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Supporting Information

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Novel Reactivity of Side-On (Disulfido)Dicopper Complexes Supported by Bi- and Tridentate N-Donors: Impact of Axial Coordination

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Experimental Details

General Considerations. All solvents and reagents were obtained from commercial sources and used as received unless noted otherwise. The solvents tetrahydrofuran (THF), toluene, pentane, and dichloromethane (CH_2Cl_2) were degassed and passed through a solvent purification system (Glass Contour, Laguna CA) before use. The NMR solvents CD_2Cl_2 and C_6D_6 were dried over CaH_2 and degassed before use. All metal complexes were prepared and stored in a Vacuum Atmospheres inert atmosphere glove box under a dry nitrogen atmosphere or were manipulated using standard inert atmosphere vacuum and Schlenk techniques. The ligands *N,N,N',N'*-tetramethyl-1,3-propanediamine (Me_4pda), 1,4,7-trimethyl-1,4,7-triazacyclononane (Me_3tacn), $Cu(O_3SCF_3)_2$, and $Cu(MeCN)_4PF_6$ were purchased from Aldrich and used as received. Labeled elemental sulfur (^{34}S, 99% enrichment) was purchased from Cambridge Isotope Laboratories, Inc. The complexes $[(Me_4pda)Cu(MeCN)]O_3SCF_3$,[1] $[(Me_4chd)Cu(MeCN)]O_3SCF_3$ (Me_4chd = *N,N,N',N'*-tetramethyl-*trans*-1*R*,2*R*-diaminocyclohexane),[2] $[Cu(MeCN)_4]O_3SCF_3$,[3] sodium disulfide (Na_2S_2),[4] and the anilido-imine [*ortho*-$C_6H_4\{NLi(C_6H_3Me_2)\}(CH{=}NC_6H_3Me_2)$],[5] were synthesized according to published procedures.

Physical Methods. NMR spectra were recorded on a VXR-300, VI-500 or VI-300 spectrometer. Chemical shifts (δ) for ^1H and ^{13}C NMR spectra are reported versus tetramethylsilane and were referenced to residual protium in the deuterated solvent. $^{31}P\{^1H\}$ NMR spectra are referenced to an external H_3PO_4 standard (85%). 1,3,5-Trimethoxybenzene and triphenylphosphate were used as internal standards for peak integration. Mass spectra were obtained on a Bruker Biotof II instrument. UV-vis spectra were recorded on an HP8453 (190-1100 nm) diode array spectrophotometer equipped with a Unisoku low-temperature device. X-band EPR spectra were recorded on a Bruker E-500 spectrometer with an Oxford Instruments EPR-10 liquid helium cryostat (4-20K, 9.61 GHz). Solutions were made anaerobicaly in CH_2Cl_2 (1.0-4.0 mM). Quantitation of EPR signal intensity was accomplished by comparing the integration with that of $[\{(o\text{-}^iPr_2C_6H_3)NC(CH_3)\}_2CHCuCl]$ (1 mM in CH_2Cl_2).[6] Resonance Raman spectra were collected on an Acton AM-506 spectrometer using a Princeton Instruments LN/CCD-11100-PB/UVAR detector and ST-1385 controller interfaced with Winspec software. A Spectra-Physics BeamLok 2065-7S Ar laser provided excitation at 457.9 nm. The spectra were obtained at –196 °C using a backscattering geometry. Samples were frozen in an NMR tube submerged in liquid N_2, or frozen in a copper cup attached to a coldfinger Dewar filled with liquid nitrogen. Raman shifts were externally referenced to liquid indene. FT-IR spectra were recorded using a CaF_2 solution cell (International Crystal Labs) in a ThermoNicolet Avatar 370 spectrometer. Cyclic voltammograms were recorded using Pt working and auxiliary electrodes, a Ag wire / $AgNO_3$ (0.001 M in CH_2Cl_2) reference electrode, and a BAS Epsilon potentiostat connected to a glass cell in an inert-atmosphere glovebox. Experiments were performed on analyte solutions of 1 mM in CH_2Cl_2 with 0.4 M Bu_4NPF_6 (sample volume of ~ 5 mL) at room temperature. The ferrocene/ferrocenium couple was recorded for reference, using the reported value of $E_{1/2}$ = + 0.46 V *vs*. SCE (for 0.1 M Bu_4NPF_6 in CH_2Cl_2).[7] Elemental analyses were performed by Robertson Microlit (Madison, NJ). GC-MS analyses were done by injection of 1μL aliquots into a HP G1800A MSD instrument. Electrical conductivity measurements were performed in CH_2Cl_2 for **1**, **2**, and $(Bu_4N)(O_3SCF_3)$ using a Fischer Scientific Accumet Portable AP65 model conductivity bridge with a cell constant of 1.0 cm^{-1}. The equivalent conductance, Λ_e, was calculated from the conductance measurements and plotted against the square root of the concentration for each sample. Extrapolation of the linear portion to zero concentration resulted in the determination of the equivalent conductance at infinite dilution, Λ_0. A plot of (Λ_0 - Λ_e) vs. the square root of the concentration gave the Onsager plots[8] shown in Figure S7.

X-Ray Crystallography. CCDC-657470 and -657471 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Crystals of an appropriate size were placed onto the tip of a 0.1 mm diameter glass fiber and mounted on either a Siemens or Bruker SMART Platform CCD diffractometer. Data collections were carried out using Mo Kα radiation at 173 K, with a detector distance of ~ 4.9 cm. A randomly oriented region of reciprocal space was surveyed to the extent of one sphere and to a resolution of 0.84 Å. Four major sections of frames were collected with 0.30° steps in ω at 4 different ϕ setting and a detector position of -28° in 2θ. The intensity data were corrected for absorption and decay (SADABS).[9] Final cell constants were calculated from the xyz centroids of strong reflections from the actual data collection after integration (SAINT).[10] The structures were solved by direct methods using SHELXL-97 software.[11] Full-matrix least squares/difference Fourier cycles were performed, which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. Space groups were determined based on systematic absences and intensity statistics. The data collection for $[(Me_3tacn)_2Cu_2(\mu\text{-}S_2)](SbF_6)_2$ (**2**) was carried out with a detector distance of 8.0 cm due to initial frames collection that suggested a long axis presence in the unit cell. A randomly oriented region of reciprocal space was surveyed to the extent of one sphere and to a resolution of 0.84 Å by the collection of five sets of frames at 72° initials in ϕ. In addition, with the detector set at 0°, a 108° ω and 360° ϕ set of frames were collected. However, the specimen was found to be a non-merohedral twin with Cell-now, with the twin law used to treat the data being a rotation of 180° around the b-axis. The structure was solved in the space group P-1, with the final BASF value of 0.306.

$[(Me_4pda)_2Cu_2(\mu\text{-}S_2)](OTf)_2$ (1). The preparation of this compound is described in the Experimental section of the main text. Samples could also be prepared by reaction of $[(Me_4pda)Cu(MeCN)]OTf$ with elemental sulfur in THF but lower yields were usually obtained. A sample of $[(Me_4pda)_2Cu_2(\mu\text{-}^{34}S_2)](OTf)_2$ for characterization by resonance Raman spectroscopy was prepared as follows: $^{34}S_8$ (1.8 mg, 0.05 mmol) was added to a solution of $[(Me_4pda)Cu(MeCN)]OTf$ (20 mg, 0.05 mmol) in THF (5 mL). The reaction was stirred for 2 hours during which time an orange precipitate formed. The precipitate was collected, washed with THF (7 mL) and dried under reduced pressure. The product was dissolved in CH_2Cl_2 (1 mL) for resonance Raman spectroscopy measurements. UV-vis and resonance Raman spectra are shown in Figures S1 and S2, respectively. A cyclic voltammogram of **1** (1 mM in CH_2Cl_2 with 0.4 M Bu_4NPF_6) was recorded at room temperature in an inert-atmosphere glovebox using the ferrocene/ferrocenium couple for reference (Figure S3).

$[(Me_3tacn)Cu(MeCN)](SbF_6)$. A solution of Me_3tacn (73 mg, 0.43 mmol) in THF (2 mL) was added to a solution of $[Cu(MeCN)_4]SbF_6$ (198 mg, 0.43 mmol) in THF (10 mL). The solution was stirred for 30 min and filtered through Celite. The solvent was removed under reduced pressure and the residue washed twice with pentane (2 x 10 mL). The white powder obtained (196 mg, 90%) was analyzed by NMR and ESIMS. ^{1}H NMR (CD_2Cl_2, 300 MHz): δ = 2.72 (s, 9H), 2.69 (m, 12H), 2.21 (s, 3H) ppm; ^{13}C NMR (CD_2Cl_2, 75 MHz): δ = 115.6, 54.5, 48.2, 2.5 ppm; ESI-MS: $[(Me_3tacn)Cu(MeCN)]^+$ calc. m/z 275.1291, found 275.1270. Other salts of $[(Me_3tacn)Cu(MeCN)]^+$ have been reported.[12]

$[(Me_3tacn)_2Cu_2(\mu\text{-}S_2)](SbF_6)_2$ (2). The preparation of this compound is described in the Experimental section of the main text. A sample of $[(Me_3tacn)_2Cu_2(\mu\text{-}^{34}S_2)](SbF_6)_2$ for characterization by resonance Raman spectroscopy was prepared by the same procedure using $^{34}S_8$ (1.4 mg, 0.04 mmol) and $[(Me_3tacn)Cu(MeCN)]SbF_6$ (20 mg, 0.04 mmol) in CH_2Cl_2 (5 mL). UV-vis and resonance Raman spectra are shown in Figures S1 and S2, respectively. A

cyclic voltammogram of **2** (1 mM in CH_2Cl_2 with 0.4 M Bu_4NPF_6) was recorded at room temperature in an inert-atmosphere glovebox using the ferrocene/ferrocenium couple for reference (Figure S3).

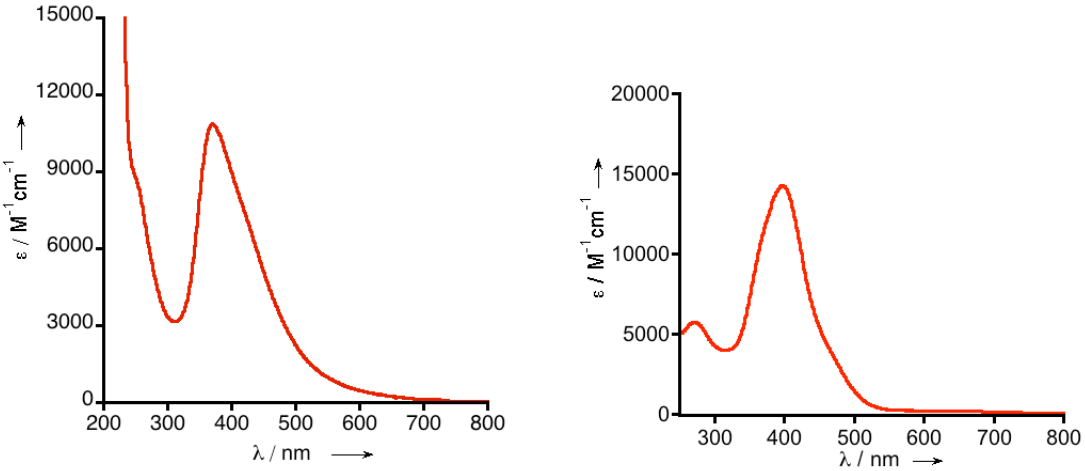


Figure S1. UV/Vis spectra of **1** (left) and **2** (right) in CH_2Cl_2 at 25 °C.

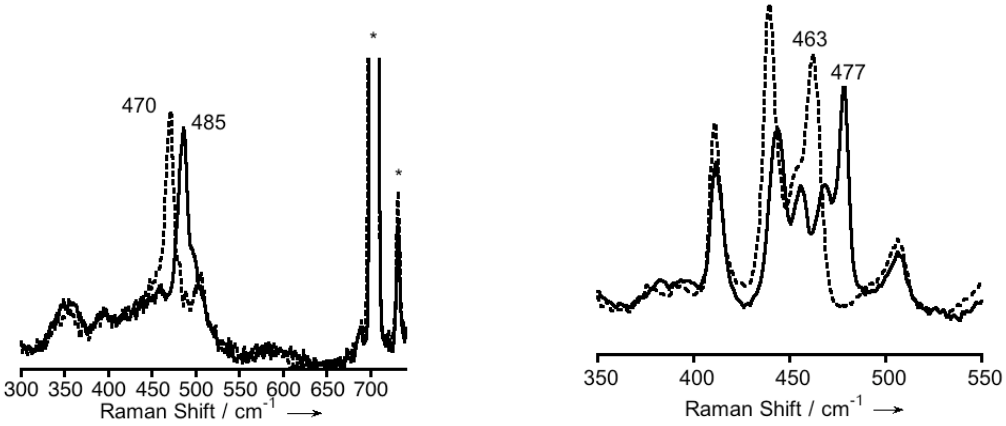
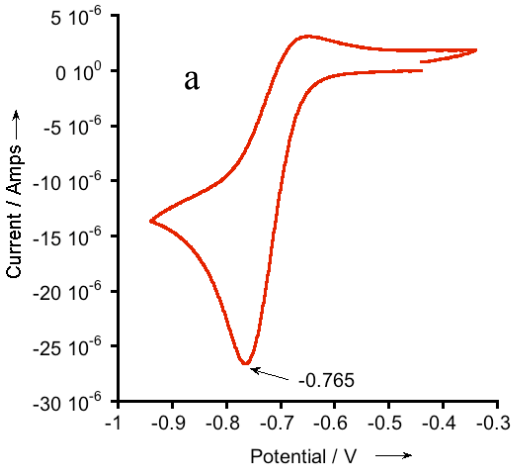


Figure S2. Resonance Raman spectra of **1** (left) and **2** (right) in CH_2Cl_2 at -196 °C, λ_{ex} = 457.9 nm (^{32}S, solid line; ^{34}S, dashed line). Asterisks denote solvent peaks.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Current / Amps
Potential / V
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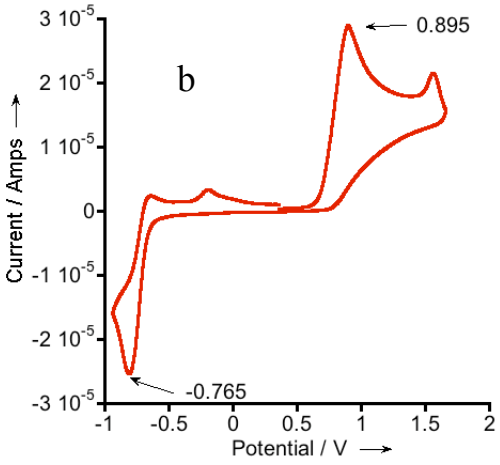
b
Current / Amps
Potential / V
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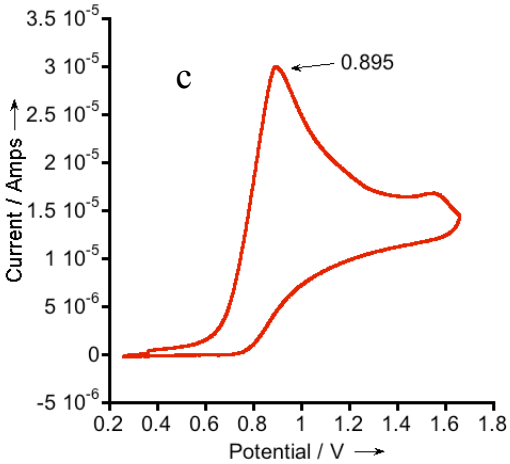
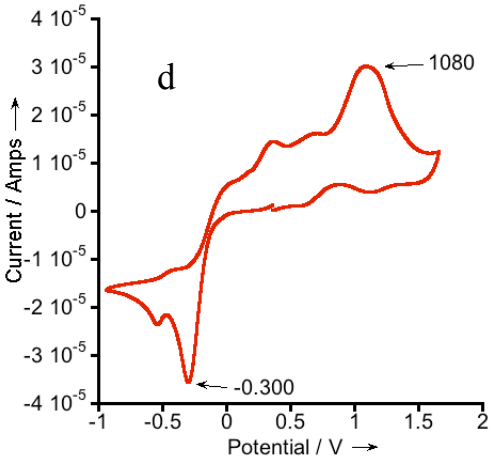
-0.765


c
Current / Amps
Potential / V
0.895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Current / Amps
Potential / V
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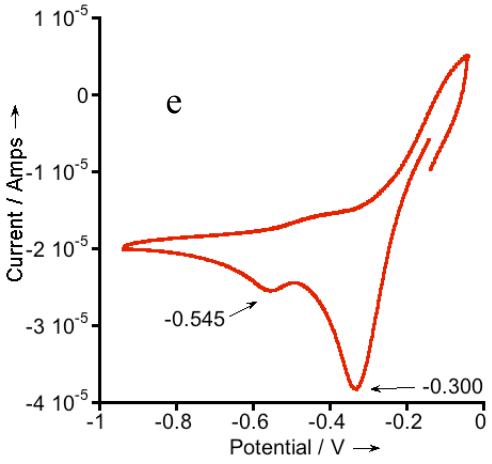
-0.300


e
Current / Amps
Potential / V
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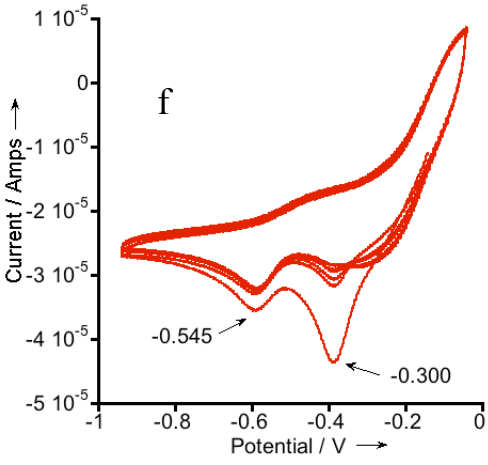
-0.300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Current / Amps
Potential / V
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-0.300

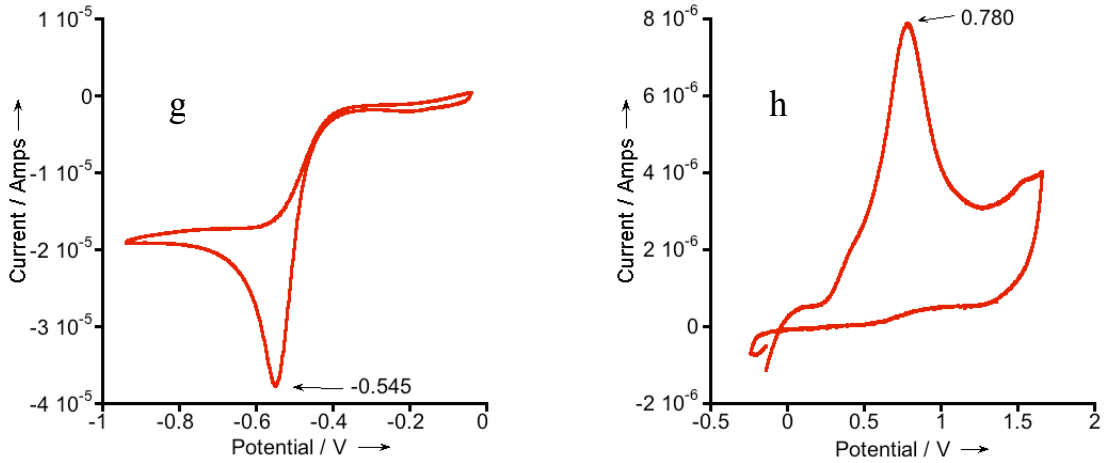

Figure S3. Cyclic voltammograms of **1** and **2**. Conditions: 1 mM in CH_2Cl_2 with 0.4 M Bu_4NPF_6, using the ferrocene/ferrocenium couple for reference, scan rate = 100 mV/s. Figures a, b and c show the cyclic voltammograms obtained for compound **2** at different starting potentials. An irreversible reduction wave occurred at −765 mV and an irreversible oxidation wave at 895 mV. In the case of compound **1**, the cyclic voltammograms are more complex (Figures d-h). Two reduction waves are seen at −545 and −300 mV (Figures d-f), with the intensity of the former increasing and the latter decreasing upon repeated scans (f) or upon standing (g). Similarly, an oxidation wave at +1080 mV decreases as one at +780 mV increases upon repeated scans or standing (d, h). We attribute this reproducible behavior (multiple runs) to compound **1** (E_{red} = −300 and E_{ox} = +1080 mV) which decomposes under the conditions of the electrochemistry experiments to some other species (E_{red} = −545 and E_{ox} = +780 mV).

Reactivity of 1. **(a) Triphenylphosphine:** Two equivalents of triphenylphosphine (7.0 mg, 0.027 mmol) dissolved in CD_2Cl_2 (1 mL) were added slowly to a solution of **1** (10.0 mg, 0.013 mmol) in CD_2Cl_2 (1 mL). The solution bleached immediately, and after stirring for 15 min it was analyzed by NMR spectroscopy, which showed quantitative formation of [(Me$_4$pda)Cu]OTf and S=PPh$_3$. ^{1}H NMR (CD_2Cl_2, 300 MHz): δ = 7.40-7.80 (m, 30H), 2.68 [t (J = 5.7 Hz), 8H], 2.00-2.50 (2s, 24H), 1.73 [t, (J = 5.7 Hz), 4H] ppm; ^{31}P{^{1}H} NMR (CD_2Cl_2, 121.373 MHz): δ = 42.65 ppm. Reaction of **1** with 4 equivalents of triphenylphosphine was performed by the same procedure and analyzed by NMR and ESIMS, which revealed the presence of a 1:1 mixture of [(Me$_4$pda)CuPPh$_3$]OTf and S=PPh$_3$ in quantitative yields. ^{1}H NMR (CD_2Cl_2, 300 MHz): δ = 7.10-7.80 (m, 60H), 2.62 [t, (J = 6.0 Hz), 8H], 2.33 (s, 24H), 1.71 [t, (J = 6.0 Hz), 4H] ppm; ^{31}P{^{1}H} NMR (CD_2Cl_2, 121.373 MHz): δ = 43.53, 0.45 ppm; ESIMS: calcd for [(Me$_4$pda)CuPPh$_3$]$^+$: m/z 455.1672; found: 455.1680. The identity of [(Me$_4$pda)CuPPh$_3$]OTf was confirmed by comparison of the spectroscopic and MS data to those of independently synthesized material: One equivalent of triphenylphosphine (6.3 mg, 0.024 mmol) dissolved in CD_2Cl_2 (1 mL) was added to a solution of [(Me$_4$pda)Cu(MeCN)]OTf (9.2 mg, 0.024 mmol) in CD_2Cl_2 (1 mL). The mixture was stirred for 15 min and then analyzed by NMR and ESIMS (quantitative yields). ^{1}H NMR (CD_2Cl_2, 300 MHz): δ = 7.20-7.60 (m, 15H), 2.66 [t, (J = 6.0 Hz), 4H], 2.33 (s, 12H), 1.99 (s, 3H), 1.71 [t, (J = 6.0 Hz), 2H] ppm; ^{31}P{^{1}H} NMR (CD_2Cl_2, 121.373 MHz): δ = 0.50 ppm; ESIMS: calcd for [(Me$_4$pda)CuPPh$_3$]$^+$: m/z 455.1672; found: 455.1677.

(b) 2,6-dimethylphenylisocyanide: Two equivalents of 2,6-dimethylphenylisocyanide (6.2 mg, 0.047 mmol) dissolved in CD_2Cl_2 (1 mL) were added slowly to a solution of **1** (17.6 mg, 0.023 mmol) in CD_2Cl_2 (1 mL). The bleached solution was stirred for 15 min and then

analyzed by NMR and ESIMS (quantitative yields). ^{1}H NMR (CD_2Cl_2, 300 MHz): δ = 7.28 [t, (J = 7.8 Hz), 2H], 7.16 [d, (J = 7.8 Hz), 4H], 2.66 [t, (J = 5.1 Hz), 8H], 2.57 (s, 24H), 2.41 (s, 12H), 1.77 [t, (J = 5.1 Hz), 4H] ppm; ESIMS: calcd for $[(Me_4pda)Cu(2,6\text{-}Me_2C_6H_3NC)]^+$: m/z 324.1496; found: 324.1503. To confirm the formation of $[(Me_4pda)Cu(2,6\text{-}Me_2C_6H_3NC)]OTf$, it was prepared and characterized independently: One equivalent of 2,6-dimethylphenylisocyanide (5.8 mg, 0.045 mmol) dissolved in CD_2Cl_2 (1 mL) was added to a solution of $[(Me_4pda)Cu(MeCN)](OTf)$ (17.1 mg, 0.045 mmol) in CD_2Cl_2 (1 mL). The mixture was stirred for 15 min and then analyzed by NMR and ESIMS (quantitative yields). ^{1}H NMR (CD_2Cl_2, 300 MHz): δ = 7.29 [t, (J = 7.8 Hz), 1H], 7.16 [d, (J = 7.8 Hz), 2H], 2.66 [t, (J = 5.1 Hz), 4H], 2.56 (s, 12H), 2.42 (s, 6H), 2.01 (s, 3H), 1.77 [t, (J = 5.1 Hz), 2H] ppm; ESIMS: calcd for $[(Me_4pda)Cu(2,6\text{-}Me_2C_6H_3NC)]^+$: m/z 324.1496; found: 324.1438.

(c) Carbon monoxide: 1 (6.0 mg, 0.008 mmol), dissolved in CD_2Cl_2 (1 mL) under inert atmosphere, was reacted with carbon monoxide (1 atm) at room temperature for 15 min. The bleached solution was then analyzed by NMR and FT-IR (CH_2Cl_2 solution), which indicated quantitative formation of $[(Me_4pda)CuCO]OTf$. ^{1}H NMR (CD_2Cl_2, 300 MHz): δ = 2.59 [t, (J = 5.4 Hz), 4H], 2.55 (s, 12H), 1.71 [t, (J = 5.4 Hz), 2H] ppm; FT-IR (CH_2Cl_2): ν_{co} = 2095 cm^{-1}. To confirm the formation of $[(Me_4pda)CuCO]OTf$, it was independently prepared: $[(Me_4pda)Cu(MeCN)](OTf)$ (6.0 mg, 0.016 mmol), dissolved in CD_2Cl_2 (1 mL) under inert atmosphere, was reacted with carbon monoxide (1 atm) at room temperature for 15 min. The bleached solution was then analyzed by NMR (quantitative yields). ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 2.59 [t, (J = 5.4 Hz), 4H], 2.55 (s, 12H), 1.99 (s, 3H), 1.71 [t, (J = 5.4 Hz), 2H] ppm.

(d) 9,10-Dihydroanthracene, THF, aniline, and benzyl bromide: Two to four equivalents of substrate dissolved in CD_2Cl_2 were added to one equivalent of a solution of **1** in CD_2Cl_2. The reaction mixtures were stirred for 2 – 4 hours at room temperature, filtered through Celite and analyzed by NMR spectroscopy. No reaction was observed in all cases. In addition, no reaction was observed when two equivalents of 9,10-dihydroanthracene were reacted with one equivalent of **1** in CH_2ClCH_2Cl at 70 °C for 2 hours (NMR).

(e) $[(Me_3tacn)Cu(MeCN)](SbF_6)$. Two equivalents of $[(Me_3tacn)Cu(MeCN)](SbF_6)$ (13.7 mg, 0.027 mmol) dissolved in CH_2Cl_2 (2 mL) was added to a solution of **1** (10.0 mg, 0.013 mmol) in CH_2Cl_2 (10 mL) at –20 °C. The reaction mixture was stirred for 30 min, filtered through Celite, and the filtrate was removed under reduced pressure. Analysis of the crude product by NMR and UV/Vis spectroscopy indicated clean formation of **2** (> 95% yield based on NMR). The reaction stochiometry was confirmed by a UV-vis spectrophotometric titration; maximum intensity of the 397 nm peak was obtained upon addition of 2 equivalents of $[(Me_3tacn)Cu(MeCN)](SbF_6)$.

(f) Anilido-imine ligand salt: Two equivalents of the lithium salt of *ortho*-$C_6H_4\{NLi(C_6H_3Me_2)\}(CH{=}NC_6H_3Me_2)$ (35 mg, 0.105 mmol) dissolved in THF (1 mL) were added to a solution of **1** (38.7 mg, 0.052 mmol) in CH_2Cl_2 (10 mL) and stirred for 1 hour. The solvent was removed under reduced pressure and the residue washed with pentane (2 x 10 mL). Comparison of the NMR and UV/Vis spectra for the resulting green compound to literature data revealed it to be **3** (>95% yield).[13] In addition, slow diffusion of pentane at -20 °C into the toluene solution result in formation of dark green block crystals of **3** as confirmed by X-ray crystallography (data not provided).

(g) $[(Me_4chd)Cu(MeCN)]OTf$: One equivalent of $[(Me_4chd)Cu(MeCN)]OTf$ (11.0 mg, 0.026 mmol) dissolved in CH_2Cl_2 (2 mL) was added to **1** (19.4 mg, 0.026 mmol) solution in CH_2Cl_2. The green reaction mixture was stirred for 30 min, filtered through Celite, and the filtrate was concentrated under reduced pressure to ~ 2 mL. Slow diffusion of pentane at -20 °C into the CH_2Cl_2 solution result in formation of dark green block crystals, identified as $[(Me_4chd)_3Cu_3(\mu\text{-}S)_2](CF_3SO_3)_3$ (**4**) by X-ray crystallography,[14] and a brown powder

(unidentified). A UV-Vis spectrophotometric titration indicated the stoichiometry of the reaction. Thus, up to 5 equivalents of [(Me_4chd)Cu(MeCN)]OTf (0.71 mg, 0.167 μmol) dissolved in CH_2Cl_2 (0.5 mL, 3.33 mM) were injected by syringe into a stirred anaerobic CH_2Cl_2 (2.0 mL, 0.167 mM) solution of **1** (0.25 mg, 0.33 μmol) placed in a UV/Vis cuvette at -20 °C. The yield of the reaction (> 95%) was determined by following the growth of the feature at 610 nm associated with the $[(Me_4chd)_3Cu_3(\mu\text{-}S)_2]^{3+}$ cluster formation[14,15] after the addition of 3 equivalents [(Me_4chd)Cu(MeCN)]OTf (no additional growth in the 610 nm peak intensity was recorded beyond the addition of 3 equivalents, Figure S4).

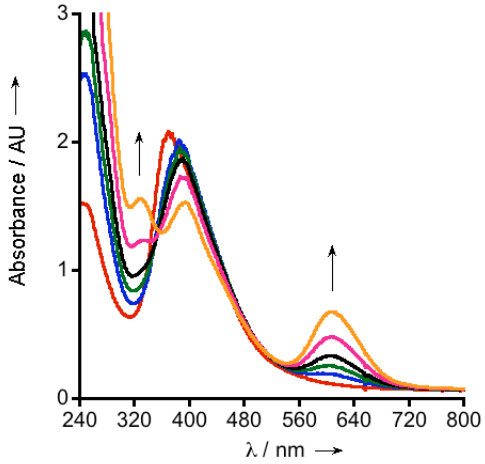

Figure S4. UV/Vis spectra obtained during the reaction of **1** (red line) in CH_2Cl_2 (2.0 mL, 0.167 mM) with up to 3 equivalents of [(Me_4chd)Cu(MeCN)]OTf (orange line) in CH_2Cl_2 (0.5 mL, 3.33 mM) at -20 °C. No further changes in the spectra were observed upon addition of further amounts of [(Me_4chd)Cu(MeCN)]OTf.

(h) 3,5-Di-*tert*-butyl catechol: One equivalent of 3,5-di-*tert*-butyl catechol (2.5 mg, 0.011 mmol) dissolved in CD_2Cl_2 (1 mL) was added to **1** (8.5 mg, 0.011 mmol). The mixture was stirred for 15 min, filtered through Celite, and then analyzed by ^{1}H NMR spectroscopy, GC-MS and ESIMS, which indicated stochiometric formation of 3,5-Di-*tert*-butyl-1,2-benzoquinone. When two equivalents of 3,5-di-*tert*-butyl catechol were added to **1** under the same conditions formation of one equivalent of 3,5-di-*tert*-butyl-1,2- benzoquinone and one equivalent of unreacted 3,5-di-*tert*-butyl catechol was observed (^{1}H NMR).

(i) 3,5-Di-*tert*-butyl catecholate disodium salt: One equivalent of 3,5-di-*tert*-butyl catecholate disodium salt (5.4 mg, 0.020 mmol) dissolved in CH_2Cl_2 (3 mL) was added to a solution of **1** (15.3 mg, 0.020 mmol) in CH_2Cl_2 (4 mL). The mixture was stirred for 15 min and then quenched by the addition of 0.5 M aqueous H_2SO_4 solution (2 mL). The reaction mixture was stirred for another 15 min and extracted with CH_2Cl_2 (3 x 10 mL). The organic fractions were combined, dried over Na_2SO_4, and filtered through Celite. The solvent was removed under reduced pressure, and the residue was analyzed by ^{1}H NMR spectroscopy, GC-MS and ESIMS. Stoichiometric formation of 3,5-di-*tert*-butyl-1,2-benzoquinone was observed. When two equivalents of 3,5-di-*tert*-butyl catecholate disodium salt were used under the same conditions one equivalent of 3,5-di-*tert*-butyl-1,2-benzoquinone and one equivalent of 3,5-di-*tert*-butyl catechol were observed (NMR).

(j) *tert*-Butylhydroquinone: One equivalent of *tert*-butylhydroquinone (2.2 mg, 0.013 mmol) dissolved in CD_2Cl_2 (1 mL) was added to $[Cu_2(\mu\text{-}S_2)(Me_4pda)_2](OTf)_2$ (10 mg, 0.013 mmol). The mixture was stirred for 15 min, filtered through a plug of neutral alumina, and then analyzed by ^{1}H NMR spectroscopy and GC-MS. 2-*tert*-butyl-1,4-benzoquinone obtained stochiometrically. One equivalent of 2-*tert*-butyl-1,4-benzoquinone was analyzed by ^{1}H NMR spectroscopy when two equivalents of *tert*-butylhydroquinone were added to $[Cu_2(\mu\text{-}S_2)(Me_4pda)_2](OTf)_2$ under the same reaction procedure.

(k) 2,4-Di-*tert*-butyl phenol: Two equivalents of 2,4-di-*tert*-butyl phenol (4.6 mg, 0.022 mmol) dissolved in CH_2Cl_2 (3 mL) were added to a solution of **1** (8.4 mg, 0.011 mmol) in CH_2Cl_2 (4 mL). The mixture was stirred for 15 min and then quenched by the addition of 0.5 M aqueous H_2SO_4 solution (2 mL). The reaction mixture was stirred for another 15 min and extracted with CH_2Cl_2 (3 x 10 mL). The organic fractions were combined, dried over Na_2SO_4, and filtered through Celite. The solvent was removed under reduced pressure, and the residue was analyzed by ^{1}H NMR spectroscopy (Figure S5), GC-MS and ESIMS. The ^{1}H NMR spectrum showed a formation of 0.43 equivalent of 2,2'-thiobis(4,6-di-*tert*-butylphenol),[16,17] 0.29 equivalent of 3,3',5,5'-tetra-*tert*-butyl-(1,1'-biphenyl)-2,2'-diol and 0.59 equivalent of unreacted 2,4-di-*tert*-butyl phenol. The conversion of 2,4-di-*tert*-butyl phenol to products was 72 % (based on NMR). Reaction of **1** with 4 equivalents 2,4-di-*tert*-butyl phenol formed 0.46 equivalent of 2,2'-thiobis(4,6-di-*tert*-butylphenol), 0.46 equivalent of 3,3',5,5'-tetra-*tert*-butyl-(1,1'-biphenyl)-2,2'-diol and 2.16 equivalent of unreacted 2,4-di-*tert*-butyl phenol. The conversion (based on NMR) of 2,4-di-*tert*-butyl phenol to products was 46% (50% is the theoretical maximum yield in this reaction).

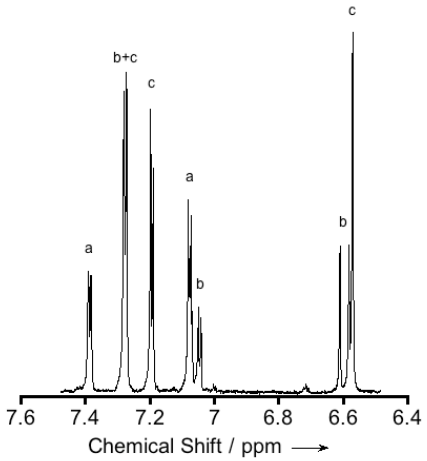

Figure S5. The ^{1}H NMR spectra (only the aromatic region is shown for simplification) obtained for the crude reaction mixture of **1** with 2 equivalents 2,4-di-*tert*-butyl phenol in CD_2Cl_2. The reaction products are all assigned: 2,2'-thiobis(4,6-di-*tert*-butylphenol) (c), 3,3',5,5'-tetra-*tert*-butyl-(1,1'-biphenyl)-2,2'-diol (a), and 2,4-di-*tert*-butyl phenol (b).

(l) 2,4-Di-*tert*-butyl phenolate disodium salt: Two equivalents of 2,4-di-*tert*-butyl phenolate disodium salt (4.8 mg, 0.021 mmol) dissolved in 3 mL CH_2Cl_2:THF mixture (2:1), were added to a solution of **1** (7.9 mg, 0.011 mmol) in CH_2Cl_2 (4 mL). The mixture was stirred for 15 min and then quenched by the addition of 0.5 M aqueous H_2SO_4 solution (2 mL). The reaction mixture was stirred for another 15 min and extracted with CH_2Cl_2 (3 x 10 mL). The

organic fractions were combined, dried over Na_2SO_4, and filtered through Celite. The solvent was removed under reduced pressure, and the residue was analyzed by ^1H NMR spectroscopy, GC-MS and ESIMS. The ^1H NMR spectrum showed formation of 0.63 equivalent of 2,2'-thiobis(4,6-di-*tert*-butylphenol), 0.25 equivalent of 3,3',5,5'-tetra-*tert*-butyl-(1,1'-biphenyl)-2,2'-diol and 0.25 equivalent of unreacted 2,4-di-*tert*-butyl phenol. The conversion of 2,4-di-*tert*-butyl phenolate disodium salt to products was 88% (based on NMR). Reaction of **1** with 4 equivalents 2,4-di-*tert*-butyl phenolate disodium salt formed 0.60 equivalent of 2,2'-thiobis(4,6-di-*tert*-butylphenol), 0.40 equivalent of 3,3',5,5'-tetra-*tert*-butyl-(1,1'-biphenyl)-2,2'-diol and 2.00 equivalent of unreacted 2,4-di-*tert*-butyl phenol. The conversion (based on NMR) of 2,4-di-*tert*-butyl phenolate disodium salt to products was 50% (the theoretical maximum yield in this reaction).

(m) 4-methylbenzenethiol: Two equivalents of 4-methylbenzenethiol (2.4 mg, 0.019 mmol) dissolved in CD_2Cl_2 (1 mL) was added to **1** (7.2 mg, 0.010 mmol). The reaction mixture was stirred for 15 min, filtered through Celite, and then analyzed by ^1H NMR spectroscopy, which indicated stoichiometric formation of (*p*-tolyl)disulfide.

(n) 4-methylbenzenethiolate sodium salt: Four equivalents of 4-methylbenzenethiolate sodium salt (8.1 mg, 0.055 mmol) were added to a solution of **1** (10.4 mg, 0.014 mmol) in CH_2Cl_2 (4 mL). The mixture was stirred for 15 min and then quenched by the addition of 0.5 M aqueous H_2SO_4 solution (2 mL). The reaction mixture was stirred for another 15 min and extracted with CH_2Cl_2 (3 x 10 mL). The organic fractions were combined, dried over Na_2SO_4, and filtered through Celite. The solvent was removed under reduced pressure, and the residue was analyzed by ^1H NMR spectroscopy, which showed the formation of one equivalent of (*p*-tolyl)disulfide.

(o) 2,4,6-Tri-*tert*-butyl phenol: Two equivalents of 2,4,6-tri-*tert*-butyl phenol (14.0 mg, 0.053 mmol) were dissolved in CH_2Cl_2 (3 mL), and added to a solution of **1** (20.0 mg, 0.027 mmol) in CH_2Cl_2 (4 mL). The mixture was stirred for 2 hours, filtered through Celite, and the filtrate was concentrated under reduced pressure to ~ 2 mL. The blue supernatant solution was analyzed by UV/Vis and X-band EPR, which confirmed formation of 2,4,6-tri-*tert*-butyl phenoxyl radical (Figure S6).[18] The conversion of 2,4,6-tri-*tert*-butyl phenol to 2,4,6-tri-*tert*-butyl phenoxyl radical based on the UV/Vis data is ~85 %.

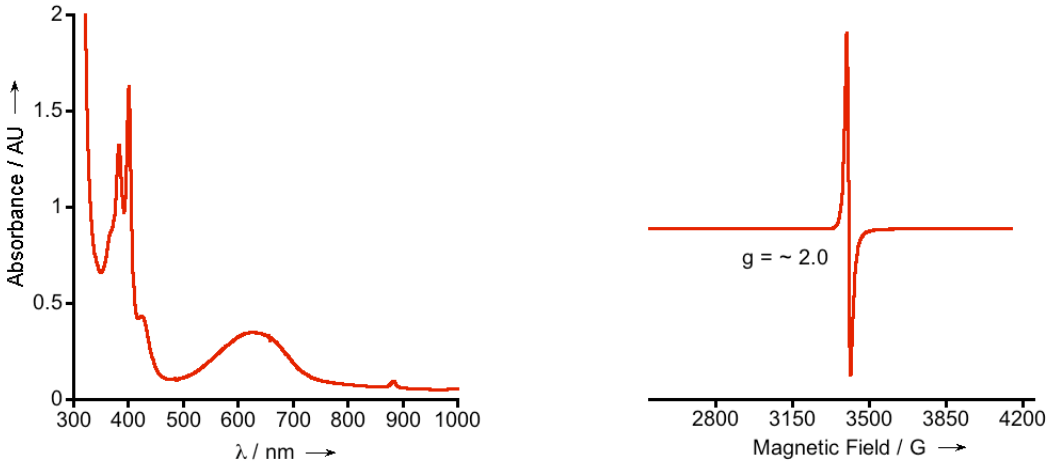

Figure S6. (Left) UV/Vis spectrum obtained from the reaction of **1** with 2,4,6-tri-*tert*-butyl phenol recorded at room temperature. (Right) X-band EPR spectrum obtained from the reaction of **1** with 2,4,6-tri-*tert*-butyl phenol in CH_2Cl_2, recorded at 5K.

(p) 2,4,6-Tri-*tert*-butyl phenolate sodium salt: Two equivalents of 2,4,6-tri-*tert*-butyl phenolate sodium salt (7.6 mg, 0.027 mmol) dissolved in CH_2Cl_2 (3 mL) were added to a solution of **1** (10.0 mg, 0.013 mmol) in CH_2Cl_2 (4 mL). The mixture was stirred for 15 min, filtered through Celite, and the blue filtrate was analyzed by UV/Vis and EPR, which confirmed the formation of 2,4,6-tri-*tert*-butyl phenoxyl radical. The conversion of 2,4,6-tri-*tert*-butyl phenol to 2,4,6-tri-*tert*-butyl phenoxyl radical based on the UV/Vis data was > 95 %.

(q) 2,6-Di-*tert*-butyl phenol: Two equivalents of 2,6-di-*tert*-butyl phenol (6.1 mg, 0.029 mmol) dissolved in CD_2Cl_2 (1 mL) was added to **1** (11.0 mg, 0.015 mmol). The mixture was stirred for 3 hours, filtered through Celite, and then analyzed by ^{1}H NMR spectroscopy, GC-MS and ESIMS. The data indicated formation of a half equivalent of 3,3',5,5'-tetra-*t*-butyldiphenoquinone and one equivalent of unreacted 2,6-di-*tert*-butyl phenol (half equivalent of coupled product is the maximum theoretical yield for a $2e^-$ and $2H^+$ process).

(r) 2,6-Di-*tert*-butyl phenolate sodium salt: Two equivalents of 2,6-di-*tert*-butyl phenolate sodium salt (12.1 mg, 0.053 mmol) dissolved in THF (3 mL) was added to a solution of **1** (19.8 mg, 0.026 mmol) in CH_2Cl_2 (4 mL) . The mixture was stirred for 15 min and then quenched by the addition of 0.5 M aqueous H_2SO_4 (2 mL). The reaction mixture was stirred for another 15 min and extracted with CH_2Cl_2 (3 x 10 mL). The organic fractions were combined, dried over Na_2SO_4, and filtered through Celite. The solvent was removed under reduced pressure, and the residue was analyzed by ^{1}H NMR spectroscopy, GC-MS and ESIMS. The data indicated formation of a half equivalent of 3,3',5,5'-tetra-*t*-butyldiphenoquinone and one equivalent of unreacted 2,6-di-*tert*-butyl phenol.

(s) (Et_3NH)(BPh_4): Two equivalents of (Et_3NH)(BPh_4) were dissolved in CH_2Cl_2 or THF (2 mL) and added slowly to one equivalent **1** in CH_2Cl_2 (3 mL). The bleached reaction mixture was stirred for 15 min, filtered through Celite, and the solvent was removed under reduced pressure. The crude reaction mixture was analyzed by NMR, which revealed formation of Me_4pdaH^+. ^{1}H NMR (CD_2Cl_2, 300 MHz): δ = 9.35 (s, 2H), 7.20 – 7.65 (m, 30H), 2.86 [q, (J = 7.2 Hz), 12H], 2.50 [t, (J = 6.6 Hz), 8H], 2.35 (s, 24H), 1.69 [m, J = 6.6 Hz), 4H], 1.90 [t, (J = 7.2 Hz), 18H] ppm. The reaction profile also was followed by a UV/Vis titration experiment: 2 equivalents of the acid, dissolved in CH_2Cl_2 (0.5 mL, 1.2 mM) were injected by syringe in portions into a stirred anaerobic solution of **1** (0.25 mg, 0.33 μmol) in CH_2Cl_2 (2 mL, 0.167 mM) placed in a UV/Vis cuvette at -20 °C. Bleaching of the 370 nm band was observed to be complete upon addition of 2 equivalents of the acid.

Reactivity of 2. **(a) Triphenylphosphine:** Two equivalents of triphenylphosphine (5.1 mg, 0.019 mmol) dissolved in CD_2Cl_2 (1 mL) were added slowly to **2** (9.8 mg, 0.010 mmol) solution in CD_2Cl_2 (1 mL). The orange solution was stirred for 15 min and then analyzed by ^{1}H and ^{31}P NMR spectroscopy and ESI-MS, which indicated the formation of one equivalent of [(Me_3tacn)$CuPPh_3$]SbF_6 and S=PPh_3, along with 0.5 equivalent of unreacted **2**. ^{1}H NMR (CD_2Cl_2, 300 MHz): δ = 7.20-7.80 (m, 30H), 2.95 (s, 12H), 2.83 (s, 9H), 2.82 (s, 12H), 2.53 (s, 9H) ppm; ^{31}P{^{1}H} NMR (CD_2Cl_2, 121.373 MHz): δ = 43.56 (1P), 8.1 (broad, 1P) ppm; ESIMS: calcd for [(Me_3tacn)$CuP(Ph)_3$]$^+$: m/z 496.1937; found: 496.1985, calcd for [(Me_3tacn)$_2Cu_2$(μ-S_2)](SbF_6)$^+$: m/z 767.0441; found: 767.0417. Reaction of **2** using 4 equivalents of triphenylphosphine was performed by the same procedure and analyzed by ^{1}H and ^{31}P NMR spectroscopy, which indicated the formation of two equivalents of [(Me_3tacn)$CuPPh_3$]SbF_6 and two equivalents of S=PPh_3. ^{1}H NMR (CD_2Cl_2, 300 MHz): δ = 7.20-7.80 (m, 60H), 2.82 (s, 24H), 2.53 (s, 18H) ppm; ^{31}P{^{1}H} NMR (CD_2Cl_2, 121.373 MHz): δ = 43.56 (2P), 8.1 (broad, 2P) ppm.

To confirm the identity of $[(Me_3tacn)CuPPh_3]SbF_6$, it was prepared independently: One equivalent of triphenylphosphine (8.4 mg, 0.032 mmol) dissolved in CD_2Cl_2 (1 mL) was added to a solution of $[(Me_3tacn)Cu(MeCN)]SbF_6$ (16.3 mg, 0.032 mmol) in CD_2Cl_2 (1 mL). The mixture was stirred for 15 min and then analyzed by ^1H and ^{31}P NMR spectroscopy and ESIMS. ^1H NMR (CD_2Cl_2, 300 MHz): δ = 7.20-7.60 (m, 15H), 2.82 (s, 12H), 2.53 (s, 9H), 1.97 (s, 3H) ppm; $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121.373 MHz): δ = 8.1 (broad) ppm; ESIMS: calcd for $[(Me_3tacn)CuP(Ph)_3]^+$: m/z 496.1937; found: 496.1976.

(b) 2,6-Dimethylphenylisocyanide: Two equivalents of 2,6-dimethylphenylisocyanide (5.0 mg, 0.038 mmol) dissolved in CD_2Cl_2 (1 mL) were added slowly to a solution of **2** (19.2 mg, 0.019 mmol) in CD_2Cl_2 (1 mL). The bleached solution was stirred for 15 min and then analyzed by NMR, ESIMS and FT-IR (quantitative yields). ^1H NMR (CD_2Cl_2, 300 MHz): δ = 7.27 [t, (J = 7.8 Hz), 2H], 7.16 [d, (J = 7.8 Hz), 4H], 2.84 (s, 18H), 2.80 (m, 24H), 2.38 (s, 12H) ppm; ESIMS: calcd for $[(Me_3tacn)Cu(2,6\text{-}Me_2C_6H_3NC)]^+$: m/z 365.1761; found: 365.1771; FT-IR (CH_2Cl_2): ν_{NC} = 2139 cm^{-1} (Figure S1). To confirm the formation of $[(Me_3tacn)Cu(2,6\text{-}Me_2C_6H_3NC)]SbF_6$, it was synthesized and characterized independently: One equivalent of 2,6-dimethylphenylisocyanide (4.31 mg, 0.033 mmol) dissolved in CD_2Cl_2 (1 mL) was added to $[(Me_3tacn)Cu(MeCN)](SbF_6)$ (16.8 mg, 0.033 mmol) solution in CD_2Cl_2 (1 mL). The mixture was stirred for 15 min and then analyzed by NMR, ESIMS and FT-IR (quantitative yields). ^1H NMR (CD_2Cl_2, 300 MHz): δ = 7.27 [t, (J = 7.8 Hz), 1H], 7.16 [d, (J = 7.8 Hz), 2H], 2.84 (s, 9H), 2.80 (m, 12H), 2.38 (s, 6H), 1.97 (s, 3H) ppm; ESIMS: calcd for $[(Me_3tacn)Cu(2,6\text{-}Me_2C_6H_3NC)]^+$: m/z 365.1761; found: 365.1793; FT-IR (CH_2Cl_2): ν_{NC} = 2139 cm^{-1}.

(c) Carbon monoxide: Complex **2** (10.0 mg, 0.010 mmol), dissolved in CD_2Cl_2 (1 mL) under an inert atmosphere, was reacted with carbon monoxide (1 atm) at room temperature for 25 min. The bleached solution was than analyzed by NMR, ESIMS and FT-IR (quantitative yields). ^1H NMR (CD_2Cl_2, 300 MHz): δ = 2.88 (s, 24H), 2.85 (m, 18H) ppm; ESIMS: calcd for $[(Me_3tacn)Cu(CO)]^+$: m/z 262.0975; found: 262.1025; FT-IR (CH_2Cl_2): ν_{co} = 2091 cm^{-1}.[19] To confirm the formation of $[(Me_3tacn)Cu(CO)]SbF_6$, it was synthesized independently: $[(Me_3tacn)Cu(MeCN)](SbF_6)$ (8.0 mg, 0.016 mmol), dissolved in CD_2Cl_2 (1 mL) under inert atmosphere, was reacted with carbon monoxide (1 atm) at room temperature for 15 min. The solution was analyzed by NMR, ESIMS and FT-IR (quantitative yields). ^1H NMR (CD_2Cl_2, 300 MHz): δ = 2.88 (s, 12H), 2.85 (m, 9H), 1.97 (s, 3H) ppm; ESIMS: calcd for $[(Me_3tacn)Cu(CO)]^+$: m/z 262.0975; found: 262.1059; FT-IR (CH_2Cl_2): ν_{co} = 2091 cm^{-1}.

(d) 3,5-Di-*tert*-butyl catechol: Two equivalents of 3,5-di-*tert*-butyl catechol (2.0 mg, 0.009 mmol) dissolved in CD_2Cl_2 (1 mL) were added to **2** (4.3 mg, 0.004 mmol). The mixture was stirred for 20 hours, filtered through Celite, and then analyzed by ^1H NMR spectroscopy, which indicated that no reaction had occurred.

(e) 3,5-Di-*tert*-butyl catecholate disodium salt: Two equivalents of 3,5-di-*tert*-butyl catecholate disodium salt (1.8 mg, 6.77 μmol) dissolved in CH_2Cl_2 (2 mL) were added to a solution of **2** (3.4 mg, 3.38 μmol) in CH_2Cl_2 (10 mL). The mixture was stirred for 2 hours and then quenched by the addition of 0.5 M aqueous H_2SO_4 solution (2 mL). The reaction mixture was stirred for another 15 min and extracted with CH_2Cl_2 (3 x 10 mL). The organic fractions were combined, dried over Na_2SO_4, and filtered through Celite. The solvent was removed under reduced pressure, and the residue was analyzed by ^1H NMR spectroscopy, which indicated complete recovery of 3,5-di-*tert*-butyl catechol.

(f) $(Et_3NH)(BPh_4)$: 2 equivalents of $(Et_3NH)(BPh_4)$, dissolved in THF (0.5 mL, 1.4 mM) were gradually injected by syringe into a stirred anaerobic solution of solution of **2** (0.34 mg, 0.34 μmol) in CH_2Cl_2 placed in a UV/Vis cuvette at room temperature. The peak at 397 nm changed its intensity as expected upon dilution, but no additional spectral changes were recorded after stirring the solution for 1 hour at room temperature (no discernable reaction).

(g) Benzyl bromide: Two equivalents of benzyl bromide (2.6 mg, 0.015 mmol) dissolved in CD_2Cl_2 (1 mL) was added to **2** (7.7 mg, 0.008 mmol). The mixture was stirred for 1 hour and analyzed by ^1H NMR spectroscopy, which confirmed that no reaction took place.

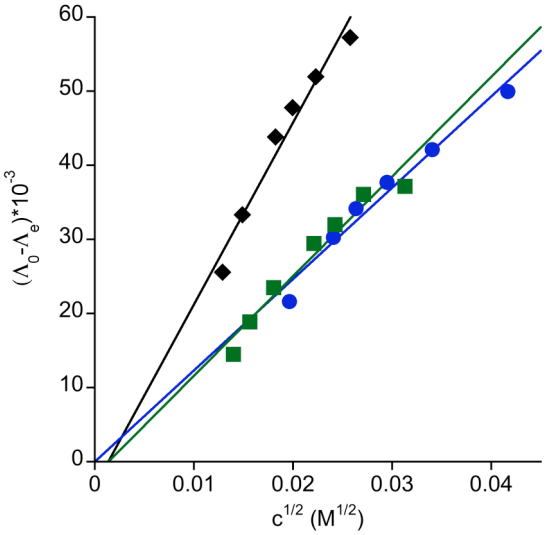

Figure S7. Onsager plot of conductivity data, where c = concentration, for **2** (black diamonds), **1** (green squares), and $(Bu_4N)(O_3SCF_3)$ (blue circles). The overlapping slopes for the plots for **1** and $(Bu_4N)(O_3SCF_3)$ indicate that the former is a 1:1 electrolyte, and are consistent with the steeper slope for the plot of the 2:1 electrolyte **2**.

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