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$_2$Cl$_2$) were degassed and passed through a solvent purification system (Glass Contour, Laguna CA) before use. The NMR solvents CD$_2$Cl$_2$ and C$_6$D$_6$ 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 $N,N',N''$-tetramethyl-1,3-propanediamine (Me$_4$pdada), 1,4,7-trimethyl-1,4,7-triazacyclononane (Me$_2$tacn), Cu(O$_2$SCF$_3$)$_2$, and Cu(MeCN)$_2$PF$_6$ were purchased from Aldrich and used as received. Labeled elemental sulfur (34$\%$, 99% enrichment) was purchased from Cambridge Isotope Laboratories, Inc. The complexes [(Me$_4$pdada)Cu(MeCN)]O$_2$SCF$_3$,[1] [(Me$_4$chd)Cu(MeCN)]O$_2$SCF$_3$ (Me$_4$chd = $N,N',N''$-tetramethyl-trans-1R,2R-diaminocyclohexane),[2] [Cu(MeCN)$_2$]O$_2$SCF$_3$,[3] sodium disulfide (Na$_2$S$_2$),[4] and the anilido-imine [ortho-C$_6$H$_4${NLi(C$_6$H$_3$Me$_2$)}(CH=NC$_6$H$_3$Me$_2$)],[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 ($\delta$) for $^1$H and $^{13}$C NMR spectra are reported versus tetramethyilsilane and were referenced to residual protium in the deuterated solvent. $^{31}$P{$^1$H} NMR spectra are referenced to an external H$_3$PO$_4$ 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 anaerobically in CH$_2$Cl$_2$ (1.0-4.0 mM). Quantitation of EPR signal intensity was accomplished by comparing the integration with that of [(o-Pr$_2$C$_6$H$_3$)NC(CH$_3$)]$_2$CHCl (1 mM in CH$_2$Cl$_2$).[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 Thermo Nicolet Avatar 370 spectrometer. Cyclic voltammograms were recorded using Pt working and auxiliary electrodes, a Ag wire / AgNO$_3$ (0.001 M in CH$_2$Cl$_2$) 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$_2$Cl$_2$ with 0.4 M Bu$_4$NPF$_6$ (sample volume of ~ 5 mL) at room temperature. The ferrocene/ferrocnium couple was recorded for reference, using the reported value of $E_{1/2}$ = + 0.46 V vs. SCE (for 0.1 M Bu$_4$NPF$_6$ in CH$_2$Cl$_2$).[7] Elemental analyses were performed by Robertson Microlit (Madison, NJ). GC-MS analyses were done by injection of 1$\mu$L aliquots into a HP G1800A MSD instrument. Electrical conductivity measurements were performed in CH$_2$Cl$_2$ for 1, 2, and (Bu$_4$N)(O$_2$SCF$_3$) using a Fischer Scientific Accumet Portable AP65 model conductivity bridge with a cell constant of 1.0 cm$^{-1}$. The equivalent conductance, $\Lambda_e$, 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, $\Lambda_0$. A plot of (\$\Lambda_0 - \Lambda_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). Final cell constants were calculated from the xyz centroids of strong reflections from the actual data collection after integration (SAINT). The structures were solved by direct methods using SHELXL-97 software. 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 [(Me₃tacn)₂Cu₂(μ-S₂)](SbF₆)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.

[(Me₄pda)₂Cu₂(μ-S₂)](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 [(Me₄pda)Cu(MeCN)]OTf with elemental sulfur in THF but lower yields were usually obtained. A sample of [(Me₄pda)₂Cu₂(μ-S₂)](OTf)₂ for characterization by resonance Raman spectroscopy was prepared as follows: 34S₈ (1.8 mg, 0.05 mmol) was added to a solution of [(Me₄pda)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 CH₂Cl₂ (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 CH₂Cl₂ with 0.4 M Bu₄NPF₆) was recorded at room temperature in an inert-atmosphere glovebox using the ferrocene/ferrocinium couple for reference (Figure S3).

[(Me₃tacn)Cu(MeCN)](SbF₆). A solution of Me₃tacn (73 mg, 0.43 mmol) in THF (2 mL) was added to a solution of [Cu(MeCN)₄]SbF₆ (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. ¹H NMR (CD₂Cl₂, 300 MHz): δ = 2.72 (s, 9H), 2.69 (m, 12H), 2.21 (s, 3H) ppm; ¹³C NMR (CD₂Cl₂, 75 MHz): δ = 115.6, 54.5, 48.2, 2.5 ppm; ESI-MS: [(Me₃tacn)Cu(MeCN)]⁺ calc. m/z 275.1291, found 275.1270. Other salts of [(Me₃tacn)Cu(MeCN)]⁺ have been reported.12

[(Me₃tacn)₂Cu₂(μ-S₂)](SbF₆)₂ (2). The preparation of this compound is described in the Experimental section of the main text. A sample of [(Me₃tacn)₂Cu₂(μ-S₂)](SbF₆)₂ for characterization by resonance Raman spectroscopy was prepared by the same procedure using 34S₈ (1.4 mg, 0.04 mmol) and [(Me₃tacn)Cu(MeCN)]SbF₆ (20 mg, 0.04 mmol) in CH₂Cl₂ (5 mL). UV-vis and resonance Raman spectra are shown in Figures S1 and S2, respectively. A

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cyclic voltammogram of 2 (1 mM in CH$_2$Cl$_2$ with 0.4 M Bu$_4$NPF$_6$) was recorded at room temperature in an inert-atmosphere glovebox using the ferrocene/ferrocenium couple for reference (Figure S3).

![Figure S1](image1)

**Figure S1.** UV/Vis spectra of 1 (left) and 2 (right) in CH$_2$Cl$_2$ at 25 °C.

![Figure S2](image2)

**Figure S2.** Resonance Raman spectra of 1 (left) and 2 (right) in CH$_2$Cl$_2$ at -196 °C, $\lambda_{ex} = 457.9$ nm ($^{32}$S, solid line; $^{34}$S, dashed line). Asterisks denote solvent peaks.
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**Figure S3.** Cyclic voltammograms of 1 and 2. Conditions: 1 mM in CH$_2$Cl$_2$ with 0.4 M Bu$_4$NPF$_6$, 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 ($E_{\text{red}}$ = −300 and $E_{\text{ox}}$ = +1080 mV) which decomposes under the conditions of the electrochemistry experiments to some other species ($E_{\text{red}}$ = −545 and $E_{\text{ox}}$ = +780 mV).

**Reactivity of 1. (a) Triphenylphosphine:** Two equivalents of triphenylphosphine (7.0 mg, 0.027 mmol) dissolved in CD$_2$Cl$_2$ (1 mL) were added slowly to a solution of 1 (10.0 mg, 0.013 mmol) in CD$_2$Cl$_2$ (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$_2$Cl$_2$, 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$_2$Cl$_2$, 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$_2$Cl$_2$, 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$_2$Cl$_2$, 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$_2$Cl$_2$ (1 mL) was added to a solution of [(Me$_4$pda)Cu(MeCN)]OTf (9.2 mg, 0.024 mmol) in CD$_2$Cl$_2$ (1 mL). The mixture was stirred for 15 min and then analyzed by NMR and ESIMS (quantitative yields). $^1$H NMR (CD$_2$Cl$_2$, 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$_2$Cl$_2$, 121.373 MHz): δ = 0.50 ppm; ESIMS: calcd for [(Me$_4$pda)Cu(MeCN)]$: m/z$ 455.1672; found: 455.1677.

**(b) 2,6-dimethylphenylisocyanide:** Two equivalents of 2,6-dimethylphenylisocyanide (6.2 mg, 0.047 mmol) dissolved in CD$_2$Cl$_2$ (1 mL) were added slowly to a solution of 1 (17.6 mg, 0.023 mmol) in CD$_2$Cl$_2$ (1 mL). The bleached solution was stirred for 15 min and then
analyzed by NMR and ESIMS (quantitative yields). \(^1\)H NMR (CD\(_2\)Cl\(_2\), 300 MHz): \(\delta = 7.28\) [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: calc'd for [(Me\(_4\)pda)Cu(2,6-Me\(_2\)C\(_6\)H\(_3\)NC)]\(^+\): m/z 324.1496; found: 324.1503. To confirm the formation of [(Me\(_4\)pda)Cu(2,6-Me\(_2\)C\(_6\)H\(_3\)NC)]OTf, it was independently prepared: One equivalent of 2,6-dimethylphenylisocyanide (5.8 mg, 0.045 mmol) dissolved in CD\(_2\)Cl\(_2\) (1 mL) was added to a solution of [(Me\(_4\)pda)Cu(MeCN)]OTf (17.1 mg, 0.045 mmol) in CD\(_2\)Cl\(_2\) (1 mL). The mixture was stirred for 15 min and then analyzed by NMR and ESIMS (quantitative yields). \(^1\)H NMR (CD\(_2\)Cl\(_2\), 300 MHz): \(\delta = 7.29\) [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: calc'd for [(Me\(_4\)pda)Cu(2,6-Me\(_2\)C\(_6\)H\(_3\)NC)]\(^+\): m/z 324.1496; found: 324.1438.

(c) Carbon monoxide: 1 (6.0 mg, 0.008 mmol), dissolved in CD\(_2\)Cl\(_2\) (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\(_2\)Cl\(_2\) solution), which indicated quantitative formation of [(Me\(_4\)pda)CuCO]OTf. \(^1\)H NMR (CD\(_2\)Cl\(_2\), 300 MHz): \(\delta = 2.59\) [t, (J = 5.4 Hz), 4H], 2.55 (s, 12H), 1.99 (s, 3H), 1.71 [t, (J = 5.4 Hz), 2H] ppm; FT-IR (CH\(_2\)Cl\(_2\)): \(v_{\text{CO}} = 2095\) cm\(^{-1}\). To confirm the formation of [(Me\(_4\)pda)CuCO]OTf, it was independently prepared: [(Me\(_4\)pda)Cu(MeCN)](OTf) (6.0 mg, 0.016 mmol), dissolved in CD\(_2\)Cl\(_2\) (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\(_2\)Cl\(_2\), 300 MHz): \(\delta = 2.59\) [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\(_2\)Cl\(_2\) were added to one equivalent of a solution of 1 in CD\(_2\)Cl\(_2\). 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\(_2\)Cl\(_2\)Cl at 70 °C for 2 hours (NMR).

(e) [(Me\(_3\)tacn)Cu(MeCN)](SbF\(_6\)). Two equivalents of [(Me\(_3\)tacn)Cu(MeCN)](SbF\(_6\)) (13.7 mg, 0.027 mmol) dissolved in CH\(_2\)Cl\(_2\) (2 mL) was added to a solution of 1 (10.0 mg, 0.013 mmol) in CH\(_2\)Cl\(_2\) (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 stoichiometry was confirmed by a UV-vis spectrophotometric titration; maximum intensity of the 397 nm peak was obtained upon addition of 2 equivalents of [(Me\(_3\)tacn)Cu(MeCN)](SbF\(_6\)).

(f) Anilido-imine ligand salt: Two equivalents of the lithium salt of ortho-C\(_6\)H\(_4\){NLi(C\(_6\)H\(_3\)Me\(_2\))}CH=NC\(_6\)H\(_3\)Me\(_2\) (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\(_2\)Cl\(_2\) (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\(_4\)chd)Cu(MeCN)]OTf: One equivalent of [(Me\(_4\)chd)Cu(MeCN)]OTf (11.0 mg, 0.026 mmol) dissolved in CH\(_2\)Cl\(_2\) (2 mL) was added to 1 (19.4 mg, 0.026 mmol) solution in CH\(_2\)Cl\(_2\). 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\(_2\)Cl\(_2\) solution result in formation of dark green block crystals, identified as [(Me\(_4\)chd)Cu\(_3\)(µ-S\(_2\))]CF\(_3\)SO\(_3\))\(_3\) (4) by X-ray crystallography,\(^{14}\) and a brown powder.
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A UV-Vis spectrophotometric titration indicated the stoichiometry of the reaction. Thus, up to 5 equivalents of ([Me₄chd]Cu(MeCN))OTf (0.71 mg, 0.167 µmol) dissolved in CH₂Cl₂ (0.5 mL, 3.33 mM) were injected by syringe into a stirred anaerobic CH₂Cl₂ (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 ([Me₄chd]₃Cu₃(µ-S)₂]⁺ cluster formation após the addition of 3 equivalents ([Me₄chd]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 CH₂Cl₂ (2.0 mL, 0.167 mM) with up to 3 equivalents of ([Me₄chd]Cu(MeCN))OTf (orange line) in CH₂Cl₂ (0.5 mL, 3.33 mM) at -20 °C. No further changes in the spectra were observed upon addition of further amounts of ([Me₄chd]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 CD₂Cl₂ (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 ¹H 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, one equivalent of 3,5-di-tert-butyl-1,2-benzoquinone and one equivalent of 3,5-di-tert-butyl catechol was observed (¹H 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 CH₂Cl₂ (3 mL) was added to a solution of 1 (15.3 mg, 0.020 mmol) in CH₂Cl₂ (4 mL). The mixture was stirred for 15 min and then quenched by the addition of 0.5 M aqueous H₂SO₄ solution (2 mL). The reaction mixture was stirred for another 15 min and extracted with CH₂Cl₂ (3 x 10 mL). The organic fractions were combined, dried over Na₂SO₄, and filtered through Celite. The solvent was removed under reduced pressure, and the residue was analyzed by ¹H NMR spectroscopy, GC-MS and ESIMS. Stochiometric 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 CD₂Cl₂ (1 mL) was added to [Cu₂(µ-S₂)(Me₄pda)](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 ¹H NMR spectroscopy and GC-MS. 2-tert-butyl-1,4-benzoquinone obtained stoichiometrically. One equivalent of 2-tert-butyl-1,4-benzoquinone was analyzed by ¹H NMR spectroscopy when two equivalents of tert-butylhydroquinone were added to [Cu₂(µ-S₂)(Me₄pda)](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 CH₂Cl₂ (3 mL) were added to a solution of 1 (8.4 mg, 0.011 mmol) in CH₂Cl₂ (4 mL). The mixture was stirred for 15 min and then quenched by the addition of 0.5 M aqueous H₂SO₄ solution (2 mL). The reaction mixture was stirred for another 15 min and extracted with CH₂Cl₂ (3 x 10 mL). The organic fractions were combined, dried over Na₂SO₄, and filtered through Celite. The solvent was removed under reduced pressure, and the residue was analyzed by ¹H NMR spectroscopy (Figure S5), GC-MS and ESIMS. The ¹H 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).

(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 CH₂Cl₂:THF mixture (2:1), were added to a solution of 1 (7.9 mg, 0.011 mmol) in CH₂Cl₂ (4 mL). The mixture was stirred for 15 min and then quenched by the addition of 0.5 M aqueous H₂SO₄ solution (2 mL). The reaction mixture was stirred for another 15 min and extracted with CH₂Cl₂ (3 x 10 mL). The

Figure S5. The ¹H 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 CD₂Cl₂. 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).
organic fractions were combined, dried over Na$_2$SO$_4$, 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 $^1$H 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$_2$Cl$_2$ (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 $^1$H 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$_2$Cl$_2$ (4 mL). The mixture was stirred for 15 min and then quenched by the addition of 0.5 M aqueous H$_2$SO$_4$ solution (2 mL). The reaction mixture was stirred for another 15 min and extracted with CH$_2$Cl$_2$ (3 x 10 mL). The organic fractions were combined, dried over Na$_2$SO$_4$, and filtered through Celite. The solvent was removed under reduced pressure, and the residue was analyzed by $^1$H 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$_2$Cl$_2$ (3 mL), and added to a solution of 1 (20.0 mg, 0.027 mmol) in CH$_2$Cl$_2$ (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 phenoxy radical (Figure S6). The conversion of 2,4,6-tri-tert-butyl phenol to 2,4,6-tri-tert-butyl phenoxy 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 CH₂Cl₂, 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 CH₂Cl₂ (3 mL) were added to a solution of 1 (10.0 mg, 0.013 mmol) in CH₂Cl₂ (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 CD₂Cl₂ (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 ¹H NMR spectroscopy, GC-MS and ESI-MS. The data indicated formation of a half equivalent of 3,3’,5,5’-tetra-tert-butylidiphenoquinone 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 CH₂Cl₂ (4 mL). The mixture was stirred for 15 min and then quenched by the addition of 0.5 M aqueous H₂SO₄ (2 mL). The reaction mixture was stirred for another 15 min and extracted with CH₂Cl₂ (3 x 10 mL). The organic fractions were combined, dried over Na₂SO₄, and filtered through Celite. The solvent was removed under reduced pressure, and the residue was analyzed by ¹H NMR spectroscopy, GC-MS and ESI-MS. The data indicated formation of a half equivalent of 3,3’,5,5’-tetra-tert-butylidiphenoquinone and one equivalent of unreacted 2,6-di-tert-butyl phenol.

(s) (Et₃NH)(BPh₄): Two equivalents of (Et₃NH)(BPh₄) were dissolved in CH₂Cl₂ or THF (2 mL) and added slowly to one equivalent 1 in CH₂Cl₂ (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 Me₄PdH⁺. ¹H NMR (CD₂Cl₂, 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 CH₂Cl₂ (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 CH₂Cl₂ (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 CD₂Cl₂ (1 mL) were added slowly to 2 (9.8 mg, 0.010 mmol) solution in CD₂Cl₂ (1 mL). The orange solution was stirred for 15 min and then analyzed by ¹H and ³¹P NMR spectroscopy and ESI-MS, which indicated the formation of one equivalent of [(Me₃tacn)CuPPh₃]SbF₆ and S=PPh₃, along with 0.5 equivalent of unreacted 2. ¹H NMR (CD₂Cl₂, 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; ³¹P{¹H} NMR (CD₂Cl₂, 121.373 MHz): δ = 43.56 (1P), 8.1 (broad, 1P) ppm; ESI-MS: cycled for [(Me₃tacn)CuP(Ph₃)]⁺: m/z 496.1937; found: 496.1985, calcld for [(Me₃tacn)CuP(Ph₃)]⁺: m/z 767.0441; found: 767.0417. Reaction of 2 using 4 equivalents of triphenylphosphine was performed by the same procedure and analyzed by ¹H and ³¹P NMR spectroscopy, which indicated the formation of two equivalents of [(Me₃tacn)CuPPh₃]SbF₆ and two equivalents of S=PPh₃. ¹H NMR (CD₂Cl₂, 300 MHz): δ = 7.20-7.80 (m, 60H), 2.82 (s, 24H), 2.53 (s, 18H) ppm; ³¹P{¹H} NMR (CD₂Cl₂, 121.373 MHz): δ = 43.56 (2P), 8.1 (broad, 2P) ppm.
To confirm the identity of [(Me₅tacn)CuPPh₃]SbF₆, it was prepared independently: One equivalent of triphenylphosphine (8.4 mg, 0.032 mmol) dissolved in CD₂Cl₂ (1 mL) was added to a solution of [(Me₅tacn)Cu(MeCN)]SbF₆ (16.3 mg, 0.032 mmol) in CD₂Cl₂ (1 mL). The mixture was stirred for 15 min and then analyzed by ¹H and ³¹P NMR spectroscopy and ESIMS. ¹H NMR (CD₂Cl₂, 300 MHz): δ = 7.20-7.60 (m, 15H), 2.82 (s, 12H), 2.53 (s, 9H), 1.97 (s, 3H) ppm; ³¹P{¹H} NMR (CD₂Cl₂, 121.373 MHz): δ = 8.1 (broad) ppm; ESIMS: calcd for [(Me₅tacn)Cu(PPh₃)]⁺: 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 CD₂Cl₂ (1 mL) were added slowly to a solution of 2 (19.2 mg, 0.019 mmol) in CD₂Cl₂ (1 mL). The bleached solution was stirred for 15 min and then analyzed by NMR, ESIMS and FT-IR (quantitative yields). ¹H NMR (CD₂Cl₂, 300 MHz): δ = 7.27 [t, (J = 7.8 Hz), 2H], 7.16 [d, (J = 7.8 Hz), 4H], 2.84 (s, 18H), 2.38 (s, 12H) ppm; ESIMS: calcd for [(Me₅tacn)Cu(2,6-Me₂C₆H₃NC)]⁺: m/z 365.1761; found: 365.1771; FT-IR (CH₂Cl₂): νNC = 2139 cm⁻¹ (Figure S1). To confirm the formation of [(Me₅tacn)Cu(2,6-Me₂C₆H₃NC)]SbF₆, it was synthesized and characterized independently: One equivalent of 2,6-dimethylphenylisocyanide (4.31 mg, 0.033 mmol) dissolved in CD₂Cl₂ (1 mL) was added to [(Me₅tacn)Cu(MeCN)](SbF₆) (16.8 mg, 0.033 mmol) solution in CD₂Cl₂ (1 mL). The mixture was stirred for 15 min and then analyzed by NMR, ESIMS and FT-IR (quantitative yields). ¹H NMR (CD₂Cl₂, 300 MHz): δ = 7.27 [t, (J = 7.8 Hz), 2H], 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 [(Me₅tacn)Cu(CO)]²⁻: m/z 365.1761; found: 365.1793; FT-IR (CH₂Cl₂): νCO = 2139 cm⁻¹.

(c) Carbon monoxide: Complex 2 (10.0 mg, 0.010 mmol), dissolved in CD₂Cl₂ (1 mL) under an inert atmosphere, was reacted with carbon monoxide (1 atm) at room temperature for 25 min. The bleached solution was then analyzed by NMR, ESIMS and FT-IR (quantitative yields). ¹H NMR (CD₂Cl₂, 300 MHz): δ = 2.88 (s, 24H), 2.85 (m, 18H) ppm; ESIMS: calcd for [(Me₅tacn)Cu(CO)]⁺: m/z 262.0975; found: 262.1025; FT-IR (CH₂Cl₂): νCO = 2091 cm⁻¹. To confirm the formation of [(Me₅tacn)Cu(CO)]SbF₆, it was synthesized independently: [(Me₅tacn)Cu(MeCN)](SbF₆) (8.0 mg, 0.016 mmol), dissolved in CD₂Cl₂ (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 (CD₂Cl₂, 300 MHz): δ = 2.88 (s, 12H), 2.85 (m, 9H), 1.97 (s, 3H) ppm; ESIMS: calcd for [(Me₅tacn)Cu(CO)]⁺: m/z 262.0975; found: 262.1059; FT-IR (CH₂Cl₂): νCO = 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 CD₂Cl₂ (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 CH₂Cl₂ (2 mL) were added to a solution of 2 (3.4 mg, 3.38 µmol) in CH₂Cl₂ (10 mL). The mixture was stirred for 2 hours and then quenched by the addition of 0.5 M aqueous H₂SO₄ solution (2 mL). The reaction mixture was stirred for another 15 min and extracted with CH₂Cl₂ (3 x 10 mL). The organic fractions were combined, dried over Na₂SO₄, 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) (Et₃NH)(BPh₄): 2 equivalents of (Et₃NH)(BPh₄), 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 CH₂Cl₂ 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$_2$Cl$_2$ (1 mL) was added to 2 (7.7 mg, 0.008 mmol). The mixture was stirred for 1 hour and analyzed by $^1$H NMR spectroscopy, which confirmed that no reaction took place.

![Figure S7](image)

Figure S7. Onsager plot of conductivity data, where c = concentration, for 2 (black diamonds), 1 (green squares), and (Bu$_4$N)(O$_3$SCF$_3$) (blue circles). The overlapping slopes for the plots for 1 and (Bu$_4$N)(O$_3$SCF$_3$) 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.

References

[4] The compound was synthesized according to T. Takata, D. Saeki, Y. Makita, N. Yamada, N. Kihara, Inorg. Chem. 2003, 42, 3712-3714. Elemental sulfur was reacted with 1.1 atom equivalent of sodium dispersion and 0.18 equivalent of benzophenone in DME at 70 °C for 4 hours under dry and inert atmosphere. The yellow precipitate was washed with DME, diethyl ether and pentane before it was dried under reduced pressure. The purity of the compound was determined by its reaction with benzyl chloride followed by GC-MS analysis as described in the original procedure (>95% dibenzyl disulfane and <5% dibenzyl sulfane were identified).
[19] This value differs from that reported in the literature for [(Me₃tacn)CuCO]ClO₄ (2082 cm⁻¹, KBr), which may be due to differences in the nature of the counterions and media: M. Kujime, T. Kurahashi, M. Tomura, H. Fujii, Inorg. Chem. 2007, 46, 541-551.