Supporting information

Materials and methods

Starting materials were commercially available unless otherwise noted. $[Cu(CH_3CN)_4](CF_3SO_3)$ was synthesized by adaptation of a literature procedure (Kubas, G.J. *Inorg. Synth.* **1979**, *19*, 90-92). Organometallic procedures were carried out under N_2 using Schlenk techniques and dried, distilled solvents.

^{1}H- and ^{13}C-NMR spectra were obtained on a Varian XL-400 spectrometer operating at 400 MHz for ^{1}H and 100 MHz for ^{13}C; all samples were dissolved in $CDCl_3$. X-band EPR spectra were obtained using a Bruker EMX spectrometer, a ER041XG microwave bridge and ER4102ST cavity, with samples held in a liquid nitrogen-filled finger Dewar; spectral parameters were obtained by simulation using WinEPR SimFonia v1.25 (Bruker). Cyclic voltammetry was performed using a BAS CV-40 potentiometer, a AgCl/Ag wire reference electrode, a graphite disk working electrode, and a Pt wire counter electrode; Fc was added as an internal standard. UV-Vis spectroscopy was performed using a Polytec X-DAP fibre-optic diode array spectrophotometer with an immersible probe (Hellma, Inc.) or a 1 cm cell adapter. High resolution mass spectra were obtained from the Mass Spectrometry Facility (UCSF) supported by the NIH Division of Research and Resources, and low resolution mass spectra were collected by Stanford University Mass Spectrometry or using an HP6890/5973 tandem GC/MS. Analytical services were provided by Desert Analytics (Tucson, AZ). Computations were performed with PC Spartan 2002 (Wavefunction, Inc.).

Synthetic procedures

2-*tert*-butyl-1,10-phenanthroline: *tert*-Butyllithium (1.5 M in pentane, 4.0 mL, 6.0 mmol) was slowly added to 1,10-phenanthroline (360 mg, 2.0 mmol) suspended in toluene (10 mL) at room temperature and the solution stirred for 12 hours. The reaction mixture was cooled (0°C), treated with 10 mL water, and extracted with 3x20 mL CH_2Cl_2. The organic layer was stirred over activated MnO_2 (20 g) for 3 h, then dried ($MgSO_4$), filtered, and evaporated. The resulting red-orange oil was separated by column chromatography (silica, 2% MeOH in CH_2Cl_2) to give the product (last fraction) as an amber oil (140 mg, 30% yield). ^{1}H-NMR: δ 1.60 (s, 9H, Bu^t), 7.61 (dd, 1H, H^8, J = 8.0, 4.3 Hz), 7.74 (m, 3H,

$H^{3=4=5}$), 8.18 (d, 1H, H^4, J=8.0 Hz), 8.23 (dd, 1H, H^7, J = 8.0, 1.6 Hz), 9.24 (dd, 1H, H^9, J=4.3, 1.6 Hz). ESI-MS: *m*/*z* 259 (M+Na).

2-bromo-4,6-di-*tert*-butylphenol: A solution of 2,4-di-*tert*-butylphenol (12.3 g, 60 mmol) in CS_2 (75 mL) was treated with Br_2 (9.9 g, 62 mmol) in CS_2 (50 mL) at 0°C and stirred for 12 h at room temperature. Dry N_2 was bubbled through the solution to remove HBr (trapped with aqueous alkali). After then evaporating the solvent, the residue was redissolved in hexanes (100 mL) and stored over $MgSO_4$ to help remove residual Br_2, then again evaporated under vacuum to give a white solid (15.8 g, 92% yield). ^{1}H-NMR: δ 1.29 (s, 9H, Bu^t), 1.40 (s, 9H, Bu^t), 5.66 (s, 1H, OH), 7.24 (d, 1H, Ar*H*, J=2.4 Hz), 7.32 (d, 1H, Ar*H*, J=2.3 Hz). EI-MS: *m*/*z* 286/284 (M^+(^{81}Br/^{79}Br).

2-bromo-4,6-di-*tert*-butylanisole: To a solution of 2-bromo-4,6-di-*tert*-butylphenol (4.0 g, 13.9 mmol) in acetone (50 mL) was added K_2CO_3 (10 g), then dropwise a solution of Me_2SO_4 (2.0 g, 15 mmol) in acetone (30 mL). The suspension was stirred overnight, then filtered. Water (100 mL) was added, and the solution was extracted with hexanes (3x50 mL). The combined hexanes fractions were dried over $MgSO_4$ and evaporated to give a colorless oil (4.15 g, 99% yield). ^{1}H-NMR: δ 1.30 (s, 9H, Bu^t), 1.40 (s, 9H, Bu^t), 3.92 (s, 3H, OCH_3), 7.28 (d, 1H, Ar*H*, J=2.4 Hz), 7.40 (d, 1H, Ar*H*, J=2.4 Hz). EI-MS: *m*/*z* 300/298 (M^+(^{81}Br/^{79}Br)).

2-(3,5-di-*tert*-butyl-2-hydroxy)-9-*tert*-butyl-1,10-phenanthroline (**HL^{Phen}**): *tert*–Butyllithium (1.5 M in pentane, 2.67 mL, 4.0 mmol) was added to 2-bromo-4,6-di-*tert*-butylanisole (598 mg, 2.0 mmol) in diethyl ether (15 mL) at –78°C and stirred for 1 h. This solution was then allowed to warm and added to a suspension of 2-*tert*-butyl-1,10-phenanthroline (236 mg, 1.0 mmol) in toluene (10 mL) at room temperature, then stirred for 12 hours. The reaction mixture was cooled (0°C), treated with 10 mL water, and extracted with 3x20 mL CH_2Cl_2. The organic layer was stirred over activated MnO_2 (20 g) for 3 h, dried ($MgSO_4$), filtered, and evaporated. The resulting orange oil was separated by column chromatography (silica, 2% MeOH in CH_2Cl_2) to give an amber oil (last fraction). This product was dissolved in CH_2Cl_2 (30 mL) and treated with excess BBr_3 (2.6 mL, 6.9 g, 28 mmol) for 2 h at –78°C, then 12 h at room temperature, before being quenched with water (10 mL) at 0°C. The organic layer was washed with saturated $NaHCO_3$(aq) (2x10 mL) and water (1x10 mL), dried ($MgSO_4$), filtered and evaporated. The resulting orange oil was

separated by column chromatography (silica, 2% MeOH/CH_2Cl_2). The third colorless fraction gave the product as a yellow powder (280 mg, 64% yield overall). ^{1}H-NMR: δ 1.41 (s, 9H, Bu^t), 1.58 (s, 9H, Bu^t), 1.64 (s, 9H, Bu^t), 7.47 (d, 1H, Ar*H*, J = 2.4 Hz), 7.73–7.78 (m, 3H, Phen*H*), 7.87 (d, 1H, Ar*H*, J = 2.4 Hz), 8.19 (d, 1H, Phen*H*, J = 8.5 Hz), 8.25 (d, 1H, Phen*H*, J = 8.7 Hz), 8.31 (d, 1H, Phen*H*, J = 8.7 Hz). ^{13}C-NMR ($CDCl_3$, 125 MHz, 25^o C): δ 29.58, 30.27, 31.67, 34.35, 35.47, 38.82, 118.42, 120.19, 120.61, 124.64, 125.61, 126.03, 126.63, 135.84, 136.81, 138.24, 138.83, 158.23, 159.08, 169.93. EI-HRMS: Calcd. for $C_{30}H_{36}N_2O$: *m/z* 440.2828. Found: *m/z* 440.2829.

[$L^{Phen}Cu^{II}Cl$]: Under N_2, a solution of triethylamine (32 µL, 23 mg, 230 µmol) and HL^{Phen} (100 mg, 230 µmol) in CH_2Cl_2 (10 mL) was added to a suspension of CuCl (22.5 mg, 230 µmol) in dry MeOH (10 mL0 and stirred for 2 h. The yellow solution was then exposed to air and stirred for 5 h, changing color to dark green. The solution was evaporated and recrystallization (CH_2Cl_2/diethyl ether) gave a dark green solid (100 mg, 80% yield). X-ray quality crystals were grown by slow evaporation of a CH_2Cl_2 solution. UV-Vis (CH_2Cl_2, 25°C; λ_{max}, ε/M^{-1} cm^{-1}): 312 (32 000), 452 (8000), 665 (700). EI-MS: *m/z* 502 ($L^{Phen}Cu^+$). For $C_{30}H_{35}ClCuN_2O$: C, 66.90; H, 6.55; N, 5.20. Found: C, 66.53; H, 6.50; N, 5.12.

[$L^{Phen}Cu^{II}(CF_3SO_3)$]—*Method A:* Under N_2, a solution of triethylamine (7.7 µL, 5.5 mg, 55 µmmol) and HL^{Phen} (24 mg, 54 µmol) in CH_2Cl_2 (10 mL) was added to a solution of $[Cu(CH_3CN)_4](CF_3SO_3)$ (21 mg, 55 µmol) in CH_3CN (10 mL) and stirred for 1 h. The solutions was then exposed to air and stirred for 24 h, giving a green solution. Evaporation of the solution and recrystallization of the solid residue (acetone/diethyl ether) gave green plate crystals (5 mg, 14% yield), suitable for crystallographic analysis.

Method B: A solution of $AgCF_3SO_3$ (24 mg, 90 µmol) in MeOH (10 mL) was added to a solution of [$L^{Phen}Cu^{II}Cl$] (50 mg, 90 µmol) in MeOH (10 mL) and stirred for 8 h. Precipitated AgCl was removed by filtration (Celite) and the solvent was evaporated. Dark green crystals were obtained from recrystallization of the solid residue (acetone/pentane) (53 mg, 90% yield). UV-Vis (CH_2Cl_2, 25°C; λ_{max}, ε/M^{-1} cm^{-1}): 312 (33 000), 444 (7500), 650 (400). EI-MS: *m/z* 502 ($L^{Phen}Cu^+$). For $C_{31}H_{35}CuFN_2O_4S{\cdot}H_2O$: C, 55.55; H, 5.56; N, 4.18. Found: C, 55.78; H, 5.62; N, 4.35.

Figure S1. ORTEP representation of [$L^{Phen}Cu^{II}Cl$] shown with 50% ellipsoids. Hydrogen atoms and a disordered CH_2Cl_2 solvate molecule are omitted for clarity. The *para*-*tert*-butyl substituent of the phenolate is disordered over two positions; only one conformer is shown. Selected bond lengths (Å) and angles (°): Cu(1)-N(1) 2.060(5), Cu(1)-N(2) 1.919(5), Cu(1)-O(1) 1.847(4), Cu(1)-Cl(1) 2.277(2), N(2)-Cu(1)-Cl(1) 134.8(2).

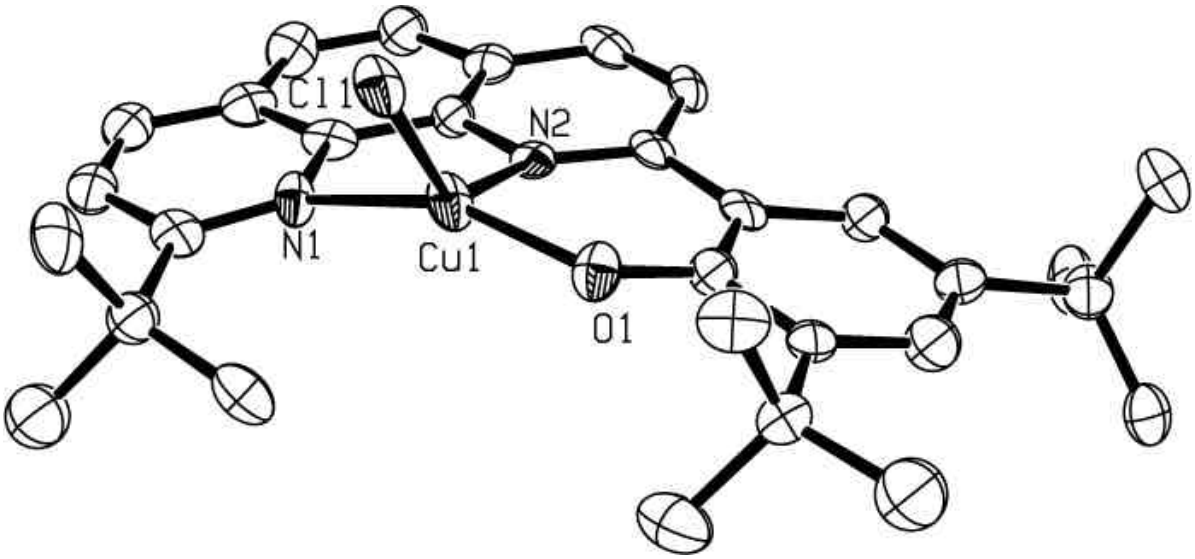

Figure S2. Overlays of the crystal structures (black) and calculated structures (grey) of [$L^{Phen}Cu^{II}Cl$]. The phenolic *tert*-butyl substituents, expected to have little electronic or steric effects for this purpose, were deleted to speed calculations; the 9-*tert*-butyl subtituent is omitted from the graphics for clarity. In (a), all atoms were included in the overlay algorithm (RMS deviation = 0.246 Å); in (b), only the coordination sphere ($CuClN_2O$) was matched (RMS deviation = 0.046 Å). Structural parameters calculated for [$L^{Phen}Cu^{II}Cl$] (lengths Å, angles °): Cu(1)-Cl(1) 2.252, Cu(1)-N(1) 2.069, Cu(1)-N(2) 1.959, Cu(1)-O(1) 1.866, N(2)-Cu-Cl(1) 134.9.

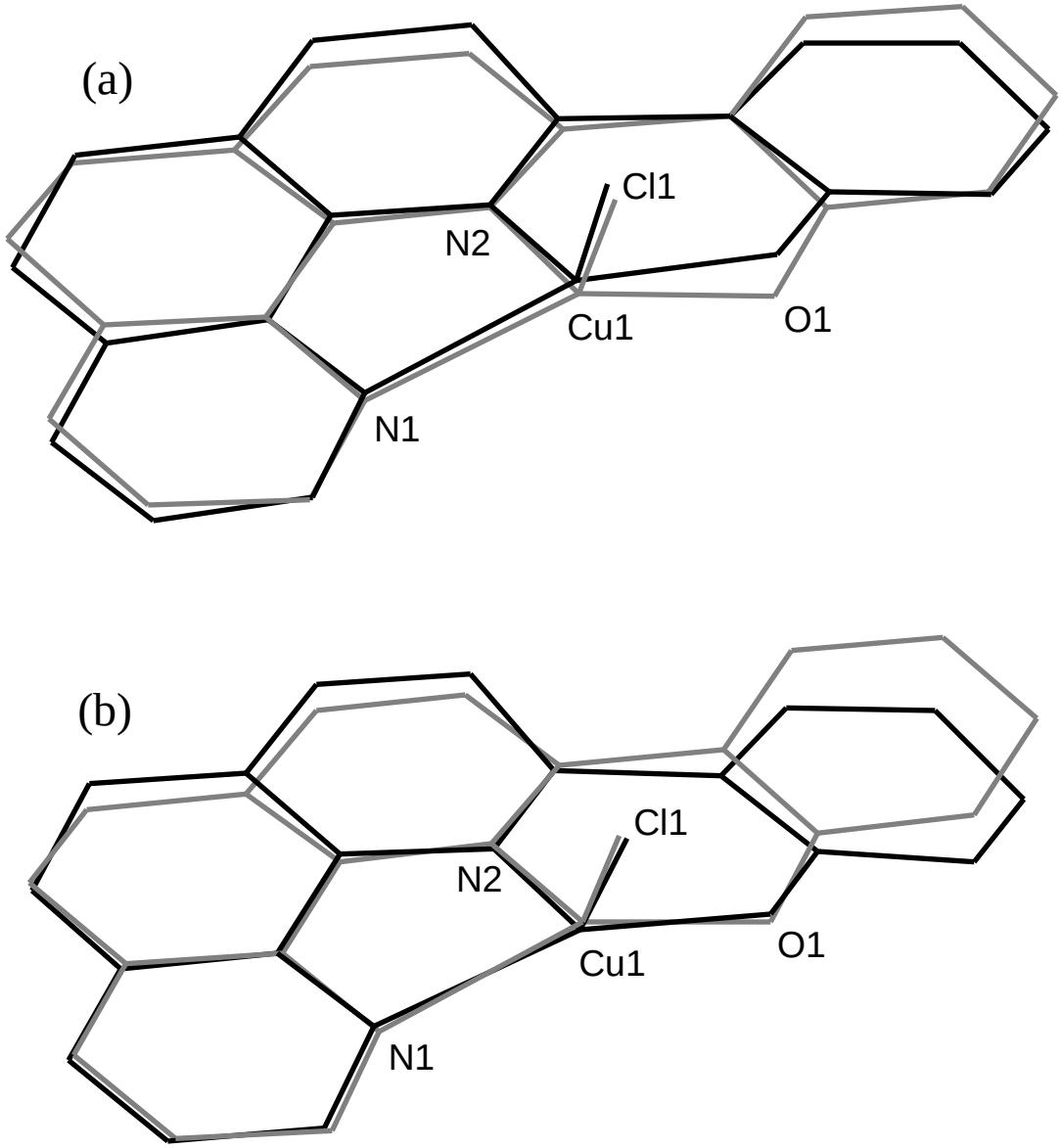

Figure S3. UV-Vis titration of [$L^{Phen}Cu^{II}Cl$] (0.1 mM in MeOH) with sodium methoxide. Inset: absorbance at 475 nm plotted versus equivalents of methoxide added, showing linear addition and a break point at 1 equivalent added.