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Supporting Information

for

Co-electrocatalytic CO₂ reduction mediated by a dibenzophosphole oxide and a chromium complex

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Materials and Methods

General

All chemicals and solvents (ACS or HPLC grade) were commercially available and used as received unless otherwise indicated. 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. Gas cylinders were obtained from Praxair (Ar as 5.0; CO₂ as 4.0). Fast mixing for variable concentration experiments was accomplished using a gas proportion rotameter from Omega Engineering. An Anton-Parr Mulitwave Pro Solv, NXF-8 microwave reactor was used for microwave syntheses.

Electrochemistry

All electroanalytical experiments were performed using a Metrohm Autolab PGSTAT302N potentiostat. A glassy carbon working electrode (\emptyset = 3 mm and non-aqueous silver/silver chloride pseudoreference electrodes were obtained from CH Instruments. The pseudoreference electrodes were prepared by depositing chloride on bare silver wire in 10% HCl at oxidizing potentials and stored in a 0.1 M tetrabutylammonium hexafluorophosphate/*N*,*N*-dimethylformamide (TBAPF₆/DMF) in the dark prior to use. Glassy carbon rods (\emptyset = 3 mm) were used as the counter electrodes. All CV experiments were performed in a scintillation vial (20 mL volume) as a single-chamber cell fitted with a modified cap with ports for all electrodes and a sparging needle. 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 (Fc⁺/Fc) reduction potential under stated conditions). Ferrocene was purified by sublimation prior to use. All voltammograms were corrected for internal resistance.

Controlled Potential Electrolysis (CPE)

CPE experiments were performed in a glass Pine Research Instrumentation H-cell with two compartments separated by a glass frit. A 75 mL stock solution of DMF with 0.1 M TBAPF₆ was prepared for each bulk electrolysis experiment. Approximately 26 mL of the stock solution was added to each half of the H-cell. One side of the H-cell contained the catalyst, any additional substrate, such as the mediator and/or PhOH, and a graphite rod working electrode. The other side of the H-cell contained approximately 0.075 M ferrocene as a sacrificial reductant along with a graphite rod counter electrode and a Ag/AgCI pseudoreference electrode. The electrolysis experiment was referenced by taking a CV of the ferrocene containing solution. The H-cell was sealed with two septa that were connected by a piece of PTFE tubing which aided to maintain equal pressure between each half of the cell during the electrolysis. Before starting the electrolysis experiment, both sides of the H-cell were sparged with CO₂ for 20 minutes and the sealed cell was allowed to equilibrate for at least 1 hour. The resistance between the two halves of the H-cell was measured using the *i*-interrupt procedure available in the NOVA software provided by Metrohm.

CPE Product Analysis

During CPE experiments, 250 µL GC injections of the headspace were periodically taken for the detection and quantification of any gaseous products produced. After each CPE experiment, the total volume of solution was measured. The total volume of the sealed H-cell was also measured to account for the total headspace volume for accurate quantification of gaseous products. A

calibration curve for CO and H₂ was used to quantify gaseous products produced during electrolysis experiments in the same manner as we previously reported.¹

Analysis of gas phase products was done by sampling electrolysis headspace through syringe injections into an Agilent 7890B GC equipped with a specialty gas split column 5 Å mol sieve/Porabond Q column (15 m length; 0.320 mm diameter; 25.0 μ m film) and thermal conductivity detector with He as a carrier gas. A calibration curve for CO and H₂ was made in the H-cell with an experimental setup containing identical volumes of DMF in 0.1 M TBAPF₆ to those used during electrolysis. Known volumes of CO and H₂ were injected into the cell with stirring and 250 μ L injections of the headspace were taken for GC injection after equilibration. The limit of detection (LOD) and limit of quantification (LOQ) for CO and H₂ in the GC were determined from seven consecutive injections at the lowest observable concentrations of each gaseous product respectively. For CO, the LOD was determined to be 1.07×10^{-5} moles and the LOQ was determined to be 3.25×10^{-5} moles.

Calculation of Overpotential for CO₂ Reduction with PhOH Present

The calculation of overpotential was performed according to reported methods.² The following equation was used for the determination of the reaction standard potential in V with respect to the Fc^+/Fc couple:

$$E_{CO2/CO} = -0.73 \text{ V} - 0.059(pK_a)$$
 Eq (1)

The pK_a for PhOH in DMF is reported as 18.8:³

$$E_{CO2/CO}(PhOH) = -1.84 \text{ V vs } Fc^{+}/Fc$$
 Eq (2)

The $E_{cat/2}$ determined experimentally for Cr(^{tbu}dhbpy)Cl(H₂O) is -1.95 V vs. Fc⁺/Fc.¹ For protic CO₂ reduction (1.0 mM catalyst and 0.1 M PhOH under CO₂ saturation); the overpotential is:

$$\eta = |E_{cat/2} - E_{CO2/CO}| \qquad \qquad \mathbf{Eq} (3)$$

 $Cr(^{tbu}dhbpy)Cl(H_2O)$ $\eta = 110 \text{ mV}^4$

Homoconjugation of the acid (PhOH) is expected to perturb the expected overpotential. The homoconjugation constant (HA₂⁻) for PhOH in DMF has been reported as $log(mK_{HA_2}) = 3.8.^5$ Thus, the overpotential equation can be modified as follows:

$$E_{CO2/CO} = -0.73V - 0.059(pK_a) - \frac{-2.303RT}{nF} \log(mK_{HA_2})$$
 Eq (4)

Where *n* = number of electrons (2) and *m* = number of proton transfers (2). The modified equation provides $E^{0}_{CO2/CO} = -1.72$ V vs Fc⁺/Fc and the following η value.

 $Cr(^{tbu}dhbpy)Cl(H_2O)$ $\eta = 230 \text{ mV}^4$

This value does not account for the possible thermodynamic contribution of the water coordinated to the pre-catalyst, the equimolar quantities of water produced for each equivalent of CO generated, or any adventitious H_2O present in the CO_2 , solvent or electrolyte. The homoconjugation effects of present water have been consider in work by Matsubara, reporting the standard potential as -1.70 V versus Fc⁺/Fc for the reduction of CO₂ to CO in DMF with PhOH and 10 mM H_2O present.⁶

Determination of TOF from Preparative Electrolysis

The integrated expression of current for a homogeneous electrocatalytic response (considering an application of steady-state condition to the substrate) has been solved previously:^{7, 8}

$$\frac{i}{FA} = \frac{n\frac{\sigma}{cat}[cat]\sqrt{(k_{obs}D_{cat})}}{1+exp\left[\frac{F}{BT}(E_{app}-E_{1/2})\right]}$$
 Eq (7)

where

 $k_{obs} = k_{cat}[CO_2]$

where *i* is the average current (Amps) specific to the reaction product of interest, *F* is Faraday's constant (96485 C mol⁻¹), *A* is the area of the electrode (cm²), η^{σ}_{cat} is the number of electrons in the catalytic process (2) with $\sigma = 0.5$ corresponds to homogeneous electron transfer occurring between catalyst molecules in solution; used here for co-electrocatalytic conditions), [*cat*] is the concentration of the catalyst (mol cm⁻³), k_{obs} is the apparent turnover frequency (s⁻¹), [*CO*₂] is the concentration of CO₂ saturated in DMF (mol cm⁻³), D_{cat} is the diffusion coefficient of the catalyst (cm² s⁻¹), *R* is the ideal gas constant (J mol⁻¹ K⁻¹), *T* is the temperature (K), E_{app} is the applied potential during preparative electrolysis (V), and $E_{1/2}$ is the standard potential of the catalyst (V).

$$\frac{i}{A} = J = CO$$
 specific current density Eq (8)

Substituting and rearranging the first expression to solve for k_{obs}

$$k_{obs} = \frac{J^2 \left(1 + exp \left[\frac{F}{RT} (E_{app} - E_{1/2})\right]\right)^2}{F^2 \left(n \frac{\sigma}{cat} [cat]\right)^2 D_{cat}}$$
 Eq (9)

with k_{obs} in hand, the TOF can be expressed for a given potential according to the following relationship

$$TOF = \frac{k_{obs}}{1 + exp\left[\frac{F}{RT}(E_{app} - E_{1/2})\right]}$$
 Eq (10)

Parameters for CPE experiments reported in Table 1.

- E_{1/2} catalyst: -1.95 V vs Fc⁺/Fc for Cr(^{tbu}dhbpy)Cl(H₂O) 1
 Temperature: 298.15 K
 [CO₂]: 2.3 x 10⁻⁴ mol cm⁻³
 Diffusion coefficient: 2.0 x 10⁻⁶ cm² s⁻¹ for Cr(^{tbu}dhbpy)Cl(H₂O) 1
 Electrode area: 2.29 cm²

Calculation of Diffusion Coefficients

The calculation of the diffusion coefficient for each redox mediator was performed by reported methods.⁹ Cyclic voltammetry (CV) experiments were done with a solution of 2.5 mM RM in 0.1 M TBAPF₆/DMF under Ar saturation conditions. The scan rate of these CVs was varied from 25 mV/s to 5000 mV/s (**Figure S3**). The increase in current observed as the scan rate increases can be represented by the following equation where i_p is the peak current, *n* is the number of electrons, *A* is the area of the electrode, *D* is the diffusion coefficient, *C* is the concentration of analyte, and *v* is the scan rate:

$$i_p = (2.69 \ x \ 10^5) n^{3/2} A C D^{1/2} v^{1/2}$$
 Eq (11)

By plotting the current density as a function of $v^{1/2}$ (**Figure S4**), the slope can be used to find *D*.

$$D_{cat} = \frac{(slope)^2}{n^3 C^2 (2.69 \times 10^5)^2}$$
 Eq (12)

Computational Methods

Geometry optimizations were performed without geometry constraints at the DFT level with the Gaussian 16 program, Rev B.01,¹⁰ employing the hybrid functional B3LYP¹¹⁻¹⁴ and the def2-SVP basis set was used for all atoms.^{15, 16} Dispersion and bulk solvent effects (*N*,*N*-dimethylformamide = DMF; ϵ = 37.219) were accounted for at the optimization stage, by using Grimme's D3 parameter set with Becke-Johnson (BJ) damping^{17, 18} and the CPCM continuum model,¹⁹ respectively. The stationary points and their nature as minima (no imaginary frequencies) were characterized by vibrational analysis using the IGRRHO approach as implemented by default in the software package, which also produced enthalpy (H), entropy (S) and Gibbs energy (G) data at 298.15 K. The minima connected by a given transition state were determined by perturbing the transition states along the TS coordinate and optimizing to the nearest minimum. Free energies were corrected (ΔG_{ab}) to account for concentration effects and for errors associated with the harmonic oscillator approximation. Thus, according to Truhlars's quasi-harmonic approximation for vibrational entropy and enthalpy, all vibrational frequencies below 100 cm⁻¹ were set to this value.²⁰ These anharmonic and concentration corrections were calculated with the Goodvibes code.²¹ Concentrations were set at 0.001 M for metal complexes, 0.005 for RM and RM⁻, and 12.92 M for DMF. Energies were refined by means of single point calculations with the larger def2-TZVP basis set. The stability of the wavefunction and spin contamination were studied at the double- and triple-zeta levels of theory. Kohn-Sham orbital projections and spin densities were plotted with isovalues of 0.045 and 0.005, respectively.

Single crystal X-ray diffraction

A single crystal of the sample was coated with Paratone oil and mounted on a MiTeGen MicroLoop. The X-ray intensity data were measured on a Bruker Kappa APEXII Duo system equipped with an Inoatec Microfocus IµS (Cu K_a, $\lambda = 1.54178$ Å) and a multi-layer mirror monochromator, and a fine-focus sealed tube (Mo K_a, $\lambda = 0.71073$ Å) and a graphite monochromator or Bruker D8 Venture Kappa four-circle diffractometer system equipped with an

Inocoatec IµS 3.0 micro-focus sealed X-ray tube (Mo K_{α}, λ = 0.71073 Å) and a HELIOS double bounce multilayer mirror monochromator.

The frames were integrated with the Bruker SAINT software package²² using a narrow-frame algorithm. Data were corrected for absorption effects using the Multi-Scan method (SADABS or TWINABS).²³ Each Structure was solved and refined using the Bruker SHELXTL Software Package²³ with APEX3²² and OLEX2.²⁴ Non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in geometrically calculated positions with *I*_{iso} = 1.2*U*_{equiv} of the parent atom (*U*_{iso} = 1.5*U*_{equiv} for methyl).

CCDC number	2219200
Formula	C ₁₈ H ₁₃ OP
FW (g/mol)	276.27
Temp (K)	100.03
λ (Å)	0.71073
Size (mm)	0.075 × 0.128 × 0.293
Crystal habit	white blocks
Crystal system	monoclinic
Space group	P21/c
A (Å)	10.0250(12)
B (Å)	9.5951(11)
C (Å)	14.1127(17)
α (°)	90
β (°)	93.226(4)
γ (°)	90
Volume (Å ³)	1355.4(3)
Ζ	4
Density (g/cm ³)	1.364
μ (mm ⁻¹)	0.194
F(000)	584.0
Θ range (°)	4.07 to 66.734
Index ranges	-15 ≤ h ≤ 15, -14 ≤ k ≤ 14, -21 ≤ l ≤ 21
Data / restraints / parameters	5048 / 0 / 233
GOF on F ²	1.026
R ₁ (I>2σ(I))	0.0461
wR ₂ (all data)	0.1099

Table S1. Crystallographic data for PhBPO



Figure S1— Single Crystal Structure of PhBPO. H atoms omitted for clarity. Ellipsoids represented at 50% probability. Grey = Carbon, red = oxygen, and yellow = phosphorous. CCDC 2219200.

Synthesis and Characterization

Synthesis of 6,6'-Di(3,5-di-*tert*-butyl-2-hydroxybenzene)-2,2'-bipyridine, ^{tbu}dhbpy(H)₂

The synthesis of ^{tbu}dhbpy(H)₂ was carried out as previously reported.¹

Synthesis of Cr(^{tbu}dhbpy)Cl(H₂O) (1)

The metalation of $^{tbu}dhbpy(H)_2$ to generate Cr($^{tbu}dhnpy)Cl(H_2O)$ (1) was carried out as previously reported.⁴

Synthesis of PhBPO

The synthesis of PhBPO was carried out following a previously reported method.²⁵

Electrochemistry



Figure S2— Cyclic voltammograms of the first redox couple representing DBTD^{0/-} and PhBPO^{0/-}. [DBTD] and [PhBPO] (2.5 mM) in 0.1 M TBAPF₆/DMF solution under Ar saturation conditions. Conditions: 100 mV/s scan rate; referenced to an internal ferrocene standard.



Figure S3— CVs of PhBPO first redox couple (2.5 mM) in 0.1 M TBAPF₆/DMF solution under Ar saturation conditions, varying the scan rate from 25 mV/s to 5000 mV/s and referenced to internal ferrocene standard.



Figure S4— Linear Fit of variable scan rate data from **Figure S3** demonstrating that PhBPO shows a diffusion limited current response. The data was obtained from the reversible redox feature at -2.49 V vs Fc⁺/Fc and the slope was used to calculate the diffusion coefficient.



Figure S5— CVs of PhBPO (2.5 mM) under saturated Ar and CO₂ conditions, with and without PhOH (0.1 M) as a H-donor in 0.1 M TBAPF₆/DMF. Conditions: 100 mV/s scan rate; referenced to an internal ferrocene standard.



Figure S6— CVs of **1** (1.0 mM), **1** (1.0 mM) with PhOH (H-donor) (0.1 M), **1** (1.0 mM) with DBTD (RM) (2.5 mM), and **1** (1.0 mM) with PhBPO (RM) (2.5 mM) under saturated Ar conditions in 0.1 M TBAPF₆/DMF. Conditions: 100 mV/s scan rate; referenced to an internal ferrocene standard.



Figure S7— CVs of 1 (1.0 mM), 1 (1.0 mM) with PhOH (0.1 M), 1 (1.0 mM) with DBTD (2.5 mM), and 1 (1.0 mM) with PhBPO (2.5 mM) under saturated CO₂ conditions in 0.1 M
 TBAPF₆/DMF. Conditions: 100 mV/s scan rate; referenced to an internal ferrocene standard.



Figure S8— CVs of **1** (1.0 mM), **1** (1.0 mM) with PhOH (0.1 M), **1** (1.0 mM) with DBTD (2.5 mM) and PhOH (0.1 M), and **1** (1.0 mM) with PhBPO (2.5 mM) and PhOH (0.1 M) under saturated Ar conditions in 0.1 M TBAPF₆/DMF. Conditions: 100 mV/s scan rate; referenced to an internal ferrocene standard.



Figure S9— CVs of **1** (1.0 mM), **1** (1.0 mM) with PhOH (0.1 M), **1** (1.0 mM) with DBTD (2.5 mM) and PhOH (0.1 M), and **1** (1.0 mM) with PhBPO (2.5 mM) and PhOH (0.1 M) under saturated CO_2 conditions in 0.1 M TBAPF₆/DMF. Conditions: 100 mV/s scan rate; referenced to an internal ferrocene standard.



Figure S10— CVs of **1** at varying concentrations with PhBPO (2.5 mM) and PhOH (0.1 M) under saturated Ar conditions in 0.1 M TBAPF₆/DMF. Conditions: 100 mV/s scan rate; referenced to an internal ferrocene standard.



Figure S11— CVs of **1** at varying concentrations with PhBPO (2.5 mM) and PhOH (0.1 M) under saturated CO_2 conditions in 0.1 M TBAPF₆/DMF. Conditions: 100 mV/s scan rate; referenced to an internal ferrocene standard.



Figure S12— Plot of log(current density) vs. log[1] from variable [1] CV under saturated CO_2 conditions from peak at –2.45 V vs. Fc⁺/Fc in **Figure S11**.



Figure S13— CVs of **1** (1.0 mM) and PhOH (0.1 M) with variable concentration PhBPO under Ar saturation conditions in 0.1 M TBAPF₆/DMF. Conditions: 100 mV/s scan rate; referenced to an internal ferrocene standard.



Figure S14— CVs of **1** (1.0 mM) and PhOH (0.1 M) with variable concentration PhBPO under CO_2 saturation conditions in 0.1 M TBAPF₆/DMF. Conditions: 100 mV/s scan rate; referenced to an internal ferrocene standard.



Figure S15— Plot of log(current density) vs. log[PhBPO] from variable [PhBPO] CV under saturated CO₂ conditions from peak at -2.45 V vs. Fc⁺/Fc in **Figure S14**.



Figure S16— CVs of variable concentrations of **1** and PhBPO at a 1:5 ratio with PhOH (0.1 M) under Ar saturation conditions in 0.1 M TBAPF₆/DMF. Conditions: 100 mV/s scan rate; referenced to an internal ferrocene standard.



Figure S17— CVs of variable concentrations of **1** and PhBPO at a 1:5 ratio with PhOH (0.1 M) under CO_2 saturation conditions in 0.1 M TBAPF₆/DMF. Conditions: 100 mV/s scan rate; referenced to an internal ferrocene standard.



Figure S18— Plot of log(current density) vs. log[**1**+PhBPO] from variable [**1**+PhBPO] CV under saturated CO₂ conditions from peak at -2.45 V vs. Fc⁺/Fc in **Figure S17**.



Figure S19— CVs of **1** (1.0 mM) with PhBPO (2.5 mM) and PhOH (0.1 M) under variable CO_2 concentrations in 0.1 M TBAPF₆/DMF. Conditions: 100 mV/s scan rate; referenced to an internal ferrocene standard.



Figure S20— Current versus time trace from CPE experiment of 0.5 mM **1** with 1.25 mM PhBPO under protic (0.6 M PhOH) saturated CO₂ conditions. Conditions: -2.58 V vs Fc⁺/Fc in 0.1 M TBAPF₆/DMF; working and counter electrodes were a graphite rod and the reference was a nonaqueous Ag/AgCl pseudoreference electrode; 0.075 M Fc was used as sacrificial oxidant.



Figure S21— Charge versus time trace from CPE experiment in Figure S20.

Time (s)	Charge (coulombs)	Moles (e ⁻)	Moles of CO	FE _{co}
17675	15.7	1.63 x 10 ⁻⁴	7.70 x 10 ⁻⁵	94.4
17698*	15.8	1.63 x 10 ⁻⁴	8.55 x 10 ⁻⁵	104.7
17698*	15.8	1.63 x 10 ⁻⁴	8.39 x 10 ⁻⁵	102.8
17698*	15.8	1.63 x 10 ⁻⁴	8.22 x 10 ⁻⁵	100.7

Table S2. Results from CPE experiment in Figure S20, 1 with PhBPO and PhOH.

* indicates a triplicate series of injections carried out upon completion of electrolysis.



Figure S22— Current versus time trace from CPE experiment of 1.25 mM PhBPO under aprotic saturated CO₂ conditions. Conditions: -2.58 V vs Fc⁺/Fc in 0.1 M TBAPF₆/DMF; working and counter electrodes were a graphite rod and the reference was a nonaqueous Ag/AgCl pseudoreference electrode; 0.075 M Fc was used as sacrificial oxidant.



Figure S23— Charge versus time trace from CPE experiment in Figure S22.

Table S3. Results from CPE experiment in Figure	\$ \$22 , 1.25mM PhBPO under saturated CO ₂
conditions.	

Time (s)	Charge (coulombs)	Moles (e ⁻)	Moles of CO
16710	5.31	5.50 x 10 ⁻⁵	<loq< td=""></loq<>
16740*	5.32	5.51 x 10 ^{−5}	<loq< td=""></loq<>
16740*	5.32	5.51 x 10 ^{−5}	<loq< td=""></loq<>
16740*	5.32	5.51 x 10 ^{−5}	<loq< td=""></loq<>

* indicates a triplicate series of injections carried out upon completion of electrolysis.



Figure S24— Current versus time trace from CPE experiment of 1.25 mM PhBPO under protic (0.6 M PhOH) saturated CO₂ conditions. Conditions: -2.58 V vs Fc⁺/Fc in 0.1 M TBAPF₆/DMF; working and counter electrodes were a graphite rod and the reference was a nonaqueous Ag/AgCI pseudoreference electrode; 0.075 M Fc was used as sacrificial oxidant.



Figure S25— Charge versus time trace from CPE experiment in Figure S24.

Table S4. Results from CPE experiment in **Figure S24**, 1.25mM PhBPO under protic (0.6 M PhOH) saturated CO₂ conditions.

Time (s)	Charge (coulombs)	Moles (e ⁻)	Moles of CO
23243*	9.93	1.03 x 10 ⁻⁴	<loq< td=""></loq<>
23243*	9.93	1.03 x 10 ⁻⁴	<loq< td=""></loq<>
23243*	9.93	1.03 x 10 ⁻⁴	<loq< td=""></loq<>

* indicates a triplicate series of injections carried out upon completion of electrolysis.



Figure S26— Current versus time trace from CPE experiment of rinse test under protic (0.6 M PhOH) saturated CO₂ conditions. Conditions: -2.58 V vs Fc⁺/Fc in 0.1 M TBAPF₆/DMF; working electrode was graphite rod from experiment in **Figure S22** counter electrode was a graphite rod, and the reference was a nonaqueous Ag/AgCl pseudoreference electrode; 0.075 M Fc was used as sacrificial oxidant.



Figure S27— Charge versus time trace from CPE experiment in Figure S26.

Table S5. Results from CPE experiment in Figure S26	, rinse test under protic (0.6 M PhOH)
saturated CO ₂ conditions.	

Time (s)	Charge (coulombs)	Moles (e⁻)	Moles of CO
9645	-0.009	–9.52 x 10 ^{−8}	<loq< td=""></loq<>
14500*	-0.012	−1.25 x 10 ⁻⁷	<loq< td=""></loq<>
14500*	-0.012	−1.25 x 10 ⁻⁷	<loq< td=""></loq<>

* indicates a duplicate series of injections carried out upon completion of electrolysis.

³¹P-NMR

³¹P-NMR spectra were collected on a Varian NMRS 600 MHz instrument using the standard phosphorous method with ¹H NOE decoupling. An internal reference of 80% aqueous phosphoric acid solution was used to reference the collected spectra to 0 ppm.



Figure S28— ³¹P-NMR (243 MHz) of **1** with PhBPO (RM) and PhOH (H-donor) pre-CPE solution from experiment in **Figure S20**.



Figure S29—³¹P-NMR (243 MHz) of **1** with PhBPO (RM) and PhOH (H-donor) post-CPE solution from experiment in **Figure S20**.



Figure S30—³¹P-NMR (243 MHz) spectrum of TBAPF₆ control.



Figure S31—³¹P-NMR (243 MHz) spectrum of PhBPO control.



Figure S32— ³¹P-NMR (243 MHz) spectrum of phenylbenzophosphindole (the precursor to PhBPO) control.

Density Functional Theory (DFT)



Figure S33— Comparison of the geometry of the reduced PhBPO⁻ radical (A) and the spin density distribution (B). H atoms have been omitted for clarity; C = black, P = orange, O = red.



Figure S34— Comparison of the geometry of the reduced PhBPO⁻ radical (A) and the KS orbital of the SOMO (B). H atoms have been omitted for clarity; C = black, P = orange, O = red.



Figure S35— Comparison of the geometry of the key $[Cr(^{tbu}dhbpy)(CO_2H)(PhBPO)]^{2-}$ adduct from the side (A) and top (B), highlighting the poor aromatic overlap. Select H atoms have been omitted for clarity.



Figure S36— Comparison of the geometry of the key proposed rate-determining transition state for C–OH bond cleavage from $[Cr(^{tbu}dhbpy)(CO_2H)(PhBPO)]^{2-}$ •PhOH adduct (A) with the predicted spin density (B). Select H atoms and all tBu groups have been omitted for clarity.



Figure S37— Change in energy determined by DFT methods for all stable configurations as a dihedral angle involving the PPhBPO mediator and Cr center (pink) is rotated in $[Cr(^{tbu}dhbpy)(CO_2H)^{2-} S = 3/2$. Structure shown is the lowest energy configuration.



Figure S38— Change in energy determined by DFT methods for all stable configurations as a dihedral angle involving the PPhBPO mediator and Cr center (pink) is rotated in $[Cr(^{tbu}dhbpy)(CO_2H)^{2-} S = 3/2$. Structure shown is the lowest energy configuration.

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