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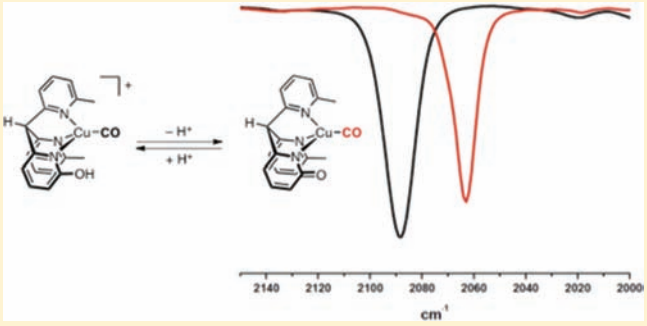
Influence of Second Coordination Sphere Hydroxyl Groups on the Reactivity of Copper(I) Complexes

Christopher S. Letko, Thomas B. Rauchfuss,* Xiaoyuan Zhou, and Danielle L. Gray

School of Chemical Sciences, University of Illinois, Urbana, Illinois 61801, United States

Supporting Information

ABSTRACT: We report the enhanced reactivity of hydroxyl substituted CuN_3^+ derivatives, where N_3 = tris(picolinyl)-methane (tripic) and related derivatives, upon deprotonation of the O−H functionality. The work capitalizes on new methodology for incorporating hydroxyl groups into the second coordination sphere of copper centers. The key synthetic methodology relies on Pd-catalyzed coupling reactions of dilithiated 6-methyl-2-pyridone with bromopyridyl derivatives. These building blocks allow the preparation of tridentate N_3 ligands with OH and OMe substituents flanking the fourth coordination site of a tetrahedral complex. Coupling of these tridendate ligands gives the corresponding hydroxy- and methoxy-functionalized bistripodal ligands. [Cu[bis(2-methylpyrid-6-yl)(2-hydroxypyrid-6-yl)methane](NCMe)]$^+$ ([Cu(**2**H)(NCMe)]$^+$) oxidizes readily in air to afford the mixed valence $Cu^{1,5}$ dimer ([Cu_2(**2**)$_2$]$^+$). Formation of [Cu_2(**2**)$_2$]$^+$ is accelerated in the presence of base and can be reversed with a combination of decamethylferrocene and acid. The reactivity of [Cu(**2**H)(NCMe)]$^+$ with dioxygen requires deprotonation of the hydroxyl substituent: neither [Cu(tripic)(NCMe)]$^+$ nor the methoxy-derivatives displayed comparable reactivity. A related mixed valence dimer formed upon oxidation of the dicopper(**I**) complex of a tetrahydroxy bis(tridentate) ligand, [Cu_2(**6**H_4)(NCMe)$_2$]$^{2+}$. The dicopper(**I**) complex of the analogous tetramethoxy N_6-ligand, [Cu_2(**5**)(NCMe)$_2$]$^{2+}$, instead reversibly binds O_2. Deprotonation of [Cu(**2**H)(CO)]$^+$ and [Cu(**2**H)(NCMe)]$^+$ afforded the neutral derivatives Cu(**2**)(CO) and Cu_2(**2**)$_2$, respectively. The dicopper(**I**) derivative Cu_2(**2**)$_2$ can be reoxidized, reprotonated, and carbonylated. The silver(**I**) complex, [Ag(**2**H)(NCMe)]BF_4, forms an analogous neutral dimer (Ag_2(**2**)$_2$) upon deprotonation of the hydroxyl group. The structures of ligand **2**H, [Cu_2(**5**)(NCMe)$_2$]$^+$, [Cu_2(**2**)$_2$]$^+$, [Cu_2(**6**H_2)]$^+$, [Ag(**2**H)(NCMe)]BF_4, and Ag_2(**2**)$_2$ were confirmed by single crystal X-ray diffraction.



INTRODUCTION

The metal-catalyzed reduction of O_2 is a central reaction in many energy harvesting schemes.[1] Because aerobic life depends on this process, nature has evolved elaborate catalysts for this reduction.[2] Synthetic catalysts for the catalytic reduction of O_2 are few however.[3,4] Catalysts are required components of fuel cells, which operate optimally when the oxygen reduction reaction (ORR) is effected at low pH and close to the thermodynamic potential (1.23 V at pH = 0).[5] Since even platinum-based catalysts require overpotentials of several hundred millivolts, interest in improved catalysts remains high.[6] Modeling enzyme active sites has been one the most promising approaches to the development of replacements for platinum in fuel cells.[7]

In the quest for biomimetic O_2 reduction catalysts, obvious approaches involve iron and copper centers capitalizing on the affinity of biological cuprous and ferrous centers for O_2.[8] Impressive advances have been made in constructing functional O_2 reduction catalysts based on cytochrome oxidase.[9] In some respects laccase, a multicopper oxidase containing a trinuclear Cu site O_2 receptor,[10] presents a simpler design than cytochrome oxidase, although less progress has been reported in developing functional models.[11]

Dioxygen has been observed to bridge pairs of Cu centers in two modes: μ-κ^1:κ^1 and μ-κ^2:κ^2, depending on the coordination number of the copper center.[12] CuN_2 and CuN_3 sites favor μ-κ^2:κ^2-O_2 derivatives, whereas CuN_4 sites, which do not occur naturally, give complexes with μ-κ^1:κ^1 O_2 ligands. The μ-κ^1:κ^1-peroxide ligand, like nonbridging η^2-peroxides,[13] is generally nucleophilic. Thus, protonation of [Cu_2(tpa)$_2$(μ-κ^1:κ^1-O_2)]$^{2+}$ (tpa = tris(2-pyridylmethyl)-amine) affords hydrogen peroxide.[14] In contrast, we have shown that μ-κ^2:κ^2-O_2 complexes resist protonation.[4]

The premier example of a thermally stable Cu_2−O_2 complex is [Cu_2(bistripic)(O_2)]$^{2+}$ (bistripic = 1,2-bis[2-(bis(6-methylpyrid-2-yl)methyl)pyrid-6-yl]ethane), as described by Kodera and co-workers (Figure 1).[15,16] This dicopper complex mimics the behavior of the O_2-carrier hemocyanin.[17] In the bistripic system, two CuN_3 sites cooperate in binding O_2. The related monocopper derivative [Cu(tripic)(NCMe)]$^+$ (tripic = tris(6-methylpyrid-2-yl)methane) is unreactive toward O_2.[18]

We hypothesized that by augmenting the bistripic system with proton donors, the corresponding hemocyanin model might acquire laccase-like properties. Our hypothesis was informed by the role of hydrogen-bonding in the enzymatic reduction of O_2,[19] which is thought to involve proton-coupled

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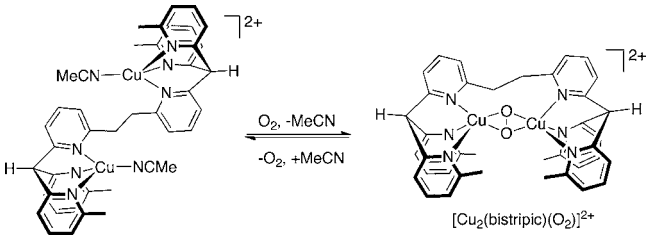


Figure 1. Reaction of O_2 with $[Cu_2(bistripic)(NCMe)_2]^{2+}$.

electron-transfer (PCET).[20] Several studies have examined the role of hydrogen-bonding substituents in the second coordination sphere of copper complexes, but with variable success.[21−23] A Cu-hydroperoxide is stabilized by hydrogen-bonding to a pendant pivalamide N−H group.[23] The stability of $[Cu_2(tpa)_2(\mu\text{-}\kappa^1{:}\kappa^1\text{-}O_2)]^{2+}$ complexes is slightly enhanced by introduction of amine groups flanking the pyridyl nitrogen centers.[22]

This Article describes the synthesis of a new set of mono- and dicopper complexes with hydroxy-functionalized tripodal ligands, along with a description of their reactivity toward dioxygen and CO. Deprotonation of the auxillairy hydroxyl groups enhances the reactivity of hemocyanin-inspired models, not only for the dicopper(I) species but for the related monocopper(I) complex.

RESULTS AND DISCUSSION

Synthesis of Hydroxy- and Methoxy-Complemented Tripodal Ligands. The preparation of copper(I) complexes of hydroxy-complemented tripodal ligands required modification of the coupling routes described by Kodera for tris-(2-picolinyl)methane.[15,24] The specific methodological innovation is based on the generation and use of the dilithiated derivative of 2-hydroxy-6-methylpyridine. This dilithiated derivative was found to couple with 2-bromo-6-methylpyridine using $ZnCl_2$ as the transmetallating agent and $PdCl_2$(dppf) as catalyst to afford (2-picolin-6-yl)(2-pyridon-6-yl)methane (**1**). The coupled product **1**, which exists as the pyridone tautomer, proved to be a versatile precursor to other tripodal N_3-ligands that contain flanking hydrogen-bonding functionality. For example, **1** was cross-coupled with an additional equiv of 2-bromo-6-methylpyridine to afford ligand **2**H (Scheme 1).

Crystallographic analysis confirmed that **2**H exists as the pyridone tautomer. An intramolecular bifurcated hydrogen-bond exists between the pyridone N−H and the two picolinyl nitrogen atoms with a N1−N2 distance of 2.902(2) Å (Figure 2). Even stronger bifurcated hydrogen-bonds have been observed for

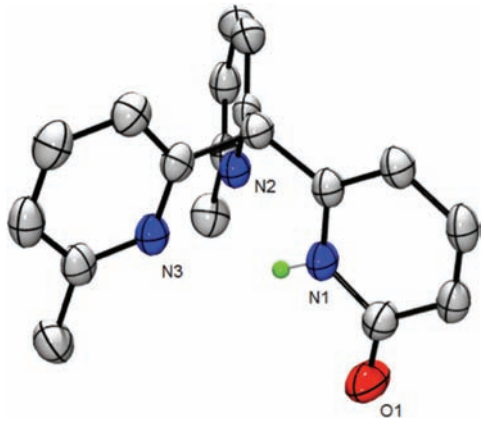


Figure 2. Structure of the pyridone tautomer of **2**H with ellipsoids shown at 50% probability. The hydrogen atom (green) bound to N1 was located crystallographically. Other hydrogen atoms were omitted for clarity.

a related amide-pyridine-pyrazine ligand ($d(N_{amide}{-}N_{pyridine}$ = 2.598(6), $d(N_{amide}{-}N_{pyrazine}$ = 2.667(5) Å).[25] Amine proton N1−*H* was located in the difference map at a short distance of 2.41(2) Å from N2. The presence of hydrogen-bonding in **2**H is consistent with its ^{1}H NMR spectrum, which exhibits a D_2O-exchangeable signal at δ 11.8.[26] Thus, ligand **2**H adopts a conformation similar to complexes of its tautomer.

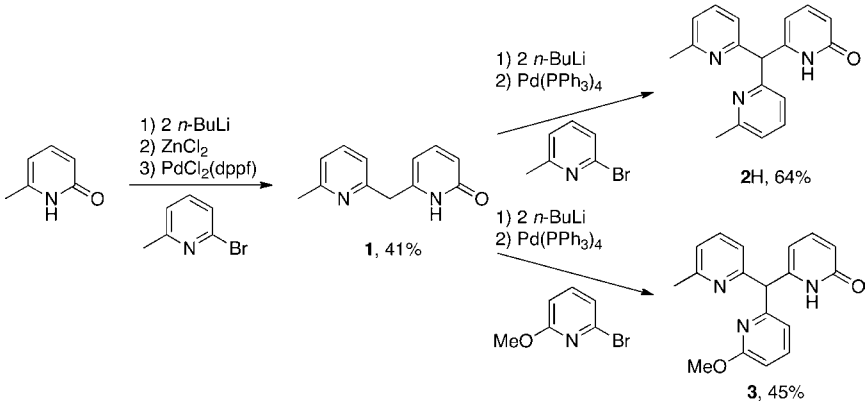
Pd-catalyzed cross-coupling of the dilithiated derivative of **1** with 2-bromo-6-methoxypyridine gave **3**, a chiral tripodal ligand where the binding pocket is flanked by methyl, methoxy, and hydroxy substituents (Scheme 1).

Hexadentate ligands capable of hosting two copper centers were prepared via the homocoupling of two tripodal ligands such as **2**H. To avoid complications with the coupling of chiral precursors, we converted **3** into the dimethoxy tripod **4** by methylation of **3** with Ag_2CO_3 and MeI. Dilithiation of **4** using *t*-BuLi followed by oxidation of this intermediate with 1,2-dibromoethane afforded the homodimeric ligand **5** (Scheme 2).

Analogous to the behavior of 2-methoxypyridine,[27] **5** was efficiently demethylated with HBr to yield the tetrahydroxy ligand **6**H_4. Coordination of Cu^I to hydroxy-decorated tripodal ligands occurs with tautomerization of pyridone to hydroxypyridine (see below), as commonly observed when combining pyridone ligands and soft metal cations.[28] The abbreviations **2**H and **6**H_4 are used here to describe all tautomers of these ligands.

Complexes of Methoxy- and Hydroxy-Functionalized Ligands. The tripodal ligands **2**H and **3** readily formed 1:1

Scheme 1. Synthesis of Hydroxyl-Functionalized Tripodal Ligands



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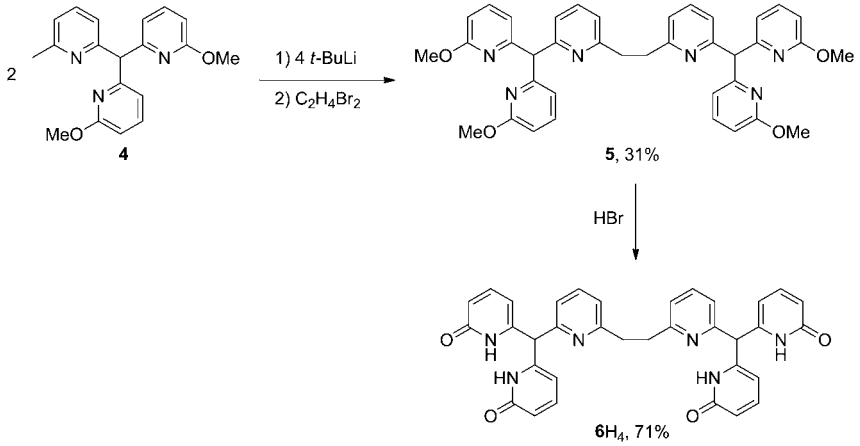
Scheme 2. Synthesis of Methoxy- and Hydroxy-Functionalized Bistripodal Ligands



complexes upon treatment with salts of $[Cu(MeCN)_4]^+$. Spectroscopic analysis indicated that these species are similar to $[Cu(tripic)(MeCN)]^+$.[18] A silver(I) derivative, $[Ag(\mathbf{2}H)(MeCN)]BF_4$, was also prepared, the ^1H NMR spectrum of which displays a broad singlet at δ 9.1 assigned to the phenolic O*H*. X-ray crystallography confirmed the tetrahedral coordination with an uncoordinated OH group (Figure 3).

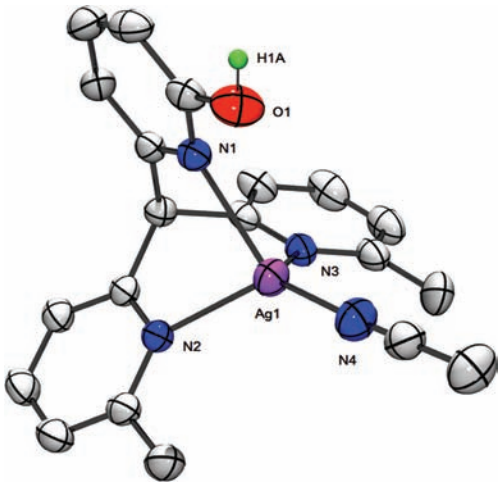


Figure 3. Structure of $[Ag(\mathbf{2}H)(MeCN)]BF_4$ with ellipsoids shown at 50% probability level. Counteranions and solvent molecules were omitted for clarity. Selected distances (Å): Ag(1)−N(1), 2.090(4); Ag(1)−N(2), 2.09(4); Ag(1)−N(3), 2.060(3); Ag(1)−N(4), 6.7784(9). The O*H* group was located in the refinement.

Upon treatment with copper(I), the binucleating ligands **5** and $\mathbf{6}H_4$ gave 2:1 derivatives. Although the PF_6^- salts of these dicationic complexes proved poorly soluble in CH_2Cl_2, the corresponding tetrakis(3,5-trifluoromethylphenyl)borate ($BAr^F{}_4^-$) and tetrakis(pentafluorophenyl)borate ($BAr^{F5}{}_4^-$) salts exhibited satifactory solubility. Crystallographic analysis of $[Cu_2(\mathbf{5})(NCMe)_2](BAr^F{}_4)_2$ confirmed the CuN_4 environment provided by two methoxypyridyl groups, one picolinyl group, and an acetonitrile ligand (Figure 4).

Unlike $[Cu_2(\mathbf{5})(NCMe)_2](BAr^F{}_4)_2$, the salt of the tetrahydroxy complex, tentatively assigned as $[Cu_2(\mathbf{6}H_4)(NCMe)_x](BAr^F{}_4)_2$, appears to adopt an asymmetric structure indicated by its complex ^1H NMR spectrum. The −55 °C NMR spectrum of a CD_2Cl_2 solution exhibits four equally intense but

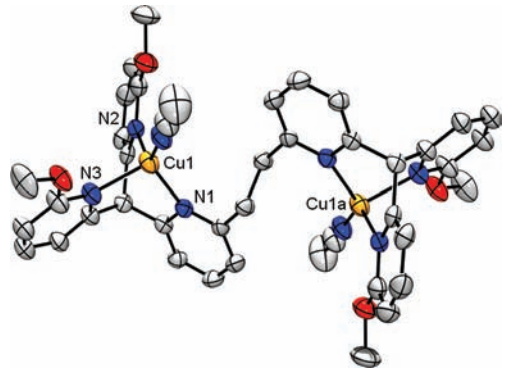
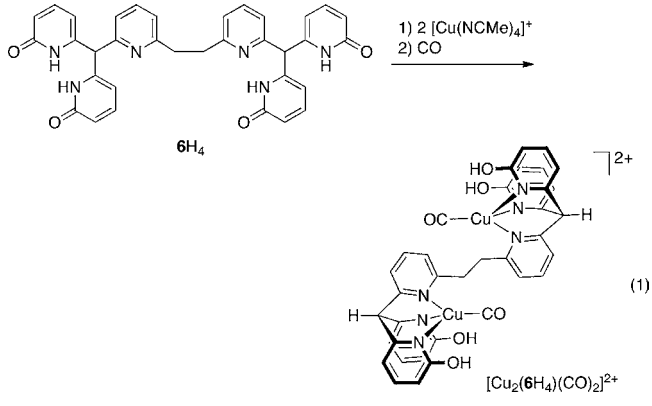


Figure 4. Structure of $[Cu_2(\mathbf{5})(NCMe)_2](BAr^F{}_4)_2$ with ellipsoids shown at 50% probability. Hydrogen atoms and counteranions were omitted for clarity. Selected distances (Å): Cu(1)−N(1), 2.090(4); Cu(1)−N(2), 2.09(4); Cu(1)−N(3), 2.060(3); Cu(1)−Cu(1a), 6.7784(9).

broad singlets in the range of δ ∼10−15 assigned to the four nonequivalent O*H* groups.[29] The indicated asymmetric structure is attributed to intramolecular hydrogen-bonding. Consistent with this view, CD_3CN solutions at 70 °C display a simplified ^1H NMR spectrum, featuring an O*H* signal at δ 6.7 which decreases in intensity upon addition of D_2O. Treatment of a CH_2Cl_2 solution of $[Cu_2(\mathbf{6}H_4)(NCMe)_x](BAr^F{}_4)_2$ with CO afforded the dicarbonyl derivative $[Cu_2(\mathbf{6}H_4)(CO)_2](BAr^F{}_4)_2$ (ν_{CO} = 2104 cm^{-1}, eq 1).



(1)

This salt exhibits a simple ^1H NMR spectrum indicative of high symmetry at room temperature, in contrast to the MeCN adduct.

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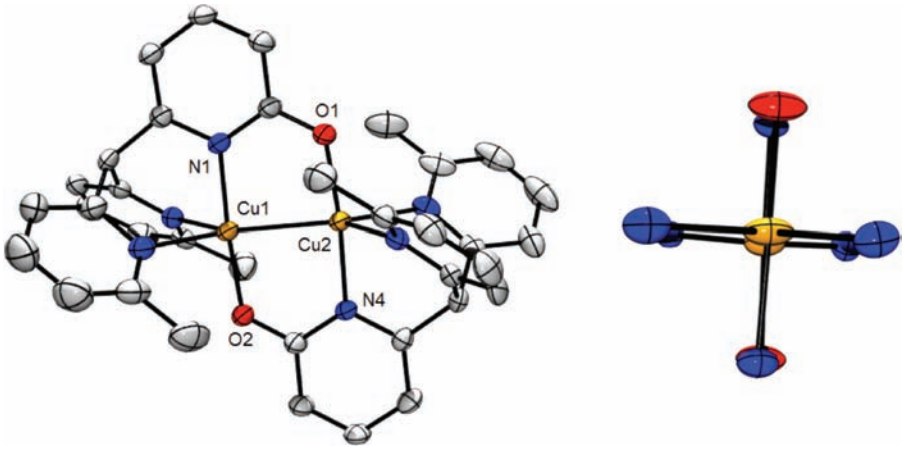
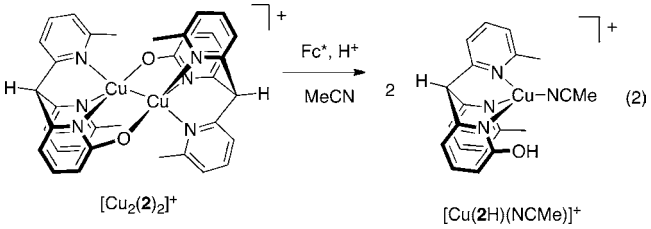


Figure 5. Left: Structure of the cation in $[Cu_2(\mathbf{2})_2]BAr^F_4$ with ellipsoids shown at 50% probability. The counteranion and hydrogen atoms have been omitted for clarity. Right: View down the Cu2−Cu1 bond vector with carbon atoms omitted.

Oxygenation of Mononuclear Cu(I) Complexes. As reported for $[Cu(tripic)(NCMe)]^+$, the methoxylated complex $[Cu(\mathbf{2}Me)(NCMe)]^+$ is unreactive toward O_2. In contrast, solutions of $[Cu(\mathbf{2}H)(NCMe)]PF_6$ oxidized upon exposure to oxygen, a process that was accelerated by bases such as 2,6-lutidine. Although the PF_6^- salt of the green oxidized product was insoluble in common solvents, the corresponding $BAr^F_4{}^-$ salt was soluble. ESI-MS analysis indicated that this species has the formula $[Cu_2(\mathbf{2})_2]^+$. Reversion of $[Cu_2(\mathbf{2})_2]^+$ to $[Cu(\mathbf{2}H)(NCMe)]^+$ is effected by $H(OEt_2)_2BAr^F_4$ in the presence of decamethylferrocene (−0.59 V,[30] eq 2).



The structure of the mixed valence complex $[Cu_2(\mathbf{2})_2]BAr^F_4$ was determined by X-ray crystallography. Each $(Cu^{1.5})_2$ center is enveloped in an N_3 pocket of the tripyridine ligand but is linked to a second complex via the pyridonate oxygen centers (Figure 5). The cationic complex has C_{2h} symmetry with a short Cu−Cu distance of 2.458(1) Å, comparable to the Cu−Cu distance found in the Cu_A site of cytochrome oxidase (~2.5 Å).[31] The Cu centers are trigonal bipyramidal, with each pyridonate ligand occupying an apical position. The Cu(1)−Cu(2)−N(4) angle is 86.8(2)°, slightly distorted from 90° for a trigonal bipyramid. The trigonal bipyramidal geometry of Cu in $[Cu_2(\mathbf{2})_2]^+$ is reminiscent of the geometry found for the $(Cu^{1.5})_2$ center in an octaaza-cryptand complex.[32]

The magnetic moment for $[Cu_2(\mathbf{2})_2]^+$ was determined to be μ_{eff} = 1.85 μ_B, appropriate to S = 1/2. Electron paramagnetic resonance (EPR) spectra at 77 K display a seven-line pattern, as expected for a Cu(1.5)Cu(1.5) complex where the unpaired electron is delocalized over the two I = 3/2 centers (Figure 6). In fluid solution at 298 K, the seven-line pattern remains discernible and was simulated with g_{iso} = 2.137 and A_{Cu} = −159 MHz. EPR parameters for $[Cu_2(\mathbf{2})_2]BAr^F_4$ were similar g-factors to those for other mixed valence Cu dimers.[33]

The coordination geometry, short Cu−Cu distance, and seven-line EPR spectrum all indicate that $[Cu_2(\mathbf{2})_2]BAr^F_4$ is a type III mixed valence dimer.[34]

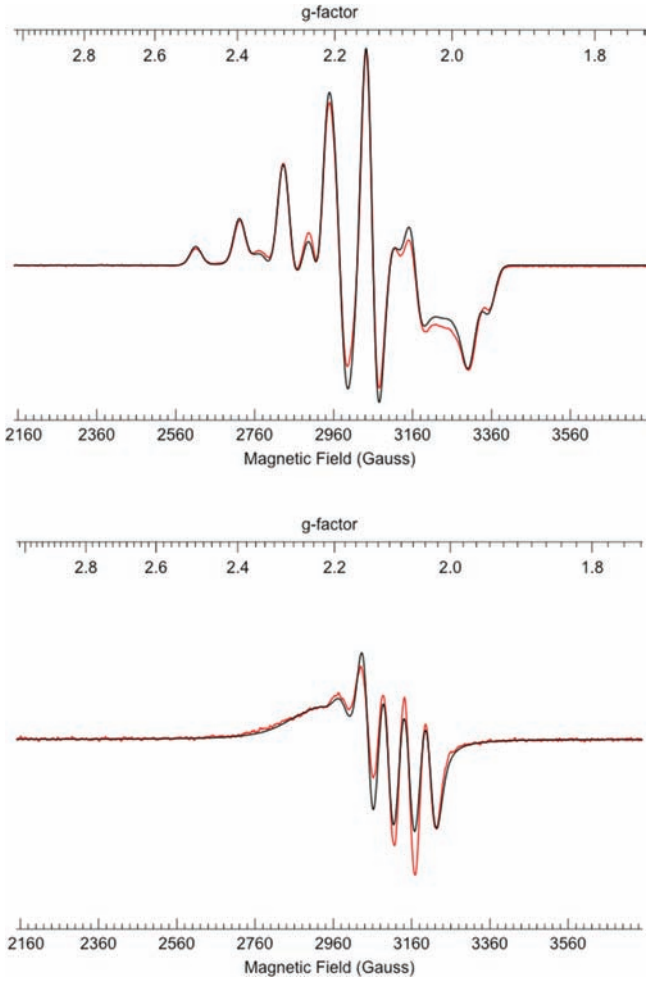


Figure 6. Experimental (red) and simulated (black) X-band EPR spectra (top = 77 K, bottom = 298 K) for $[Cu_2(\mathbf{2})_2]BAr^F_4$ in CH_2Cl_2:toluene (1:1). Simulation parameters for 77 K: g = 2.002, 2.185, and 2.214, A_{Cu} = 56.3, −195, −344, 92.0, 1.0, and −92.0 MHz; 298 K: g = 2.137, A_{Cu} = −159 MHz.

In addition to absorptions at 460 and 655 nm, the UV−vis spectrum of $[Cu_2(\mathbf{2})_2]BAr^F_4$ displays a strong feature 1040 nm (ε_M = 1160). Such intense bands are characteristic of intervalence charge transfer and are observed in other $Cu^{1.5}$ dimers.[35]

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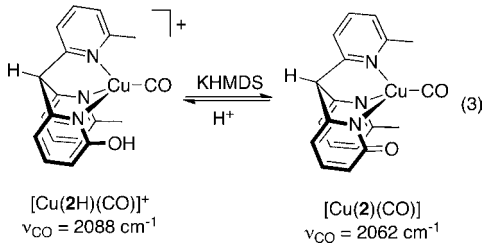
Carbonylation and Deprotonation of Cu(I) Complexes. Although substitution of a methyl for hydroxyl does not affect the Cu−CO bonding, deprotonation of the hydroxyl group has dramatic effects. In CH_2Cl_2 solution, $[Cu(\mathbf{2}H)(CO)]^+$ exhibits a ν_{CO} of 2094 cm^{-1} (2088 cm^{-1} in tetrahydrofuran (THF)), similar to $[(\kappa^3\text{-tpa})Cu(CO)]^+$ (ν_{CO} = 2091, 2074 cm^{-1}) and $[(tripic)Cu(CO)]^+$ (ν_{CO} = 2090 cm^{-1}).[18,36] Deprotonation of $[Cu(\mathbf{2}H)(CO)]BAr^F_4$ with $KN(SiMe_3)_2$ (KHMDS, pK_a^{THF} = 26)[37] led to precipitation of $Cu(\mathbf{2})(CO)$ as an off-white solid (eq 3, Figure 7).



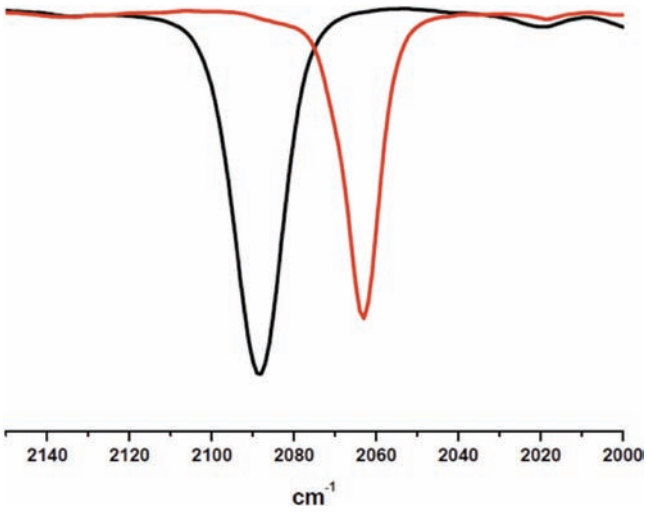


Figure 7. IR spectra before and after deprotonation of $[Cu(\mathbf{2}H)(CO)]^+$ with KHMDS (black = $[Cu(\mathbf{2}H)(CO)]^+$, red = $Cu(\mathbf{2})(CO)$). The lower intensity of the red band is attributed to the lower solubility of $Cu(\mathbf{2})(CO)$.

Deprotonation is reflected by a decrease in ν_{CO} of 26 cm^{-1} to ν_{CO} = 2062 cm^{-1}. For comparison, single deprotonation of $[Rh(CO)_2(3,3'\text{-dihydroxy-}2,2'\text{-bipy})]^+$ shifts ν_{CO} from 2108 and 2052 to 2072 and 2002 cm^{-1}.[38]

Deprotonations with tetramethylguanidine (pK_a^{MeCN} = 23)[39] and NEt_3 (pK_a^{MeCN} = 18)[40] produced species with hydrogen-bonds to the conjugate acid or to $Cu(\mathbf{2})(CO)$ as indicated by ν_{CO} bands in the region 2084−2076 cm^{-1}. Deprotonations were reversed by the addition of $HBAr^F_4{\cdot}2Et_2O$.

Deprotonation of $[Cu(\mathbf{2}H)(NCMe)]^+$ also gave encouraging results relevant to $[Cu_2(\mathbf{2})_2]^+$. Addition of 1 equiv of KHMDS to a THF solution of $[Cu(\mathbf{2}H)(NCMe)]^+$ resulted in immediate precipitation of a brick-red solid. Unlike $Cu(\mathbf{2})(CO)$, this species was CH_2Cl_2-soluble. NMR spectra showed that this red compound was a MeCN-free, symmetrical species. We propose that this new compound is the dimer $Cu_2(\mathbf{2})_2$, structurally related to $[Cu_2(\mathbf{2})_2]^+$, but lacking the Cu−Cu bond. A Cu^I dimer similarly bridged by two pyridonate ligands has been reported by Zhang and co-workers.[41] In CH_2Cl_2 solution, $Cu_2(\mathbf{2})_2$ reacts with CO to give $Cu(\mathbf{2})(CO)$. In MeCN solution, protonation of $Cu_2(\mathbf{2})_2$ efficiently gave $[Cu(\mathbf{2}H)(NCMe)]^+$. Deprotonation of $[Ag(\mathbf{2}H)(MeCN)]BF_4$ also afforded a similar dimeric species as evidenced by mass spectrometry. Although we were unable to obtain single crystals of $Cu_2(\mathbf{2})_2$, suitable crystals were obtained for $Ag_2(\mathbf{2})_2$ (Figure 8), analysis of which confirmed the expected bitetrahedral structure.

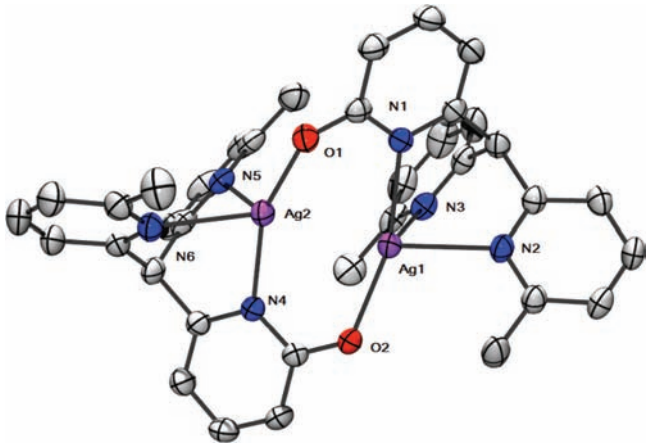


Figure 8. Molecular structure of one of two (similar) independent molecules of $Ag_2(\mathbf{2})_2$ with ellipsoids at 50% probability. Selected distances (Å): Ag(1)−Ag(2), 2.7847(3); Ag(1)−N(1), 2.253(2); Ag(1)−N(2), 2.400(2); Ag(1)−N(3), 2.513(2); Ag(1)−O(2), 2.211(2); Ag(2)−N(4), 2.281(2); Ag(2)−N(5), 2.474(2); Ag(2)−N(6), 2.380(2); Ag(2)−O(1), 2.204(2).

Oxygenation of Dinuclear Cu(I) Complexes. Solutions of the dicopper tetrahydroxy species $[Cu_2(\mathbf{6}H_4)(NCMe)_2](BAr^F_4)_2$ instantly turned dark blue upon exposure to O_2. The product $[Cu_2(\mathbf{6}H_2)]BAr^F_4$ was obtained in analytical purity. The EPR spectra for $[Cu_2(\mathbf{6}H_2)]BAr^F_4$ and $[Cu_2(\mathbf{2})_2]BAr^F_4$ closely match. The UV−vis spectrum of the intensely blue solution of $[Cu_2(\mathbf{6}H_2)]BAr^F_4$ displays an intervalence charge transfer absorption at 1100 nm (ε_M = 1810, 1,2-dichloroethane), which is red-shifted in comparison to that of $[Cu_2(\mathbf{2})_2]BAr^F_4$. Crystallographic analysis of the blue oxidation product revealed that $[Cu_2(\mathbf{6}H_2)]^+$ has idealized C_2-symmetry (Figure 9). The structure of $[Cu_2(\mathbf{6}H_2)]^+$ is similar to that of

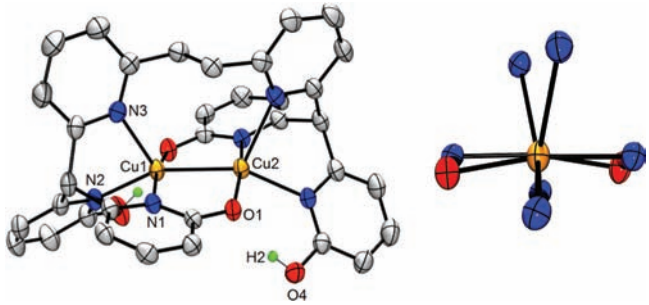


Figure 9. Left: Structure of the cation in $[Cu_2(\mathbf{6}H_2)]BAr^F_4$ with ellipsoids shown at 50% probability. The hydrogen atoms (green) bound to O2 and O4 were observed crystallographically. Other hydrogen atoms and the counteranion have been omitted for clarity. Right: View down the Cu2−Cu1 bond vector with carbon atoms omitted.

$[Cu_2(\mathbf{2})_2]^+$, having a Cu−Cu distance of 2.4939(5) Å. The mixed valence Cu dimer is additionally stabilized by hydrogen-bonding between a hydroxypyridyl group and the coordinated

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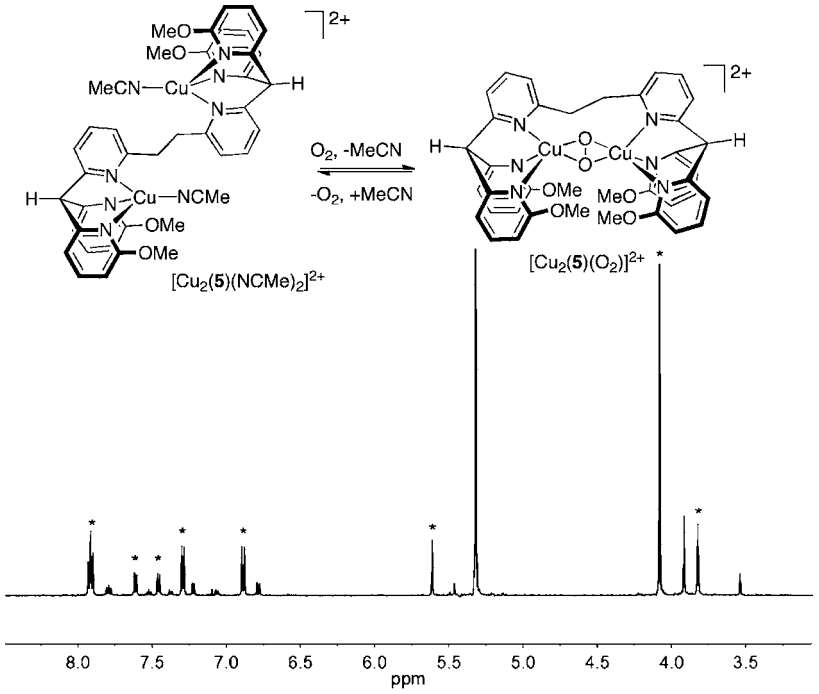

Figure 10. 500 MHz ^{1}H NMR spectrum of $[Cu_2(\mathbf{5})(MeCN)_2](BAr^{FS}{}_4)_2$ (CD_2Cl_2, 293 K) under 0.4 atm of O_2. Signals assigned to the dioxygen adduct are indicated with *.

O-center of the pyridonate ligands (d_{O1-O4} = 2.591(3) Å). Because of this intramolecular hydrogen-bonding, the Cu centers are enveloped in a cryptand-like cage. Structural perturbations imposed by the ethylene bridge in $[Cu_2(\mathbf{6H_2})]$-$BAr^F{}_4$ distort the idealized trigonal bipyramidal geometry at Cu from that observed in $[Cu_2(\mathbf{2})_2]BAr^F{}_4$. The resulting coordination sphere of each Cu center is nearly square pyramidal.

The methoxy-substituted salt $[Cu_2(\mathbf{5})(MeCN)_2](BAr^F{}_4)_2$ was found to reversibly react with dioxygen. Binding is indicated by a change from the colorless dicuprous species to purple upon introducing 1 atm of O_2. The UV−vis spectrum of a CH_2Cl_2 solution of $[Cu_2(\mathbf{5})(O_2)](BAr^F{}_4)_2$ (298 K) displays bands at 355 and 509 nm (see Supporting Information), blue-shifted with respect to $[Cu_2(bistripic)(O_2)](PF_6)_2$ (360 and 532 nm). The ^{1}H NMR spectrum is consistent with a symmetric diamagnetic adduct (Figure 10), consistent with a μ-κ^2:κ^2-O_2 ligand. At 0.4 atm O_2 (293 K), the equilibrium constant, K_{O2}, for the binding of O_2 by $[Cu_2(\mathbf{5})(MeCN)_2]^{2+}$ was found to be 0.012 M. For comparison, $[Cu_2(bistripic)$-$(NCMe)_2]^{2+}$ has a larger binding affinity for O_2 indicated by complete conversion to the μ-κ^2:κ^2-O_2 complex at 298 K. The oxygenation of $[Cu_2(\mathbf{5})(MeCN)_2]^+$ is fully reversible in contrast to the behavior of the dicopper(I) adducts of the hydroxylated ligand.

Electrochemical Studies. Cyclic voltammetry revealed that the mixed valence dimer $[Cu_2(\mathbf{2})_2]BAr^F{}_4$ oxidizes at 0.99 V (all potentials vs $Fc^{0/+}$, where Fc = ferrocene). It exhibits a reversible 1e$^-$ reduction at −1.03 V (i_{pa}/i_{pc} = 0.88) in CH_2Cl_2 solutions. The mixed valence complex of the binucleating ligand $[Cu_2(\mathbf{6H_2})]^+$ is reversibly reduced at −0.56 V (i_{pa}/i_{pc} = 0.99) and irreversibly oxidized at +0.99 V, the latter being similar to the irreversible oxidation waves observed for both $[Cu_2(\mathbf{2})_2]^{+/2+}$ and $[Cu(\mathbf{2H})(NCMe)]^{+/2+}$ couples.

Consistent with the electrochemical measurements, treatment of $Cu_2(\mathbf{2})_2$ with $[Fc]^+$ gave $[Cu_2(\mathbf{2})_2]^+$ (Figure 11). The analogous silver complex, $Ag_2(\mathbf{2})_2$, exhibits an irreversible

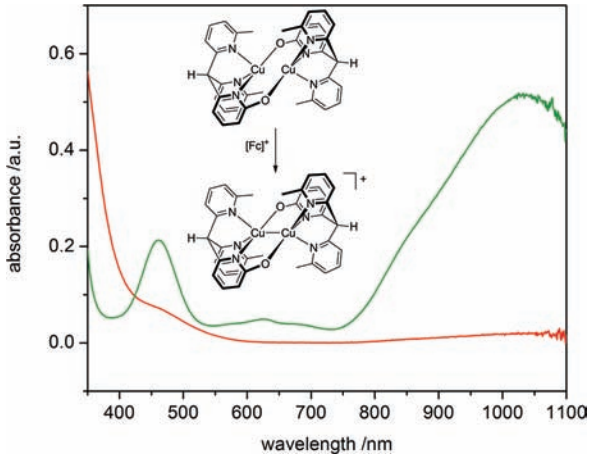

Figure 11. UV−vis spectrum of $Cu_2(\mathbf{2})_2$ before (red) and after (green) the addition of 1 equiv of $[Fc]BAr^F{}_4$ (CH_2Cl_2 solution) to afford the mixed valence salt $[Cu_2(\mathbf{2})_2]BAr^F{}_4$.

oxidation wave at a more positive potential of 0.65 V. Addition of strong oxidants, such as $[NO]BF_4$ (E = 1.0 V), to a CH_2Cl_2 solution of $Ag_2(\mathbf{2})_2$ did not appear to give mixed valence derivatives.

■ CONCLUSIONS

New families of pyridine-based tripodal ligands, developed from the dilithiated derivative of 6-methyl-2-pyridone, give rise to a family of mono- and dicopper complexes wherein the fourth coordination site is flanked by a mix of methyl, methoxy, and hydroxy groups. The methoxy substituents exert little influence, but deprotonation of the hydroxy groups profoundly affects the behavior of the copper centers by facilitating their oxidation to bimetallic derivatives. The new N_3-pyridonate scaffold stabilizes binuclear derivatives that give mixed valence species. Pyridonates and structurally related anionic ligands such as

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amide and urea derivatives, are well-known to bridge pairs of metals.[42] For example, Borovik and co-workers have generated square planar $(Cu^{1.5})_2$ complexes by oxidation of a $(Cu^1)_2$ precursor using O_2 and Fc^+.[43]

The highly negative potential for the $[Cu_2(\mathbf{2})]^{+/0}$ couple (−1.03 V) is indicative of the stability of the mixed valence derivative. The second oxidation, corresponding to the $[Cu_2(\mathbf{2})]^{2+/+}$ couple, is not observed until 0.99 V. The milder redox couple (−0.56 V) for $[Cu_2(\mathbf{6H}_2)]^{+/0}$ more closely matches that for the binuclear Cu_A site (−0.39 V vs $Fc^{0/+}$, pH = 8).[44] The 0.41 V difference in $E(Cu_2^{2+/3+})$ for these two complexes illustrates the sensitivity of this redox couple to relatively subtle steric constraints imposed by the ligand. A reversible one-electron reduction observed for $[Cu_2(\mathbf{2})_2]^+$ suggests that the conversion of $[Cu(\mathbf{2H})(MeCN)]^+$ to $[Cu_2(\mathbf{2})_2]^+$ proceeds via $Cu_2(\mathbf{2})_2$. The modulation of a complex's oxidation potential via deprotonation of a coordinated ligand has also been established for some Fe and Ru complexes of N-heterocyclic ligands.[45,46] For example, Carina and co-workers have demonstrated that deprotonation of a Fe^{II}−tetraimidazolyl dication with four equiv of base shifts the oxidation potential of the $Fe^{II/III}$ couple negative by 1.38 V.[46] Despite its highly negative reduction potential, $[Cu_2(\mathbf{2})_2]^+$ is readily reduced by weak reductants in the presence of acids.

EXPERIMENTAL SECTION

All manipulations were performed under an Ar atmosphere using standard Schlenk techniques, unless otherwise noted. Reagents were purchased from Sigma-Aldrich and Matrix Scientific. Solvents were HPLC-grade and dried by filtration through activated alumina or distilled under nitrogen over an appropriate drying agent. $ZnCl_2$ was dried by refluxing the solid in $SOCl_2$. $[Cu(NCMe)_4]BAr^{Fn}{}_4$ (n = 20 or 24) was prepared according to literature.[47] All other commercial reagents were used as received without further purification. ^{1}H NMR spectra were acquired using a Varian 500 spectrometer. ^{1}H NMR signals are quoted in ppm (δ) referenced to the residual solvent signal.[48] FT-IR spectra were recorded on a Perkin-Elmer Spectrum 100 FT-IR spectrometer. Chromatography was conducted with Siliaflash P60 from Silicycle (230−400 mesh). UV−vis spectra were acquired on either a Cary Bio 50 UV−vis or Cary 5000 UV−vis-NIR spectrophotometer. Electrochemical data were collected using either a BAS CV-50W or CH Instruments 600D potentiostat. Cyclic voltammetry was conducted under an inert atmosphere in CH_2Cl_2 solution using $[TBA]BAr^F{}_4$ (0.1 M) as the electrolyte, iR compensation, a glassy carbon electrode (diameter =1 cm), a Ag wire quasi-reference electrode, and a Pt counter electrode. Redox couples are referenced vs internal $Fc^{+/0}$.

(6-Picolinyl)(6-pyridonyl)methane (1). A hexanes solution of n-BuLi (50.4 mL, 1.6 M) was added to a suspension of 2-hydroxy-6-methylpyridine (4.0 g, 37 mmol) in 40 mL of THF at 0 °C. The resulting red-orange solution was stirred at room temperature for 1 h, followed by the addition of 50 mL of a THF solution of $ZnCl_2$ (11.0 g, 81 mmol) at 0 °C (An attempt to synthesize **1** in the absence of the transmetalating agent $ZnCl_2$ resulted in no conversion). The yellow mixture was allowed to warm to room temperature and then stirred for 1 h. The yellow mixture was treated with $PdCl_2$(dppf) (0.27 g, 0.37 mmol) (dppf = 1,1′-bis(diphenylphosphino)ferrocene) and 2-bromo-6-methylpyridine (4.6 mL, 40 mmol). After heating under reflux for 15 h, the reaction mixture was cooled to room temperature, and the THF was removed under vacuum. CH_2Cl_2 (100 mL) was added to the remaining yellow residue, followed by the addition of 25 mL aqueous solutions of $Na_2S{\cdot}9H_2O$ (9.7 g) and NaOH (1.6 g). After 1 h of stirring, the frothy mixture was filtered and the remaining solid was washed with 50 mL of CH_2Cl_2. The filtrate layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (2 × 50 mL). The combined organic layers were dried over $MgSO_4$ and filtered. Concentration of the filtrate under vacuum afforded a light brown solid. Dissolution of the solid in a minimal quantity of CH_2Cl_2, followed by the addition of hexanes (ca. 100 mL) afforded a light tan precipitate. Filtration of the suspension afforded **1** as a light tan solid. Yield: 3.0 g (41%). *Note:* Additional **1** can be isolated through acidification of the aqueous portion of the filtrate during workup; however, this requires separation from unreacted 2-hydroxy-6-methylpyridine. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.59 (s, 3H), 3.92 (s, 2H), 6.06 (d, J = 7.0 Hz, 1H), 6.41 (d, J = 9.2 Hz, 1H), 7.07 (pt, J = 7.3 Hz, 2H), 7.32 (dd, J = 6.8, 9.2 Hz, 1H), 7.54 (pt, J = 7.7 Hz, 1H), 11.20 (br s, 1H). Anal. Calcd for $C_{12}H_{12}N_2O$ (found): C, 71.98 (71.28); H, 6.04 (5.95); N, 13.99 (13.78).

Bis(2-methylpyrid-6-yl)(2-pyridon-6-yl)methane (2H). A suspension of **1** (1.0 g, 5.0 mmol) in 25 mL of THF was cooled in an ice bath to 0 °C. Addition of a hexanes solution of n-butyllithium (3.1 mL, 1.6 M) afforded a dark red mixture, which was warmed to room temperature and stirred for 1 h. 2-Bromo-6-methylpyridine (0.63 mL, 5.5 mmol) and $Pd(PPh_3)_4$ (58 mg, 0.05 mmol) were added to the mixture, which was then heated at reflux for 15 h. The dark mixture was cooled to room temperature, and the solvent was removed under vacuum. The remaining dark residue was extracted into a mixture of 30 mL of CH_2Cl_2 and 30 mL of H_2O. The layers were separated, and the aqueous phase was extracted with CH_2Cl_2 (2 × 30 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under vacuum to afford a light brown solid. Dissolution of the light brown solid in a minimum portion of CH_2Cl_2, followed by the addition of hexanes (ca. 100 mL) precipitated an off-white solid. The solid can be further purified by column chromatography on silica gel, eluting with EtOAc/MeOH (10:1). Yield: 0.93 g (64%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.57 (s, 6H), 5.33 (s, 1H), 6.23 (d, J = 6.7 Hz, 1H), 6.43 (d, J = 9.3 Hz, 1H), 7.04 (d, J = 7.8 Hz, 2H), 7.26 (d, J = 7.8 Hz, 2H), 7.30 (ddd, J = 0.5, 6.9, 9.3 Hz, 1H), 7.53 (t, J = 7.8 Hz, 2H), 11.72 (br s, 1H). Anal. Calcd for $C_{18}H_{17}N_3O$ (found): C, 74.20 (74.26); H, 5.88 (5.89); N, 14.42 (14.37). ESI-MS (MeOH, 25 °C): m/z 292 ($[M+H]^+$). mp 201 °C. Single crystals were obtained by cooling an EtOAc solution to −35 °C.

(±)-(2-Methoxypyrid-6-yl)(2-methylpyrid-6-yl)(2-pyridon-6-yl)methane (3). This compound was synthesized following the procedures outlined for **2H**, using 2-bromo-6-methoxypyridine in place of 2-bromo-6-methylpyridine. A quantity of 1.35 g of **1** yielded 0.92 g (45%) of **3**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.57 (s, 6H), 5.34 (s, 1H), 6.23 (d, J = 7.0 Hz, 1H), 6.42 (dd, J = 0.8, 9.2 Hz, 1H), 7.04 (d, 7.8 Hz, 1H), 7.26 (d, 7.7 Hz, 2H), 7.30 (dd, J = 6.7, 9.2 Hz, 2H), 7.53 (t, J = 7.8 Hz, 2H), 11.73 (br s, 1H). Anal. Calcd for $C_{18}H_{17}N_3O_2$ (found): C, 70.34 (70.10); H, 5.58 (5.48); N, 13.67 (13.38). ESI-MS (MeOH, 25 °C): m/z 308 ($[M+H]^+$).

[Cu(2H)(NCMe)]PF_6. A solution of $[Cu(NCMe)_4]PF_6$ (192 mg, 0.5 mmol) in 5 mL of MeCN was treated with a solution of **2H** (150 mg, 0.5 mmol) in 5 mL of MeCN. After stirring this yellow solution for 1 h, it was diluted with 40 mL of Et_2O to precipitate a light-yellow solid, which was washed with two 20-mL portions of Et_2O before storing under vacuum. Yield: 211 mg (78%). ^{1}H NMR (500 MHz, CD_2Cl_2): δ 2.44 (s, 3H), 2.76 (s, 6H), 5.61 (s, 1H), 6.66 (s, 1H), 6.82 (d, J = 8.3 Hz, 1H), 7.24 (d, J = 7.7 Hz, 2H), 7.28 (d, J = 7.4 Hz, 1H), 7.50 (d, J = 7.7 Hz, 2H), 7.68−7.76 (m, 3H). ESI-MS (MeCN, 25 °C): m/z 395 ($[M]^+$). Preliminary crystallographic data for single crystals of $[Cu(\mathbf{2H})(NCMe)]PF_6$ (grown from layering a MeCN solution of $[Cu(\mathbf{2H})(NCMe)]PF_6$ with Et_2O) indicated coordination of the Cu center to the picoline and pyridone group N-atoms of **2H** with MeCN occupying the fourth coordination site (see characterization of $[Ag(\mathbf{2H})(MeCN)]BF_4$).

[Cu(2H)(NCMe)]$BAr^F{}_4$. A 3-mL CH_2Cl_2 solution of **2H** (100 mg, 0.34 mmol) was treated with a 5-mL CH_2Cl_2 solution of $[Cu(NCMe)_4]$-$BAr^F{}_4$ (311 mg, 0.34 mmol). After being stirred for 1 h, the light-yellow solution was diluted with 25 mL of hexanes to precipitate a colorless solid, which was collected by filtration and washed with hexanes before storage under vacuum. Yield: 310 mg (85%). ^{1}H NMR (500 MHz, CD_2Cl_2): δ 2.44 (s, 3H), 2.73, (s, 6H), 5.50 (s, 1H), 6.48 (br s, 1H), 6.81 (d, J = 8.4 Hz, 1H), 7.22 (d, J = 7.6 Hz, 1H), 7.23 (d, J = 8.0 Hz, 2H), 7.42 (d, J = 7.7 Hz, 2H), 7.56 (br s, 4H), 7.67−7.75 (m, 19H). Anal. Calcd for $C_{52}H_{32}N_4BCuF_{24}O$ (found): C, 49.60 (49.35); H, 2.56 (2.57); N, 4.45 (4.34). The salt $[Cu(\mathbf{2H})(NCMe)]BAr^{FS}{}_4$ was prepared analogously.

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[Cu(3)(NCMe)]BAr$^{F5}_4$. This off-white salt was prepared following procedures outlined for [Cu(**2**H)(NCMe)]BAr$^F_4$, from **3** (52 mg, 0.17 mmol) and [Cu(NCMe)$_4$]BAr$^{F5}_4$ (154 mg, 0.17 mmol). Yield: 157 mg (85%). ^{1}H NMR (500 MHz, CD_2Cl_2): δ 2.42 (br s, 3H), 2.74 (s, 3H), 3.95 (s, 3H), 5.45 (s, 1H), 6.50 (s, 1H), 6.80 (d, J = 8.6 Hz, 1H), 6.82 (d, J = 8.5 Hz, 1H), 7.23 (d, J = 7.8 Hz, 1H), 7.25 (d, J = 8.4 Hz, 1H), 7.41 (d, J = 7.8 Hz, 1H), 7.70 (t, J = 7.8 Hz, 1H), 7.72 (t, J = 7.8 Hz, 1H), 7.81 (dd, J = 7.6, 8.3 Hz, 1H). Anal. Calcd for $C_{44}H_{20}BCuF_{20}N_4O_2$ (found): C, 48.44 (48.00); H, 1.85 (1.52); N, 5.14 (5.08).

[Ag(2H)(MeCN)]BF$_4$. A solution of **2**H (0.44 g, 1.5 mmol) and $AgBF_4$ (0.30 g, 1.5 mmol) in 20 mL of MeCN was prepared. After stirring for 30 min, the solution was evaporated. The white solid residue was washed with Et_2O (30 mL) and hexanes (20 mL). Yield: 0.69 g (87%). Crystals of [Ag(**2**H)(MeCN)]BF_4 suitable for X-ray diffraction were obtained by vapor diffusion of Et_2O into a MeCN solution of [Ag(**2**H)(MeCN)]BF_4 at −25 °C. ^{1}H NMR (400 MHz, CD_3CN): δ 9.10 (br, 1H), 7.74 (t, 2H), 7.61 (t, 1H), 7.47 (d, 2H), 7.28 (d, 2H), 6.88 (br, 1H), 6.64 (d, 1H), 5.74 (s, 1H), 2.64 (s, 6H), 1.96 (s, 3H). ESI-MS (m/z): calcd for $C_{20}H_{20}AgN_4O$ $[M]^+$ 439.07, found 439.3. Anal. Calcd for $C_{20}H_{20}AgN_4BF_4O$ (found): C, 45.58 (44.99); H, 3.82 (3.91); N, 10.63 (10.43).

(2-Methoxypyrid-6-yl)-bis(2-methylpyrid-6-yl)methane (2Me). This compound, isolated as a yellow oil, was prepared following the procedures for **4** starting with **3** (500 mg). Yield: 130 mg (25%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.53 (s, 3H), 3.80 (s, 6 H), 5.72 (s, 1H), 6.56 (d, J = 8.3 Hz, 2H), 6.86 (d, J = 7.4 Hz, 2H), 6.99 (d, J = 7.6 Hz, 1H), 7.33 (d, J = 8.0 Hz, 1H), 7.45 (t, J = 7.9 Hz, 2H), 7.49 (t, J = 8.2 Hz, 1H). ESI-MS (MeOH, 25 °C): m/z 306 ($[M+H]^+$).

[Cu(2Me)(NCMe)]BAr$^{F5}_4$. This light-yellow solid was synthesized following the procedures outlined for [Cu(**2**H)(NCMe)]BAr$^F_4$. Starting with (2-methoxypyrid-6-yl)-bis(2-methylpyrid-6-yl)methane (110 mg, 0.36 mmol). Yield: 325 mg (83%). ^{1}H NMR (500 MHz, CD_3CN): δ 2.71 (s, 6H), 3.95 (s, 3H), 5.87 (s, 1H), 6.89 (d, J = 8.5 Hz, 1H), 7.27 (d, J = 7.8 Hz, 2H), 7.36 (d, J = 7.5 Hz, 1H), 7.54 (d, J = 7.7 Hz, 2H), 7.73 (t, J = 7.7 Hz, 2H), 7.85 (t, J = 7.9 Hz, 1H). Anal. Calcd for $C_{45}H_{22}BCuF_{20}N_4O{\cdot}0.25CH_2Cl_2$ (found): C, 48.95 (48.88); H, 2.04 (1.66); N, 5.05 (4.87).

Bis(2-methoxy-6-pyridyl)(2-methyl-6-pyridyl)methane (4). A slurry of Ag_2CO_3 (904 mg, 3.3 mol) and **2** (746 mg, 2.4 mmol) in 40 mL of $CHCl_3$ was treated with MeI (1.52 mL, 24 mmol). The mixture was stirred in the absence of light for 48 h. The resulting tan slurry was filtered through a ∼6-cm pad of Celite, which was rinsed with an additional 50 mL of $CHCl_3$. Concentration of the dark filtrate afforded a blue oil, which was further purified via elution through a 7.5-cm plug of silica using EtOAc as the eluent. Concentration of the first band to elute from the plug afforded **4** as a blue oil. Yield: 550 mg (71%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.53 (s, 3H), 3.80 (s, 6 H), 5.72 (s, 1H), 6.56 (d, J = 8.3 Hz, 2H), 6.86 (d, J = 7.4 Hz, 2H), 6.99 (d, J = 7.6 Hz, 1H), 7.33 (d, J = 8.0 Hz, 1H), 7.45 (t, J = 7.9 Hz, 2H), 7.49 (t, J = 8.2 Hz, 1H). Chromatographic separation of **4** from the blue side product was unsuccessful, although the ^{1}H NMR spectrum of the blue oil showed signals only assignable to **4**. Blue-colored samples of **4** were used in the subsequent homocoupling reactions.

Bis[bis(2-methoxy-6-pyridyl)(2-methyl-6-pyridyl)methane] (5). A flame-dried flask was charged with **4** (550 mg, 1.7 mmol) followed by 70 mL of THF to afford a blue solution. To the blue solution was added t-BuLi (2.1 mL, 1.7 M) at −78 °C. Upon completion of the addition, the resulting dark red solution was warmed to 0 °C and stirred for 1 h. The red solution was cooled to −78 °C and slowly treated with 1,2-dibromoethane (0.3 mL, 3.4 mmol). The solution was allowed to warm to room temperature and stirred for a further 14 h. Solvent was removed from the reaction mixture under reduced pressure to afford a dark red residue. A mixture of 40 mL of CH_2Cl_2 and 40 mL of H_2O was used to dissolve the residue. The aqueous layer was further extracted with CH_2Cl_2 (2 × 40 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated to afford a green oil. The oil was purified by silica chromatography using a gradient eluent of 4:1 EtOAc/hexanes to 2:1 EtOAc/hexanes to afford **5** as a light yellow oil. Yield: 170 mg (31%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.17 (s, 4H), 3.79 (s, 12 H), 5.72 (s, 2H), 6.56 (d, J = 8.2 Hz, 4H), 6.79 (dd, J = 0.9, 7.6 Hz, 2H), 6.85 (d, J = 7.4 Hz, 4H), 7.24 (dd, J = 0.9, 7.8 Hz, 2H), 7.34 (t, J = 7.7 Hz, 2H), 7.47 (dd, J = 7.4, 8.2 Hz, 4H).

[Cu$_2$(5)(NCMe)$_2$](PF$_6$)$_2$. Solutions of [Cu(NCMe)$_4$]PF_6 (198 mg, 0.53 mmol) and **5** (170 mg, 0.26 mmol), each in 5 mL of MeCN, were combined to afford a yellow solution. After 1 h of stirring, 30 mL of Et_2O was added to the solution to precipitate a light-yellow solid, which was washed with two 20-mL portions of Et_2O. Yield: 136 mg (43%). ^{1}H NMR (500 MHz, CD_3CN): δ 1.96 (s, 6H), 3.45 (s, 4H), 3.90 (s, 12H), 5.73 (s, 2H), 6.85 (d, J = 8.5 Hz, 4H), 7.14 (d, J = 8.0 Hz, 2H), 7.22 (d, J = 6.4 Hz, 4H), 7.42 (d, J = 7.8 Hz, 2H), 7.64 (t, J = 7.8 Hz, 2H), 7.82 (t, J = 8.0 Hz, 4H).

[Cu$_2$(5)(NCMe)$_2$](BAr$^F_4$)$_2$. A suspension of [Cu$_2$(**5**)(NCMe)$_2$]PF_6 (100 mg, 0.084 mmol) and KBAr$^F_4$ (152 mg, 0.17 mmol) in CH_2Cl_2 (10 mL) was stirred for 1 h and then filtered via cannula. Concentration of the filtrate under reduced pressure afforded a white solid. The product was extracted into 5 mL of CH_2Cl_2 and reprecipitated with hexanes. Yield: 175 mg (81%). Treatment of **5** with [Cu(NCMe)$_4$]BAr$^F_4$ afforded the same salt. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 2.16 (s, 6H), 3.54 (s, 4H), 3.87 (s, 12 H), 5.46 (s, 2H), 6.74 (d, J = 8.5 Hz, 4H), 7.02 (dd, J = 1.0, 7.8 Hz, 2H), 7.21 (dd, J = 0.6, 7.5 Hz, 4H), 7.37 (dd, J = 1.0, 7.8 Hz, 2H), 7.50 (t, J = 7.8 Hz, 2H), 7.53 (s, 8H), 7.72 (br t, 16H), 7.76 (dd, J = 7.4, 8.4 Hz, 4H). Anal. Calcd for $C_{106}H_{66}N_8B_2Cu_2F_{40}O_4$ (found): C, 49.42 (49.73); H, 2.58 (2.65); N, 4.35 (4.28).

Bis[bis(2-pyridon-6-yl)(2-methylpyrid-6-yl)methane] (6H$_4$). A solution of **5** (420 mg, 0.66 mmol) in 5 mL of HBr (49%) was heated at reflux for 4 h. After cooling to room temperature, the tan solution was neutralized by slow addition to a 200 mL saturated aqueous solution of $NaHCO_3$. The aqueous solution was extracted with CH_2Cl_2 (3 × 100 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated to afford a tan solid. Yield: 271 mg (71%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.31 (s, 4H), 5.30 (s, 2H), 6.01 (d, J = 6.8 Hz, 4H), 6.39 (d, J = 9.2 Hz, 4H), 7.03 (d, J = 8.0 Hz, 2H), 7.18 (dd, J = 0.9, 7.8 Hz, 2H), 7.33 (dd, J = 6.8, 9.3 Hz, 4H), 7.37 (t, J = 7.7 Hz, 4H), 11.23 (br s, 4H). ESI-MS (MeOH, 25 °C): m/z 585 ($[M+H]^+$), 607 ($[M+Na]^+$). mp 230 °C.

[Cu$_2$(2)$_2$]PF$_6$. A solution of [Cu(**2**H)(NCMe)]PF_6 (100 mg, 0.18 mmol) in 5 mL of CH_2Cl_2 under an atmosphere of air was treated with 2,6-lutidine (21 μL, 0.18 mmol), resulting in the formation of a green precipitate. After 30 min of stirring, the green suspension was filtered, and the solids were washed with CH_2Cl_2 (2 × 5 mL). Yield: 67 mg (85%). Anal. Calcd for $C_{36}H_{32}N_6Cu_2F_6O_2P{\cdot}0.5CH_2Cl_2$ (found): C, 48.97 (48.58); H, 3.72 (3.39); N, 9.39 (9.26). ESI-MS (MeOH, 25 °C): m/z 706 ($[M]^+$). [Cu$_2$(**2**)$_2$]BAr$^F_4$ could be generated in a similar manner, but separation of the conjugate acid proved to be difficult. Single crystals were obtained by slow evaporation of a MeCN solution of [Cu$_2$(**2**)$_2$]BAr$^F_4$. UV−vis (BAr$^F_4$ salt, 1,2-dichloroethane), λ (ε_M): 460 (460), 655 (120), 1110 (1810).

[Cu$_2$(6H$_2$)]BAr$^F_4$. A 5 mL CH_2Cl_2 solution of [Cu(NCMe)$_4$]BAr$^F_4$ (373 mg, 0.34 mmol) was added to a 5 mL suspension of **6**H$_4$ (100 mg, 0.17 mmol) to afford a bright yellow mixture. After stirring the solution for 10 min, 30 mL of hexanes was added to precipitate a yellow oil. The oil was isolated via decantation and redissolved in 10 mL of CH_2Cl_2 to afford a turbid yellow solution, which was filtered. The filtrate was evaporated to yield 325 mg a yellow-green solid of [Cu$_2$(6H$_4$)(NCMe)$_x$](BAr$^F_4$)$_2$. ^{1}H NMR (500 MHz, CD_3CN, 70 °C): δ 3.41 (s, 4H), 5.52 (s, 2H), 6.60 (d, J = 8.5 Hz, 4H), 6.75 (br s, 2H), 7.28 (d, J = 7.7 Hz, 2H), 7.43 (d, J = 7.5 Hz, 2H), 7.58 (br t, J = 7.7 Hz, 4H), 7.74 (t, J = 7.7 Hz, 2H). A solution of [Cu$_2$(**6**H$_4$)(NCMe)$_x$](BAr$^F_4$)$_2$ (50 mg, 0.02 mmol) in 3 mL of CH_2Cl_2 was exposed to air, resulting in an immediate color change to dark blue. The dark blue solution was layered with 3 mL of hexanes and stored at room temperature to afford dark blue crystals of [Cu$_2$(**6**H$_2$)]BAr$^F_4$. EPR (CH_2Cl_2:Toluene [1:1], 77 K): g = 2.012, 2.165, 2.250; A_{Cu} = 30, −164, −361, 72.1, 3.8, −72.6 MHz. EPR (CH_2Cl_2:Toluene [1:1], 298 K): g = 2.144, A_{Cu} = −170 MHz. UV−vis, 1,2-dichloroethane, λ nm (ε_M): 495 (994), 590 (938), 1040 (1510), 1110 (1810). ESI-MS (CH_2Cl_2,

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25 °C): m/z 708 ([M]$^+$). Anal. Calcd for $C_{66}H_{38}BCu_2F_{24}N_6O_4$ (found): C, 50.40 (50.08); H, 2.43 (2.40); N, 5.34 (5.10).

Oxygenation of $[Cu_2(5)(NCMe)_2](BAr^F{}_4)_2$. A solution of $[Cu_2(5)(NCMe)_2](BAr^F{}_4)_2$ (8.0 mg) in about 0.75 mL of CD_2Cl_2 in a J. Young NMR tube was saturated with O_2, resulting in a purple solution. ^{1}H NMR data were acquired immediately, as the purple oxygenated species quickly reverted back to $[Cu_2(5)(NCMe)_2](BAr^F{}_4)_2$. Prolonged oxygenations resulted in the formation of green NMR-silent products. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 3.80 (s, 4H), 4.04 (s, 12 H), 5.59 (s, 2H), 6.83 (d, J = 8.5 Hz, 4H), 7.27 (d, J = 7.4 Hz, 2H), 7.42 (d, J = 7.7 Hz, 4H), 7.59 (d, J = 7.6 Hz, 2H), 7.53 (s, 8H), 7.72 (br t, 16H), 7.83−7.89 (m, 6H).

Deprotonation of $[Cu(2H)(CO)]BAr^F{}_4$ with NEt_3 or TMG. A solution of $[Cu(2H)(CO)]BAr^F{}_4$ in 10 mL of CH_2Cl_2 was generated by carbonylation of a solution of 30 mg (0.024 mmol) of $[Cu(2H)(NCMe)]BAr^F{}_4$ for approximately one min. Varying equiv of NEt_3 or TMG were added from stock CH_2Cl_2 solutions followed immediately by recording IR spectra.

Cu(2)(CO). A solution of $[Cu(2H)(CO)]BAr^{F5}{}_4$ in 5 mL of THF was generated in situ by carbonylation of 100 mg (0.093 mmol) of the MeCN complex. Formation of $[Cu(2H)(CO)]BAr^{F5}{}_4$ was verified by IR spectroscopy (ν_{CO} = 2088 cm^{-1}). The solution was titrated with a 0.05 M THF solution of KHMDS, monitoring IR spectra in the CO region. Upon adding a total of 1 equiv of KHMDS (2 mL, 0.05 M THF solution) a colorless solid precipitated. The resulting suspension was filtered, and the isolated colorless solids were washed with THF (2 × 3 mL) and dried under vacuum. Yield: 26 mg (73%). The addition of 1 equiv of $HBAr^F{}_4{\cdot}2Et_2O$ to a THF suspension of Cu(2)(CO) resulted in the regeneration of $[Cu(2H)(CO)]BAr^F{}_4$, as indicated by IR spectroscopy (ν_{CO} = 2088 cm^{-1}).

$Cu_2(2)_2$. A THF solution of $[Cu(2H)(NCMe)]PF_6$ (5 mL, 0.056 M) was treated with a THF solution of KHMDS (5.5 mL, 0.05 M), immediately resulting in the evolution of a red precipitate. After 30 min of stirring, the red mixture was concentrated to afford a dark residue. The residue was extracted with CH_2Cl_2 (3 × 5 mL), and the combined extracts were concentrated to about 5 mL. Addition of 20 mL hexanes to the red-orange CH_2Cl_2 solution precipitated a red-orange solid, which was washed with hexanes (3 × 5 mL) and dried under vacuum. Yield: 42 mg (42%). ^{1}H NMR (500 MHz, CD_2Cl_2): δ 2.44 (s, 6H), 5.37 (s, 1H), 6.44 (s, 2H), 7.01 (s, 2H), 7.22 (s, 1H), 7.30 (s, 2H), 7.56 (s, 2H). Anal. Calcd for $C_{36}H_{32}N_6Cu_2O_2{\cdot}0.8CH_2Cl_2$ (found): C, 56.98 (56.89); H, 4.37 (4.14); N, 10.83 (10.90). Cyclic voltammetry (CH_2Cl_2, $NBu_4BAr^F{}_4$): $E_{1/2}$ = −1.03 V (i_{pa}/i_{pc} = 0.99), +0.97 V (irreversible) at 50 mV/s.

$Ag_2(2)_2$. A flask was charged with $[Ag(2H)(MeCN)]BF_4$ (0.40 g, 0.76 mmol), KHMDS (0.15 g, 0.76 mmol), and 35 mL of THF. After 1 h, this solution was evaporated. The dark brown solid residue was extracted into 40 mL of CH_2Cl_2, and this solution was filtered through Celite. The colorless filtrate was evaporated under vacuum to afford a colorless solid. Yield: 0.15 g (49%). Crystals of $Ag_2(2)_2$ suitable for X-ray diffraction were obtained by vapor diffusion of Et_2O into a CH_2Cl_2 solution of $Ag_2(2)_2$ at −25 °C. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 2.25 (s, 6H), 5.32 (m, 1H), 6.44 (dd, 2H), 6.92 (d, 2H), 7.23 (m, 3H), 7.52 (t, 2H). FD-MS: calcd 796.41, found 796.0.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional experimental details and data. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: rauchfuz@illinois.edu.

Notes

The authors declare no competing financial interest.

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