Cu(I)/O$_2$ Chemistry Using a β-Diketiminate Supporting Ligand Derived from *N,N*-Dimethylhydrazine: A [Cu$_3$O$_2$]$^{3+}$ Complex with Novel Reactivity

Aalo K. Gupta and William B. Tolman*

Department of Chemistry and Center for Metals in Biocatalysis, University of Minnesota, 207 Pleasant Street SE, Minneapolis, Minnesota 55455, United States

Ⓢ *Supporting Information*

ABSTRACT: A Cu(I) complex, LCu(CH$_3$CN), was prepared and characterized, where L$^-$ is a sterically unencumbered β-diketiminate ligand, the deprotonated version of 4-(2,2-dimethylhydrazino)dimethylhydrazone-3-penten-2-one (LH). Analysis of FTIR spectra of the products of the reaction of LCu(CH$_3$CN) with CO indicate that L$^-$ is strongly electron donating, and support an equilibrium in solution between monomeric and dimeric forms with terminal and bridging CO ligands, respectively. Low temperature oxygenation of LCu(CH$_3$CN) generated a bis-(μ-oxo)tricopper complex with a $S = 1$ [Cu$_3$O$_2$]$^{3+}$ core that was identified on the basis of UV−vis (λ_{max} (ε, M^{-1} cm^{-1} per Cu) = 328 (10700), 420 (1500), 590 (835) nm) and X-band electron paramagnetic resonance (EPR) spectroscopy ($\Delta m_s = 2$ transition at 1500 G), electrospray ionization (ESI) mass spectrometry, and spectrophotometric titration (0.35(2) equiv of O$_2$ per copper atom), magnetic susceptibility ($\mu_{eff} = 2.8(1)$ BM), and H$_2$O$_2$ detection experiments (no H$_2$O$_2$ evolved upon acidification). Unlike other reported variants supported by neutral N-donor ligands, L$_3$Cu$_3$O$_2$ is not reduced by ferrocene, does not abstract H-atoms from phenols or 1,2-dihydroanthracene, oxidizes PPh$_3$ to Ph$_3$P=O, and generates carbonate species upon exposure to CO$_2$. This unique reactivity for a [Cu$_3$O$_2$]$^{3+}$ complex may be traced to the anionic charge and strong electron donating characteristics of L$^-$.
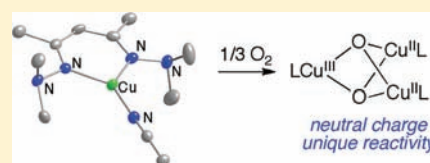
■ INTRODUCTION

Studies of the reactions of O$_2$ with Cu(I) complexes have led to important insights into the nature of possible intermediates in oxidation catalysis.[1] Thus, species with the core structures shown in Chart 1 have been characterized by spectroscopy and,

Chart 1. Selected Well-Characterized Copper−Oxygen Intermediate Cores Derived from Reactions of Cu(I) Complexes with O$_2$
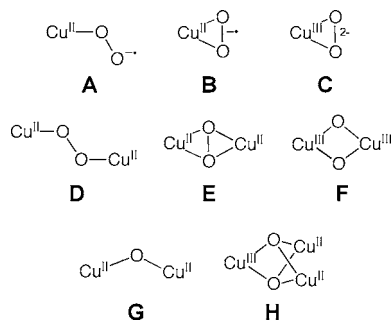
in some cases, by X-ray crystallography, and several of these cores have been identified in biological or other catalytic oxidation systems.[2] Of the various factors that influence which core forms in oxygenations of Cu(I) complexes, the nature of the supporting ligand is paramount. For example, the monoanionic, strongly electron donating β-diketiminates (e.g., **1−7**, Chart 2) are

Chart 2. Selected β-Diketiminate Ligands Used in Studies of the Reactivity of Cu(I) Complexes with O$_2$
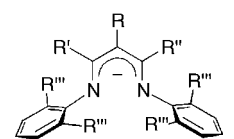
Ligand	R	R'	R"	R'''
1	H	Me	Me	iPr
2	H	tBu	tBu	iPr
3	H	Me	CF$_3$	iPr
4	H	CF$_3$	CF$_3$	iPr
5	H	CF$_3$	CF$_3$	Me
6	H	Me	Me	Me
7	Ph	H	H	iPr

a well-studied class of ligands[3] which yield Cu(I) complexes that are highly reactive with O$_2$. For the most sterically hindered β-diketiminates (**1−3**) and related anilido-imines, reactions of their Cu(I) complexes with O$_2$ yield isolable monocopper-peroxo species (**C**, Chart 1).[1e,4,5] Copper(I) complexes of less hindered variants (**6** and **7**) form bis(μ-oxo)dicopper(III) complexes (**F**).[6]

No examples of related isomeric (μ-η^2:η^2-peroxo)dicopper(II) compounds (**E**) have been identified with β-diketiminate ligands, presumably because their strong electron donating capabilities stabilize the more oxidized metal centers of the bis(μ-oxo)-dicopper(III) core.[7] Effects of replacing backbone methyl groups of the β-diketiminate frame with electron withdrawing CF_3 groups (**3−5**) have been evaluated through comparisons of electrochemical data, $\nu(CO)$ values and ^{13}C NMR chemical shifts for CO adducts, and Cu(I)/O_2 reactivity.[5,8] The expected effects of CF_3 substitution on spectroscopic properties were observed (e.g., $\nu(CO)$ increase of ~13 cm^{-1} per CF_3 group),[5] but for **3** and **5** the type of complex formed upon oxygenation of their Cu(I) complexes was the same as for the analogues **1** and **6**, respectively. Finally, it is notable that bis(μ-oxo)tricopper species **H**[9,10] has not been accessed using β-diketiminate ligands, presumably because even the most unhindered aryl-substituted β-diketiminates are too bulky to allow formation of the compact tricopper cluster.

In an extension of our previous work using ligands **1−7** and congeners,[1e,4−6,8] we sought to examine a derivative that would be more electron donating and less sterically encumbered. We hypothesized that a Cu(I) complex of a strongly electron donating ligand would be highly reactive with O_2 and other oxidants, and that the small steric profile would allow for the formation of potentially unique multinuclear copper−oxygen species. Herein, we describe the synthesis and characterization of a Cu(I) complex of the deprotonated version of 4-(2,2-dimethylhydrazino)dimethylhydrazone-3-penten-2-one (LH, Figure 1), a ligand precursor used previously to generate
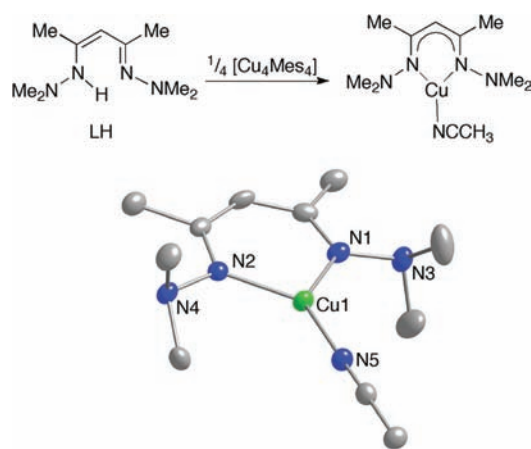

Figure 1. Synthesis of LCu(CH$_3$CN) and representation of its X-ray structure with nonhydrogen atoms shown as 50% thermal ellipsoids. Selected interatomic distances (Å) and angles (deg): Cu(1)−N(1), 1.937(3); Cu(1)−N(2), 1.941(3); Cu(1)−N(5), 1.884(3); N(1)−N(3), 1.454(4); N(2)−N(4), 1.462(4); N(1)−Cu(1)−N(2), 98.23(12); N(5)−Cu(1)−N(1), 129.23(12); N(5)−Cu(1)−N(2), 132.54(12).

volatile group IIA metal complexes for chemical vapor or atom layer deposition experiments.[11] The Cu(I) complex LCu-(CH$_3$CN) reacts with O_2 at low temperatures to yield a thermally unstable intermediate, which we propose on the basis of spectroscopic and other results contains precedented core **H**. However, this intermediate is unusual because it has an overall neutral charge, unlike previously reported trications supported by neutral N-donor ligands.[9,10] This difference underlies new reactivity for the intermediate distinct from that reported previously for complexes with core **H**, thus demonstrating

an important effect of the supporting ligand L$^-$ on Cu/O_2 chemistry.

■ EXPERIMENTAL SECTION

General Considerations. All solvents and reagents were obtained from commercial sources unless otherwise noted. Solvents were thoroughly degassed via three cycles of freezing, evacuating, and thawing. The solvents tetrahydrofuran (THF) and d_8-THF were dried over Na/benzophenone and distilled under vacuum, and CH$_2$Cl$_2$ and CH$_3$CN were dried over CaH$_2$ and distilled under vacuum; CH$_3$CN was stored over molecular sieves (4 Å). Acetone was dried over 4 Å molecular sieves, distilled, and stored over sieves (4 Å) in the glovebox. Toluene, Et$_2$O, and pentanes were passed through solvent purification columns (Glass Contour, Laguna, CA) and stored over CaH$_2$ in the glovebox. All metal complexes were prepared and stored in a Vacuum Atmospheres inert atmosphere glovebox under dry nitrogen or were manipulated under argon or dry nitrogen using standard Schlenk techniques. The proligand LH was prepared according to literature procedures,[11] dried over 4 Å molecular sieves, and distilled under vacuum prior to use.

Physical Methods. NMR spectra were recorded on either Varian VI-300, VXR-300, or VI-500 spectrometers at room temperature unless indicated otherwise. Chemical shifts (δ) for ^{1}H and ^{13}C NMR spectra were referenced to residual protium in the deuterated solvent (^{1}H) or the characteristic solvent resonances of the solvent nuclei (^{13}C). Variable temperature ^{1}H NMR spectra were obtained on a Varian VI-300 spectrometer fitted with a liquid nitrogen cryostat. Stem coaxial inserts used for Evans method experiments were purchased from Wilmad Lab Glass. UV−vis spectra were collected on a HP8453 (190−1000 nm) diode array spectrophotometer. Low temperature UV−vis experiments were performed using an Unisoku low temperature UV−vis cell holder. UV−vis spectra that had drifting baselines because of minor frosting caused by the low-temperature device were corrected when necessary by subtracting the average of a region with no absorbance from the entire spectrum. X-band electron paramagnetic resonance (EPR) spectra were recorded on a Bruker E-500 spectrometer with an Oxford Instruments EPR-10 liquid-helium cryostat (4−20 K, 9.61 GHz). Elemental analysis was performed by Robertson Microlit Lab (Madison, NJ). Electrospray ionization mass spectrometry (ESI-MS) was performed on a Bruker BioTOF II instrument with high-resolution data acquired by internally referencing samples to a polyethylene glycol standard. All GC-MS experiments were conducted on an Agilent Technologies 7890A GC system and 5975C VL MSD. The GC column was a HP-5 ms with dimensions 30 m × 0.250 mm. The standard method used for all runs involved an initial oven temperature of 60 °C (held for 4 min) followed by a 20 °C/min ramp to 230 °C that was held for 15 min. Infrared spectra were collected on a Nicolet Avatar 370 FT-IR equipped with an attenuated total reflectance attachment, using a CaF$_2$ solution cell (International Crystal Laboratories) or a Smart OMNI-Sampler for solid samples.

LCu(CH$_3$CN). LH (145 mg, 0.79 mmol) was dissolved in CH$_3$CN (5 mL) and added to a slurry of Cu$_4$Mes$_4$ (142 mg, 0.19 mmol) in THF (5 mL). The cloudy solution became clear over 20 min yielding a golden solution. After stirring for 2 h the solution became dark brown with a brown precipitate. The solution was filtered and solvent removed in vacuo yielding a brown residue. The residue was dissolved in approximately 2 mL of fresh THF and cooled to −20 °C. Addition of pentanes to this solution resulted in the rapid formation of yellow needle crystals of product that were isolated by vacuum filtration (128 mg, 66%). ^{1}H NMR (d_8-THF, 300 MHz, −80 °C): δ 2.89 (s, 1H), 2.46 (s, 3H), 2.28 (s, 12 H), 1.91 (s, 6H). ^{13}C{^{1}H} NMR (75.0 MHz, d_8-THF): δ 165.1, 121.95, 86.37, 49.53, 21.84, 2.36. Anal. Calc. for C$_9$H$_{19}$CuN$_4$ (LCu; the CH$_3$CN ligand was lost upon drying of the crystals under vacuum prior to analysis): C, 43.80; H, 7.76; N, 22.70. Found: C, 42.73; H, 7.37; N, 22.43.

Reaction of LCu(CH$_3$CN) with CO. A 5 mL Schlenk flask was charged with a 40 mM solution of LCu(NCCH$_3$) in THF and sealed by a septum. Carbon monoxide was bubbled through the solution at

1882

dx.doi.org/10.1021/ic202214c | *Inorg. Chem.* 2012, 51, 1881−1888

room temperature until all solvent had evaporated, leaving a solid residue. Samples of this residue were transferred by spatula to the FTIR spectrometer and infrared spectra collected on an attenuated total reflectance attachment. For characterization in solution, THF was added to the residue under an inert atmosphere to obtain a concentration of approximately 40 mM, and the solution was loaded and sealed in a CaF_2 solution cell (International Crystal Laboratories) for analysis by FTIR spectroscopy.

Low Temperature Oxygenations of LCu(CH$_3$CN). Anaerobically prepared solutions of LCu(CH$_3$CN) in THF or acetone (1 mM or 0.1 mM) were cooled to −80 °C in a septum sealed quartz cuvette under a constant argon purge. Dry O_2 was bubbled through the cooled solutions, and the reaction was monitored by UV−vis spectroscopy. **(a) Spectrophotometric Titrations.** In titration experiments, a 3.5 mL solution of LCu(CH$_3$CN) in THF (1 mM) was placed in a 1 cm path length cuvette and cooled to −80 °C under an argon atmosphere. An O_2 saturated THF solution was prepared by bubbling dry O_2 through argon saturated THF for 20 min.[12] Aliquots (70 μL) of the THF solution were transferred by gastight syringe to the cuvette, and the sample was allowed to equilibrate under stirring. The absorption band at 590 nm was monitored by UV−vis spectroscopy. **(b) EPR Spectroscopy.** Solutions for examination by parallel X-band EPR spectroscopy were prepared by first charging a 5 mL Schlenk flask with LCu(CH$_3$CN) in THF (60 mM) to obtain a 20 mM final concentration of the putative product $L_3Cu_3O_2$. The flask was sealed with a septum and cooled to −78 °C in a dry ice/acetone bath under argon. Dry O_2 was bubbled through the solution for 10 min followed by 45 min of an argon purge to remove excess O_2. Samples were transferred to precooled EPR tubes taking care to avoid any bubbles and rapidly frozen in liquid N_2 and stored for analysis. Samples were examined with the spectrometer set in the parallel mode (9.3970 GHz) at a temperature of 13 K. **(c) ESI-MS Analysis.** A 5 mL Schlenk flask was charged with a 1 mM solution of LCu(CH$_3$CN) and cooled to −78 °C under argon in a dry ice/acetone bath. Dry O_2 was bubbled through the solution for 10 min followed by 20 min of an argon purge. An aliquot (40 μL) of the dark green solution was rapidly loaded into 100 μL gastight syringe followed by 40 μL of fresh methanol and the sample directly injected into the spectrometer while continuously collecting spectra in the positive ion detection mode. As the deep green portion entered the instrument the peaks of interest were observed and became more intense. Samples prepared from PhIO were prepared by placing 1 equiv of PhIO in a 5 mL Schlenk flask with THF (3.2 mL) and a stir bar. After sealing with a septum, the heterogeneous mixture was cooled to −78 °C in a dry ice/acetone bath under argon. A solution of LCu(CH$_3$CN) in THF was added to this mixture by gastight syringe to yield a final copper concentration of 1 mM in the flask. The solution was stirred for 5 h at −78 °C. The insoluble solids were removed by rapidly passing the solution through a 0.45 μm PTFE filter into a precooled 5 mL Schlenk flask. This process caused an instantaneous color change in the solution from deep green to a pale gold/green, and no peaks in the ESI-MS spectrum were assignable to $L_3Cu_3O_2$. **(d) Evans Method Determination of Magnetic Susceptibility.** A stock solution of LCu(CH$_3$CN) (38.4 mg, 0.133 mmol) and 1,3,5-trimethoxybenzene (22.4 mg, 0.133 mmol) in d_8-THF (2.5 mL) was prepared in the glovebox. An aliquot of the stock solution (0.6 mL) was sealed in an NMR tube by a septum and cooled to −78 °C in a dry ice/acetone bath under a positive argon atmosphere. The solution was oxygenated by bubbling dry O_2 through the solution for 5 min followed by an argon purge (15 min) to remove excess O_2. A separate stock solution of 1,3,5-trimethoxybenzene (22.5 mg, 0.134 mmol) in d_8-THF (2.5 mL) was prepared and loaded into a coaxial NMR insert and sealed in the glovebox. The insert was placed into the NMR tube containing the oxygenated solution and the ^{1}H NMR spectrum obtained of the combined apparatus at −80 °C.

Photometric H$_2$O$_2$ Detection with Ti(IV)Oxysulfate. A stock solution of aqueous H_2O_2 (1.96 mM) was prepared from a H_2O_2 solution (30% in H_2O) and serially diluted to known concentrations (0.899, 0.448, and 0.268 mM). Aliquots from the H_2O_2 solution (3 mL) were loaded into a UV−vis cuvette, and 0.1 mL of Ti(IV)oxysulfate added (15% in dilute sulfuric acid). The UV−vis

spectra of the solutions were recorded, and the absorbance at λ_{max} = 408 nm was recorded and plotted against the concentration of H_2O_2 to obtain a standard curve. This standard curve was used to detect and/or quantitate peroxide species derived from Cu/O_2 reactions as described in the literature.[13] To validate the method, a solution of [(TMPA)Cu(NCCH$_3$)]OTf in THF (22 mM) at −78 °C was oxygenated for 20 min, which resulted in the formation of a characteristic purple solution for [(TMPA)$_2$Cu$_2$O$_2$]$^{2+}$.[14] Formic acid (2.4 equiv per dicopper species) was added, and the solution warmed to room temperature. Addition of Ti(IV)oxysulfate and quantification of the chromophore observed at λ_{max} = 408 nm to a standard curve showed the recovery of 79% of the expected amount of H_2O_2 (Supporting Information, Figure S1). An identical procedure was used to evaluate the blue/green species resulting from oxygenation of LCu(CH$_3$CN), and in this case no absorbance at 408 nm was observed, indicating no formation of H_2O_2 (Supporting Information, Figure S2).

Reactions of Oxygenated Product with Exogenous Substrates. Solutions of $L_3Cu_3O_2$ in 3.5 mL of THF (1 mM) were generated as described above. After complete formation of $L_3Cu_3O_2$ as determined by UV−vis spectroscopy, samples were purged for 20 min with argon. Substrates were introduced as THF solutions by syringe (9,10-dihydroanthracene, 2,6-di-*tert*-butylphenol, 2,4,6-tri-*tert*-butylphenol, 2,4-di-*tert*-butylphenol, ferrocene, triphenylphosphine), added as a 30% by weight in water solution (H_2O_2), or bubbled through the reaction as a gas (CO_2). Reactions were monitored by UV−vis spectroscopy for 2 h and then warmed to room temperature and analyzed by GC-MS. Samples for GC-MS analysis were demetalated by the following steps. Solvent was removed under vacuum, and the remaining residue dissolved in CH_2Cl_2 (∼ 5 mL). The solution was washed with dilute aqueous HCl (3 × 5 mL of 0.1 M HCl). The organic layer was dried over K_2CO_3, filtered, and injected into the GC-MS instrument.

RESULTS AND DISCUSSION

Synthesis and Characterization of LCu(CH$_3$CN). Reaction of LH with Cu$_4$Mes$_4$ in CH$_3$CN/THF (1:1 v/v) generated LCu(CH$_3$CN), which was isolated as a crystalline solid in 66% yield and characterized by NMR spectroscopy, CHN analysis, and X-ray crystallography (Figure 1). The anticipated peaks were observed in the room temperature ^{1}H NMR spectrum of the complex in d_8-THF (Supporting Information, Figure S3), although the signal for the hydrogen atoms on the CH$_3$CN ligand overlap with those for the −NMe$_2$ groups of L$^-$ (2.32 ppm). These peaks were resolved in a spectrum recorded at −80 °C, suggesting lability of the CH$_3$CN group or an ill-defined fluxional process in solution. In support of the former possibility, extended drying of the crystals of the complex under vacuum resulted in loss of the CH$_3$CN ligand (CHN analysis). Air-sensitive crystals of the complex suitable for X-ray diffraction analysis were obtained from THF/ pentanes solutions kept at −80 °C (Figure 1). Similar to other reported Cu(I) complexes of β-diketiminates,[1e,4−6,8] LCu-(CH$_3$CN) contains a 3-coordinate Cu ion in a trigonal planar geometry (sum of donor angles = 360°) ligated by two nitrogen atoms from L$^-$ and one nitrogen from bound CH$_3$CN. The structural parameters of L$^-$ are similar to those reported for η^2-bound complexes of group IIA metals (cf. N−N distances of 1.45−1.46 Å, N-methyl groups splayed away from the β-diketiminate backbone substituents).

To evaluate the electron donating characteristics of L$^-$, we examined the reaction of LCu(CH$_3$CN) with CO with the aim of preparing a simple CO adduct and comparing its ν(CO) value to those reported for Cu(I)-CO complexes (Table 1).[5,8,15−26] Thus, solutions of LCu(CH$_3$CN) in THF were treated with CO (1 atm) and examined by FTIR spectroscopy,

Table 1. IR Data for Selected Copper(I)-CO Adducts

entry	compound[a]	$\nu(CO)$ (cm^{-1})	ref
1	Cu(CO)$_2$AsF$_6$	2177, 2164	15
2	Zeolite ZSM-5$^-$ [Cu(CO)$_2$]$^+$	2178, 2151	16
3	[(TMPA)Cu(CO)]$^+$	2091, 2077	17
4	LCu(CH$_3$CN) + CO in THF	2056, 1968	this work
5	[(TMEN)$_2$Cu$_2$(μ-CO)]$^{2+}$ in THF	2060, 1930	18
6	[(TMPDA)$_2$Cu$_2$(μ-CO)]$^{2+}$ in THF	2065, 1925	18
7	Cu(CO)OTf in TfOH	2155	19
8	CO	2143	20
9	Tp$^{(CF3)2}$Cu(CO)	2137	21
10	[Cu(CO)]Cl	2127	22
11	Tp^{CF3,H}Cu(CO)	2100	23
12	(**5**)Cu(CO)	2100	8
13	[Cu(Me$_6$tren)CO]PF$_6$ (Nujol)	2098	24
14	[(tach)Cu(CO)]PF$_6$	2092	25
15	[Cu(Me$_6$tren)CO]PF$_6$ in THF	2078	24
16	(**6**)Cu(CO)	2071	8
17	Tp^{iPr2}Cu(CO)	2056	26
18	LCu(CH$_3$CN) + CO (solid)	2047	this work
19	[(TMEN)$_2$Cu$_2$(μ-CO)]$^{2+}$ (Nujol)	1926	18
20	[(TMPDA)$_2$Cu$_2$(μ-CO)]$^{2+}$ (Nujol)	1925	18

[a]Abbreviations: TMPA = tris(methylpyridyl)amine; TMEN = N,N,N′,N′-tetramethylethylenediamine; TMPDA = N,N,N′,N′-tetramethylpropylenediamine; OTf$^-$ = CF$_3$SO$_3^-$; Tp$^{R,R'}$ = tris(3-R, 5-R′-pyrazolyl)hydroborate; Me$_6$tren = tris(N,N-dimethylaminoethyl)-amine; tach =1,3,5-triazacyclohexane.

both in solution and, after removal of THF, in the solid state (Figure 2). The solid-state sample (solid line) displays a single
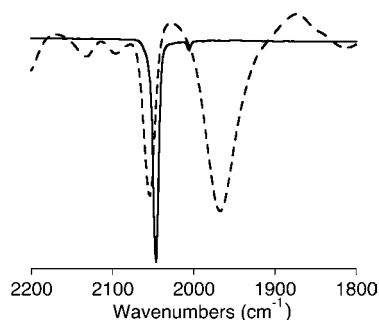

Figure 2. FTIR spectra of the product of the reaction of LCu(CH$_3$CN) in THF with CO, in the solid state (*solid line*) and in solution (*dashed line*).

sharp peak at 2047 cm^{-1} consistent with formation of LCu(CO). This feature is lower in energy than reported $\nu(CO)$ values for CO bound in terminal fashion to Cu(I) centers in a variety of ligand environments, including complexes supported by other β-diketiminates (Table 1, entries 9−18). The data thus demonstrate the exceptionally strong electron donating properties of L$^-$.

The solution state spectrum (dotted line, Figure 2) displays two peaks at 2056 and 1968 cm^{-1}, indicating either (a) binding of two CO molecules to the LCu(I) moiety to yield LCu-(CO)$_2$, or (b) the presence of two types of CO adducts, possibly in equilibrium. Rationale (a) seems unlikely because while several [Cu(CO)$_2$]$^+$ species have been reported (cf. entry 2, Table 1),[16,27−31] they display $\nu(CO)$ values higher in energy than free CO (2143 cm^{-1}) because of competition between the multiple CO ligands for dπ electron density at the metal

center.[27] In support of rationale (b), equilibria between Cu(I) species with bridging or terminal CO ligands (Figure 3)
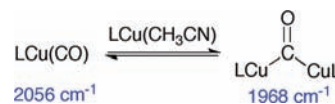

Figure 3. Proposed equilibrium between CO adducts in solution.

have been described for complexes supported by bidentate peralkylated diamines, which exhibit a pattern of $\nu(CO)$ values similar to that which we observe (entries 4−6, Table 1).[18] We deem it likely that a similar equilibrium occurs for our system, with the caveat that we have not performed more extensive characterization to support this hypothesis unambiguously. An alternative hypothesis reported recently[17] for tris(methyl-pyridyl)amine (TMPA) complexes involving adducts with a ligand arm either bound or dissociated (entry 3, Table 1) would seem less likely for L$^-$, as dissociation of one donor in a β-diketiminate complex of copper has yet to be observed.[32]

O$_2$ Reactivity. Oxygenation of LCu(NCCH$_3$) in THF or acetone at −80 °C resulted in a rapid color change of the solution from pale yellow to deep blue/green. This color remained unchanged at low temperature for many hours, but bleached upon warming, with an approximate half-life of 1 h at −10 °C (Supporting Information, Figure S4). Attempts to isolate the blue/green species as a pure solid were unsuccessful, so characterization in solution was pursued. UV−vis spectra measured for the oxygenation (1 mM Cu(I), THF, −80 °C, using 1 or 0.2 cm path length cells) are presented in Figure 4 with the starting complex (*dashed*), a transient species (*dotted*), and the final oxygenation product shown (*solid*). The transient species (Figure 4, *dotted*) forms instantaneously and gives way to the final blue/green product (Figure 4, *solid*) in seconds; because of its instability, further characterization of the transient species was not possible. The λ_{max} values and extinction coefficients for the blue/green final product are compared to those of [Cu$_3$O$_2$]$^{3+}$ species reported previously in Table 2. Despite differences in detail that likely arise from divergent supporting ligand donor characteristics, the overall patterns of the features are roughly similar, consistent with analogous core structures. To test this notion, we sought to determine the nuclearity (Cu:O ratio) of the blue/green product species through a spectrophotometric titration. Aliquots of THF saturated with O$_2$ (10 mM)[12] were added to a solution of LCu(NCCH$_3$) in THF (10 mM) at −80 °C and the spectral feature at 590 nm was monitored (Figure 5). The absorption feature reached a maximum intensity (intersection of shown best fit lines) at 0.35(2) equiv of O$_2$ per copper atom (~3:2 Cu:O ratio), consistent with a [Cu$_3$O$_2$]$^{3+}$ core.

Further evidence in favor of the formulation of the blue/green oxygenation product as L$_3$Cu$_3$O$_2$ was obtained using ESI-MS. The starting sample solution was kept at −78 °C, and the sample transfer tube that is typically used to introduce an ESI-MS sample was removed to minimize sample warming/decomposition and maximize the peak intensities of the species of interest. Initial spectra of THF or acetone solutions did not display any signal in either the positive or the negative ion detection modes, indicating that no easily ionizable species were present under these conditions. Samples doped with methanol lost their characteristic blue/green color when warmed and displayed a strong peak envelope at m/z = 429.2640 in the mass spectrum that we assign on the basis of simulation as an
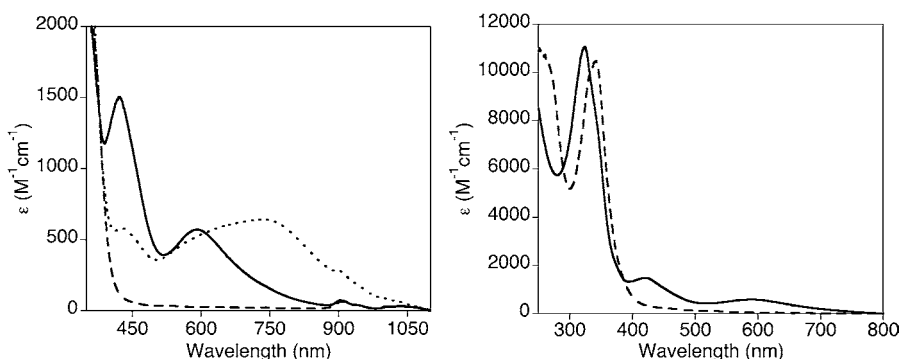
Figure 4. UV–vis spectra of the oxygenation of LCu(CH$_3$CN) at −80 °C in THF (1 mM) in a 1 cm path length cuvette (*left*) and a 0.2 cm path length cuvette (*right*). Dashed line = LCu(CH$_3$CN); dotted line = transient intermediate; solid line = final oxygenated product. The transient intermediate was not observed in the experiment using the 0.2 cm path length cuvette because of experimental difficulties associated with baseline drift and solution warming during oxygenation.

Table 2. UV-vis Data for $[(Ligand)_3Cu_3O_2]^{n+}$ Complexes^a

ligand	n	solvent	λ_{max}, nm (ε, M^{-1} cm^{-1} per Cu)	ref
TMCD	3	CH$_2$Cl$_2$	355(5000), 480(470), 620(270)^b	9a
TMEN	3	acetone	345(4200), 500(440), 620(300)	33
^{H}Py1^{Me,Me}	3	acetone	342(4000), 515(333), 685(270)	10
L	0	THF	328(10700), 420(1500), 590(835)	this work

^{a}TMCD = N,N,N',N'-(R,R)-1,2-cyclohexanediamine; TMEN = N,N,N',N'-tetramethylethylenediamine; ^{H}Py1^{Me,Me} = N,N-dimethyl-2-(2-pyridyl)ethylamine. ^{b}Additional peak reported at 290 (4200).
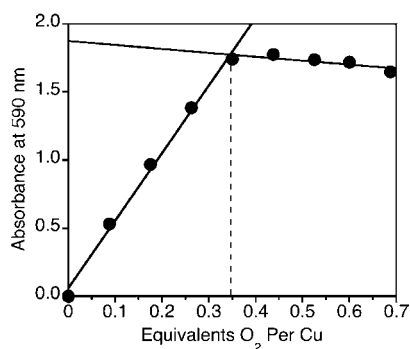

Figure 5. Data from titration of solution of LCu(CH$_3$CN) in THF (10 mM) with O$_2$ at −80 °C, with best linear fits (solid lines). The intersection point is mapped to the x-axis (dashed line) to yield the Cu:O ratio (0.35(2) equiv O$_2$ per Cu = ~3:2 Cu:O ratio).

apparent decomposition product [L$_2$Cu]$^+$ (Supporting Information, Figure S5). However, by first loading a 100 μL sample syringe with 40 μL of an acetone solution of the blue/green species (at −80 °C), followed by 60 μL of MeOH, and rapidly injecting the solution into the spectrometer a mass spectrum was obtained with multiple peak envelopes indicative of multicopper species (high m/z region in Figure 6; full spectrum in Supporting Information, Figure S6). The highest m/z peak envelopes feature isotope patterns diagnostic for three copper atoms and were identified on the basis of simulations as L$_3$Cu$_3$O$_2$ plus variable solvent molecules: C$_{32}$H$_{68}$Cu$_3$N$_{14}$O$_3$ [L$_3$Cu$_3$O$_2$ + MeOH + 2CH$_3$CN + H$^+$]$^+$ (mass 887.1967; Figure 6) and C$_{34}$H$_{72}$Cu$_3$N$_{13}$O$_4$ [L$_3$Cu$_3$O$_2$ + MeOH + CH$_3$CN + THF + H$^+$]$^+$ (mass 917.2197; Supporting Information, Figure S7). These results support the presence of L$_3$Cu$_3$O$_2$ in the blue/green oxygenation product solutions.
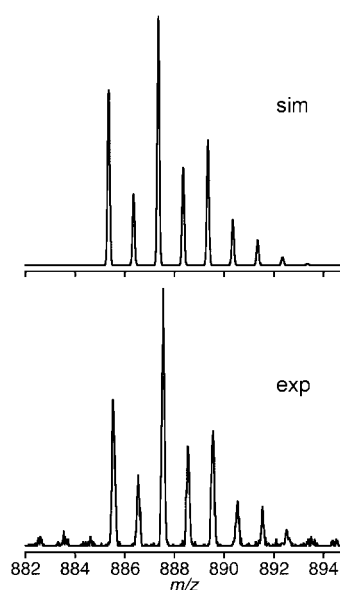

Figure 6. Peak envelope in the ESI mass spectrum (bottom) and simulation (top) for the blue/green oxygenation product solution corresponding to C$_{32}$H$_{68}$Cu$_3$N$_{14}$O$_3$ [L$_3$Cu$_3$O$_2$ + MeOH + 2CH$_3$CN + H$^+$]$^+$. The full spectrum is presented in the Supporting Information, Figure S6.

Previous work demonstrated that the [Cu$_3$O$_2$]$^{3+}$ core contains one Cu(III) and two Cu(II) ions in a valence localized S = 1 ground state.[9,33,34] For comparison, we examined the electronic structure of the blue/green oxygenation product through solution state magnetic susceptibility (Evans method)[35−38] and EPR spectroscopy measurements. In the Evans method experiment, a 54 mM solution of LCu(NCCH$_3$) was oxygenated in d$_8$-THF at −78 °C in the presence of an internal standard 1,3,5-trimethoxybenzene. Comparison of the peak assignable to the aryl proton originating from 1,3,5-trimethoxybenzene appearing between 5 and 7 ppm for this sample and one for an inserted coaxial tube with only the internal standard provided a peak separation that upon analysis (Supporting Information, Figure S8 and associated text) yielded μ$_{eff}$ = 2.8(1) BM. This value is indicative of an S = 1 ground state (μ$_{eff}$ = 2.83 μ$_B$)[39] and is in agreement with the value determined via similar methodology for [(TMCD)$_3$Cu$_3$O$_2$]$^{3+}$.[9a]

The parallel mode X-band EPR spectrum of the blue/green product solution is shown in Figure 7 with the g ~ 4 region

enlarged and shown in the inset. The feature observed at ~1500 G is attributed to a $\Delta m_s = 2$ transition and the high field
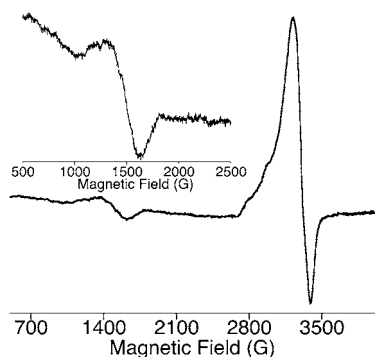

Figure 7. X-Band EPR spectrum (9.3970 GHz) of the oxygenation product of LCu(NCCH₃) (60 mM) in THF in parallel mode at 13 K. The inset displays an expanded view of the $g \sim 4$ region.

signal at ~3300 G is a $\Delta m_s = 1$ transition, consistent with what would be expected for a triplet ground state species.[34,40] These features are qualitatively similar to those reported previously for $[(TMCD)_3Cu_3O_2]^{3+}$, which exhibits a strong derivative feature at 3525 G and a $\Delta m_s = 2$ transition at 1400 G.[34]

To evaluate the possibility that the blue/green species is a peroxide complex, we attempted to detect H_2O_2 after treatment with protic acid using a precedented Ti(IV)oxysulfate titration procedure (see Experimental Section for details).[13] We first validated the procedure by testing the known 1,2-peroxide complex $[(TMPA)_2Cu_2O_2](OTf)_2$,[14] and from the absorbance at 408 nm obtained a 79% yield of the expected amount of H_2O_2. The same method applied to the blue/green solution derived from oxygenation of LCu(CH₃CN) did not display any absorbance at 408 nm, indicating that, within the limits of detection, no H_2O_2 was formed.

In sum, the similarities of the UV−vis spectrum, EPR signal, and magnetic moment in solution to those reported previously for $[Cu_3O_2]^{3+}$ complexes, in combination with the spectrophotometric titration, ESI-MS, and H_2O_2 detection results, provide compelling evidence that the oxygenation of LCu-(CH₃CN) results in the formation of $L_3Cu_3O_2$ featuring core **H** (Figure 1). This complex is novel insofar as it is supported by monoanionic rather than neutral N-donor ligands, resulting in an overall neutral rather than a +3 charge. The implications of this disparity on reactivity with exogenous substrates are explored below.

Reactivity with Exogenous Substrates. The reactions of two $[Cu_3O_2]^{3+}$ species supported by either TMCD or $^{H}Pyl^{Me,Me}$ with a few substrates have been described.[9a,10] The complex supported by TMCD was reduced by ferrocene but not acetylferrocene at −80 °C and a redox potential for the complex was estimated to be between 0.48 and 0.79 V vs SCE.[9a] Both complexes react with 2,4-di-*tert*-butylphenol via a radical pathway to form the coupled product 3,3′,5,5′-tetra-*tert*-butyl-2,2′-biphenol in high yield (>97%). Thus, they are electrophilic and are capable of performing H-atom abstractions from molecules with relatively weak O−H bonds, similar to their bis(μ-oxo)dicopper(III) relatives.[1a,b]

For comparison, we examined the reactivity of $L_3Cu_3O_2$ toward reductants (ferrocene, decamethylferrocene) and substrates with weak O−H or C−H bonds (2,4- and 2,6-di-*tert*-butylphenols, 2,4,6-tri-*tert*-butylphenol, and 9,10-dihydroanthracene). In these

experiments solutions of $L_3Cu_3O_2$ were generated by the oxygenation of LCu(CH₃CN) in THF at −80 °C (1 mM) and then purged with argon for approximately 20 min to remove excess O_2. Substrates were introduced at −80 °C and stirred for 2 h while the reactions were monitored by UV−vis spectroscopy. The solutions were then gradually warmed to room temperature, subjected to an acidic workup to remove copper-containing species, and the residue examined by GC-MS or ^{1}H NMR spectroscopy. Unlike the $[Cu_3O_2]^{3+}$ species supported by TMCD or $^{H}Pyl^{Me,Me}$, no reactions occurred with the aforementioned substrates; no decay of UV−vis spectra were seen at −80 °C and no oxidized organic products were identified by GC-MS or ^{1}H NMR spectroscopy for the reactions with the phenols or 9,10-dihydroanthracene. Apparently, $L_3Cu_3O_2$ is not nearly as potent an oxidant nor as electrophilic as the $[Cu_3O_2]^{3+}$ species supported by TMCD or $^{H}Pyl^{Me,Me}$. Yet, $L_3Cu_3O_2$ was found to be capable of transferring an O-atom to PPh_3, reactivity typical of electrophilic copper−oxygen complexes.[1c] Thus, addition of 5 equiv of PPh_3 at −80 °C to solutions of $L_3Cu_3O_2$ followed by warming to room temperature and examination by ^{31}P NMR spectroscopy[41] and GC-MS led to identification of $Ph_3P{=}O$ in ~40% yield (based on $L_3Cu_3O_2$). On the other hand, the UV−vis spectroscopic features of $L_3Cu_3O_2$ changed instantaneously upon exposure to CO_2. Carbonate-containing species formed according to ESI-MS and FT-IR data (Supporting Information, Figures S9−S11), although we have been unable to unambiguously identify their structures despite repeated attempts to isolate the products from the reaction. These results are indicative of "nucleophilic" reactivity, and contrast with the typical reaction patterns for electrophilic copper−oxygen intermediates.[1c,42] We conclude that the strong electron donating capabilities of L^- stabilize the $[Cu_3O_2]^{3+}$ core and perturb its reactivity relative to other known examples.

■ CONCLUSIONS

A Cu(I) complex of the hydrazine-derived β-diketiminate L^- was prepared and characterized, and the FTIR spectra of the products of its reaction with CO were analyzed. The data indicate that L^- is strongly electron donating, and support an equilibrium in solution between monomeric and dimeric forms with terminal and bridging CO ligands, respectively (Figure 3). Low temperature oxygenation of LCu(CH₃CN) generated a species formulated as $L_3Cu_3O_2$ with core **H** on the basis of UV−vis and EPR spectroscopy, ESI mass spectrometry, and spectrophotometric titration, magnetic susceptibility, and H_2O_2 detection experiments. The observation of a monomer/dimer equilibrium for the Cu(I)-CO adduct and formation of core **H** upon oxygenation attest to the small steric profile of L^- relative to other β-diketiminates (cf. **1−7**) that have been used previously to study Cu/O_2 chemistry. The anionic charge and strong electron donating characteristics of L^- result in unique reactivity for core **H** in $L_3Cu_3O_2$. Thus, unlike other reported variants supported by neutral N-donor ligands, $L_3Cu_3O_2$ is not reduced by ferrocene, does not abstract H-atoms from phenols or 1,2-dihydroanthracene, oxidizes PPh_3 to $Ph_3P{=}O$, and generates carbonate species upon exposure to CO_2. The new reactivity for core **H** that results from the properties of L^- illustrate key influences of supporting ligands on the structure and function of Cu/O_2 intermediates relevant to copper-catalyzed oxidations in catalysis and biology.

ASSOCIATED CONTENT

S Supporting Information

Experimental details and spectroscopic data (pdf) and X-ray crystallographic information (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: wtolman@umn.edu.

ACKNOWLEDGMENTS

REFERENCES

(1) (a) Mirica, L. M.; Ottenwaelder, X.; Stack, T. D. P. *Chem. Rev.* **2004**, *104*, 1013−1045. (b) Lewis, E. A.; Tolman, W. B. *Chem. Rev.* **2004**, *104*, 1047−1076. (c) Hatcher, L.; Karlin, K. D. *J. Biol. Inorg. Chem.* **2004**, *9*, 669−683. (d) Itoh, S. *Curr. Opin. Chem. Biol.* **2006**, *10*, 115−122. (e) Cramer, C. J.; Tolman, W. B. *Acc. Chem. Res.* **2007**, *40*, 601−608. (f) Himes, R. A.; Karlin, K. D. *Curr. Opin. Chem. Biol.* **2009**, *13*, 119−131.

(2) (a) Prigge, S. T.; Eipper, B. A.; Mains, R. E.; Amzel, L. M. *Science* **2004**, *304*, 864−867. (b) Magnus, K. A.; Ton-That, H.; Carpenter, J. E. *Chem. Rev.* **1994**, *94*, 727−735. (c) Sánchez-Ferrer, A.; Rodríguez-López, J. N.; García-Cánovas, F.; García-Carmona, F. *Biochim. Biophys. Acta* **1995**, *1247*, 1−11. (d) Woertink, J. S.; Smeets, P. J.; Groothaert, M. H.; Vance, M. A.; Sels, B. F.; Schoonheydt, R. A.; Solomon, E. I. *Proc. Natl. Acad. Sci. U.S.A.* **2009**, *106*, 18908−18913. (e) Gamez, P.; Aubel, P. G.; Driessen, W. L.; Reedijk, J. *Chem. Soc. Rev.* **2001**, *30*, 376−385.

(3) Bourget-Merle, L.; Lappert, M. F.; Severn, J. R. *Chem. Rev.* **2002**, *102*, 3031−3065.

(4) (a) Spencer, D. J. E.; Aboelella, N. W.; Reynolds, A. M.; Holland, P. L.; Tolman, W. B. *J. Am. Chem. Soc.* **2002**, *124*, 2108−2809. (b) Aboelella, N. W.; Lewis, E. A.; Reynolds, A. M.; Brennessel, W. W.; Cramer, C. J.; Tolman, W. B. *J. Am. Chem. Soc.* **2002**, *124*, 10660−10661. (c) Aboelella, N. W.; Kryatov, S. V.; Gherman, B. F.; Brennessel, W. W.; Young, V. G. Jr.; Sarangi, R.; Rybak-Akimova, E. V.; Hodgson, K. O.; Hedman, B.; Solomon, E. I.; Cramer, C. J.; Tolman, W. B. *J. Am. Chem . Soc.* **2004**, *126*, 16896−16911. (d) Reynolds, A. M.; Gherman, B. F.; Cramer, C. J.; Tolman, W. B. *Inorg. Chem.* **2005**, *44*, 6989−6997. (e) Aboelella, N. W.; Gherman, B. F.; Hill, L. M. R.; York, J. T.; Holm, N.; Young, V. G. Jr.; Cramer, C. J.; Tolman, W. B. *J. Am. Chem. Soc.* **2006**, *128*, 3445−3458.

(5) Hill, L. M. R.; Gherman, B. F.; Aboelella, N. W.; Cramer, C. J.; Tolman, W. B. *Dalton Trans.* **2006**, 4944−4953.

(6) Spencer, D. J. E.; Reynolds, A. M.; Holland, P. L.; Jazdzewski, B. A.; Duboc-Toia, C.; Pape, L. L.; Yokota, S.; Tachi, Y.; Itoh, S.; Tolman, W. B. *Inorg. Chem.* **2002**, *41*, 6307−6321.

(7) DuBois, J. L.; Mukherjee, P.; Stack, T. D. P.; Hedman, B.; Solomon, E. I.; Hodgson, K. O. *J. Am. Chem. Soc.* **2000**, *122*, 5775−5787.

(8) Hong, S.; Hill, L. M. R.; Gupta, A. K.; Naab, B. D.; Gilroy, J. B.; Hicks, R. G.; Cramer, C. J.; Tolman, W. B. *Inorg. Chem.* **2009**, *48*, 4514−4523.

(9) (a) Cole, A. P.; Root, D. E.; Mukherjee, P.; Solomon, E. I.; Stack, T. D. P. *Science* **1996**, *273*, 1848−1850. (b) Root, D. E.; Henson, M. J.; Machonkin, T.; Mukherjee, P.; Stack, T. D. P.; Solomon, E. I. *J. Am. Chem. Soc.* **1998**, *120*, 4982−4990.

(10) Taki, M.; Teramae, S.; Nagatomo, S.; Tachiu, Y.; Kitagawa, T.; Itoh, S.; Fukuzumi, S. *J. Am. Chem. Soc.* **2002**, *124*, 6367−6377.

(11) (a) Domnin, N. A.; Yakimovich, S. I. *Zh. Org. Khim.* **1965**, *1*, 658−666. (b) Sedai, B.; Heeg, M. J.; Winter, C. H. *Organometallics*

2009, *28*, 1032−1038. (c) Sedai, B.; Heeg, M. J.; Winter, C. H. *J. Organomet. Chem.* **2008**, *693*, 3495−3503.

(12) Battino, R., Ed.; *Solubility Data Series*; Pergamon: Oxford, U.K., 1981; Vol. 7: Oxygen and Ozone.

(13) (a) Halime, Z.; Kieber-Emmons, M. T.; Qayyum, M. F.; Mondal, B.; Gandhi, T.; Puiu, S. C.; Chufan, E. E.; Sarjeant, A. A. N.; Hodgson, K. O.; Hedman, B.; Solomon, E. I.; Karlin, K. D. *Inorg. Chem.* **2010**, *49*, 3629−3645. (b) Sanyal, I.; Strange, R. W.; Blackburn, N. J.; Karlin, K. D. *J. Am. Chem. Soc.* **1991**, *113*, 4692−4693. (c) Chaudhuri, P.; Hess, M.; Mueller, J.; Hildenbrand, K.; Bill, E.; Weyhermueller, T.; Wieghardt, K. *J. Am. Chem. Soc.* **1999**, *121*, 9599−9610. (d) Eisenberg, G. M. *Ind. Eng. Chem., Anal. Ed.* **1943**, *15*, 327−328.

(14) Jacobson, R. R.; Tyeklár, Z.; Farooq, A.; Karlin, K. D.; Liu, S.; Zubieta, J. *J. Am. Chem. Soc.* **1988**, *110*, 3690−3692.

(15) Rack, J. J.; Webb, J. D.; Strauss, S. H. *Inorg. Chem.* **1996**, *35*, 277−278.

(16) Zecchina, A.; Bordiga, S.; Salvalaggio, M.; Spoto, G.; Scarano, D.; Lamberti, C. *J. Catal.* **1998**, *173*, 540−542.

(17) Fry, H. C.; Lucas, H. R.; Sarjeant, A. N.; Karlin, K. D.; Meyer, G. J. *Inorg. Chem.* **2008**, *47*, 241−256.

(18) Pasquali, M.; Floriani, C.; Venturi, G.; Gaetani-Manfredotti, A.; Chiesi-Villa, A. *J. Am. Chem. Soc.* **1982**, *104*, 4092−4099.

(19) Scott, A. F.; Wilkening, L. L.; Rubin, B. *Inorg. Chem.* **1969**, *8*, 2533−2534.

(20) Lupinetti, A. J.; Strauss, S. H.; Frenking, G. *Prog. Inorg. Chem.* **2001**, *49*, 1−112.

(21) Dias, H. V. R.; Lu, H.-L. *Inorg. Chem.* **1995**, *34*, 5380−5382.

(22) Haakansson, M.; Jagner, S. *Inorg. Chem.* **1990**, *29*, 5241−5244.

(23) Dias, R. H. V.; Kim, H.-J.; Lu, H.-L.; Rajeshwar, K.; de Tacconi, N. R.; Derecskei-Kovacs, A.; Marynick, D. S. *Organometallics* **1996**, *15*, 2994−3003.

(24) Chu, L.; Hardcastle, K. I.; MacBeth, C. E. *Inorg. Chem.* **2010**, *49*, 7521−7529.

(25) Ebrahimpour, P.; Cushion, M.; Haddow, M. F.; Hallett, A. J.; Wass, D. F. *Dalton Trans.* **2010**, *39*, 10910−10919.

(26) Kitajima, N.; Fujisawa, K.; Fujimoto, C.; Morooka, Y.; Hashimoto, S.; Kitagawa, T.; Toriumi, K.; Tatsumi, K.; Nakamura, A. *J. Am. Chem. Soc.* **1992**, *114*, 1277−1291.

(27) Polyakov, O. G.; Ivanova, S. M.; Gaudinski, C. M.; Miller, S. M.; Anderson, O. P.; Strauss, S. H. *Organometallics* **1999**, *18*, 3769−3771.

(28) Rack, J. J.; Webb, J. D.; Strauss, S. H. *Inorg. Chem.* **1996**, *35*, 277−278.

(29) Iwamoto, M.; Hoshino, Y. *Inorg. Chem.* **1996**, *35*, 6918−6921.

(30) Borovkov, V. Y.; Karge, H. G. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 2035−2039.

(31) (a) Lamberti, C.; Bordiga, S.; Zecchina, A.; Salvalaggio, M.; Geobaldo, F.; Otero Arean, C. *J. Chem. Soc., Faraday Trans.* **1998**, *94*, 1519−1525. (b) Kuroda, Y.; Maeda, H.; Yoshikawa, Y.; Kumashiro, R.; Nagao, M. *J. Phys. Chem. B* **1997**, *101*, 1312−1316.

(32) Another option suggested by a reviewer would be for the peak at 1968 cm^{-1} to arise from LCu(CO)THF. We view this notion to be unlikely relative to the more precedented equilibrium in Figure 3 because it is not clear why such a species would exhibit a broadened ν(CO) shifted 88 cm^{-1} from the sharp peak at 2056 cm^{-1} (a much smaller shift would be anticipated; see ref 17).

(33) Kang, P.; Bobyr, E.; Dustman, J.; Hodgson, K. O.; Hedman, B.; Solomon, E. I.; Stack, T. D. P. *Inorg. Chem.* **2010**, *49*, 11030−11038.

(34) Machonkin, T.; Mukherjee, P.; Henson, M.; Stack, T. D. P.; Solomon, E. I. *Inorg. Chim. Acta* **2002**, *341*, 39−44.

(35) Piguet, C. *J. Chem. Educ.* **1997**, *74*, 815−816.

(36) Sur, S. K. *J. Magn. Reson.* **1989**, *82*, 169−173.

(37) Evans, D. F. *J. Chem. Soc.* **1959**, 2003−2005.

(38) Taktak, S.; Ye, W.; Herrera, A. M.; Rybak-Akimova, E. V. *Inorg. Chem.* **2007**, *46*, 2929−2942.

(39) Que, L. *Physical Methods in Bioinorganic Chemistry*; University Science Books: Sausalito, CA, 2000.

(40) Yang, F.-A.; Guo, C.-W.; Chen, Y.-J.; Chen, J.-H.; Wang, S.-S.; Tung, J.-Y.; Hwang, L.-P.; Elango, S. *Inorg. Chem.* **2007**, *46*, 578−585.

(41) Zeldin, M.; Mehta, P.; Vernon, W. D. *Inorg. Chem.* **1979**, *18*, 463−466.

(42) As suggested by a reviewer, reaction of $L_3Cu_3O_2$ with CO_2 may involve initial reaction with the dimethylamino group of the ligand. We cannot rule out this possibility on the basis of the available data.

1888

dx.doi.org/10.1021/ic202214c | *Inorg. Chem.* 2012, 51, 1881−1888