Supporting Information

for

Reactivity of a 1:1 Copper-Oxygen Complex: Isolation of a Cu(II)-*o*-Iminosemiquinonato Species

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Experimental Details and Characterization Data

S1. General Considerations

All solvents and reagents were obtained from commercial sources and used as received unless otherwise stated. The solvents tetrahydrofuran (THF), toluene and pentane were passed through solvent purification columns (Glass Contour, Laguna, CA). Hexamethyldisiloxane (HMDSO) was distilled from calcium hydride. Acetone was distilled twice from anhydrous calcium sulfate and stored under N_2 no longer than two weeks before use. Deuterated benzene (C_6D_6) was distilled from Na/benzophenone. All metal complexes were prepared and stored in a Vacuum Atmospheres inert atmosphere glove box under a dry N_2 atmosphere or using standard Schlenk and vacuum line techniques. The complex LCu(MeCN)[i] and $[Cu(MeCN)_4]O_3SCF_3$[ii] were prepared *via* literature procedures.

S2. Physical Methods

NMR spectra were recorded on a Varian VI-300 or VXR-300 spectrometer. Chemical shifts (δ) for ^1H and ^{13}C NMR spectra were referenced to residual protium in the deuterated solvent. UV-vis spectra were recorded on a HP8453 (190–1100 nm) diode array spectrophotometer. Low temperature spectra were acquired using a custom manufactured vacuum dewar equipped with quartz windows, with low temperatures maintained using a low temperature methanol bath circulator, or a Unisoku low-temperature UV-vis cell holder. X-band EPR spectra were acquired on a Bruker E-500 spectrometer, with an Oxford Instruments EPR-10 liquid helium cryostat (4-20 K, 9.61 GHz). Quantitation of EPR signal intensity was accomplished by comparing the double integration of the derivative spectrum to that of LCuCl[iii] in toluene. Elemental Analyses were performed by Atlantic Microlabs of Norcross, GA. GC/MS experiments were performed on a HP GCD series G1800A GC/MS equipped with a 30 m HP-5 (crosslinked PhMe-silicone) column, using helium as a carrier gas and a flow rate of 1.0 mL min^{-1}.

UV-vis experiments were performed in THF at –80 °C. For all reactivity studies, **1a** was generated by bubbling O_2 through solutions of LCu(MeCN) (~0.2 mM) for 5 min to form $LCuO_2$. Excess O_2 was removed from the UV-vis cell by evacuating the headspace, backfilling with N_2 (3×) and bubbling Ar through the solution for 20-30 min. The UV-vis spectrum of the solution was recorded after this procedure to confirm that no degradation of **1a** had occurred. The substrate(s) were then added as solutions *via* syringes. For kinetics experiments, solutions of degassed **1a** (3.1 mM in THF) were treated with excess amounts (15 - 35 eq) of $PMePh_2$ as solutions in THF. The decrease in absorbance at 595 nm was followed to determine pseudo first order rate constants (k_{obs}) *via* non-linear least squares fits performed using the program Kaleidagraph.

S3. Experimental Procedures

Isolation of Ligand Fragments from the Decomposition of 1a. An anaerobic solution of LCu(MeCN) (typically 10.0 mg, 0.019 mmol) in THF (5 mL) in a Schlenk flask was cooled to –80 °C. Dry $^{16}O_2$ was bubbled through the solution for 10 min, resulting in the development of a pale blue-green color. Experiments with $^{18}O_2$ were performed by freezing the anaerobic solution at –196 °C, transferring *ca.* 10 mL $^{18}O_2$ onto the solid, and warming to –80 °C. Excess O_2 was removed by evacuating the headspace and backfilling with N_2 (3x), and then bubbling Ar for 30 min. The solution was then allowed to warm to room temperature, causing a color change to dark brown, and was stirred for 1 hour. An equal volume of concentrated aqueous ammonia was added and the mixture was stirred vigorously for about 10 minutes, giving blue aqueous and yellow-brown organic layers. After the addition of 10 mL CH_2Cl_2, the organic layer was separated and the aqueous layer was further extracted with 5 mL CH_2Cl_2. The organic layers were combined and the above ammonia treatment and extraction were repeated two additional times. The final organic layers were dried over $MgSO_4$, filtered, and the solvent was removed under reduced pressure. The oily brown residue was dissolved in EtOAc (~5 mL) and filtered through a plug of activated Alumina. The resulting yellow-brown solution was subjected to GC/MS analysis, revealing more than 25 fragments of the ligand, in varying amounts depending on the experiment.

Reactivity Studies with Organic Substrates. Solutions of **1a** in THF were prepared and degassed at –80 °C as described above. One equivalent of the organic substrate in THF (*ca.* 0.25 mL) was then introduced *via* syringe. No obvious color changes were observed. For organic product analysis, the solutions were allowed to warm to room temperature and subjected to the ammonia treatment described above to remove the copper ions. GC/MS analysis of the resulting solutions revealed the presence of more than 25 fragments of the ligand, as well as intact substrate starting material, except in the case of the reaction with HBF_4, in which case the only product was ligand (*m/z* 418).

Reactivity Studies with Phosphines. Solutions of **1a** were prepared and degassed at –80 °C as described above. 1 equivalent of phosphine in THF (*ca.* 0.25 mL) was then introduced *via* syringe.

Methyldiphenylphosphine. The color faded from pale blue-green to colorless after stirring for 30 minutes at –80 °C. The solution was warmed to room temperature and the solvent was removed under reduced pressure. The solid was taken up in dry C_6D_6. $^{31}P\{^1H\}$ NMR (C_6D_6, 121.5 MHz) δ –15.98 ppm ($LCuPMePh_2$). The identity of the product was further confirmed by comparison of its ^1H NMR spectrum to independently isolated material (see below).

Triphenylphosphine. No color change was observed at –80 °C after stirring for 1 hour. The solution was allowed to warm to room temperature, causing a color change from pale blue-green to colorless. The solvent was removed under reduced pressure, and the solid completely dissolved in dry C_6D_6. $^{31}P\{^1H\}$ NMR (C_6D_6, 121.5 MHz) δ 3.36 ($LCuPPh_3$, 92 %), 29.85 ($OPPh_3$, 8 %) ppm. The identity of the product was further confirmed by comparison of its ^1H NMR spectrum to independently isolated material (see below).

Trimesitylphosphine. No immediate color change was observed. The solution was allowed to warm to room temperature, causing a color change from pale blue-green to brown. The solvent was removed under reduced pressure and the solid was completely dissolved in dry C_6D_6. $^{31}P\{^1H\}$ NMR (C_6D_6, 121.5 MHz) δ–35.91 ppm ($PMes_3$).

Synthesis of LCu(PPh_3). To a stirred solution of LCu(MeCN) (0.098 g, 0.19 mmol) in toluene (6 mL) was added a solution of PPh_3 (0.049 g, 0.19 mmol) in toluene (3 mL), causing the yellow color of the solution to fade. After stirring for 90 minutes, the solvent was removed under reduced pressure. The pale yellow residue was extracted into pentane (10 mL) and filtered through a plug of Celite. The solvent volume was reduced to 4 mL under vacuum. The solution was stored at –20 °C overnight, causing the deposition of colorless crystals that were isolated and dried under reduced pressure. Concentration of the mother liquor and further cooling led to the isolation of a second crop of colorless crystals. Total yield = 0.082 g (58 %). ^1H NMR (C_6D_6, 300 MHz): δ 7.10 (m, 6H), 6.90 (m, 15H), 5.13 (s, 1H), 3.60 (septet, J = 6.9 Hz, 4H), 1.86 (s, 6H), 1.23 (d, J = 6.9 Hz, 12 H), 0.81 (d, J = 6.9 Hz, 12 H) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6, 75 MHz): δ 171.4, 164.1, 151.1, 141.4, 134.5, 134.2, 134.1, 129.8, 129.2, 129.1, 124.3, 124.2, 95.5, 66.2, 28.6, 24.8, 24.5, 24.3, 18.2 ppm. $^{31}P\{^1H\}$ NMR (C_6D_6, 121.5 MHz): δ 3.58 ppm. Anal. Calcd for $C_{47}H_{56}CuN_2P$: C, 75.93; H, 7.59; N, 3.77. Found: C, 76.04; H, 7.64; N, 3.80.

Synthesis of LCu($PMePh_2$). To a stirred solution of LCu(MeCN) (0.044 g, 0.084 mmol) in THF (3 mL) was added a solution of $PMePh_2$ (0.017 g , 0.084 mmol) in THF (2 mL), causing the yellow color of the solution to fade. After stirring for 30 minutes, the solvent was removed under reduced pressure to yield a colorless oil. 4 mL pentane was added, and the solvent was removed under vacuum to yield a white oily solid. This solid was dissolved in 2 mL pentane, and 4 mL HMDSO was added. Storage at –20 °C overnight led to the deposition of colorless crystals that were isolated and dried under reduced pressure. Yield = 0.028 g (49 %). ^1H NMR (C_6D_6, 300 MHz): δ 7.13 (m, 6 H), 6.93 (m, 10 H), 5.12 (s, 1H), 3.57 (septet, J = 6.9 Hz, 4H), 1.90 (s, 6H), 1.22 (d, J = 6.9 Hz, 12 H), 0.98 (d, J = 6.9 Hz, 12 H), 0.93 (d, J_{H-P} = 5.1 Hz, 3 H) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6, 75 MHz): δ 163.60, 150.93, 141.02, 136.57 (d, J = 34 Hz), 132.78 (d, J = 15 Hz), 129.76, 129.07 (d, J = 9 Hz), 124.03, 123.95, 28.58, 24.55, 24.03, 24.02, 12.71 (d, J =

22 Hz) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6, 121.5 MHz): δ -15.93 ppm. Anal. Calcd for $C_{42}H_{54}CuN_2P$: C, 74.03; H, 7.99; N, 4.11. Found: C, 73.58; H, 8.04; N, 4.11.

Synthesis, Isolation and Spectroscopic Characterization of 2. Crystalline samples of **2** were typically prepared by bubbling O_2 through a solution of LCu(MeCN) (≈ 13 mg, 0.025 mmol) in THF (*ca.* 1 mL) at –80 °C in a Schlenk tube for *ca.* 20 min to give a green solution of **1a**. Excess O_2 was then removed following the procedure described above. Equimolar amounts of 3,5-diphenylpyrazole (≈ 5 mg, 0.025 mmol) followed by $[Cu(MeCN)_4]O_3SCF_3$ (≈ 9 mg, 0.025 mmol) were then added to **1a** either as solutions (*ca.* 0.5 mL/compound) in THF/acetone mixtures (acetone was added to increase solubility) or directly as the solids. After *ca.* 20 min the resulting dark brown solution was layered with pentane and left to stand at –80 °C for three days after which time dark brown crystals were obtained (≈ 10 mg, 0.011 mmol or 43%). The crystals were isolated by filtration and washed with dry, degassed pentane, maintaining the temperature at –80 °C in an inert atmsophere. The pyrazole was included as an additional coordinating ligand to aid in the growth of X-ray quality crystals, which could not be formed in its absence. We note that UV spectra are identical for: 1) the reaction with $[Cu(MeCN)_4]O_3SCF_3$ only; 2) the reaction done first with $[Cu(MeCN)_4]O_3SCF_3$, followed by the addition of pyrazole; and 3) the reaction done first with pyrazole (which produces no change in the UV spectrum of **1a**) and subsequent addition of $[Cu(MeCN)_4]O_3SCF_3$.

UV-vis: Crystals of **2** (≈ 10 mg) were dissolved in THF (5 mL) at –80 °C under a N_2 atmosphere. An aliquot (0.1 mL) of the stock solution was then diluted by addition to a UV-vis cell containing THF (3.4 mL) at –80 °C. From the UV-vis spectra of this solution, the extinction coefficient at 385 nm is calculated to be ≈ 17000 $M^{-1}cm^{-1}$.

EPR: Crystals of **2** were dissolved in THF at –80 °C (2.1 mM) and transferred to an EPR tube also at –80 °C *via* a syringe. The resulting yellow/brown solution was then frozen in liquid nitrogen. The EPR signal intensity integrated to 2% compared to a standard sample as described above; integrations of 5% or less are considered to be silent.

S4. Spectroscopy and Kinetics Figures

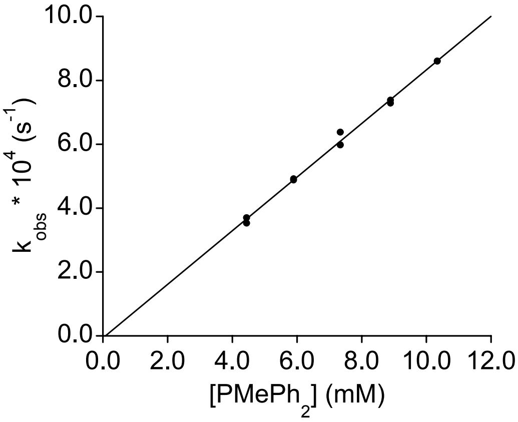

Figure S1 Kinetic plot for the reaction of **1a** with $PMePh_2$, with linear fit. Slope = $8.4 \pm 0.4 \times 10^{-3}$ $M^{-1}s^{-1}$ (R = 0.99798.)

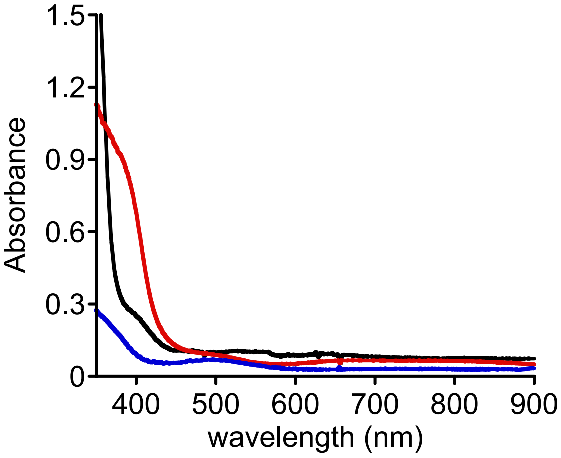

Figure S2 UV-vis spectra of (a) **1a** (black, ≈ 0.1 mM); (b) solution of crystals of **2** isolated and then redissolved in THF at –80 °C (red, ≈ 0.05 mM); (c) on warming to RT (blue).

S5. X-Ray Crystallography

Each crystal of the appropriate size was placed onto the tip of a 0.1 mm diameter glass capillary and mounted on a Siemens or Bruker SMART Platform CCD diffractometer for a data collection at 173(2) K. Data collections were carried out using MoKα radiation (graphite monochromator) with a detector distance of 4.9 cm. A randomly oriented region of reciprocal space was surveyed to the extent of one hemisphere and to a resolution of 0.84 Å. Three or four major sections of frames were collected with 0.30° steps in ω at three different ϕ settings and a detector position of -28°

in 2θ. The intensity data were corrected for absorption and decay (SADABS).[iv] Final cell constants were calculated from the xyz centroids of strong reflections from the actual data collection after integration (SAINT).[v] Please refer to the CIF files for additional crystal and refinement information.

The structures were solved using direct methods (SIR97[vi] or SHELXS-97[vii]), which located most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed using SHELXL-97,[vii] which located the remaining non-hydrogen atoms. Space groups *C*2/*c* for structure **2** and *P*2(1)/*n* for both LCu(PPh$_3$) and LCu(PMePh$_2$) were determined based on systematic absences and intensity statistics. 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 (with one exception, see below). Pertinent details for each structure are noted below.

2. Crystals suitable for X-ray crystallography were grown by slow diffusion of pentane into a THF mixture of **1a**, 3,5-diphenylpyrazole and [Cu(MeCN)$_4$]O$_3$SCF$_3$ at –80 °C. A highly disordered THF molecule, which could not be modeled, was removed using program PLATON, function SQUEEZE.[viii] It determined that there were 319 electrons in a volume of 1230.9 Å per unit cell, corresponding to the expected number of eight THF molecules. The triflate anion is disordered over two positions (90:10). EADP and SAME restraints were placed on the triflate to aid in modeling the disorder and refinement. The hydrogen atom H1, located on atom N4, was found in the E-map and refined. Crystal data are indicated in the text; See the CIF file for full crystallographic information.

LCu(PPh$_3$). Crystals suitable for X-ray crystallography were grown from a 50:50 mixture of pentane and HMDSO at –20 °C. Two independent molecules were found in the asymmetric unit. Crystal data: $C_{47}H_{56}CuN_2P$, M = 743.45, monoclinic, a = 23.439(2), b = 15.9011(15), c = 24.217(2) Å, β = 111.850(2), V = 8377.2(14), T = 173 K, space group $P2_1/n$, Z = 8, μ(Mo-Kα) = 0.593 mm^{-1}, 79358 reflections measured, 14812 unique (R_{int} = 0.0497), $R1$ = 0.0416, $wR2$ = 0.0978 (F^2, all data). See the CIF file for full crystallographic information.

LCu(PMePh$_2$). Crystals suitable for X-ray crystallography were grown from a 50:50 mixture of pentane and HMDSO at –20 °C. One phenyl group of the methyldiphenylphosphine moiety was disordered, and was successfully modeled as two phenyl groups in a 50:50 ratio. EADP, SAME, and FLAT restraints were placed on both phenyl groups to aid in modeling the disorder and refinement. Crystal data: $C_{42}H_{54}CuN_2P$, M = 681.38, monoclinic, a = 11.6105(10), b = 21.0202(12), c = 15.9832(9) Å, β = 97.837(2), V = 3864(1) Å^3, T = 173 K, space group $P2_1/n$, Z = 4, μ(Mo-Kα) = 0.636 mm^{-1}, 37565 reflections measured, 6828 unique (R_{int} = 0.0543), $R1$ = 0.0452, $wR2$ = 0.0907 (F^2, all data). See the CIF file for full crystallographic information.

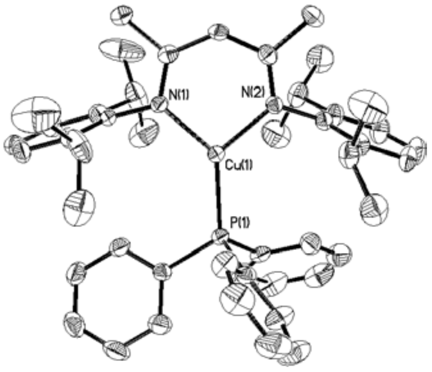

Figure S3. X-ray crystal structure representation of LCu(PPh_3), with nonhydrogen atoms shown as 50% thermal ellipsoids. Selected bond distances (Å) and angles (deg): Cu1-P1, 2.1813(7); Cu1-N1, 1.9683(19); Cu1-N2, 1.975(2); N1-Cu1-N2, 97.84(8); N1-Cu1-P1, 134.46(6); N2-Cu1-P1, 127.65(6).

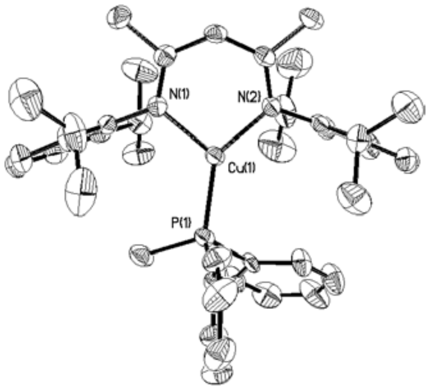

Figure S4. X-ray crystal structure representation of LCu($PMePh_2$), with nonhydrogen atoms shown as 50% thermal ellipsoids. Selected bond distances (Å) and angles (deg): Cu1-P1, 2.1581(9); Cu1-N1, 1.964(2); Cu1-N2, 1.941(2); N1-Cu1-N2, 98.31(8); N1-Cu1-P1, 123.76(6); N2-Cu1-P1, 137.88(6).

S6. Bond Valence Sum Analysis

A Bond Valence Sum (BVS) analysis can be used to quantitatively correlate structural parameters with oxidation state.[ix] The BVS for a metal ion is the sum of the valences, s_{ij}, for each metal-ligand bond and is described by eq. 1, where r_0 is an empirical constant determined for a particular bond and r_{ij} is the structurally determined bond distance between atoms i and j.

$$\mathrm{BVS} = \sum s_{ij} = \sum \exp[(r_0 - r_{ij})/0.37] \qquad (1)$$

Values for r_0 are typically calculated by solving eq. 1 for r_0 using experimentally determined values for r_{ij} in compounds of known oxidation states, and averaging these r_0

values to give the best r_0 value for a given metal-ligand bond.[9a] Many values of r_0 have been previously tabulated.[ix] By using the r_0 values for the correct oxidation state of the metal, a BVS corroborating that oxidation state should result. Good agreement between the BVS and the metal oxidation state is considered to be values varying by ± 0.25 units.

BVS values for **2** were calculated for both the Cu(I) and Cu(II) states. Using r_0 values of 1.567 for Cu(I)–O,[9e] and 1.587 for Cu(I)–N,[9c] a BVS value of 1.49 is obtained. This is not within ± 0.25 of 1.0, and therefore not in good agreement. Using r_0 values of 1.679 for Cu(II)-O,[9a,b,d] and 1.719 for Cu(II)–N,[9c] a BVS value of 2.11 is obtained. This is in very good agreement with an oxidation state of +2.

S7. References

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