 (4H, t), 1.53 (18H, s), 1.31 (18H, s). ¹³C NMR (600 MHz): δ 160.68, 158.47, 156.88, 152.02, 144.63, 140.29, 139.85, 138.39, 129.30, 125.62, 125.35, 122.70, 120.61, 115.60, 36.82, 34.62, 31.65, 31.01.

Synthesis of $\text{Co}(\text{t}^{\text{bu}}\text{d}^{\text{hbpy}})_3$

A two-necked round-bottom flask (100 mL) was charged with stir bar, $\text{t}^{\text{bu}}\text{d}^{\text{hbpy}}(\text{H})_2$ (0.150 g, 0.266 mmol), and methanol (25 mL). The suspension was capped with a septum and a condenser was attached before it was brought to reflux (65 °C) under aerobic conditions. $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (0.066 g, 0.27 mmol) was dissolved in minimal MeOH (~5 mL) and added to the suspension via syringe. A color change from yellow (ligand) to black was observed. The suspension was then refluxed for 3 h prior to cooling to room temperature. Product was obtained via vacuum filtration: 100 mg (60.6% yield). Elemental Analysis for $\text{C}_{38}\text{H}_{46}\text{N}_2\text{O}_2\text{Co}$ Calc'd: C 73.41 H 7.46 N 4.51; Found: C 73.67 H 7.50 N 4.41.

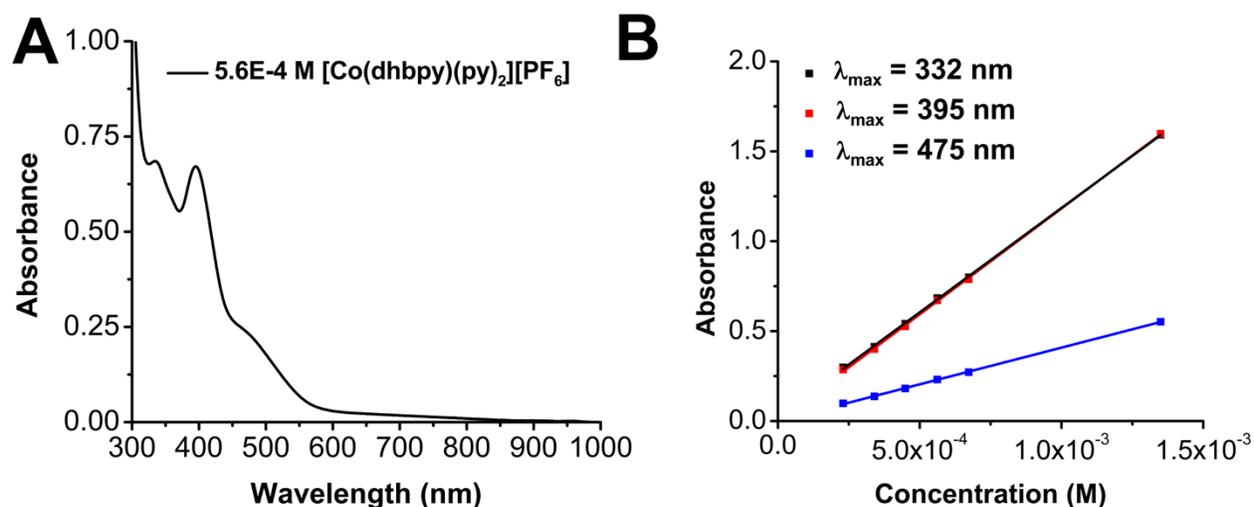


Figure S1. A) UV-Vis spectra of **1** in MeOH. B) determination of ϵ for **1**.

Equation	$y = mx + b$		
		Value	Std Err
Abs @ 322 nm	b	2.42E-02	5.5E-03
--	m	1.16E+03	1E+01
Adj. R-Square	0.99977		
		Value	Std Err
Abs @ 395 nm	b	4.34E-03	6.86E-03
	m	1.18E+03	1E+01
Adj. R-Square	0.99966		
		Value	Std. Err
Abs @ 475 nm	b	1.08E-04	2.4E-03
	m	4.08E+02	3E+00
Adj. R-Square	0.99966		

20200312_codhbppy2pf6_1H_CD2Cl2.1.fid

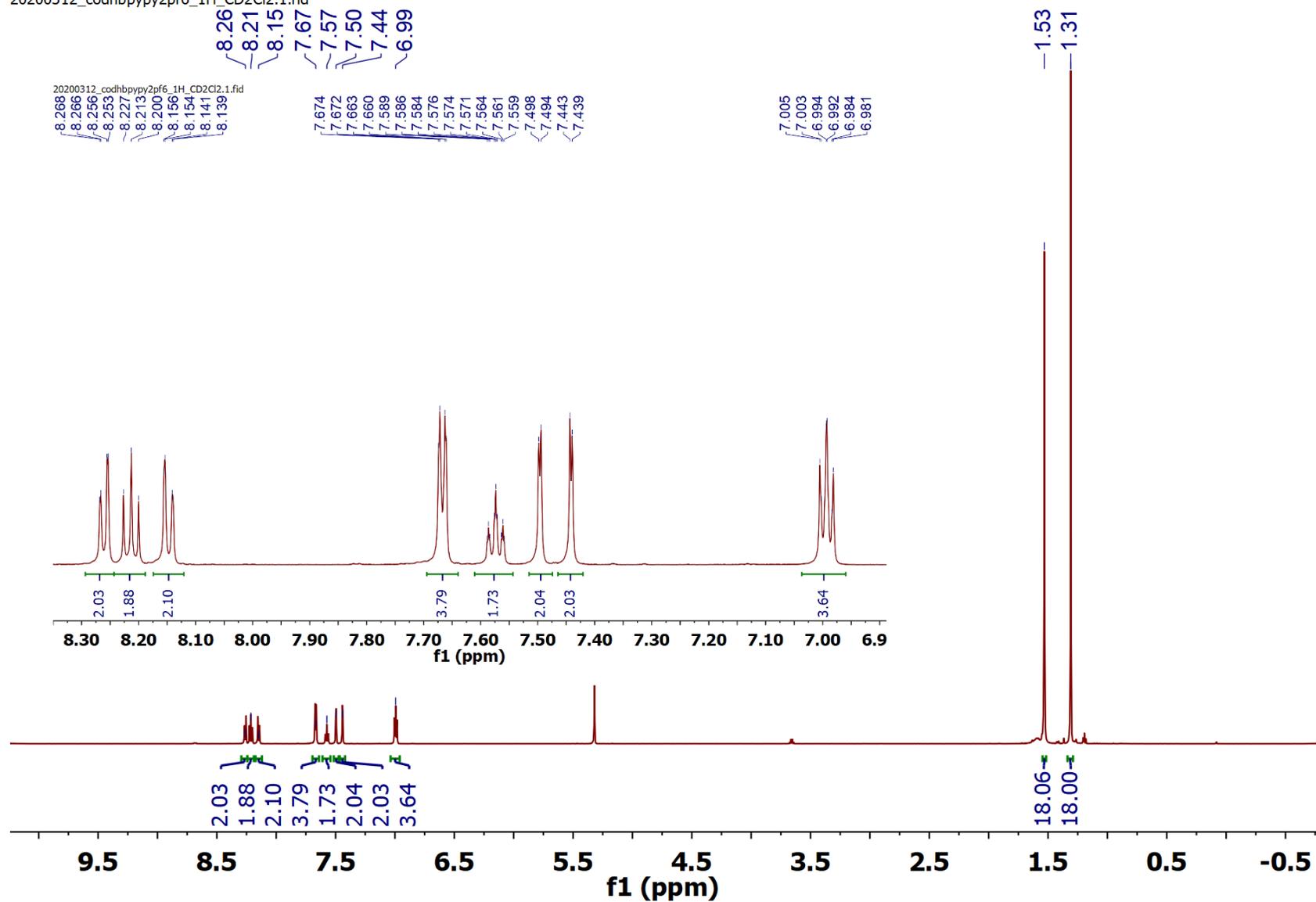


Figure S2. ^1H NMR spectra of **1** in CD_2Cl_2 . (600 MHz, Varian)

20200312_CoDhbppy2pf6_13c_CD2Cl2
Gradient Shimming

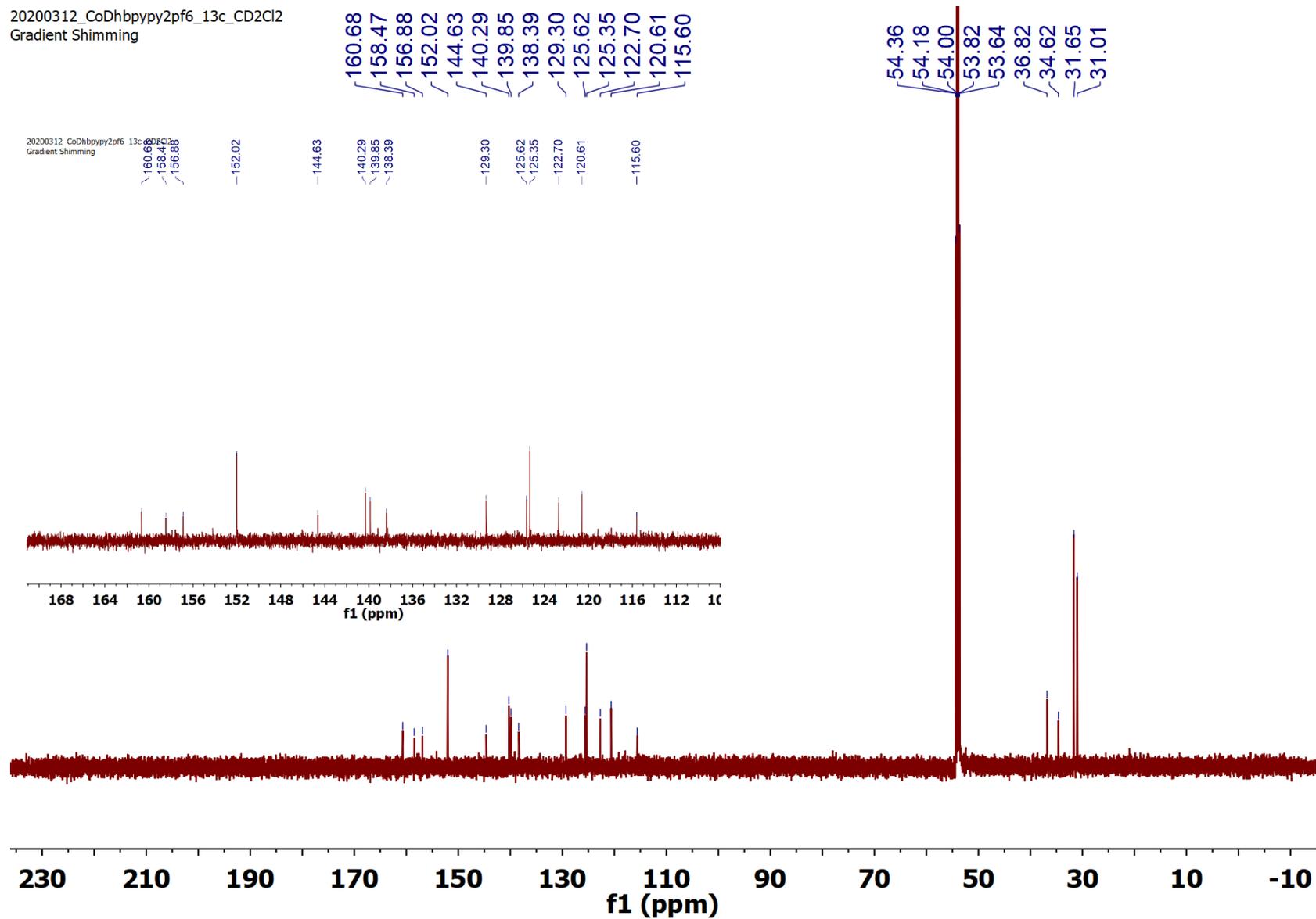


Figure S3. ^{13}C NMR of **1** in CD_2Cl_2 . (600 MHz, Varian). Inset is region from 110-170 ppm.

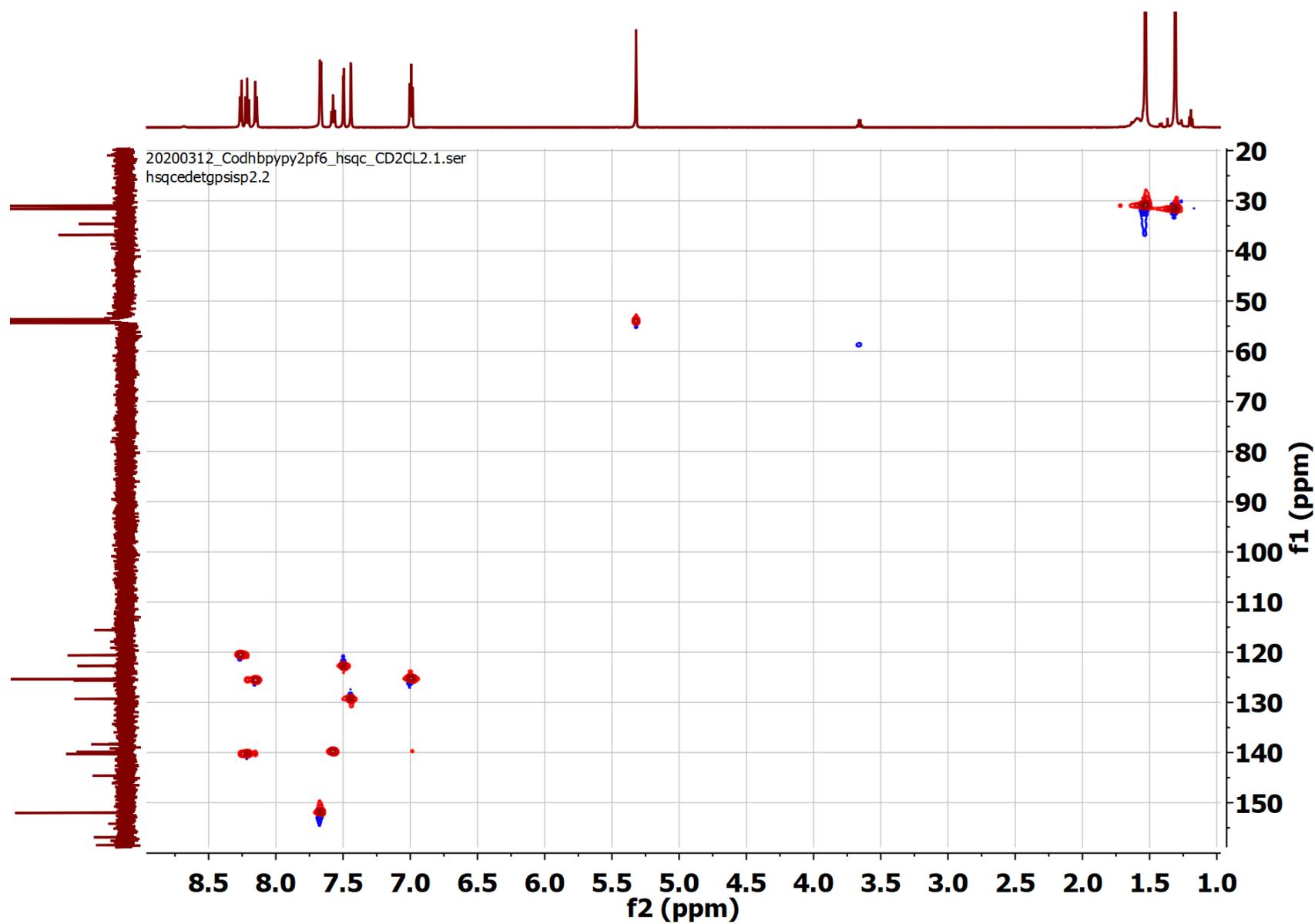


Figure S4. ^1H - ^{13}C HSQC NMR of **1** in CD_2Cl_2 . (600 MHz, Bruker).

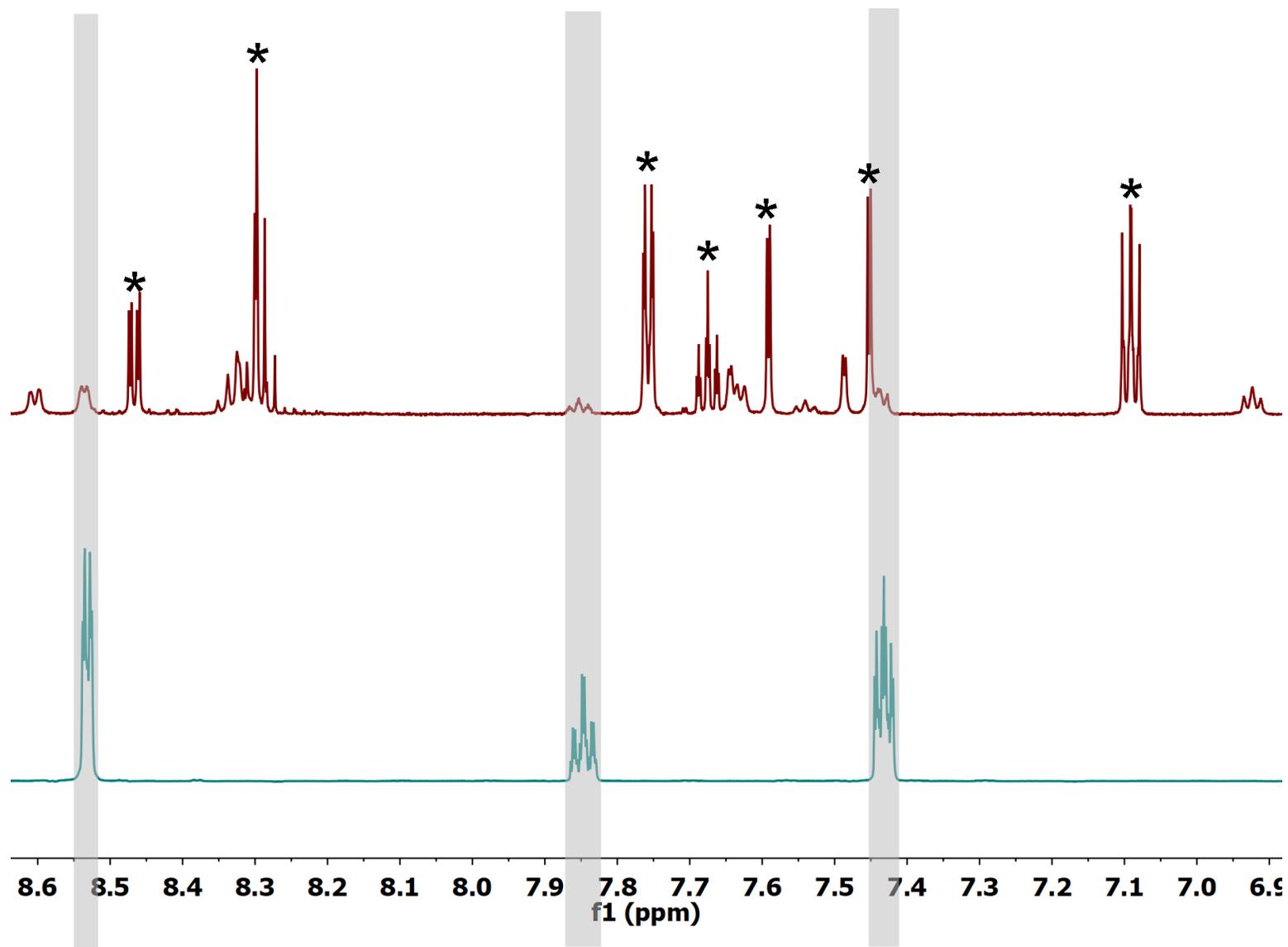


Figure S5. Stacked ^1H NMR spectra of **1** and py in d_4 -MeOH. (600 MHz, Varian). Grey boxes indicate free py; asterisks indicate $[\text{Co}(\text{t}^{\text{bu}}\text{dhbpy})(\text{py})_2]^+$.

Electrochemical Experiments

Complex **1** was analyzed by differential pulse voltammetry and cyclic voltammetry in 0.1 M TBAPF₆/MeOH electrolyte under Ar with no additional additives, 25 mM AcOH, and 25 mM AcOH/TBAOAc buffer to ensure the redox potential did not shift upon addition of AcOH or under catalytic conditions once AcO⁻ is generated.

Standard reduction potentials ($E_{1/2}$) were determined from DPV utilizing the Parry-Osteryoung Equation⁴ where E_p is the peak potential and ΔE is the modulation amplitude:

$$E_{1/2} = E_p + \frac{\Delta E}{2}$$

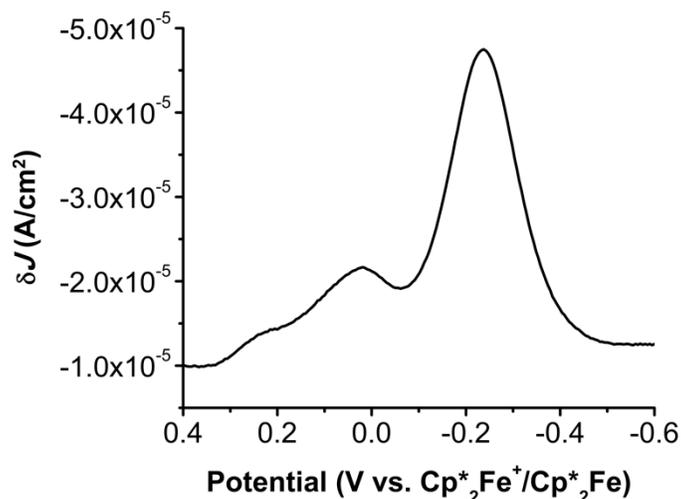


Figure S6. DPV of 1 mM **1** under Ar. Conditions: 0.1 M TBAPF₆/MeOH, glassy carbon working electrode, glassy carbon counter electrode, Ag/AgCl pseudoreference electrode, $\Delta E = 0.025$ V, modulation time 0.01 s, interval time 0.1 s, scan rate 50.354 mV/s. Referenced to external Cp^*_2Fe solution under the same conditions.

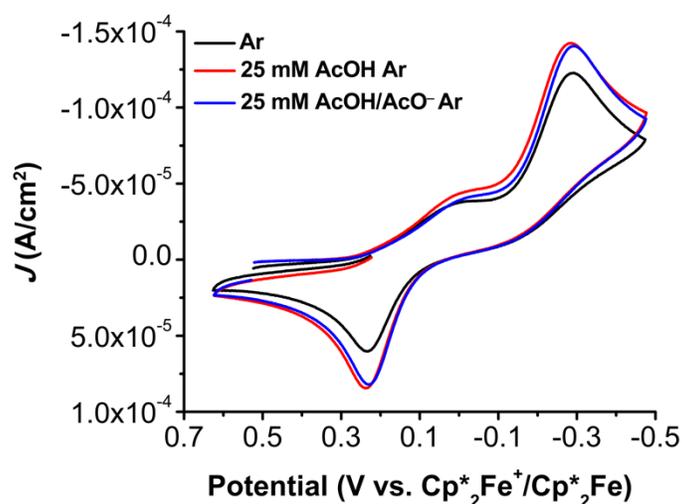


Figure S7. CVs of **1** under Ar (black), with added 25 mM AcOH (red), and with an added buffer comprised of 25 mM AcOH and 25 mM TBAOAc (blue). Conditions: 1 mM **1**, 0.1 M TBAPF₆/MeOH; glassy carbon working electrode, glassy carbon counter electrode, Ag/AgCl pseudoreference electrode, scan rate 100 mV/s; referenced to external decamethylferrocene standard.

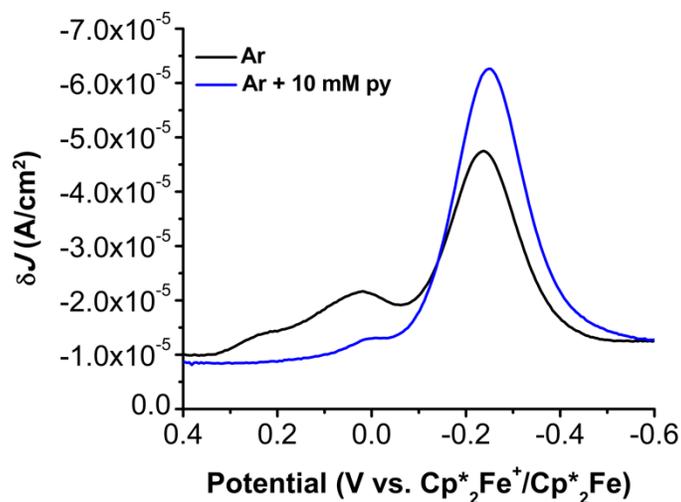


Figure S8. DPVs of **1** under Ar (black), and with 10 mM py under aprotic conditions. Conditions: 1 mM **1**, 0.1 M TBAPF₆/MeOH; glassy carbon working electrode, glassy carbon counter electrode, Ag/AgCl pseudoreference electrode, $\Delta E = 0.025$ V, modulation time 0.01 s, interval time 0.1 s, scan rate 50.354 mV/s. Referenced to external Cp*₂Fe solution under the same conditions.

Iodometric Titration for Determination of Product Selectivity for ORR.

The concentration of catalytically produced H_2O_2 was determined by titration with NaI as previously reported in the literature.⁵⁻⁶ A calibration curve was obtained through a serial dilution of a stock solution of $\text{urea}\cdot\text{H}_2\text{O}_2$ in MeOH while monitoring the appearance of the I_3^- absorbance at 361 nm. For each dilution, 30 μL of the stock solution was added to 2.97 mL of acetonitrile (MeCN). An initial UV-vis spectrum was collected to ensure no background absorbance occurred, and then excess NaI (0.1-0.2 M) was added to the solution, and a final UV-Vis spectrum was collected after approximately 1 h.

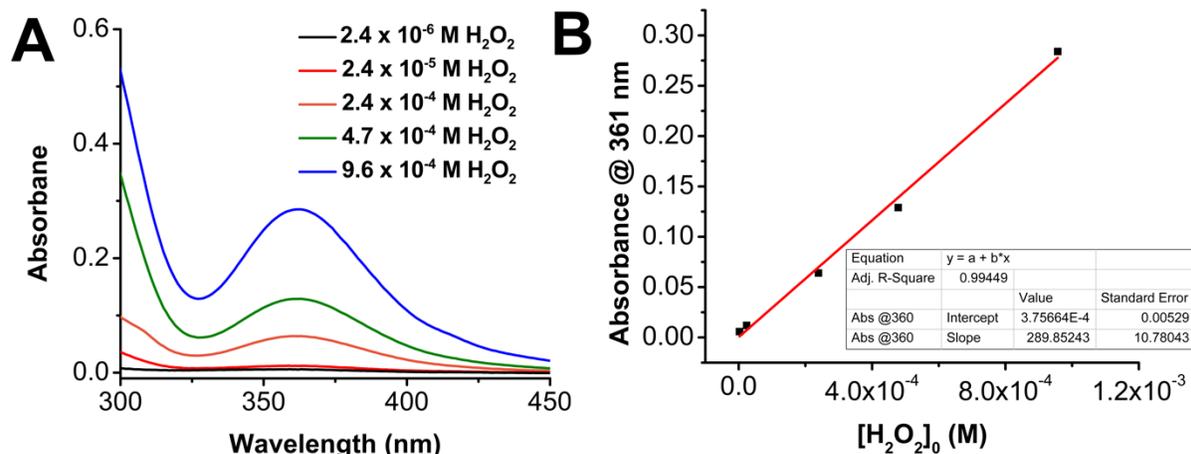


Figure S9. Iodometric titration calibration curve. (A) Serial dilution of $\text{urea}\cdot\text{H}_2\text{O}_2$ in methanol treated using the above method for iodometric titration. (B) Calibration curve made utilizing a serial dilution of $\text{urea}\cdot\text{H}_2\text{O}_2$ in MeOH , the observed slope of 290 ± 10 is consistent with reported molar absorptivity of $2.8 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$.

To ensure Co complex **1** does not facilitate H_2O_2 disproportionation or interfere with iodometric titrations, a known amount of urea• H_2O_2 in MeOH (0.5 mM final concentration) was added to each Co complex (40 μM final concentration) in MeOH along with 25 mM AcOH/TBAOAc buffer. These were then left for the full reaction time of a catalytic run (30 min) prior to diluting a 30 μL aliquot with 2.97 mL of MeCN. A UV-vis spectrum was collected before excess NaI (0.1-0.2 M) was added to the solution and the quantification reaction monitored utilizing scanning kinetics. The difference between the final and initial traces was taken at 361 nm, and used to quantify the final H_2O_2 concentration. With no cobalt complex present, 98% of the H_2O_2 was recovered; for **1**, 100% H_2O_2 was recovered.

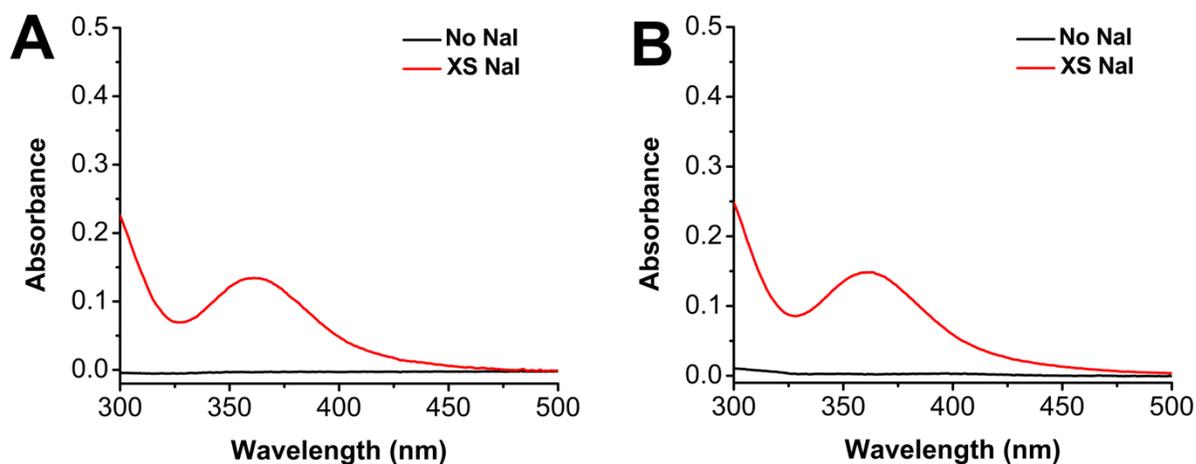


Figure S10. H_2O_2 disproportionation test. Iodometric titrations of MeOH solutions of 0 (**A**) or 40 μM (**B**) of **1** in the presence of 25 mM AcOH/TBAOAc and 0.5 mM urea• H_2O_2 to determine if the **1** interacted with I_3^- or urea• H_2O_2 .

To determine the selectivity of **1** for the ORR reaction, catalytic reaction mixtures (40 μM Co, 0.45 mM $\text{Cp}^*\text{}_2\text{Fc}$, 0.9 mM O_2 , 25 mM AcOH in MeOH) were run to completion (30 min) prior to obtaining a 30 μL aliquot and diluting it into 2.97 mL of MeCN. A UV-vis spectrum was obtained, and excess NaI (0.1-0.2 M) was added. The solution was then monitored by scanning kinetics to determine when a stable concentration of I_3^- had formed.

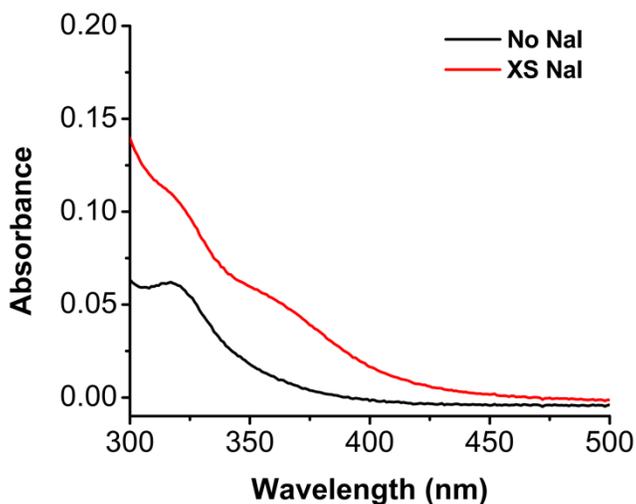


Figure S11. Iodometric titration of **1**. Black trace is prior to the addition of NaI. Red trace is after the addition of NaI.

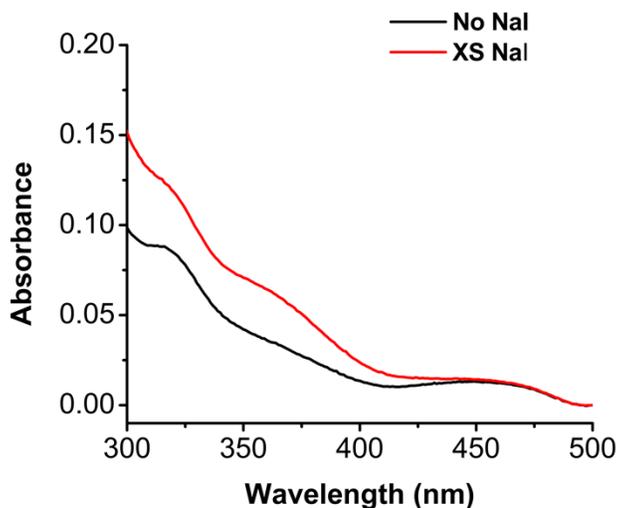


Figure S12. Iodometric titration of **1** in the presence of 20 equivalents of py. Black trace is prior to the addition of NaI. Red trace is after the addition of NaI.

Mechanistic Studies of the 2+2 Mechanism.

A 0.15 mL volume of 4 mM urea•H₂O₂ in MeOH was added to a 2.7 mL N₂-saturated MeOH solution containing 1 mM Cp*₂Fe. To this mixture, a 0.15 mL N₂-saturated MeOH solution of cobalt complex **1** (800 μM) and 0.5 M AcOH was rapidly added. The reaction mixture was vigorously shaken for 30 sec and the absorbance was monitored at 780 nm by UV-vis spectroscopy, minimal changes were observed. An Iodometric titration, as described above was performed and indicated 97% of H₂O₂ remained.

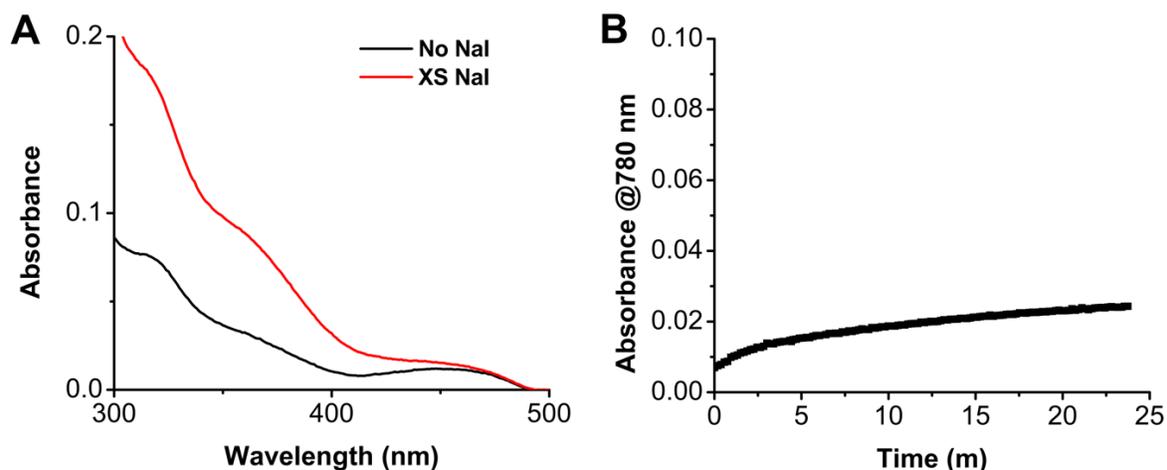


Figure S13. Iodometric titration of 40 μM **1** in MeOH. **(A)** Effect of NaI addition after 30 min reaction time in the presence of 0.9 mM Cp*₂Fe, 0.2 mM urea•H₂O₂, and 25 mM AcOH under anaerobic conditions. **(B)** Monitoring of the growth of [Cp*₂Fe]⁺ at 780 nm, which indicates that a negligible amount of catalytic reduction of H₂O₂ occurs.

Determination of the Catalytic Rate Law for 1.

[1]

A 0.3 mL N₂-saturated MeOH solution of cobalt complex **1** (100, 200, 300, 400, and 500 μM) was rapidly added to a 2.7 mL O₂-saturated (O₂ saturation concentration in MeOH is 10 mM)⁶⁻⁹ MeOH solution containing 1 mM Cp*₂Fe before 4.2 μL AcOH was added. The reaction mixture was vigorously shaken for 30 sec and the absorbance was monitored at 780 nm by UV-vis spectroscopy. Experiments were repeated in triplicate, figure axes show final concentrations; initial rates procedure described on Page S18.⁵⁻⁶

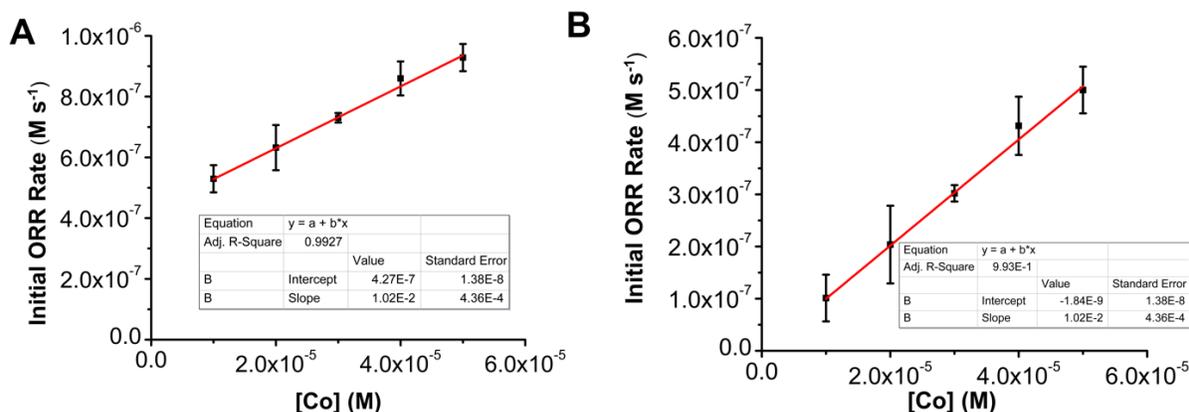


Figure S14. Determination of ORR reaction dependence upon [1]. (A) Uncorrected for background O₂ reduction. (B) Corrected for background O₂ reduction.

[AcOH]

A 0.3 mL N₂-saturated MeOH solution of complex **1** (400 μM) was rapidly added into a 2.7 mL O₂-saturated MeOH solution containing 1 mM Cp*₂Fe before AcOH (0.9, 1.6, 2.6, 3.2, 5.2 μL) was added to the reaction mixture. The reaction mixture was vigorously shaken for 30 sec and the absorbance was monitored at 780 nm by UV-visible spectroscopy. Experiments were repeated in triplicate, figure axes show final concentrations; initial rates procedure described on Page S18.

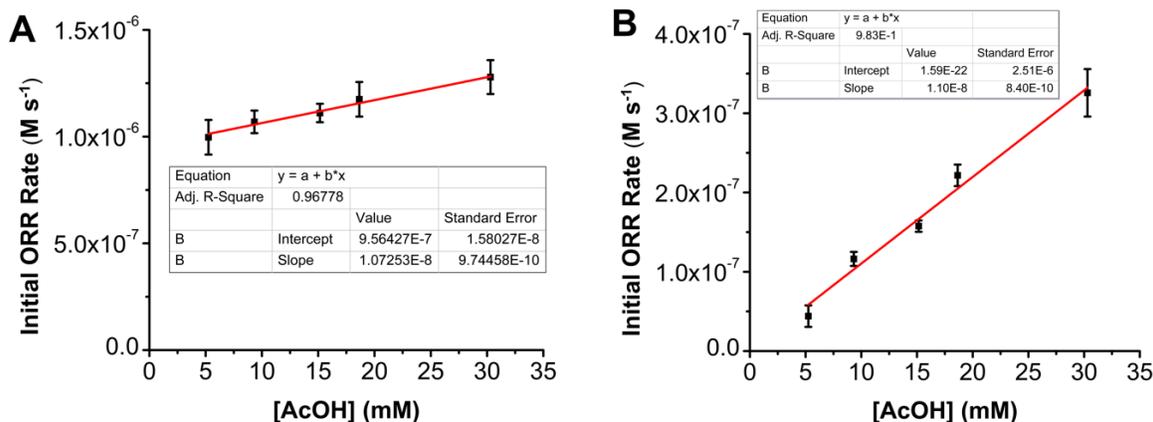


Figure S15. Determination of ORR reaction dependence upon [AcOH]. (A) Uncorrected for background O₂ reduction. (B) Corrected for background O₂ reduction, note that the background reaction is assumed to have minimal initial ORR rate dependence on [AcOH] relative to the reaction catalyzed by **1**.

[Cp*₂Fe]

A 0.3 mL N₂-saturated MeOH solution of cobalt complex **1** (400 μM) and AcOH (4.2 μL) were rapidly added into a 2.7 mL O₂-saturated MeOH solution containing Cp*₂Fe (0.37, 0.52, 0.63, 0.78 and 1 mM) before AcOH (4.2 μL) was added to the reaction mixture. Then the reaction mixture was vigorously shaken for 30 sec and the absorbance was monitored at 780 nm by UV-visible spectroscopy. Experiments were repeated in triplicate, figure axis shows final concentration; initial rates procedure described on Page S18.

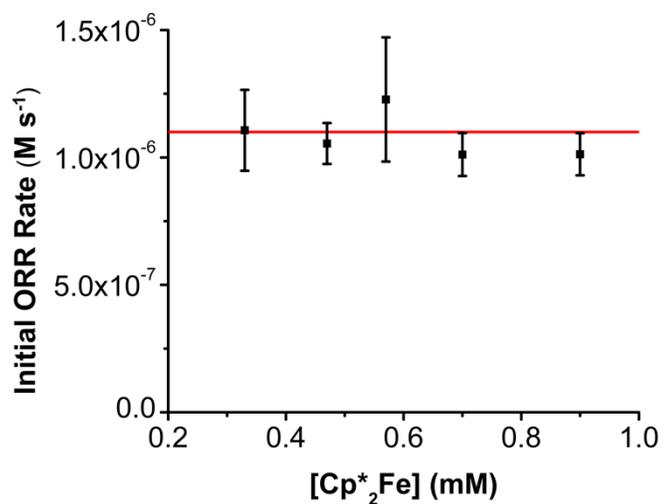


Figure S16. Determination of ORR reaction dependence upon [Cp*₂Fe]. Horizontal line represents the global average rate observed across all experiments described for variable [Cp*₂Fe].

[O₂]

(1) A 0.3 mL N₂-saturated MeOH solution of cobalt complex **1** (400 μM) was rapidly added into an O₂-saturated MeOH solution of 1 mM Cp*₂Fe before 4.2 μL of AcOH was added to the reaction mixture. Then the reaction mixture was vigorously shaken for 30 sec and the absorbance was monitored at 780 nm by UV-visible spectroscopy ([O₂] 9 mM). Experiments were repeated in triplicate, figure axis shows final concentration; initial rates procedure described on Page S18.

(2) A 0.3 mL air-saturated MeOH (20% O₂) solution of cobalt complex **1** (400 μM) was rapidly added into an air-saturated MeOH solution of 1 mM Cp*₂Fe before 4.2 μL of AcOH was added to the reaction mixture. Then the reaction mixture was vigorously shaken for 30 sec and the absorbance was monitored at 780 nm by UV-visible spectroscopy ([O₂] 2 mM). Experiments were repeated in triplicate, figure axis shows final concentration; initial rates procedure described on Page S18.

(3) A 1.5 mL O₂-saturated MeOH solution containing 0.9 mM Cp*₂Fe and 40 μM cobalt complex **1** was mixed with a 1.5 mL N₂-saturated MeOH solution containing 0.9 mM Cp*₂Fe and 40 μM cobalt complex **1**. A 4.2 μL volume of AcOH was rapidly added into the above mixed solution (3 mL), then the reaction mixture was vigorously shaken for 30 sec and the absorbance was monitored at 780 nm by UV-visible spectroscopy ([O₂] 5 mM). Experiments were repeated in triplicate, figure axis shows final concentration; initial rates procedure described on Page S18.

(4) A 2 mL O₂-saturated MeOH solution containing 0.9 mM Cp*₂Fe and 40 μM cobalt complex **1** was mixed with a 1 mL N₂-saturated MeOH solution containing 0.9 mM Cp*₂Fe and 40 μM cobalt complex **1**. A 4.2 μL volume of AcOH was rapidly added into the above mixed solution (3 mL), then the reaction mixture was vigorously shaken for 30 sec and the absorbance was monitored at 780 nm by UV-visible spectroscopy ([O₂] 6.7 mM). Experiments were repeated in triplicate, figure axis shows final concentration; initial rates procedure described on Page S18.

(5) A 1 mL O₂-saturated MeOH solution containing 0.9 mM Cp*₂Fe and 40 μM cobalt complex **1** was mixed with a 2 mL N₂-saturated MeOH solution containing 0.9 mM Cp*₂Fe and 40 μM cobalt complex **1**. A 4.2 μL volume of AcOH was rapidly added into the above mixed solution (3 mL), then the reaction mixture was vigorously shaken for 30 sec and the absorbance was monitored at 780 nm by UV-visible spectroscopy ([O₂] 3.3 mM). Experiments were repeated in triplicate, figure axis shows final concentration; initial rates procedure described on Page S18.

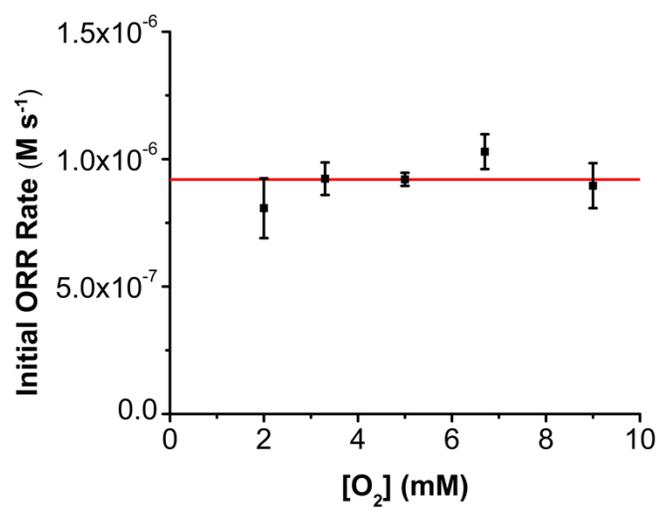


Figure S17. Determination of ORR reaction dependence upon [O₂]. Horizontal line represents the global average rate observed across all experiments described for variable [O₂].

[py]

A 0.15 mL N₂-saturated MeOH to solution of py (0.8, 1.6, 4.0, 8.0, and 16 mM) was added to a 2.7 mL O₂-saturated MeOH solution containing 1 mM Cp*₂Fe. A 0.15 mL N₂-saturated MeOH solution of cobalt complex 1 (800 μM) and 0.5 M acetic acid was rapidly added. The reaction mixture was vigorously shaken for 30 sec and the absorbance was monitored at 780 nm by UV-vis spectroscopy. Experiments were repeated in triplicate, figure axis shows final concentration; initial rates procedure described on Page S18.

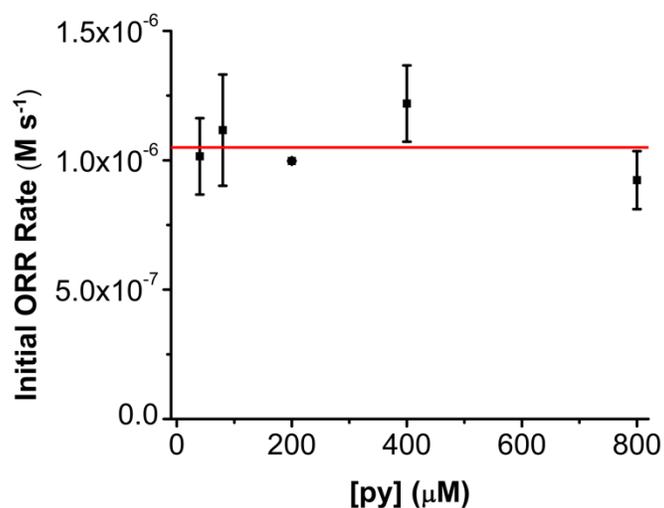


Figure S18. Determination of ORR reaction dependence upon [py].

Horizontal line represents the global average rate observed across all experiments described for variable [py].

Determination of rate constant, k_{cat} (adapted⁶).

The initial observed rate of ORR ($Rate_{obs}$, units of $M s^{-1}$) is a combination of the catalytic rate ($Rate_{cat}$) and background rate ($Rate_{background}$) of Cp^*_2Fe oxidation as follows:

$$Rate_{obs} = Rate_{cat} + Rate_{background}$$

In all cases, $Rate_{obs}$ values were obtained by taking the results of a linear fit of the initial region of $[Cp^*_2Fe]^+$ growth at 780 nm (units = relative absorbance/minute) to a minimum R^2 of 0.99. The results of the linear fit were processed to reflect the rate of ORR by converting relative absorbance units to concentration using the molar extinction coefficient of $[Cp^*_2Fe]^+$ ($\epsilon = 440 M^{-1} cm^{-1}$ as determined by serial dilution of a chemically prepared sample of $[Cp^*_2Fc][BF_4]$), correcting for the number of electrons passed during catalysis ($n_{cat} = 3.4$), and converting from minutes to seconds.

$Rate_{cat}$ is equivalent to the following based on the experimentally determined rate law:

$$Rate_{cat} = k_{cat}[1][AcOH]$$

By substitution:

$$Rate_{obs} = k_{cat}[1][AcOH] + Rate_{background}$$

Utilizing **Figure S14**, both k_{cat} and $Rate_{background}$ can be determined. At $[1] = 0$, (y-intercept), $Rate_{background}$ is the only observed rate, so $Rate_{background} = 4.3 \pm 0.2 \times 10^{-7} M s^{-1}$ (rate of O_2 reduction). To determine k_{cat} , we can simply divide the slope ($Rate/[1]$) by $[AcOH]$ ($2.5 \times 10^{-2} M$), giving a second-order rate constant $k_{cat} = 4.1 \pm 0.2 \times 10^{-1} M^{-1} s^{-1}$.

We can also determine the TOF for this complex utilizing the individual initial rates ($Rate_{[0]}$) from this graph, subtracting the background rate, and dividing by the catalyst concentration.

$$TOF = \frac{Rate_{[0]} - Rate_{background}}{[1]}$$

This gives $TOF = 1.03 \pm 0.03 \times 10^{-2} s^{-1}$ at 0.025 M AcOH.

Using an identical procedure, an estimated $Rate_{background} = 9.5 \pm 0.1 \times 10^{-7} M s^{-1}$ was obtained from **Figure S15**. Given that the background reaction is expected to have a dependence on $[AcOH]$, this value was not used to determine k_{cat} , but was used as an approximate correction to establish the rate dependence of the catalytic reaction mediated by **1** as described above. We note, however, that it shows good agreement with the value obtained from **Figure S14**.

Py Controls for Selectivity Testing with Co(salen) and Co(^{tbu}dhbpy)

A 0.15 mL volume of N₂-saturated MeOH solution of 1.6 μM py was added to 2.7 mL of an O₂-saturated MeOH solution containing 1 mM Cp*₂Fe. To this solution, a 0.15 mL volume of N₂-saturated MeOH solution of Co(salen) (800 μM) and 0.5 M acetic acid was rapidly added. The reaction mixture was vigorously shaken. After 30 min an iodometric titration was performed. Co(salen) with two equiv of pyridine present was determined to be 98±4% selective for H₂O₂ under these conditions (experiments were run in triplicate).

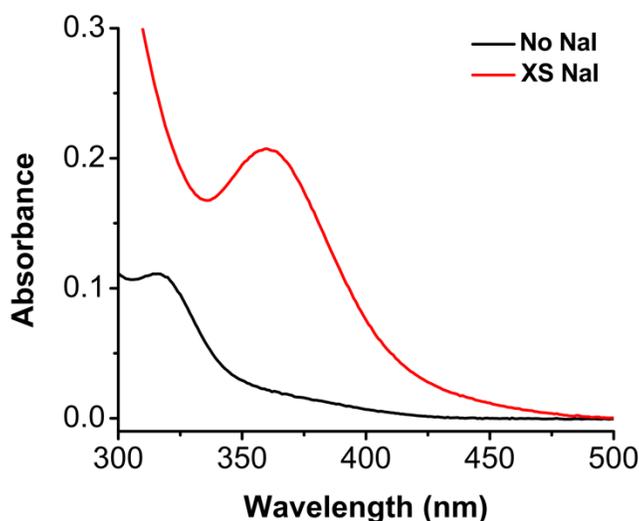


Figure S19. Iodometric titration of Co(salen) in the presence of two equiv of py under conditions identical to testing of **1**.

A 20 μM solution of $\text{Co}(\text{t}^{\text{bu}}\text{dhbpy})$ was degassed for 15 minutes by bubbling with Ar. A 6.8 mg sample of Cp^*Fe was placed under Ar in a round-bottom flask and 21 mL of the degassed $\text{Co}(\text{t}^{\text{bu}}\text{dhbpy})$ solution was added under positive Ar pressure. The solution was degassed for another 5 min. To a 3 mL aliquot of this solution, 4.2 μL AcOH was added and the mixture sparged with O_2 for 60 s. The reaction mixture was then vigorously shaken. After 45 min, an iodometric titration was performed: the reaction was determined to be $27\pm 3\%$ selective for H_2O_2 under these conditions (experiment was run in triplicate).

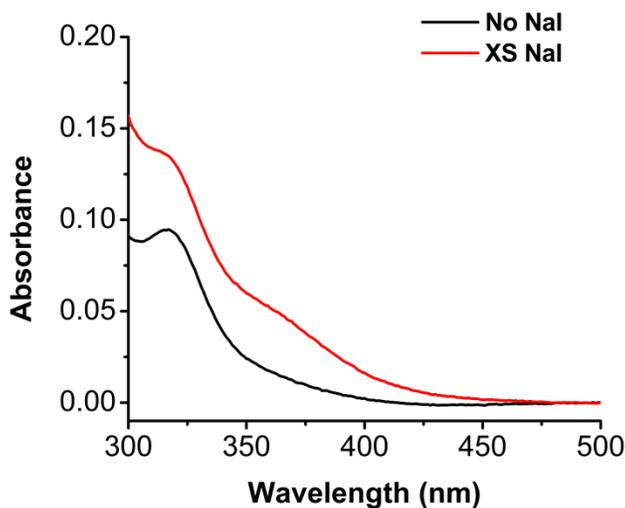


Figure S20. Iodometric titration of 20 μM $\text{Co}(\text{t}^{\text{bu}}\text{dhbpy})$ in the presence of 25 mM AcOH and O_2 saturation.

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