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Tripodal Bis(imidazole) Thioether Copper(I) Complexes: Mimics of the Cu_M Site of Copper Hydroxylase Enzymes

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Tripodal bis(imidazole) thioether ligands, (*N*-methyl-4,5-diphenyl-2-imidazolyl)$_2$C(OR)C(CH$_3$)$_2$SR′ (BIT$^{OR,SR'}$; R = H, CH$_3$; R′ = CH$_3$, C(CH$_3$)$_3$, C(C$_6$H$_5$)$_3$), have been prepared, offering the same N_2S donor atom set as the Cu_M binding site of the hydroxylase enzymes, dopamine beta hydroxylase and peptidylglycine hydroxylating monooxygenase. Isolable copper(I) complexes of the type [(BIT^{OR,SMe})Cu(CO)]PF$_6$ (**3a** and **3b**) are produced in reactions of the respective tripodal ligands **1a** (R = H) and **1b** (R = Me) with [Cu(CH$_3$CN)$_4$]PF$_6$ in CH_2Cl_2 under CO (1 atm); the pyramidal structure of **3a** has been determined crystallographically. The infrared (IR) ν(CO)'s of **3a** and **3b** (L = CO) are comparable to those of the Cu_M-carbonylated enzymes, indicating similar electronic character at the copper centers. The reaction of [(BIT^{OH,SMe})Cu(CH$_3$CN)]PF$_6$ (**2a**) with dioxygen produces [(BIT^{O,SOMe})$_2$-Cu$_2$(DMF)$_2$](PF$_6$)$_2$ (**4**), whose X-ray structure revealed the presence of bridging BIT–alkoxo ligands and terminal –SOMe groups. In contrast, oxygenation of **2b** (R = Me) affords crystallographically defined [(BIT^{OMe,SMe})$_2$Cu$_2$(μ-OH)$_2$](OTf)$_2$ (**5**), in which the copper centers are oxygenated without accompanying sulfur oxidation. Complex **5** in DMF is transformed into five-coordinate, mononuclear [Cu^{II}(BIT^{OMe,SMe})(DMF)$_2$](PF$_6$)$_2$ (**6**). The sterically hindered BIT$^{OR,SR'}$ ligands **9** and **10** (R′ = *t*-Bu; R = H, Me) and **11** and **12** (R′ = CPh$_3$; R = H, Me) were also prepared and examined for copper coordination/oxygenation. Oxygenation of copper(I) complex **13b** derived from the BIT$^{OMe,SBu-t}$ ligand is slow, relative to **2b**, producing a mixture of (BIT$^{OMe,SBu-t}$)$_2$Cu$_2$(μ-OH)$_2$-type complexes **14b** and **15b** in which the –SBu-*t* group is uncoordinated; one of these complexes (**15b**) has been ortho-oxygenated on a neighboring aryl group according to the X-ray analysis and characterization of the free ligand. Oxygenation of the copper(I) complex derived from BIT^{OMe,SCPh_3} ligand **12** produces a novel dinuclear disulfide complex, [(BIT^{OMe,S})$_2$-Cu$_2$(μ-OH)$_2$](PF$_6$)$_2$ (**17**), which is structurally characterized. Reactivity studies under anaerobic conditions in the presence of *t*-BuNC indicate that **17** is the result of copper(I)-induced detritylation followed by oxygenation of a highly reactive copper(I)–thiolate complex.

Introduction

The copper hydroxylase enzymes, dopamine beta hydroxylase (DβH) and peptidylglycine α-hydroxylating monooxygenase (PHM), catalyze the regio- and enantioselective hydroxylation of mildly activated C−H bonds by dioxygen.[1] These enzymes appear to have very similar active-site structures, featuring two copper centers separated by ca. 12 Å, the Cu_H (Cu_A) site being ligated to three histidine-derived imidazoles and the Cu_M (Cu_B) site by two histidines and a methionine residue (Figure 1).[2] Spectroscopic and amino acid mutagenesis studies suggest that upon reduction both the dioxygen and the substrate are activated at the Cu_M site and that the Cu_H site serves as an electron-transfer shuttle from ascorbate to the Cu_M site.[3] A recent X-ray structure of the O_2-bound PHM enzyme has revealed an unusual end-on coordination mode to the Cu_M center,[4–6] contrasting with

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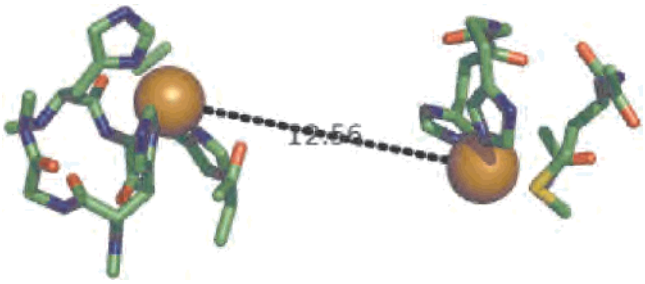

Figure 1. Copper hydroxylase active site.

the more common side-on mononuclear and bridging bimetallic bonding modes found in most synthetic complexes and in the dioxygen-binding Cu−protein hemocyanin.[7] The mechanistic details of the substrate hydroxylation are unclear, but rate-limiting C−H bond breaking with a significant tunneling component by a Cu−oxo species is supported by the large intrinsic primary D-isotope effect (10.6) for both DβH and PHM.[8] Recent computational studies suggest that either a side-on Cu-superoxo[9] or a Cu−oxo species[10] is the likely H-abstracting agent.

Although many synthetic model complexes for these (and other) copper enzymes have been prepared with a variety of polydentate amine, pyridine, and pyrazolyl-based ligands,[7] remarkably few have incorporated the biologically most relevant poly(imidazole) (from histidine) donors.[11,12] Given the significantly different basicity (pK_a: imidazolium, 6.8; pyrazolium, 2.6; pyridinium, 5.2, tertiary ammonium, 9−10)[13] and donor/acceptor properties[14] of imidazole vis-à-vis the other common nitrogen ligands, we suggest that the most accurate structural and functional mimics for histidine-rich metalloenzymes will be provided by incorporating the actual biological donor set. Regarding models for the Cu_H site of the hydroxylases, Sorrell and Borovik first reported copper(I) complexes of tripodal tris(*N*-methyl-2-imidazolyl)carbinol[12a] and tris(2-imidazolyl)phosphines.[12d] Dinuclear $[(tripod)_2Cu^I_2]Z_2$ complexes of the former ligand were found to be unreactive toward dioxygen, whereas a mononuclear copper(I) complex of the latter ligand reacts with dioxygen at low temperature to produce a reactive peroxodicopper(II) adduct, showing that steric and stereoelectronic effects are important in defining Cu^I-O_2 interactions in these systems. We recently have investigated the chemistry of copper(I) complexes of tripodal tris(*N*-methyl-4,5-diphenylimidazolyl)methane ligands.[15] Whereas these also form dinuclear Cu_2L_2-type complexes, mononuclear adducts $[(imid_3CR)CuL]Z$ are produced with L = acetonitrile, carbon monoxide, and *t*-BuNC. The structures of the isocyanide derivatives depend critically on the tripod methane substituent, R, showing trigonal and tetrahedral geometries with bi- or tridentate coordination of the tripod. Reactions of dioxygen with the dinuclear complexes or mononuclear $[(imid)_3CR]CuL]Z$ are sluggish, producing from the latter $[(imid)_3CH]Cu^{II}(acetone)(H_2O)]Z_2$.

Few complexes have been reported that possess the $(amine)_2$thioether coordination sphere relevant to the Cu_M site of the copper hydroxylases. Karlin and co-workers recently described copper(I,II) complexes of (non-imidazole) tridentate (pyridine, amine, and thioether) ligands (N_2SR); oxygenation of $[(N_2SR)Cu^I]^+$ leads to ligand sulfoxidation, demonstrating dioxygen activation and an oxygenation pathway not displayed by the enzymes.[16] Also reported was a N_3S−thioether−Cu^I complex that undergoes low-temperature oxygenation to form a spectroscopically characterized end-on peroxodicopper(II) complex.[17] A few copper(II) complexes with mixed polydentate imidazole−thioether ligands have been characterized,[18] but until our recent studies, only one copper(I) derivative had been reported.[11] In our preliminary report, we disclosed the preparation of tripodal bis(4,5-diphenylimidazolyl) thioether (BIT) ligands, corresponding copper(I) complexes, $[(BIT^{OR,SMe})Cu(L)]PF_6$ (L = CH_3CN, CO; R = H, CH_3), and the initial results of their interaction with dioxygen.[19] Herein, we describe new members of this family of ligands bearing sterically hindered thioether substituents, the novel oxygenation reactivity of

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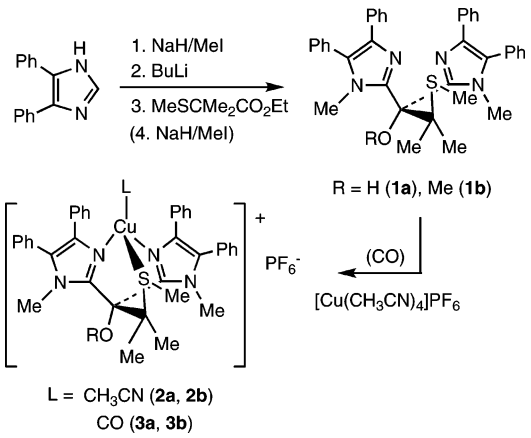
Scheme 1



the corresponding copper complexes, and provide a full account of the chemistry of the initially reported BIT−Cu complexes.

Results and Discussion

To provide the desired bis(imidazole) thioether donor set of the Cu_M center in a sterically encumbered environment that could limit the formation of bimetallic species, we first targeted the phenylated tripodal ligands $BIT^{OH,SMe}$ (**1a**) and $BIT^{OMe,SMe}$ (**1b**), which are conveniently prepared from readily available 4,5-diphenylimidazole (Scheme 1) via the addition of their 2-lithio derivatives to thiomethyl esters. These were characterized spectroscopically. Compounds **1a** and **1b** react readily with $[Cu(CH_3CN)_4]PF_6$ (CH_2Cl_2, room temperature) to produce $[(BIT^{OR,SMe})Cu(CH_3CN)]PF_6$ (**2a**, R = H; **2b**, R = Me). The former, somewhat-air-sensitive solid, was isolated and characterized spectroscopically and is presumed to have the pyramidal geometry depicted in Scheme 1.

Complexes **2a** and **2b** (generated in situ) are convenient precursors for investigating reactions with biorelevant substrates such as carbon monoxide and dioxygen. Bubbling CO into a CH_2Cl_2 solution of **2a** and **2b** (3 h, room temperature) resulted in the appearance of a strong infrared (IR) absorption near 2100 cm^{-1}. The addition of ether−petroleum ether induced crystallization of the colorless, air-sensitive carbonyl complexes $[(BIT^{OR,\ SMe})Cu(CO)]PF_6$ (**3a** and **3b**) (Scheme 1). These compounds are reasonably stable in solution with respect to CO dissociation under N_2, displaying appropriate NMR spectra and detectable molecular ions in their electrospray ionization mass spectrometry (ESIMS). The molecular structure of **3a** was established by X-ray diffraction (XRD) (Figure 2) and consists of a slightly distorted pyramidal arrangement about the copper(I) center formed by the tridentate BIT and CO ligands.[20] Notwithstanding the unique $(imidazole)_2(thioether)Cu^I$ donor atom set and a bifurcated O−H−FPF_5 hydrogen bond, the observed bond lengths and angles are unexceptional relative to reported N_3-

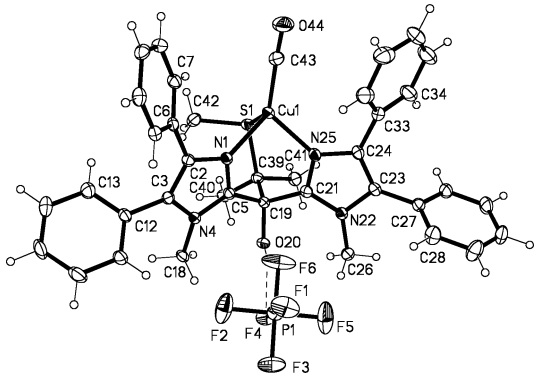


Figure 2. Crystal structure of **3a**. Selected bond lengths (angstroms) and angles (degrees): Cu(1)−C(43) 1.811(2), Cu(1)−N(25) 2.0005(19), Cu(1)−N(1) 2.0259(17), Cu(1)−S(1) 2.4392(7), C(43)−O(44) 1.123(2); C(43)−Cu(1)−N(25) 122.90(9), C(43)−Cu(1)−N(1) 132.84(10), C(43)−Cu(1)−S(1) 118.81(9), N(25)−Cu(1)−N(1) 90.67(7), N(25)−Cu(1)−S(1) 93.37(6), N(1)−Cu(1)−S(1) 87.33(5), Cu(1)−C(43)−O(44) 177.4(2).

Cu^I−CO structures.[21] An electronic similarity of the copper centers in carbonyl complexes **3a** and **3b** with the Cu_M (N_2S) site of the carbonylated copper hydroxylase enzymes is indicated by their comparable CO vibrational frequencies: PHM (2093 cm^{-1}),[22] DβH (2089 cm^{-1}),[23] **3a** (2102 cm^{-1}), and **3b** (2095 cm^{-1}). These bands lie in the range reported for N_3-type cationic [tris(pyrazolyl)methane]− and [tris(imidazolyl)methane]−Cu^I−CO complexes[12,21] but at a higher frequency than most neutral [tris(pyrazolyl)borate]−Cu−CO derivatives.[21] Although these data suggest that relatively little Cu−CO back-bonding is involved in the cationic N_2S− and N_3−Cu−carbonyl complexes vis-à-vis those of anionic N_3-type ligands, the IR data do not differentiate the electronic character of the copper centers in the N_2S complexes versus the N_3 complexes.

The reactions of hydroxy− and methoxy−tripod complexes **2a** and **2b** with dioxygen produced remarkably different results. Adventitious oxidation of **2a** occurred during its recrystallization from a DMF−ether solution over 1 week, affording green crystals of a new compound **4** whose ESIMS suggested the formation of a $Cu_2(BIT)_2$-type species. The X-ray structure of **4** (Scheme 2 and Figure 3) showed it to be a centrosymmetric dication with two five-coordinate copper(II) centers, each terminally bonded to one imidazole nitrogen, a DMF oxygen, and a sulfoxide oxygen and bridged by two alkoxo oxygens from the deprotonated tripod ligands. The bond metrics observed in the $Cu_2(OR)_2$ core of **4** (Figure 3) are comparable to those found in several $Cu_2(OH)_2$ and $Cu_2(OR)_2$ structures established crystallographically,[24] for example, Cu−(μ-OR), 1.92 (±0.02) Å; Cu−Cu 3.00 (±0.02) Å; Cu−O−Cu, 102 (±2)°. Related tris(imidazole)carbinol ligands also have been found to form polynuclear, alkoxo-

(20) (a) The geometry index τ_4, defined by Houser et al. (ref 20b), is equal to 0.74 for **3a**, a value between that of a trigonal pyramid (0.85) and a seesaw (0.64), with the former description being closer to the observed angles of **3a**. (b) Yang, L.; Powell, D. R.; Houser, R. P. *Dalton Trans.* **2007**, 955−964.

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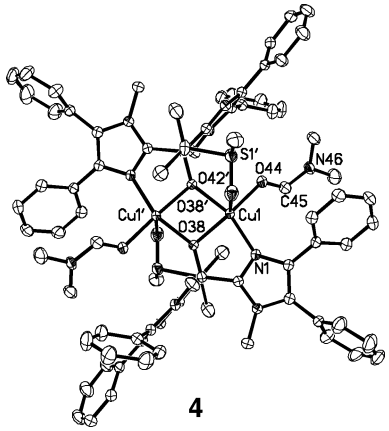

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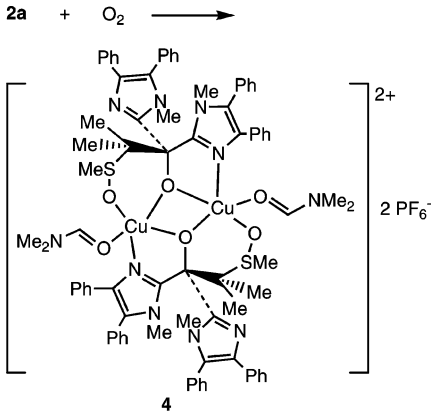
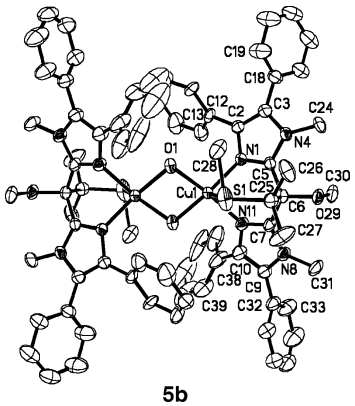
Figure 3. Crystal structure for the cation of **4**. Selected bond lengths (angstroms) and angles (degrees): Cu(1)−O(42′) 1.909(9), Cu(1)−O(44) 1.9369(18), Cu(1)−O(38) 1.9436(16), Cu(1)−N(1) 1.958(2), Cu(1)−O(38′) 1.9599(16), Cu(1)−Cu(1A) 3.0302(7); O(42′)−Cu(1)−O(38) 110.7(4), O(42′)−Cu(1)−O(44) 92.0(4), O(44)−Cu(1)−N(1) 102.53(8), O(44)−Cu(1)−O(38) 157.02(8), O(38)−Cu(1)−N(1) 81.48(8), Cu(1)−O(38)−Cu(1)′ 101.85.

Scheme 2



4

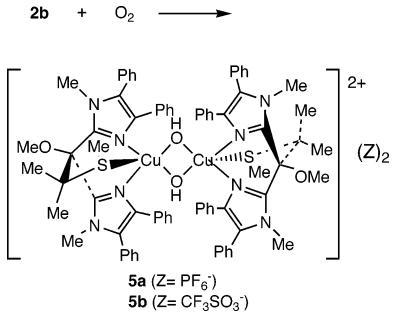
bridged copper(II) complexes.[25] Both the copper and the sulfur atoms are therefore oxidized during the conversion of **2a** to **4**. This facile sulfur oxidation can be compared to known copper-mediated oxidations of thioethers,[26] the stoichiometric sulfur ligand oxidation of a recently reported N_2S complex by the Karlin group,[17] and the copper-mediated methionine residue oxidation of the amyloid beta peptide (Aβ),[27] but it contrasts with the apparent oxidative inertness of the Cu_M active-site methionine in DβH and PHM.



5b

Figure 4. Crystal structure for the cation of **5b**. Selected bond lengths (angstroms) and angles (degrees): Cu(1)−O(1)′ 1.917(3), Cu(1)−O(1) 1.931(3), Cu(1)−N(1) 1.950(3), Cu(1)−N(11) 1.959(3), Cu(1)−S(1) 2.8683(13), Cu(1)−Cu(1)′ 3.021(3), O(1)−O(1)′ 2.383(3); O(1)′−Cu(1)−O(1) 76.55(18), O(1)′−Cu(1)−N(1) 174.66(13), O(1)−Cu(1)−N(1) 98.34(14), O(1)′−Cu(1)−N(11) 97.23(15), O(1)−Cu(1)−N(11) 173.74(13), N(1)−Cu(1)−N(11) 87.90(15), O(1)′−Cu(1)−S(1) 99.45(11), O(1)−Cu(1)−S(1) 92.73(11), N(1)−Cu(1)−S(1) 82.20(9), N(11)−Cu(1)−S(1) 87.48(9), Cu(1)′−O(1)−Cu(1) 103.44(18).

Scheme 3



In contrast, room-temperature oxygenation of the $BIT^{OMe,SMe}$ complex **2b** or **3b** (1 atm of O_2, CH_2Cl_2, 12 h), for which alkoxide formation is blocked, was accompanied by a gradual darkening of the reaction mixture. Crystallization by ether diffusion produced an amber compound **5**, whose ESIMS showed ions of $[(BIT^{OMe,SMe})CuOH]^+$ and $[(BIT^{OMe,SMe})_2Cu_2(OH)_2]^{2+}$ composition. Despite crystal disorder problems, the X-ray structure of the triflate salt **5b** was determined (Scheme 3 and Figure 4) to consist of a dinuclear dication having a Cu_2O_2 core with each copper coordinated terminally to the N_2S donor set of the $BIT^{OMe,SMe}$ ligand with separated triflate ions. Although the *O*-hydrogens were not located by XRD, **5** is formulated as a $L_2Cu^{II}_2(OH)_2$ complex based on (a) a comparison of its core metrical parameters with other $Cu_2(\mu\text{-}OH)_2$[23], $Cu_2(\mu\text{-}O)_2$, and $Cu_2(\mu\text{-}O_2)$ structures[28] [Cu−O, 1.92 (av) Å; Cu−Cu, 3.02 Å; Cu−O−Cu, 103°; O−O 2.38 Å]; (b) its mass spectrum, which showed two additional hydrogens; and (c) its thermal stability relative to typically unstable $L_nCu_2(\mu\text{-}O)_2$ complexes.[28] The hydroxo ligands of **5** are derived from dioxygen, as shown by the reaction of **2b** with $^{18}O_2/^{16}O_2$; the mass spectrum of the resulting product **5** showed appropriate higher *m*/*z* peaks. Thus, by capping of the hydroxyl group, as in the BIT^{OMe}

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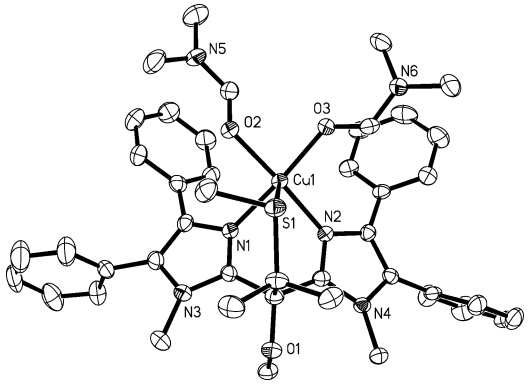
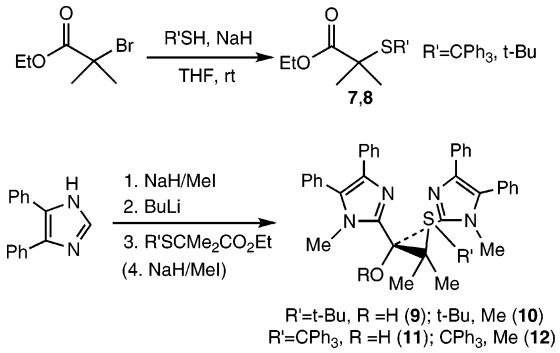


Figure 5. Crystal structure of the dication of **6**. Selected bond lengths (angstroms) and angles (degrees): Cu(1)−O(3) 1.9474(18), Cu(1)−N(2) 1.952(2), Cu(1)−O(2) 1.9527(17), Cu(1)−N(1) 1.968(2), Cu(1)−S(1) 2.6892(8); O(3)−Cu(1)−N(2) 98.75(8), O(3)−Cu(1)−O(2) 84.85(7), N(2)−Cu(1)−N(1) 84.70(9), O(2)−Cu(1)−N(1), 91.45(8).

Scheme 4



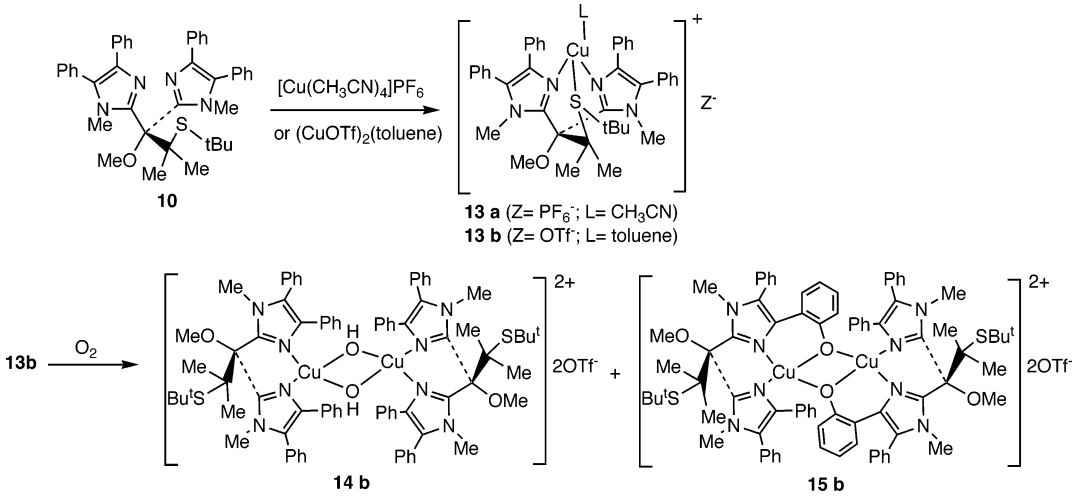
complexes, copper-centered oxygenation proceeds to give **5**, avoiding not only the alkoxo bridging tripod (as in **4**) but also sulfur oxidation as well. The source of the −OH hydrogens in **5** is uncertain but could derive from the reaction solvent, CH_2Cl_2, suggesting the intervention of a reactive mono- or dinuclear Cu−dioxygen complex. The relatively unhindered sulfur center of the $BIT^{OMe,\ SMe}$ ligand apparently is insufficient (at least at room temperature), however, to prevent the formation of a bridged dinuclear complex.

The $Cu_2(OH)_2$ linkage of **5** was found to be labile during its recrystallization from DMF−ether, from which blue crystals of a new compound **6** could be manually isolated. The ESIMS of **6** suggested a $[(BIT^{OMe,SMe})Cu^{II}(DMF)_n]^{2+}$ formulation. This was confirmed by its X-ray structure (Figure 5), which showed a mononuclear copper(II) complex cation of square-pyramidal geometry with its basal plane defined by the two imidazole nitrogens and two DMF oxygens and an apical −SMe group; two noninteracting octahedral PF_6 anions were located as well. It is noteworthy that **6** retains the N_2S coordination mode of the oxidized Cu_M site of the hydroxylase enzymes.[2,3] The Cu^{II}−S distance of **6** (2.69 Å) is considerably longer than the Cu^{I}−S length of **3a** (2.44 Å), suggestive of tighter binding of the sulfur atom to the reduced copper center. The same effect has been seen with the oxidized (2.68 Å) and reduced (2.27 Å) forms of PHM.[29] As for the formation of **6** from **5**, we speculate that DMF could assist dimer dissociation to form a mononuclear Cu−OH species, which is protonated by adventitious moisture; DMF displacement of coordinated water from such an aquo complex would provide **6**.

Because hydroxo-bridged dimers were obtained from oxygenation of the complexes derived from the −SMe ligands, we sought to inhibit dinuclear complex formation and potentially kinetically stabilize mono-Cu−O_2 species by increasing the steric demand of the tripodal ligands with bulkier S-alkyl groups. The requisite sulfur-containing esters **7** and **8** were prepared by the surprisingly effective reaction of ethyl 2-methyl-2-bromopropanoate with *tert*-butyl thiolate and trityl thiolate, respectively (Scheme 4).[30] The corresponding $BIT^{OMe,SR'}$ ligands **9** and **10** (R′ = *t*-Bu; R = H, Me) and **11** and **12** (R′ = CPh_3; R = H, Me) were then obtained by double addition of the lithiated imidazole to the esters, followed by reaction with methyl iodide. The overall conversion to the methoxy-capped tripodal ligands could be carried out sequentially in one pot or in separate steps after isolation of the intermediate alcohol. All of the new compounds had the expected compositions (by MS) and exhibited appropriate NMR and mass spectroscopic features.

The copper coordination of these two bulky ligands and the oxygenation chemistry of the copper(I) complexes proved to be strikingly different. The $BIT^{OMe,SBu-t}$ ligand **10** reacts

Scheme 5



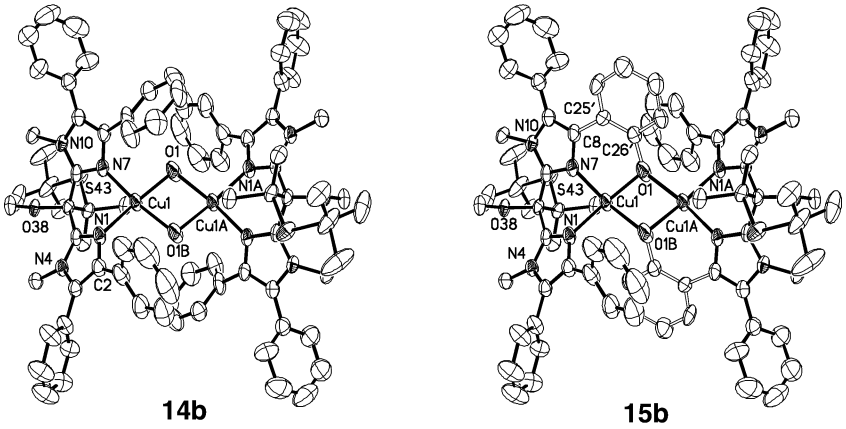
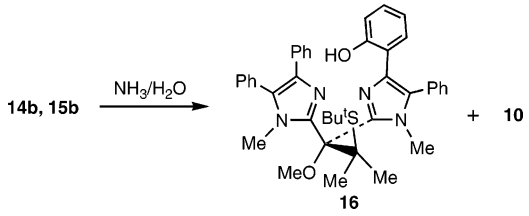


Figure 6. Crystal structures of the dications of **14b** and **15b**. Selected bond lengths (angstroms) and angles (degrees): Cu(1)−O(1) 1.898(5), Cu(1)−N(7) 1.921(5), Cu(1)−N(1) 1.927(5), Cu(1)−O(1)′ 1.952(5), Cu(1)−Cu(1)′ 3.0098(14); O(1)−Cu(1)−N(7) 95.3(2), O(1)−Cu(1)−N(1) 176.0(2), N(7)−Cu(1)−N(1) 88.6(2), O(1)−Cu(1)−O(1)′ 77.2(3), N(7)−Cu(1)−O(1)′ 167.2(2), N(1)−Cu(1)−O(1)′ 99.2(2), O(1)−Cu(1)−Cu(1)′ 39.23(17), N(7)−Cu(1)−Cu(1)′ 133.67(15), N(1)−Cu(1)−Cu(1)′ 137.07(16), O(1)′−Cu(1)−Cu(1)′ 37.93(14), Cu(1)−O(1)−Cu(1)′ 102.88(10).

with $[Cu(CH_3CN)_4]PF_6$ in CH_2Cl_2 at −20 °C to give four-coordinate $[(BIT^{OMe,SBu-t})Cu(CH_3CN)]PF_6$ (**13a**), which was characterized spectroscopically (Scheme 5). This compound was quite unreactive toward dioxygen, being largely recovered after 5 days of exposure at 20 °C (1 atm of O_2, CH_2Cl_2). To circumvent the possible inhibiting coordination competition between dioxygen and acetonitrile, the corresponding triflate salt of **13a** (**13b**) was generated in a CH_2Cl_2 solution via the reaction of **10** with $(CuOTf)_2$·(toluene). Complex **13b** reacted slowly with dioxygen at −20 °C over 72 h to give an amber solution, from which crystals were obtained upon ether diffusion. X-ray analysis of this material showed a dinuclear $Cu_2(BIT)_2$ species that was significantly disordered with respect to the orientation of the 5-aryl groups near to copper, with approximately 60% of one orientation (A) and ca. 40% of another orientation (B). This suggested the presence of two structurally similar compounds in the crystal. One, corresponding to orientation A, was determined to be hydroxo−Cu^{II} dimer **14b**, in which each copper is in a square-planar arrangement defined by the two hydroxo groups and the two imidazole nitrogens, with the SBu-*t* group being uncoordinated (Figure 6). The μ-hydroxo formulation was again supported by the atomic distances and angles within the Cu_2O_2 core[24] [Cu(1)−O(1) 1.898(5) Å; Cu(1)−O(1)′ 1.952(5) Å; Cu(1)−Cu(1)′, 3.0098(14) Å; Cu(1)−O(1)−Cu(1)′, 102.88(10)°], and the ESIMS features of the mixture.

The other molecule present in the crystal, **15b**, had the 5-position phenyl groups roughly coplanar with Cu(1), N(7), C(8), and O(1) and the *o*-phenyl carbon, C(26′), within a bonding distance (1.64 Å) of the bridging O(1), suggesting that ortho oxygenation of the ligand aryl group had occurred (Figure 6). This conclusion was confirmed by demetalation and characterization of the free ligands (Scheme 6). Thus, treatment of the mixture of complexes **14b**/**15b** with

Scheme 6



concentrated ammonium hydroxide in CH_2Cl_2 produced two organic compounds separable by thin-layer chromatography (TLC). One was found to be the original $BIT^{OMe,SBu-t}$ ligand (**10**) and the other (**16**) was found to have an extra oxygen atom from its high-resolution mass spectrum ($C_{41}H_{45}N_4O_2S$). The additional oxygen atom was incorporated at an ortho aromatic carbon, rather than at the thioether sulfur, as was apparent from the ^1H NMR spectrum of **16**, which exhibited three multiplets (4H) in the 6−7 ppm region typical of phenols, whereas the −SMe resonance was virtually unchanged relative to that of the original (unoxygenated) ligand **10**. Together, these data indicate that oxidation of the ligand occurs in part during the oxygenation of complex **13b**. Although ligand-centered C−H bond oxygenation has been observed in a number of previous dioxygen reactions of copper(I) polyamine complexes,[31] this is the first instance of such a process involving the (imidazolyl)$_2$(thioether)(BIT) or (imidazolyl)$_3$(TIC) copper complexes. The intervention of this pathway could be enabled by the sterically weakened Cu−thioether linkage that influences the reactivity of the presumed intermediate $Cu-O_2$ complex.

In contrast, when the tritylated $BIT^{OMe,SCPh_3}$ ligand **12** was combined with $[Cu(CH_3CN)_4]PF_6$ in CH_2Cl_2 at room temperature, a bright-yellow (rather than the usual colorless) solution formed immediately. The solution rapidly became purple when stirred under 1 atm of O_2 (balloon) at −50 °C. Ether diffusion into the reaction mixture produced purple crystals whose MS data suggested the formation of a

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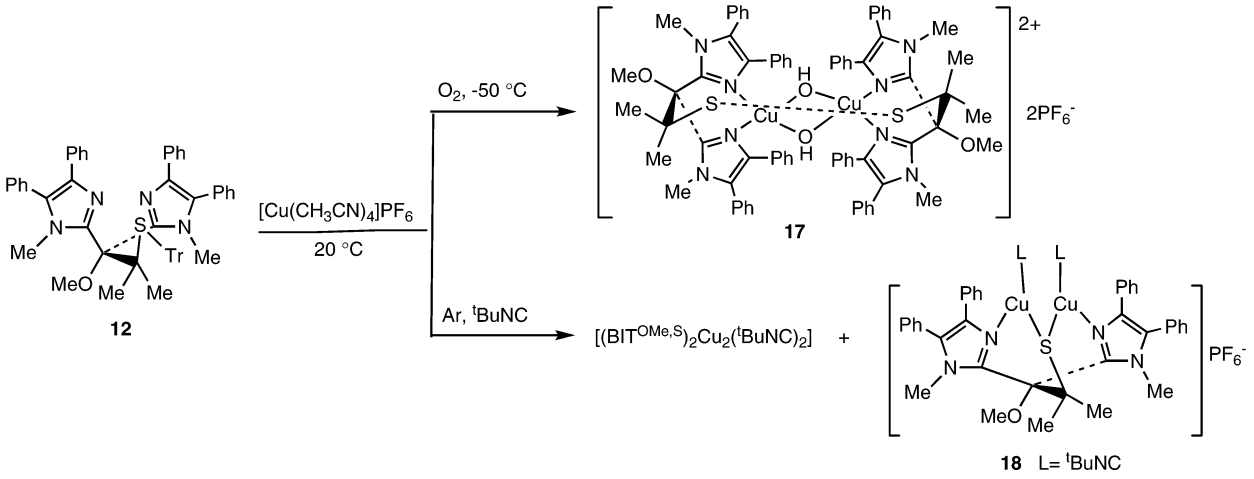
Scheme 7



dinuclear species **17**, lacking the trityl unit (Scheme 7). Indeed, XRD analysis of **17** revealed a dimeric structure (Figure 7) featuring both a $Cu^{II}(\mu\text{-OH})_2$ core (with supporting Cu−O and Cu−O−Cu bond metrics) and, most surprisingly, a bridging (noncoordinated) disulfide unit formed between the two tripodal ligands. Each copper(II) center is essentially square planar in its coordination to the two bridging hydroxo groups and the two imidazole nitrogens. Trityl alcohol was identified by TLC/NMR as the major organic product of the reaction.

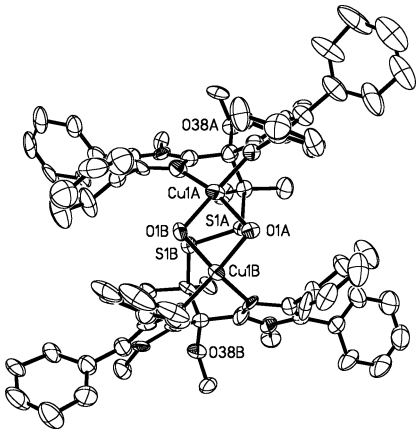


Figure 7. Crystal structure of the dication of **17**. Selected bond lengths (angstroms) and angles (degrees): Cu(1A)−O(1A) 1.918(10), Cu(1A)−O(1B) 1.962(9), Cu(1A)−N(2A) 1.971(13), Cu(1A)−N(8A) 2.007(15), Cu(1A)−Cu(1B) 2.807(3), S(1A)−S(1B) 2.051(6), Cu(1A)−Cu(1B) 2.807(3); O(1A)−Cu(1A)−O(1B) 77.7(4), O(1A)−Cu(1A)−N(2A) 99.3(5), O(1B)−Cu(1A)−N(2A) 173.5(5), O(1A)−Cu(1A)−N(8A) 157.5(5), O(1B)−Cu(1A)−N(8A) 96.2(5), N(2A)−Cu(1A)−N(8A) 88.7(6), O(1A)−Cu(1A)−Cu(1B) 43.5(3), O(1B)−Cu(1A)−Cu(1B) 44.4(3), N(2A)−Cu(1A)−Cu(1B) 136.0(4), N(8A)−Cu(1A)−Cu(1B) 118.4(4), C(40A)−S(1A)−S(1B) 108.2(6), Cu(1A)−O(1A)−Cu(1B) 93.5(4).

Hence, loss of the trityl group from the $BIT^{OMe,STr}$ ligand and oxidation of both the copper and sulfur atoms had occurred during the reaction of ligand **12** with $[Cu(CH_3CN)_4]PF_6$ and subsequent oxygenation. We wondered, how and when is the trityl group cleaved, during or prior to the oxygenation? To address these questions, we sought to identify the species produced initially, before oxygen exposure. The reaction of $BIT^{OMe,STr}$ with $[Cu(CH_3CN)_4]PF_6$ in CH_2Cl_2 was conducted under Ar followed by the addition of *tert*-butyl isocyanide (1.0 equiv) at room temperature. ESIMS analysis of the relatively air-stable reaction mixture indicated the formation of $[(BIT^{OMe,SH})_2Cu^I_2(t\text{-BuNC})_2]^{2+}$ and $[BIT^{OMe,S}Cu^I_2(t\text{-BuNC})_2]^{+}$ species, both lacking the Tr group. In addition, chromatography of this material afforded a yellow complex whose ^1H NMR and mass spectra support the formulation as a Cu^I_2(thiolate) complex **18**. It is apparent, therefore, that copper-promoted detritylation occurs before oxygenation, with the trityl unit lost as the (yellow) trityl cation, which is eventually converted by aerobic moisture to the alcohol. A highly oxygen-sensitive neutral N_2S-(thiolate)Cu^I complex, that can be stabilized by coordinating *t*-BuNC is likely produced. Lacking isocyanide, the initially formed species undergoes facile oxidation, both at sulfur to give the disulfide unit and at copper to produce a μ-oxo/peroxo species that abstracts hydrogen (presumably from solvent) to give the structurally characterized complex **17**. Although the transformations observed in the conversion of **12** to disulfide complex **17** are unusual, they find precedent in the recently reported copper(I)-catalyzed cleavage of trityl thioethers to disulfides[31] and the air-induced conversion of a related tripodal zinc thiolate complex to a dinuclear disulfide complex.[32]

The reactivity of these bis(imidazolyl)−thioether−Cu complexes is comparable in a number of respects to that of the Cu_M site of the copper hydroxylase enzymes. They form fairly stable CO adducts whose vibrational energies indicate a electronic character similar to that of the enzymes. Moreover, the CO complexes are qualitatively more stable than the corresponding tris(imidazolyl) complexes that we have recently prepared,[19] also consistent with the relative CO-adduct forming tendency of the Cu_H and Cu_M sites. The bis(imidazolyl)−thioether−Cu^I complexes are reactive to-

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ward dioxygen, undergoing oxygenation at the copper center without sulfur oxidation, as found with the Cu_M site. Here again, the N_3−tris(imidazolyl) analogues and the corresponding Cu_M centers are slower to react with dioxygen. To date, we have no visual evidence for long-lived dioxygen complex intermediates in the oxygenation reactions of the N_2S complexes. The sterically hindered, arylated imidazolyl ligands employed here do not prevent the formation of bimetallic μ-peroxo/oxo complexes that are inhibited in the enzymes, presumably because of conformational constraints by the protein ligand that limit the association of the copper centers. On the other hand, the protein probably provides a more flexible coordination geometry of the copper centers vis-à-vis these synthetic tripodal ligands that could, in turn, affect the copper center's dioxygen coordination ability and reactivity. Another structural difference between the present synthetic ligands and the donor set provided by the protein lies in the substitution pattern of the coordinating imidazole units. The 2-substituted imidazoles of the synthetic ligands are likely less basic than the 4(5)-substituted imidazole groups of the histidines of the protein,[33] again potentially affecting the reactivity of the copper-coordinated dioxygen.

Conclusions

Tripodal bis(imidazole) thioether ligands (*N*-methyl-4,5-diphenyl-2-imidazolyl)$_2$C(OR)C(CH$_3$)$_2$SR′ have been prepared that provide the same (imidazole)$_2$(thioether) ligand set as that of the Cu_M binding site of the copper hydroxylase enzymes. These complexes exhibit several close parallels with the Cu_M site of the enzymes, including the formation of electronically similar carbonyl adducts and copper-centered oxidation and oxygenation (when R = Me). [(BIT$^{OR,SR'}$)Cu(CO)]PF$_6$ have been prepared in which the IR ν(CO)'s are comparable to those of the carbonylated enzymes, indicating similar electronic character at the copper centers. The oxygenation reactivity of these complexes depends markedly on the carbinol and thioether substituents. The reaction of **2a** (R = H) with dioxygen gives dinuclear **4**, featuring bridging BIT−alkoxo ligands and terminal −SOMe groups. In contrast, oxygenation of **2b** (R = Me) affords dinuclear [(BIT^{OMe,SMe})$_2$Cu$_2$(μ-OH)$_2$](PF$_6$)$_2$ (**5**) in which the copper centers are oxygenated without accompanying sulfur oxidation. Oxygenation of the copper(I) complex derived from the sterically hindered BIT$^{OMe,SBu-t}$ ligand is slow, relative to **2b**, producing a mixture of Cu$_2$(μ-OH)$_2$-type complexes **14b** and **15b**, the latter of which has been ortho-oxygenated on a neighboring aryl group. Oxygenation of the copper(I) complex derived from the BIT^{OMe,SCPh_3} ligand produces a novel dinuclear bridged disulfide complex **17**, apparently the result of copper-induced detritylation, followed by oxygenation of a highly reactive thiolate complex.

Our ongoing efforts are focused on developing even more accurate structural and functional mimics of the copper hydroxylase enzymes and exploring the stoichiometric and catalytic oxidation reactions promoted by these and related poly(imidazole) complexes.

Experimental Section

Materials and Methods. All operations were carried out under N_2 or Ar by means of standard Schlenk and vacuum-line techniques. Organic solvents were dried by standard procedures and distilled under N_2 before use. CH_2Cl_2 was dried over CaH_2 and distilled under N_2 before use; tetrahydrofuran (THF) was dried over Na using benzophenone as an indicator and distilled under N_2 before use. Glassware was oven-dried at 150 °C overnight. A Vacuum Atmospheres glovebox was used in the handling of air-sensitive solids. Infrared (IR) spectra were recorded either in a CH_2Cl_2 solution or in KBr pellets with a Perkin-Elmer 283-B infrared spectrophotometer (resolution 4 cm^{-1}). The ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury-300 spectrometer. Mass spectra were acquired on a Finnigan TSQ 700 spectrometer in methanol or acetonitrile solution by electrospray ionization (ESI). Elemental analyses were performed by Midwest Microlab, LLC. 4,5-Diphenylimidazole[35] and *N*-methyl-4,5-diphenylimidazole[36] were prepared according to reported procedures. [Cu(CH$_3$CN)$_4$]PF$_6$ and (CuOTf)$_2$(C$_7$H$_8$) were obtained commercially. Fifty atom % $^{18}O_2$ (50% $^{16}O^{18}O$, 25% $^{16}O_2$, and 25% $^{18}O_2$) was obtained from Icon Isotopes.

1,1-Bis(*N*-methyl-4,5-diphenyl-2-imidazolyl)-2-methyl-2-methylthiopropanol (1a, BIT^{OH,SMe}). To a solution of *N*-methyl-4,5-diphenylimidazole (2.34 g, 10.0 mmol) in 40 mL of dry THF under N_2 cooled to −78 °C was added *n*-BuLi dropwise (4.6 mL in hexane, 10 mol). The mixture was stirred at −78 °C for 3 h to give a red-brown solution. After dropwise addition of dry ethyl 2-methyl-2-methylthiopropinate (0.74 mL, 5.0 mmol), the mixture was allowed to warm to room temperature overnight to give a pale-yellow solution. The reaction was quenched with 80 mL of water and extracted with diethyl ether, and the organic phase was dried over $MgSO_4$. Flash column chromatography (silica) using petroleum ether−ethyl acetate (8:1) as the eluant gave 2.0 g (68%) of the alcohol **1a** as a white solid (recrystallization from CH_2Cl_2−petroleum ether, mp 157−159 °C). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 1.88(s, 3H), 1.97(s, 6H), 3.07(s, 6H), 5.67(s, 1H), 7.18−7.52(m, 20H). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 146.68, 135.49, 135.18, 131.62, 131.43, 129.61, 129.41, 128.57, 127.03, 126.82, 77.13, 55.22, 32.46, 26.20, 13.50. HRMS (ESI): *m*/*z* 585.2621 (M + 1); calcd for C$_{37}$H$_{36}$N$_4$OS, *m*/*z* 585.2688. IR (KBr; cm^{-1}): 3410, 3100, 2927, 1603, 1442, 1027, 968, 780, 698. Anal. Calcd for C$_{37}$H$_{36}$N$_4$OS: C, 75.99; H, 6.21; N, 9.58; S, 5.48. Found: C, 75.73; H, 6.29; N, 9.56; S, 5.48.

1-Methoxy-2-methyl-1,1-bis(*N*-methyl-4,5-diphenyl-2-imidazolyl)-2-methylthiopropane (1b, BIT^{OMe,SMe}). Sodium hydride (0.024 g, 60% mineral oil suspension, 0.60 mmol, 1.2 equiv) was suspended in dry THF (10 mL) under N_2. Compound **1a** (0.292 g, 0.50 mmol) was dissolved in dry THF (10 mL) to give a light-yellow solution, which was added dropwise to the NaH suspension over 2 min, and the resulting mixture was stirred for 2 h at room temperature until no bubbles appeared. Methyl iodide (37.4 μL, 0.6 mmol, 1.2 equiv) was added dropwise, and the reaction mixture was stirred for 20 h. Then the reaction was quenched with 40 mL of deionized water and extracted twice with 25 mL portions of ether, and the organic phase was dried over $MgSO_4$. Rotary evaporation of the ether gave 0.24 g of **1b** as a light-yellow solid (80%) (recrystallization from CH_2Cl_2−petroleum ether, mp 139−141 °C). ^{1}H NMR (300 MHz, CD_2Cl_2, room temperature): δ 1.81(s, 3H), 2.11(br, 6H), 2.80(br, 3H), 3.29(br, 3H), 3.80(br, 3H), 7.13−7.46-

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(m, 20H). ^{1}H NMR (300 MHz, CD_2Cl_2, −80 °C): δ 1.58(s, 3H), 2.05(d, 6H), 2.80(s, 3H), 3.20(s, 3H), 3.80(s, 3H), 7.13−7.46(m, 20H). ^{13}C NMR (75 MHz, CD_2Cl_2, room temperature): δ 135.05, 131.29, 130.50, 128.94, 128.65, 127.96, 126.54, 126.00, 86.99, 56.94, 54.93, 26.62, 12.40. HRMS (ESI): *m*/*z* 599.2680 (M + 1); calcd for $C_{38}H_{38}N_4OS$, *m*/*z* 599.2844. IR (KBr; cm^{-1}): 3100, 2927, 1603, 1442, 1368, 1081, 776, 697.

[(BIT^{OH,SMe})Cu(NCCH$_3$)]PF$_6$ (2a). To a yellow CH_2Cl_2 solution (8 mL) of N_2S−tripod **1a** (0.467 g, 0.80 mmol) was added dropwise a CH_2Cl_2 solution (10 mL) of $[Cu(CH_3CN)_4]PF_6$ (0.29 g, 0.80 mmol) under N_2, and the resultant solution was stirred at room temperature for 2 h to give a yellow solution. The solvent was pumped off, and a pale-yellow solid was left. The solid was dissolved in 10 mL of CH_2Cl_2, and 30 mL of diethyl ether was added to precipitate 0.46 g of pale-yellow solid **2a** (84%). ^{1}H NMR (300 MHz, CD_3CN): δ 1.54(s, 6H), 1.88(s, 3H), 3.73(s, 6H), 5.20-(s, 1H), 7.30−7.56(m, 20H). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 145.40, 137.42, 133.89, 133.11, 132.53, 130.48, 130.29, 129.95, 129.72, 128.95, 128.57, 82.32, 55.25, 36.13, 25.01, 16.41. LRMS (ESI): *m*/*z* 688.2, 690.2 (100%, 52%) for $C_{39}H_{39}{}^{63}CuN_5OS^+$ and $C_{39}H_{39}{}^{65}CuN_5OS^+$, respectively. HRMS (ESI): *m*/*z* 688.2281 (M$^+$); calcd for $C_{39}H_{39}{}^{63}CuN_5OS^+$, *m*/*z* 688.2271. IR (KBr; cm^{-1}): 3100, 2927, 1657, 1444, 1389, 1105, 855, 700, 558.

[(BIT^{OH,SMe})CuCO]PF$_6$ (3a). To a CH_2Cl_2 solution (5 mL) of **1a** (0.234 g, 0.40 mmol) under N_2 was added dropwise a CH_2Cl_2 solution (5 mL) of $[Cu(CH_3CN)_4]PF_6$ (0.15 g, 0.40 mmol), and the mixture was stirred at room temperature for 1 h to give a light-yellow solution. CO was bubbled into the solution at room temperature for 3 h, during which the solution turned to light green. Colorless needle-shaped X-ray-quality crystals of **3a** were obtained overnight in a Schlenk tube under N_2 by liquid layering with CH_2Cl_2−petroleum ether. Yield: 10%. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 1.37(s, 6H), 1.77(s, 3H), 3.82(s, 6H), 4.60(s, 1H), 7.20−7.37(m, 20H). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 178.03, 143.33, 137.14, 132.72, 132.62, 131.33, 129.30, 129.22, 128.88, 128.36, 128.14, 81.78, 55.04, 35.47, 23.82, 16.38. LRMS (ESI) *m*/*z* 647.1, 649.2 (1.5%, 0.6%) for $C_{37}H_{36}{}^{63}CuN_4OS^+$ and $C_{37}H_{36}{}^{65}CuN_4OS^+$, respectively. IR (KBr; cm^{-1}): 3510, 2927, 2102, 1656, 1478, 1444, 1399, 1107, 855, 700, 558. See the X-ray experimental section for crystallographic data on **3a**.

[(BIT^{OMe,SMe})CuCO]PF$_6$ (3b). To a CH_2Cl_2 solution (5 mL) of methoxy−tripod **1b** (0.060 g, 0.10 mmol) under N_2 was added dropwise a CH_2Cl_2 solution (5 mL) of $[Cu(CH_3CN)_4]PF_6$ (0.038 g, 0.10 mmol), and the resultant mixture was stirred at room temperature for 1 h to give a light-yellow solution. CO was bubbled into the solution at room temperature for 3 h. White solid **3b** was obtained by vapor diffusion with CH_2Cl_2−diethyl ether under N_2. Yield: 44%. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.52(s, 6H), 1.69(s, 3H), 3.70(s, 3H), 3.91(s, 6H), 7.35−7.53(m, 20H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 141.45, 138.09, 132.98, 132.03, 131.05, 129.85, 129.22, 128.82, 128.49, 128.38, 127.93, 89.21, 57.01, 56.82, 35.69, 24.61, 15.12. LRMS (ESI): *m*/*z* 689.2, 691.2 (100%, 38%) for $C_{39}H_{38}{}^{63}CuN_4O_2S^+$ and $C_{39}H_{38}{}^{65}CuN_4O_2S^+$, respectively. IR (KBr; cm^{-1}): 3100, 2927, 2094, 1604, 1445, 1389, 1091, 839, 700, 558.

Oxidation of [(BIT^{OH,SMe})Cu^{I}(NCCH$_3$)]PF$_6$ (4). Crystals of 4 were obtained by slow vapor diffusion of ether into a concentrated solution of [(BIT^{OH,SMe})Cu(NCCH$_3$)]PF$_6$ (**2a**) in DMF. Green needles of **4** were obtained over 1 week. Yield: 20%. LRMS (ESI): *m*/*z* 662.1 (70%, $C_{37}H_{34}{}^{63}CuN_4O_2S^+$), 662.6 (51%, $C_{74}H_{68}{}^{63}$-$Cu_2N_8O_4S_2{}^{2+}$), 663.1 (100%), 663.6 (42%), 664.1 (26%, $C_{37}H_{35}{}^{65}$-$CuN_4O_2S^+$). See the X-ray experimental section for crystallographic data on **4**.

[(BIT^{OMe,SMe})$_2$Cu$_2$(OH)$_2$](PF$_6$)$_2$ (5a,b). To a yellow, dry CH_2-Cl_2 solution (5 mL) of tripod ether **1b** (0.060 g, 0.10 mmol) under Ar was added dropwise a colorless CH_2Cl_2 solution (5 mL) of $[Cu(CH_3CN)_4]PF_6$ (0.038 g, 0.10 mmol) or $[CuOTf]_2$(toluene) (0.10 mmol) and the mixture was stirred at room temperature for 1 h to give a light-yellow solution. Then a balloon filled with dioxygen was attached to the flask and stirring was continued overnight, during which the solution turned to yellowish brown. Amber crystals of **5a** (Z = PF_6) or **5b** (Z = OTf) were obtained after several hours by vapor diffusion with CH_2Cl_2−ether (used for XRD). Yield: 60%. LRMS (ESI): *m*/*z* 677.2 (48%, $C_{38}H_{38}{}^{63}CuN_4O_2S^+$), 677.7 (22%, $C_{76}H_{76}{}^{63}Cu_2N_8O_4S_2{}^{2+}$), 678.2 (100%), 678.7 (17%), 679.2 (23%, $C_{38}H_{38}{}^{65}CuN_4O_2S^+$). IR (KBr; cm^{-1}): 3100, 2927, 1444, 1388, 1084, 839, 701, 558. UV−vis (CH_3CN): 210 nm ($\epsilon = 7.5 \times 10^4$ M^{-1} cm^{-1}), 250 nm ($\epsilon = 4.2 \times 10^4$ M^{-1} cm^{-1}), 330 nm ($\epsilon = 4.6 \times 10^3$ M^{-1} cm^{-1}). See the X-ray experimental section for crystallographic data on **5b**. An ^{18}O labeling experiment to prepare **5a** was carried out using the same protocol with 50 atom % $^{18}O_2$ (50% $^{16}O^{18}O$, 25% $^{16}O_2$, and 25% $^{18}O_2$). Green crystals were obtained whose LRMS (ESI) showed peaks at *m*/*z* 677.2 (19%), 677.7 (9.8%), 678.2 (100%), 678.7 (29%), 679.2 (47%), 679.7 (16%), 680.2 (14%), and 680.7 (2.4%).

[(BIT^{OMe,SMe})Cu(II)(DMF)$_2$](PF$_6$)$_2$ (6). Crystals of **5a** (above) were dissolved in DMF. Vapor diffusion with DMF−ether over 1 week produced green crystals of **5a** and a small quantity of blue crystals of **6**. LRMS (ESI): *m*/*z* 367.1 (2.6%, [BIT^{OMe,SMe}]^{63}Cu-[DMF]$^{2+}$), 368.1 (1.3%, [BIT^{OMe,SMe}]^{65}Cu[DMF]$^{2+}$). See the X-ray experimental section for crystallographic data on **6**.

Ethyl 2-Methyl-2-*tert*-butylthiopropanoate (7). Sodium hydride (2.0 g, 60% mineral oil suspension, 50 mmol) was suspended in dry THF (40 mL) under N_2. *tert*-Butylthiol (5.6 mL, 50 mmol) was added dropwise to the NaH suspension over 5 min, and the resulting mixture was stirred for 10 min at room temperature. Ethyl 2-bromoisobutyrate (6.6 mL, 45 mmol) was added dropwise, and then the reaction mixture was stirred at reflux under N_2 for 20 h. After cooling, the reaction was quenched with 80 mL of deionized water and extracted twice with 50 mL portions of diethyl ether, and the organic phase was dried over $MgSO_4$. Flash column chromatography (silica gel) using petroleum ether as the eluant gave 4.1 g (45%) of **7** as a colorless oil. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 1.27(t, 3H), 1.32(s, 9H), 1.52(s, 6H), 4.12(q, 2H). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 176.0, 61.6, 49.2, 46.7, 32.4, 28.6, 14.4. HRMS (ESI): *m*/*z* 227.1075 (M + Na); calcd for $C_{10}H_{20}NaO_2S$, *m*/*z* 227.1082. IR (KBr; cm^{-1}): 2970, 2931, 2869, 1724, 1469, 1385, 1365, 1264, 1154, 1123, 1029.

Ethyl 2-Methyl-2-triphenylmethanethiopropanoate (8). Sodium hydride (0.60 g, 60% mineral oil suspension, 15 mmol) was suspended in dry THF (30 mL) under N_2. Triphenylmethanethiol (3.0 g, 11 mmol) was dissolved in dry THF (30 mL) and was added dropwise to the NaH suspension over 5 min, and the resulting mixture was stirred for 10 min at room temperature until no bubbles (H_2) appeared. Ethyl 2-bromoisobutyrate (1.6 mL, 11 mmol) was added dropwise, and then the reaction mixture was stirred at reflux under N_2 for 8 h. Then the reaction was quenched with 80 mL of deionized water and extracted twice with 50 mL portions of dichloromethane, and the organic phase was dried over $MgSO_4$. Rotary evaporation of the dichloromethane gave 1.8 g of **8** as a white solid (42%) (recrystallization from CH_2Cl_2−petroleum ether). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 1.08(t, 3H), 1.21(s, 6H), 3.74(q, 2H), 7.19−7.54(m, 15H). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 174.1, 145.1, 130.5, 128.1, 127.1, 68.6, 61.5, 51.9, 27.6, 14.1. HRMS (ESI): *m*/*z* 413.1504 (M + Na); calcd for $C_{25}H_{26}NaO_2S$, *m*/*z* 413.1551. IR (KBr; cm^{-1}): 3057, 2979, 1730, 1489, 1446, 1254,

1138, 1118, 1022, 747, 704. Anal. Calcd for $C_{25}H_{26}O_2S$: C, 76.89; H, 6.71. Found: C, 76.92; H, 6.68.

1-Methoxy-2-methyl-1,1-bis(*N*-methyl-4,5-diphenyl-2-imidazolyl)-2-*tert*-butylthiopropane (10, BIT$^{OMe,SBu-t}$). To a solution of *N*-methyl-4,5-diphenylimidazole (1.4 g, 6.0 mmol) in 30 mL of dry THF under N_2 cooled to −78 °C was added *t*-BuLi dropwise (4.1 mL in hexane, 6.0 mmol). The mixture was stirred at −78 °C for 3 h to give a red-brown solution. After the addition of a dry THF solution (10 mL) of **7** (0.41 g, 2.0 mmol), the mixture was allowed to warm to room temperature overnight to give a yellow solution. Sodium hydride (0.20 g, 60% mineral oil suspension, 5.0 mmol) was added to the solution under N_2, and the resulting mixture was stirred for 1 h at room temperature. Methyl iodide (312 μL, 5.0 mmol) was added dropwise, and then the reaction mixture was stirred at reflux under N_2 for 22 h. The mixture was quenched with 80 mL of water and extracted with CH_2Cl_2, and the organic phase was dried over $MgSO_4$. Flash column chromatography (silica gel) using petroleum ether−ethyl acetate (8:1) as the eluant gave 0.30 g (24%) of **10** as a white solid. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 1.32(s, 9H), 2.30(s, br, 6H), 2.80(s, br, 3H), 3.30(s, 3H), 3.80(s, br, 3H), 7.08−7.54(m, 20H). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 135.7, 132.0, 131.8, 131.6, 130.8, 129.5, 129.1, 128.6, 127.1, 126.5, 88.1, 63.8, 55.5, 47.8, 33.8, 22.9, 14.4. HRMS (ESI): *m*/*z* 641.3352 (M + 1); calcd for $C_{41}H_{45}N_4OS$, *m*/*z* 641.3314. IR (KBr; cm^{-1}): 3060, 2959, 1604, 1507, 1444, 1365, 1128, 1070, 1056, 1026, 964, 783, 774, 723, 697. Anal. Calcd for $C_{41}H_{44}N_4OS$: C, 76.84; H, 6.92; N, 8.74. Found: C, 76.06; H, 6.93; N, 8.77.

1-Methoxy-2-methyl-1,1-bis(*N*-methyl-4,5-diphenyl-2-imidazolyl)-2-tritylthiopropane (12, BIT^{OMe,STr}). To a solution of *N*-methyl-4,5-diphenylimidazole (1.2 g, 5.0 mmol) in 30 mL of dry THF under N_2 cooled to −78 °C was added *t*-BuLi dropwise (3.4 mL in hexane, 5.0 mmol). The mixture was stirred at −78 °C for 3 h to give a red-brown solution. After the addition of a dry THF solution (15 mL) of **8** (0.78 g, 2.0 mmol), the mixture was allowed to warm to room temperature overnight to give a yellow solution. Sodium hydride (0.20 g, 60% mineral oil suspension, 5.0 mmol) was added to the solution under N_2, and the resulting mixture was stirred for 1 h at room temperature. Methyl iodide (312 μL, 5.0 mmol) was added dropwise, and then the reaction mixture was stirred at reflux under N_2 for 20 h. The mixture was quenched with 80 mL of water and extracted with CH_2Cl_2, and the organic phase was dried over $MgSO_4$. Flash column chromatography (silica gel) using petroleum ether−ethyl acetate (8:1) as the eluant gave 0.30 g (18%) of **12** as a light-yellow solid. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 1.75 (br s, 3H), 1.80 (br, s, 3H), 2.81(s, br, 3H), 3.34(s, 3H), 3.95(s, br, 3H), 7.15−7.47(m, 35H). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 145.9, 135.6, 132.1, 131.8, 131.0, 129.6, 129.3, 128.4, 128.0, 127.8, 127.4, 126.9, 126.6, 88.9, 68.9, 67.0, 55.7, 35.4, 31.4, 29.7, 26.0. HRMS (ESI): *m*/*z* 827.3783 (M + 1); calcd for $C_{56}H_{51}N_4OS$, *m*/*z* 827.3793. IR (KBr; cm^{-1}): 3061, 2947, 1602, 1491, 1444, 1077, 773, 743, 699.

[(BIT$^{OMe,SBu-t}$)Cu(NCCH$_3$)]PF$_6$ (13a). To **10** (64 mg, 0.10 mmol) and $[Cu(CH_3CN)_4]PF_6$ (38 mg, 0.10 mmol) was added dry CH_2Cl_2 (5 mL), and the resulting light-yellow solution was stirred at room temperature for 2 h under Ar. Compound **13a** was obtained as a white solid by slow diffusion of ether into the yellow solution at room temperature under N_2 (80%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 1.29(s, 9H), 1.67(s, br, 6H), 1.76(s, 3H), 3.55(s, 3H), 3.82(s, br, 6H), 7.27−7.52(m, 20H). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 142.4, 137.2, 133.2, 133.0, 131.6, 131.0, 130.0, 129.3, 128.4, 128.1, 90.2, 61.4, 56.7, 52.6, 36.2, 34.0, 32.8, 27.6. LRMS (ESI): *m*/*z* 703.3 (2.5%) for $C_{41}H_{44}{}^{63}CuN_4OS^+$, 744.3, 746.3 (100.0%, 30.6%) for $C_{43}H_{47}{}^{63}CuN_5OS^+$ and $C_{43}H_{47}{}^{65}CuN_5OS^+$, respectively. HRMS (ESI): *m*/*z* 744.2692 (M^+); calcd for $C_{43}H_{47}{}^{63}CuN_5OS^+$, *m*/*z* 744.2797. IR (KBr; cm^{-1}): 2970, 2937, 1655, 1544, 1370, 1080, 842, 700, 558.

Reaction of 13a with Dioxygen. Compound **13a** (37 mg, 0.050 mmol) was dissolved in 5 mL of dry CH_2Cl_2, and the solution was stirred at room temperature under O_2 (1 atm) for 2 days to give a yellowish solution. A white solid precipitated overnight during diffusion of the ether vapor into the reaction solution and was found to be **13a** from its ^{1}H NMR spectrum in CD_2Cl_2.

[(BIT$^{OMe,SBu-t}$)$_2$Cu$_2$(OH)$_2$](OTf)$_2$ (14b and 15b). To **10** (52 mg, 0.080 mmol) and $(CuOTf)_2(C_7H_8)$ (21 mg, 0.080 mmol) was added dry CH_2Cl_2 (5 mL), and the resulting light-yellow solution was stirred at room temperature for 1 h under Ar. Then the solution was stirred under an O_2 atmosphere (balloon) at −50 °C for 72 h, producing an amber solution. Amber crystals of **14b** and **15b** were obtained by slow diffusion of ether into the solution at −20 °C (36%). LRMS (ESI): *m*/*z* 718.2 (47%) for $C_{82}H_{86}{}^{63}Cu_2N_8O_4S_2{}^{2+}$, 719.2, 720.2, and 721.2 (12, 22, and 4%) for $C_{82}H_{88}{}^{63}Cu_2N_8O_4S_2{}^{2+}$, $C_{82}H_{88}{}^{63}Cu^{65}CuN_8O_4S_2{}^{2+}$, and $C_{82}H_{88}{}^{65}Cu_2N_8O_4S_2{}^{2+}$, respectively. IR (KBr; cm^{-1}): 1080, 840, 701, 559. Anal. Calcd for $C_{84}H_{88}Cu_2F_6N_8O_{14}S_4$: C, 58.02; H, 5.10; N, 6.44. Found: C, 57.50; H, 5.48; N, 6.22. See the X-ray experimental section for crystallographic data on **14b** and **15b**.

Reaction of 14b/15b with NH$_4$OH (16). To a CH_2Cl_2 (10 mL) solution of complexes **14b/15b** (20 mg) was added concentrated ammonium hydroxide (20 mL). The resulting bright-blue solution was stirred at room temperature for 20 min. Then the mixture was extracted with dichloromethane, and the organic phase was dried over $MgSO_4$. Preparative TLC (silica gel) using petroleum ether−ethyl acetate (8:1) as the eluant gave two compounds. One was identified as **10** on the basis of its TLC R_f. The other was a white solid, determined to be **16**. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 1.39(s, 9H), 2.30(s, br, 6H), 2.80(s, br, 3H), 3.41(s, 3H), 3.70(s, br, 3H), 6.43(apparent t, J = 8.1 Hz, 1H), 6.81(apparent t, J = 8.1 Hz, 2H), 6.98(apparent t, J = 8.1 Hz, 1H), 7.11−7.52(m, 15H). HRMS (ESI): *m*/*z* 657.3226 (M + 1); calcd for $C_{41}H_{45}N_4O_2S$, *m*/*z* 657.3263.

[(BIT^{OMe,S})$_2$Cu$_2$(OH)$_2$](PF$_6$)$_2$ (17). To **12** (40 mg, 0.048 mmol) and $[Cu(CH_3CN)_4]PF_6$ (19 mg, 0.048 mmol) was added dry CH_2Cl_2 (5 mL), and the resulting dark-yellow solution was stirred at room temperature for 1 h under Ar. Then the solution was stirred under an O_2 atmosphere (balloon) at −50 °C for 20 h to give a purple solution. Purple crystals of **17** were obtained by slow diffusion of ether into the solution at −20 °C (40%). LRMS (ESI): *m*/*z* 662.2, 663.2, and 664.2 (66.8, 100, and 26.4%) for $C_{74}H_{70}{}^{63}Cu_2N_8O_4S_2{}^{2+}$, $C_{74}H_{70}{}^{63}Cu^{65}CuN_8O_4S_2{}^{2+}$, and $C_{74}H_{70}{}^{65}Cu_2N_8O_4S_2{}^{2+}$, respectively. IR (KBr; cm^{-1}): 1082, 839, 701, 558. See the X-ray experimental section for crystallographic data on **17**.

[(BIT^{OMe,S})Cu$_2$(CNBu^t)$_2$]PF$_6$ (18). To **12** (83 mg, 0.10 mmol) and $[Cu(CH_3CN)_4]PF_6$ (38 mg, 0.10 mmol) was added dry CH_2Cl_2 (5 mL), and the resulting dark-yellow solution was stirred at room temperature for 5 min under Ar. *tert*-Butyl isocyanide (12 μL, 0.10 mmol) was added dropwise, and the resulting yellowish solution was stirred at room temperature for 1 h. After solvent evaporation, preparative TLC (silica gel) using ethyl acetate as the eluant gave 40 mg (50%) of **18** as a light-yellow solid. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 1.22(s, 18H), 1.26(s, 6H), 3.10(s, br, 3H), 3.26(s, 3H), 3.80(s, br, 3H), 7.26−7.48(m, 20H). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 147.29, 137.77, 137.08, 136.08, 135.72, 132.99, 132.39, 131.55, 130.06, 129.91, 129.61, 128.80, 128.59, 128.45, 88.89, 57.07, 56.22, 51.68, 30.28, 21.34. LRMS (ESI): *m*/*z* 875.3, 877.3, and 879.3 (100, 93.8, and 7.30%) for $C_{47}H_{53}{}^{63}$-

$Cu_2N_6OS^+$, $C_{47}H_{53}{}^{63}Cu^{65}CuN_6\text{-}OS^+$, and $C_{47}H_{53}{}^{65}Cu_2N_6OS^+$, respectively. IR (KBr; cm^{-1}): 3061, 2960, 2179, 1445, 1376, 1076, 842, 701, 558.

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Supporting Information Available: X-ray crystallographic data for **3a**, **4**, **5**, **6**, **14b**/**15b**, and **17**. This material is available free of charge via the Internet at http://pubs.acs.org.

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