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Copper(I) Complexes of Tripodal Tris(imidazolyl) Ligands: Potential Mimics of the Cu(A) Site of Hydroxylase Enzymes

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Copper(I) complexes of tripodal tris(*N*-methyl-4,5-diphenyl-imidazolyl)methane ligands, N_3CR (**1a**–**c**, R = OH, OMe, H), have been prepared as models for the Cu(A) site of copper hydroxylase enzymes. In the absence of additional donors, the ligands **1** react with $[Cu(CH_3CN)_4]PF_6$ (**2**) to produce dinuclear complexes $[(N_3CR)_2Cu_2](PF_6)_2$ (**3**) in which the tripodal ligands bridge two trigonal Cu centers; the structures of **3b** and **3c** are established by X-ray diffraction. Mononuclear adducts $[(N_3CR)CuL]Z$ are produced with L = acetonitrile (**4**), carbon monoxide (**5**), and *t*-BuNC (**6**, **7**). The carbonyl complexes **5** are in dynamic equilibrium with the dimeric complexes **3**, but **5c** (R = H) can be isolated. The structures of the isocyanide derivatives depend critically on the tripod methane substituent, R. Thus, the X-ray structures of **6** (R = OMe) and **7** (R = H) show trigonal and tetrahedral geometries, respectively, with bi- or tridentate coordination of the tripod. A trinuclear complex $[Cu_3(N_3COH)_2(t\text{-BuNC})_2](PF_6)_3$ (**8**) is formed from N_3COH (**1a**) which features both three-coordinate and two-coordinate Cu atoms and bidentate tripod coordination. Reactions of dioxygen with dinuclear **3c** or mononuclear $[(N_3CR)CuL]Z$ are sluggish, producing from the latter in acetone $[(N_3CH)Cu^{II}(L)(L')](PF_6)_2$ (**9**, L = acetone, L′ = H_2O).

Introduction

The copper hydroxylase enzymes, dopamine β-hydroxylase (DβM) and peptidylglycine α-hydroxylating monooxygenase (PHM), catalyze the regio- and enantioselective hydroxylation of mildly activated C−H bonds by O_2.[1] These enzymes appear to have very similar active-site structures, featuring two Cu centers separated by ca. 12 Å, with the Cu(A) site ligated by three histidine-derived imidazoles and the Cu(B) site by two histidines and a methionine residue.[2] Evidence derived from studies of the enzymes suggests that the N_3−Cu(A) site is an electron-transfer relay for the N_2S−Cu(B) site, at which dioxygen and the substrate associate and are transformed.[3] Although many synthetic model complexes for these and other poly(imid)−Cu enzymes have been prepared with a variety of polydentate saturated amine, pyridine, and pyrazolylborate-based ligands,[4] rather few have incorporated the biologically most relevant bis/tris(imidazole) donors,[5] which have significantly different donor/acceptor properties.[6]

We recently described rare bis(imidazole)thioether N_2S-ligands and derived Cu(I) complexes that share close structural, electronic, and reactivity features with the Cu(B)

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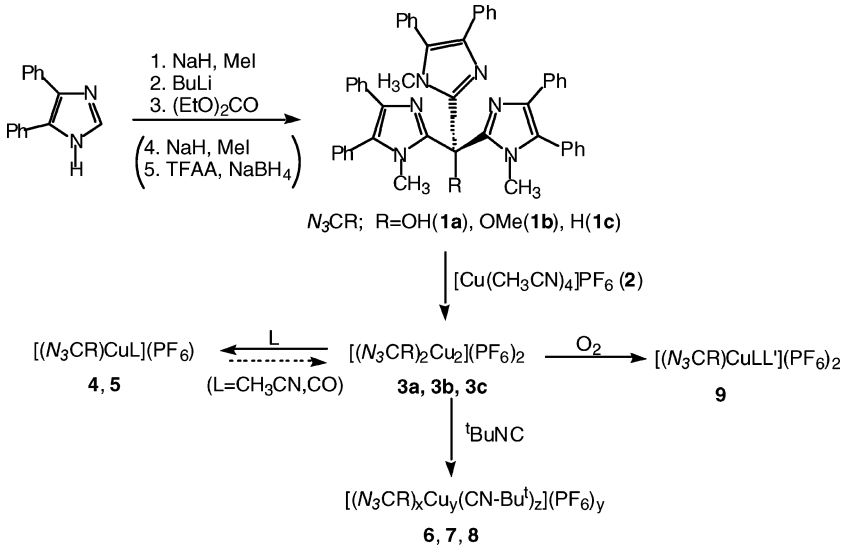
Scheme 1



site.[7] Regarding the Cu(A) site of the hydroxylases, few Cu^{I} or Cu^{II} complexes with polydentate imidazole ligands have been reported.[8] Sorrell and co-workers prepared copper(I) complexes from tris(*N*-methyl-2-imidazolyl)carbinol[5a] and substituted tris(2-imidazolyl)phosphines.[5d] From the former ligand either dinuclear $[(tripod)_2Cu_2]Z_2$ or monometallic [(tripod)CuL]Z complexes were produced, depending on the coordinating ability of L. Tris[2-(1,4-diisopropylimidazolyl)]-phosphine forms a cationic copper(I) complex that reacts with dioxygen at low temperature to produce a reactive peroxo-dicopper(II) adduct, but the corresponding complex of the *tert*-butyl-substituted ligand does not react with dioxygen, demonstrating that steric effects are important in defining $Cu^{I}-O_2$ interactions in these systems.[5d] We report here the preparation of new, sterically encumbered tripodal tris-(imidazole) ligands, characterization of the corresponding Cu(I) complexes, and their novel reactivity with isocyanides, CO, and O_2.

Results and Discussion

The tripodal tris(4,5-diphenyl-*N*-methylimidazolyl)-based ligands (**1**) were targeted since they offer a sterically hindered, hydrophobic Cu-binding pocket which could disfavor the formation of bridging, binuclear complexes. The hydroxy-substituted ligand **1a**[8b] provided a convenient source of the new -methoxy (**1b**) and -methine (**1c**) derivatives via O-alkylation or reductive substitution, respectively, as outlined in Scheme 1. Several reported methods for the reductive substitution of the hydroxyl group were ineffective[5c,9,10] for the conversion of **1a** to **1c**. However, treatment of **1a** with trifluoroacetic anhydride in CH_2Cl_2 produces an intense blue solution presumed to be the corresponding carbocation; addition of solid $NaBH_4$ gave methane derivative **1c** in good yield.

Ligands **1a**−**c** react with $[Cu(CH_3CN)_4]PF_6$ (**2**) in CH_2Cl_2 to form dinuclear complexes **3a**−**c** of composition $[(N_3CR)_2Cu_2](PF_6)_2$ on the basis of ESI-MS and NMR analysis. The ^1H NMR spectrum of **3b** shows two singlets (3H, 6H) for the *N*-methyl resonances, indicating two inequivalent *N*-methyl groups, whereas the spectrum of **3c** indicated that all methyl groups are equivalent on the NMR time scale at room temperature. Crystals of **3b** and **3c** were analyzed by X-ray diffraction, and the structure of the latter is shown in Figure 1. In both structures the two tripodal ligands bridge between nearly trigonal planar Cu(I) atoms (sum of N−Cu−N angles = 358.8° for **3b** and 358.4° for **3c**), each coordinated via three imidazole nitrogens, two from one tripod and one from the second. These structures are similar to that reported for the copper(I) complex of the non-arylated *N*-methylimidazolyl carbinol ligand.[5a] Both **3b** (in SI) and **3c** have

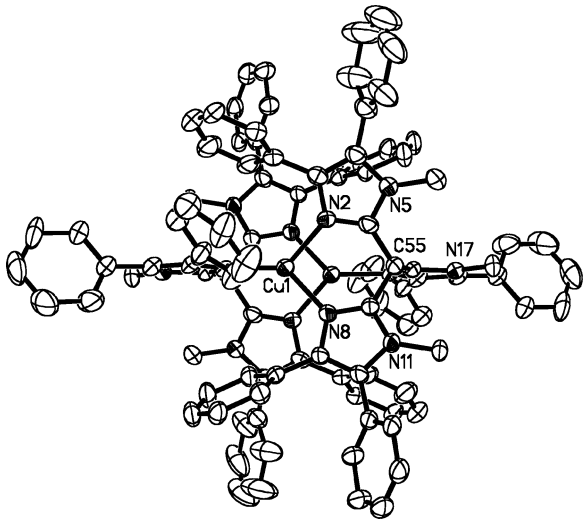


Figure 1. X-ray structure of the dication of **3c**. Selected bond lengths (Å) and angles (deg): Cu(1)−N(14) 1.950(3), Cu(1)−N(2) 2.008(3), Cu-(1)−N(8) 2.034(3); N(14)−Cu(1)-N(2) 132.56(14), N(14)−Cu(1)−N(8) 133.34(14), N(2)−Cu(1)−N(8) 92.50(14).

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inversion symmetry so that two *N*-methyl groups in each tripod are equivalent but inequivalent to the third one. The differing solution-state NMR behaviors of **3b** and **3c** suggest that the latter undergoes a dynamic process that averages the imidazole environments.

In the presence of suitable coordinating molecules, L, mononuclear [(N_3CR)CuL]Z complexes are produced, starting either from [Cu(CH_3CN)$_4$]Z (**2**), the tripodal ligands, and L or from the addition of L to the dimers **3**, indicative of an L- and tripod-dependent mono/dimer equilibrium. ^{1}H NMR and ESI mass spectra of solutions of **3c** in donor solvents, e.g., CH_3CN and acetone, indicated the presence of a new species [(N_3CR)Cu(solv)]PF_6 (**4**). Reactions between **2** and tripods **1a** and **1b** in CH_2Cl_2 under CO (1 atm) produced labile CO adducts detected by IR (**5a**, 2115 cm^{-1}; **5b**, 2100 cm^{-1}). Ether addition to these solutions precipitated only the dimers **3a** and **3b**, respectively. However, the adduct from **3c**, [(N_3CH)Cu(CO)]PF_6 (**5c**), was isolable as a solid and exhibited appropriate IR spectroscopic data (2092 cm^{-1}). Inspection of computer-generated models suggests that the apparently greater stability of the tripod complex **5c** (R = H) relative to the −OH and −OMe derivatives (**5a**, **5b**) may be the result of steric crowding between the *N*-Me groups and the larger methine substituents on the backside of the tripod caused by tridentate Cu coordination. It is noteworthy that the ν(CO) values of these complexes are ca. 40 cm^{-1} higher than those reported for some tris(His)Cu(CO) enzymes,[11] suggesting a less-electron-rich Cu in **5**. This difference may reflect a lower donicity of the 2-substituted imidazoles of **5** relative to 4-substituted His-imidazoles,[5c] a lower denticity of the tripod in [(N_3CR)Cu(CO)], coordination geometry differences, or medium/secondary sphere effects in the protein.

More stable mononuclear adducts [(N_3CR)CuL]PF_6 were formed with L = *t*-BuNC, the structures of which were remarkably dependent on the tripod substituent R. Thus, reaction of ligand **1b** (R = OMe) and **2** with 1 equiv of *t*-BuNC (CH_2Cl_2, at room temperature (rt)) produced a monometallic isocyanide derivative **6** (ν_{CN} 2189 cm^{-1}) on the basis of NMR and ES-MS analysis. Both the ^{1}H and ^{13}C NMR spectra of **6** at rt exhibit a single peak for the three *N*-methyl groups; this peak sharpened at 40 °C in the H NMR spectrum, suggesting a dynamically averaged, nearly symmetrical structure in solution. Surprisingly, the X-ray crystal structure of **6** (Figure 2) revealed the presence of a trigonal Cu(I) atom ligated by isocyanide and the tripod ligand in a bidentate mode with one imidazole group uncoordinated. The observed NMR spectra of **6** could be explained by a rapid associative/dissociative exchange of the imidazole groups in solution.

The ligand **1c** (R = H) reacted with Cu(I) and *t*-BuNC analogously to form a [(N_3CH)CuL]PF_6 derivative **7** (ν_{NC} 2186 cm^{-1}). The ^{1}H NMR spectrum of **7** shows a sharp singlet for the three *N*-methyl groups, indicating symmetric structure in solution. The X-ray structure (solid state) of **7**

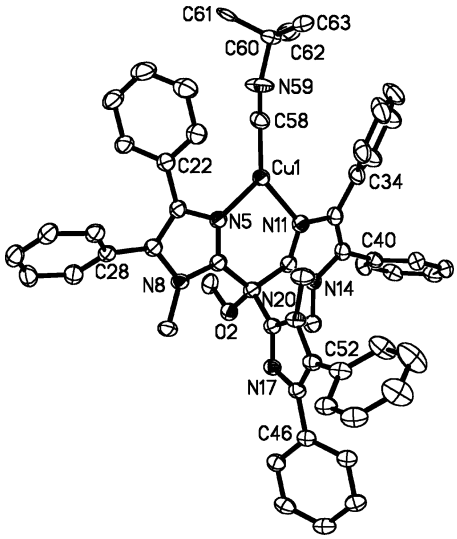

Figure 2. X-ray structure of the cation of **6.** Selected bond lengths (Å) and angles (deg): Cu(1)−C(58) 1.824(2), Cu(1)−N(5) 1.9739(17), Cu(1)−N(11) 1.9855(19), C(58)−Cu(1)−N(5) 134.91(9), C(58)−Cu(1)−N(11) 129.51(9), N(5)−Cu(1)−N(11) 93.65(7).

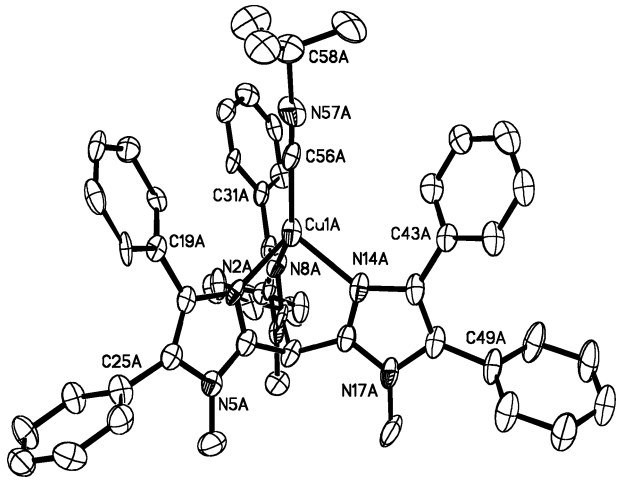

Figure 3. X-ray structure of the cation of **7**. Selected bond lengths (Å) and angles (deg): Cu(1A)−C(56A) 1.897(2), Cu(1A)−N(8A) 2.098(6), Cu(1A)−N(2A) 2.118(6), Cu(1A)−N(14A) 2.135(6), C(56A)−N(57A) 1.101(3); C(56A)−Cu(1A)−N(8A) 129.0(3), N(8A)−Cu(1A)−N(2A) 86.1(3), N(2A)−Cu(1A)−N(14A) 91.5(3).

(Figure 3) showed a four-coordinate pyramidal Cu(I) center bound to the isocyanide and all three imidazole units of the tripod ligand, consistent with the solution-state NMR spectrum. We suggest that the contrasting solid-state structures of **6** and **7** are the result of a delicate energetic balance between the stereoelectronic characteristics of the tripod's donor atom set, similar stabilities of the three- and four-coordinate copper(I) geometries, and steric crowding on the tripod backside between the methine substituent R and the imidazole *N*-methyl groups.

The reaction of **2** with tripod **1a** (R = OH) and 1 equiv of *t*-BuNC (CH_2Cl_2, rt) afforded yet a different type of complex **8**, again illustrating the subtle effects of the tripod capping group on the reaction product. The ES mass spectrum of **8** shows only a monomeric [Cu(tripod)(*t*-BuNC)]$^+$ peak, whereas its ^{1}H NMR spectrum shows a 1:1 tripod/*t*-BuNC ratio and a single somewhat broadened peak

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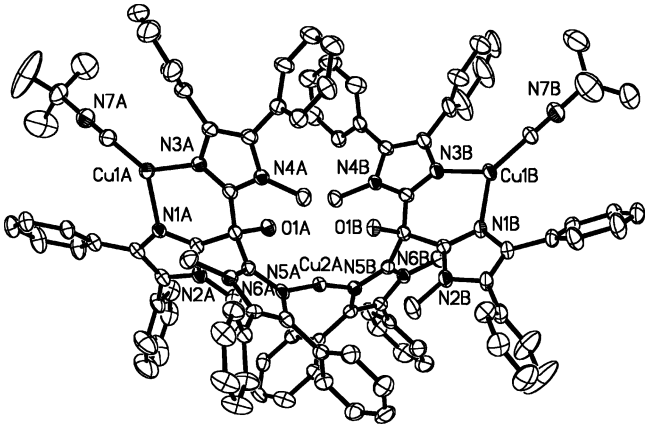

Figure 4. X-ray structure of the trication of **8**. Selected bond lengths (Å) and angles (deg): Cu(1A)−C(50A) 1.846(6), Cu(1A)−N(3A) 1.973(4), Cu(1A)−N(1A) 2.018(4), Cu(2A)−N(5B) 1.901(4), Cu(2A)−N(5A) 1.909(4), C(50A)−Cu(1A)−N(3A) 138.3(2), C(50A)−Cu(1A)−N(1A) 128.2(2), N(3A)−Cu(1A)−N(1A) 92.04(17), N(5B)−Cu(2A)−N(5A) 169.40(17).

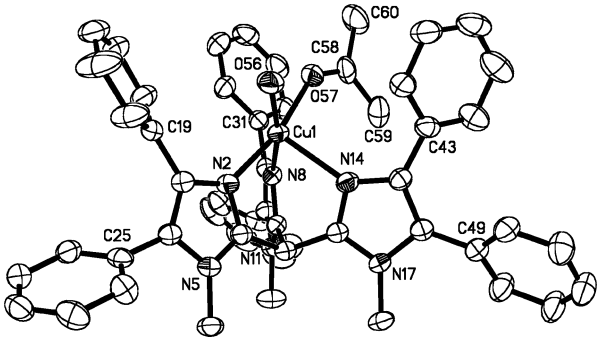

Figure 5. X-ray structure of the dication of **9**. Selected bond lengths (Å) and angles (deg): Cu(1)−O(56) 1.977(3), Cu(1)−O(57) 1.982(2), Cu(1)−N(8) 1.988(3), Cu(1)−N(2) 2.015(3), Cu(1)−N(14) 2.249(3), O(56)−Cu(1)−O(57) 84.93(11), O(57)−Cu(1)−N(8) 95.74(11), O(56)−Cu(1)−N(2) 89.71(11), N(8)−Cu(1)−N(2) 87.48(11).

for the three *N*-methyl groups. An X-ray structure determination of **8** revealed it to be more complex, containing three Cu(I) atoms, two tripod ligands, and two isocyanides, [(*t*-BuNC)$_2$Cu$_3$(*N*$_3$-COH)$_2$](PF$_6$)$_3$ (Figure 4). The structure consists of two flanking (tripod) Cu units, each having a trigonal, nearly planar Cu(I) atom bound to an isocyanide and to the tripod in a bidentate mode, with the third imidazole from each unit bridged to the central copper in a nearly linear geometry (N−Cu−N angle, 169°); secondary bonding interactions of the central copper with the tripod hydroxyl groups are suggested by the relatively short Cu−O distances (Cu−OH, 2.5−2.6 Å).

The dinuclear complexes **3b**,**c** are remarkably unreactive toward dioxygen, both largely unchanged after exposure to 1 atm of O_2 (CH_2Cl_2, rt) after 20 h, perhaps the result of a very stable trigonal Cu geometry reinforced by steric shielding of the Cu atoms by the polyaryl imidazole ligands. However, when an acetone solution of **2** and **1c** (R = H), which forms [(*N*$_3$CH)Cu(acetone)]PF$_6$, was stirred under 1 atm of O_2 at rt (24 h), it gradually turned greenish brown. Ether diffusion into the reaction solution induced crystallization of [(*N*$_3$CH)Cu^{II}(acetone)(H$_2$O)](PF$_6$)$_2$ (**9**), which was identified by X-ray diffraction (Figure 5). The five-coordinate structure of **9** is defined by the tridentate tripod, acetone, and water ligands, and the anion/Cu ratio indicates that the Cu has been oxidized by O_2. Whether the water ligand of **9** is derived from dioxygen reduction or from water present in the solvent has not been determined.

A number of factors may contribute to the relatively low dioxygen reactivity of the [(imidazolyl)$_3$CR]Cu$^+$ complexes. Their positive charge probably renders them less electron rich (and less oxidizable) than corresponding Cu(I) derivatives with anionic ligands, e.g., tris(pyrazolyl)borate,[4e] diketiminato,[4f] and those with more basic aliphatic polyamines.[5] The basis for the lower reactivity of the present poly(aryl−imidazole) complexes vis a vis Sorrell's cationic Cu[P(imid-*i*-Pr)$_3$]$^+$ complex is less apparent but could derive from a combination of steric inhibition by the aryl groups and a stereoelectronic effect from the more acute chelate bite angles of the (imid)$_3$CR vs the (imid)$_3$P ligands. It is noteworthy that dinuclear μ-oxo or hydroxo type complexes, e.g., [(*N*$_3$CR)Cu[μ-O(H)]$_2$Cu(*N*$_3$CR)]$^{2+}$, often derived from L$_n$Cu(I) reactions with dioxygen,[12,13] were not observed in the present system. Molecular models suggest that the formation of such species would be inhibited by the imidazole aryl substituents. It is also significant that no ligand oxygenation was observed, in contrast to findings in a number of other polyamine model complexes.[5f] Nonetheless, the cationic Cu-tris(imid) and bis(imid)(thioether)[7] coordination of the systems that we have investigated are the most accurate structural models presently available for the Cu(A) and Cu(B) sites of the hydroxylase enzymes. The lower reactivity toward dioxygen of the present N_3−Cu(I) complexes relative to the corresponding N_2S−tripod−Cu(I) complexes[7] is consistent with the relative reactivity of the Cu(A) and Cu(B) enzyme sites.[3]

In summary, the Cu complexes of tripodal tris(imidazolyl) ligands reported here provide rare examples of well-characterized tris(imidazole) Cu(I) and Cu(II) complexes of the type found in several metalloenzymes. The Cu(I) derivatives can form either mononuclear or polynuclear complexes, the latter with the tripod bridging, depending upon the presence (or absence) of suitable auxiliary ligands. Copper(I) derivatives of the tris(imidazolyl) ligands exhibit modest dioxygen reactivity in which the Cu center is oxidized without the formation of oxygen-bridged products or appreciable ligand oxidation. Efforts are underway to provide new, more accurate structural and functional mimics of the Cu hydroxylase enzymes and to explore their catalytic and redox activity.

Experimental Section

Materials and Methods. All operations were carried out under nitrogen or argon by means of standard Schlenk and vacuum-line techniques. Organic solvents were dried by standard procedures 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. IR spectra were recorded in either CH_2Cl_2 solution or KBr pellets with a Perkin-Elmer 283-B infrared

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Table 1. X-ray Crystal Data for Compounds **3c**, **6**, **7**, **8**, **9**

compound	**3c**	**6**	**7**	**8**	**9**
empirical formula	$C_{108}H_{104}Cl_4Cu_2F_{12}N_{12}O_2P_2$	$C_{63}H_{71}CuF_6N_7O_3P$	$C_{60}H_{64}CuF_6N_7O_{1.5}P$	$C_{118}H_{123}Cl_4Cu_3F_{18}N_{14}O_{4.5}P_3$	$C_{56}H_{58}CuF_{12}N_6O_3P_2$
fw	2160.85	1182.78	1115.69	2576.63	1216.56
crystal syst	triclinic	triclinic	monoclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$P2_1/n$
unit cell dimens					
a, Å	14.2688(18)	13.420(2)	15.141(5)	18.605(4)	15.328(4)
b, Å	14.3040(18)	15.024(2)	19.367(7)	23.695(6)	24.336(5)
c, Å	14.8469(19)	16.470(3)	40.820(15)	29.271(7)	15.890(4)
α, deg	65.390(2)	89.324(5)	90	73.480(8)	90
β, deg	65.275(2)	69.714(5)	92.987(15)	81.182(8)	100.667(8)
γ, deg	74.127(2)	68.746(5)	90	89.827(8)	90
V, Å^3	2484.3(5)	2878.1(8)	11954(7)	12214(5)	5825(2)
Z, *Z*′	1, 0.5	2, 1	8, 2	4, 2	4, 1
D, Mg/m^3	1.444	1.365	1.240	1.401	1.387
wavelength, Å	0.71073	0.71073	0.71073	0.71073	0.71073
T, K	100(2)	100(2)	100(2)	100(2)	100(2)
F(000)	1116	1240	4664	5308	2508
abs coeff, mm^{-1}	0.649	0.480	0.456	0.729	0.516
abs correction	semiemp from equiv	semiemp from equiv	semiemp from equiv	semiemp from equiv	semiemp from equiv
max, min trans	0.9321, 0.7860	0.9581, 0.8616	0.9820, 0.8211	0.9048, 0.7896	0.9648, 0.9038
θ range, deg	1.58−26.00	1.47−26.00	2.07−18.85	1.82−25.00	1.70−26.00
reflns collected	19 371	22 933	41 918	103 751	42 480
independ reflns	9635 [*R*(int) = 0.0282]	11 196 [*R*(int) = 0.0231]	9396 [*R*(int) = 0.0947]	41 983 [*R*(int) = 0.0314]	11 431 [*R*(int) = 0.0377]
data/restraints/param	9635/0/577	11196/138/680	9396/6238/1370	41983/4043/3351	11431/105/682
$R_w(F^2$ all data)	0.2652	0.1261	0.2648	0.2452	0.1917
R(*F* obsd data)	0.0823	0.0437	0.1005	0.0813	0.0612
GOF on F^2	1.046	1.035	1.047	1.024	1.005
obs data [$I > 2\sigma(I)$]	6717	8967	6594	33113	8257
largest, mean shift, s.u.	0.001, 0.000	0.001, 0.000	0.000, 0.000	0.010, 0.000	0.001, 0.000
largest diff peak, hole, e/Å^3	1.063, −1.336	0.830, −0.435	0.912, −0.595	1.823, −1.461	1.155, −0.841

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 ESI. Elemental analyses were performed by Midwest Microlab, LLC. 4,5-Diphenylimidazole,[14] *N*-methyl-4,5-diphenylimidazole,[15] and tris(1-methyl-4,5-diphenylimidazol-2-yl)methanol[8b] (**1a**) were prepared according to reported procedures.

Tris(1-methyl-4,5-diphenylimidazol-2-yl)methyl Methyl Ether (1b). Sodium hydride (48 mg, 60% mineral oil suspension, 1.2 mmol) was suspended in dry THF (10 mL) under N_2. Compound **1a** (0.73 g, 1.0 mmol) was dissolved in dry THF (10 mL) and 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 (H_2) appeared. Methyl iodide (75 μL, 1.2 mmol) was added dropwise, and then the reaction mixture was stirred for 20 h. Then the reaction was quenched with 80 mL of deionized water, the mixture was extracted twice with 50 mL portions of dichloromethane, and the organic phase was dried over $MgSO_4$. Rotary evaporation of the dichloromethane gave 0.53 g of **1b** as a light yellow solid (73%) (recrystallization from CH_2Cl_2/petroleum ether, mp 180−181 °C). ^{1}H NMR (300 MHz, CD_2Cl_2): *δ* 3.43 (s, 9H, NCH_3), 3.85 (s, 3H, OCH_3), 7.13−7.51 (m, 30H). ^{13}C NMR (75 MHz, CD_2Cl_2): *δ* 144.3, 135.5, 135.0, 131.5, 131.1, 129.0, 128.7, 128.0, 126.5, 126.1, 79.6, 54.9, 32.7. HRMS (ESI): *m*/*z* 743.3499 (M + 1); calcd for $C_{50}H_{43}N_6O$ 743.3516. IR (KBr, cm^{-1}): 3100, 2927, 1603, 1444, 1388, 1073, 777, 696.

Tris(1-methyl-4,5-diphenylimidazol-2-yl)methane (1c). To a colorless suspension of **1a** (0.218 g, 0.30 mmol) and $NaBH_4$ (114 mg, 3.0 mmol, 10 equiv) in CH_2Cl_2 (20 mL) was added trifluoroacetic anhydride (0.21 mL, 5 equiv) dropwise under Ar at 0 °C to form a dark blue solution immediately. The resulting mixture was stirred for 30 min, another portion of $NaBH_4$ (114 mg, 10 equiv) was added slowly to the blue solution, and the suspension was stirred for 1 h during which H_2 was given off and the solution became light green gradually. The mixture was quenched with water, extracted with CH_2Cl_2, and dried over $MgSO_4$. After evaporative removal of the CH_2Cl_2, a white solid was obtained. Recrystallization of the solid from CH_2Cl_2 and petroleum ether gave pure **1c** as a white solid (126 mg, 64.3%). ^{1}H NMR (300 MHz, CD_2Cl_2): *δ* 3.48 (s, 9H); 6.24 (s, 1H); 7.11−7.50 (m, 30H). ^{13}C NMR (75 MHz, CD_2Cl_2): *δ* 143.7, 136.9, 135.5, 131.6, 131.2, 129.5, 129.2, 128.5, 127.1, 126.6, 32.4, 30.3. HRMS (ESI): *m*/*z* 713.3392 (M + 1); calcd for $C_{49}H_{41}N_6$ 713.3393. IR (KBr, cm^{-1}): 3058, 2927, 1603, 1508, 1445, 1392, 1072, 1025, 966, 775, 696.

[(N_3COH)Cu]$_2$(PF_6)$_2$ (3a). To **1a** (72 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 argon. After removal of CH_2Cl_2, a white solid was obtained that was recrystallized from CH_2Cl_2 and diethyl ether to give 20 mg of **3a** as a white solid (20%). ^{1}H NMR (400 MHz, CD_2Cl_2): *δ* 3.22 (s, 9H), 5.89 (s, 1H), 7.21−7.48 (m, 30H). ^{13}C NMR (100 MHz, CD_2Cl_2): *δ* 132.8, 131.5, 130.4, 130.1, 129.9, 129.5, 129.3, 128.5, 69.7, 33.9. LRMS (ESI): *m*/*z* 791.2, 792.2 (100%, 26%) for $C_{98}H_{80}{}^{63}Cu_2N_{12}O_2{}^{2+}$ and $C_{98}H_{80}{}^{63}Cu^{65}CuN_{12}O_{22}{}^{+}$, respectively. IR (KBr, cm^{-1}): 3110, 2927, 1487, 1446, 842, 776, 699, 558.

[(N_3COMe)Cu]$_2$(PF_6)$_2$ (3b). To **1b** (0.074 g, 0.10 mmol) and [Cu(CH_3CN)$_4$]PF_6 (0.038 g, 0.10 mmol) was added dry CH_2Cl_2 (8 mL), and the resulting light yellow solution was stirred at room temperature for 2 h under argon. After removal of CH_2Cl_2, a white solid was give and then recrystallized from DMF and diethyl ether to give 50 mg of **3b** as colorless crystals (50%). ^{1}H NMR (300

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MHz, CD_2Cl_2): δ 3.33 (s, 3H), 3.79 (s, 6H), 4.23 (s, 3H), 6.31−7.48 (m, 30H). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 142.8, 139.0, 137.1, 134.5, 132.5, 131.2, 131.0, 130.9, 130.1, 129.8, 129.6, 129.1, 128.9, 128.0, 127.8, 127.4, 127.3, 127.1, 126.8, 110.0, 80.7, 36.8, 34.5. LRMS (ESI): *m*/*z* 805.3, 807.3 (54%, 27%) for $C_{100}H_{84}{}^{63}Cu_2N_{12}O_2{}^{2+}$ and $C_{100}H_{84}{}^{65}Cu_2N_{12}O_2{}^{2+}$, respectively. IR (KBr, cm^{-1}): 3110, 2927, 1478, 1444, 1075, 840, 700, 558. See Supporting Information for crystallographic data on **3b**.

[(N_3CH)Cu]$_2$(PF_6)$_2$ (3c). To **1c** (71 mg, 0.10 mmol) and [Cu(CH_3CN)$_4$]PF_6 (38 mg, 0.10 mmol, 1:1 equiv) was added dry CH_2Cl_2 (8 mL), and the resulting light yellow solution was stirred at room temperature for 2 h under argon. After removal of CH_2Cl_2, a white solid was obtained and then was recrystallized from CH_2Cl_2 and diethyl ether to give 40 mg of **3c** as colorless crystals (40%). ^1H NMR (300 MHz, CD_2Cl_2): δ 4.03 (s, 9H), 6.40−7.38 (m, 31H). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 140.7, 138.5, 132.1, 130.9, 130.3, 130.0, 129.2, 129.0, 128.8, 128.6, 128.0, 127.0, 33.3, 32.7. LRMS (ESI): *m*/*z* 775.2, 777.3 (65%, 26%) for $C_{98}H_{80}{}^{63}Cu_2N_{12}{}^{2+}$ and $C_{98}H_{80}{}^{65}Cu_2N_{12}{}^{2+}$, respectively. IR (KBr, cm^{-1}): 3110, 2927, 1487, 1446, 841, 790, 699, 558. See Supporting Information for crystallographic data on **3c**.

Formation of [(N_3CH)Cu(CH_3CN)]PF_6 (4c) from Dimer 3c. Dimer **3c** (5 mg) was dissolved in 1 mL of CD_3CN. The ^1H NMR spectrum of the resulting solution showed disappearance of the dimer and the formation of a new species assigned to [(N_3CH)Cu(CH_3CN)]PF_6. ^1H NMR (300 MHz, CD_3CN): δ 3.71 (s, 9H), 6.00 (s, 1H), 7.26−7.53 (m, 30H). LRMS (ESI in CH_3CN): *m*/*z* 816.3, 818.3 (100%, 30%) for $C_{51}H_{43}{}^{63}CuN_7{}^+$ and $C_{51}H_{43}{}^{65}CuN_7{}^+$, respectively.

[(N_3COMe)CuCNBu^t]PF_6 (6). To ligand **1b** (74 mg, 0.10 mmol) and [Cu(CH_3CN)$_4$]PF_6 (38 mg, 0.10 mmol) was added dry CH_2Cl_2 (5 mL). The resulting light yellow solution was stirred at room temperature for 2 h under argon. *tert*-Butyl isocyanide (11 μL, 0.10 mmol) was added dropwise, and the resulting yellow solution was stirred at room temperature for 2 h. Colorless crystals were obtained overnight by slow diffusion of ether vapor into the reaction solution (85%). ^1H NMR (300 MHz, CD_2Cl_2): δ 1.06 (s, 9H), 3.44 (s, 4H), 3.58 (br s, 8H), 7.20−7.50 (m, 30H). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 131.4, 130.2, 129.7, 128.7, 66.2, 30.1, 15.7. LRMS (ESI): *m*/*z* 888.3, 890.3 (100%, 32%) for $C_{55}H_{51}{}^{63}CuN_7O^+$ and $C_{55}H_{51}{}^{65}CuN_7O^+$, respectively. IR (KBr, cm^{-1}): 3059, 2927, 2186, 1446, 837, 700, 557. See Supporting Information for crystallographic data on **6.**

[(N_3CH)CuCNBu^t]PF_6 (7). To compound **1c** (15 mg, 21 μmol) and [Cu(CH_3CN)$_4$]PF_6 (8 mg, 21 μmol) was added dry CH_2Cl_2 (5 mL). The resulting light yellow solution was stirred at room temperature for 1 h under argon. *tert*-Butyl isocyanide (2.5 μL, 21 mmol) was added dropwise, and the resulting yellow solution was stirred at room temperature for 2 h. Colorless needles were obtained overnight by slow diffusion of ether vapor into the reaction solution (45%). ^1H NMR (300 MHz, CD_2Cl_2): δ 1.53 (s, 9H), 3.81 (s, 9H), 6.16 (s, 1H), 7.24−7.52 (m, 30H). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 143.4, 133.3, 131.5, 130.8, 129.8, 129.5, 128.5, 127.8, 32.5, 30.4. LRMS (ESI): *m*/*z* 858.2, 860.2 (100%, 29%) for $C_{54}H_{49}{}^{63}CuN_7{}^+$ and $C_{54}H_{49}{}^{65}CuN_7{}^+$, respectively. IR (KBr, cm^{-1}): 3059, 2927, 2178, 1509, 842, 697, 558. See Supporting Information for crystallographic data on **7**.

[(N_3COH)CuCNBu^t]PF_6 (8). To compound **1a** (146 mg, 0.20 mmol) and [Cu(CH_3CN)$_4$]PF_6 (80.0 mg, 0.20 mmol) was added dry CH_2Cl_2 (5 mL). The resulting light yellow solution was stirred at room temperature for 2 h under argon. *tert*-Butyl isocyanide (22 μL, 0.20 mmol) was added dropwise, and the resulting yellow solution was stirred at room temperature for 2 h. Colorless crystals were obtained overnight by slow diffusion of ether into the reaction solution (50%). ^1H NMR (300 MHz, CD_2Cl_2): δ 1.02 (s, 9H), 3.21 (br s, 9H), 6.00 (s, 1H), 7.22−7.48 (m, 30H). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 138.3, 134.1, 132.4, 131.0, 130.9, 130.0, 129.9, 129.6, 129.1, 128.9, 128.7, 128.2, 128.0, 69.2, 33.5, 29.5. LRMS (ESI) *m*/*z* 874.3, 876.3 (100%, 27%) for $C_{54}H_{49}{}^{63}CuN_7O^+$ and $C_{54}H_{49}{}^{65}CuN_7O^+$, respectively. IR (KBr, cm^{-1}): 3110, 2927, 2189, 1446, 840, 700, 558. See Supporting Information for crystallographic data on **8**.

Reaction of [(N_3COH)Cu]$_2$(PF_6)$_2$ with CO. To solid **1a** (72 mg, 0.10 mmol) and [Cu(CH_3CN)$_4$]PF_6 (38 mg, 0.10 mmol) was added dry CH_2Cl_2 (5 mL). The resulting light yellow solution was stirred at room temperature for 1 h under argon. Carbon monoxide was then bubbled into the solution at room temperature for 2 h. An IR spectrum of the reaction solution showed a strong absorption (ν_{CO}) at 2115 cm^{-1} (**5a**). A white solid precipitated overnight by diffusion of ether vapor into the reaction solution and was found to be dimer **3a** from its ^1H NMR spectrum in CD_2Cl_2.

Reaction of [(N_3COMe)Cu]$_2$(PF_6)$_2$ with CO (5b). To solid **1b** (74 mg, 0.10 mmol) and [Cu(CH_3CN)$_4$]PF_6 (38 mg, 0.10 mmol) was added dry CH_2Cl_2 (5 mL). The resulting light yellow solution was stirred at room temperature for 1 h under argon. Carbon monoxide was bubbled into the solution at room temperature for 2 h. An IR spectrum of the reaction solution showed a strong absorption (ν_{CO}) at 2100 cm^{-1} (**5b**). Colorless crystals, found to be dimer **3b**, were obtained overnight by slow diffusion of ether vapor into the reaction solution.

[(N_3CH)CuCO]PF_6 (5c). To compound **1c** (30 mg, 42 μmol) and [Cu(CH_3CN)$_4$]PF_6 (16 mg, 42 μmol) was added dry CH_2Cl_2 (5 mL). The resulting light yellow solution was stirred at room temperature for 1 h under argon. Carbon monoxide was bubbled into the solution at room temperature for 2 h. Colorless needles were obtained overnight by slow diffusion of ether vapor into the reaction solution (50%). ^1H NMR (300 MHz, CD_2Cl_2): δ 3.85 (s, 9H), 6.27 (s, 1H), 7.29−7.48 (m, 30H). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 142.9, 138.3, 132.9, 131.4, 130.1, 129.7, 128.9, 128.6, 32.8, 31.7. LRMS (ESI): *m*/*z* 803.3, 805.3 (100%, 31%) for $C_{50}H_{40}{}^{63}CuN_6O^+$ and $C_{50}H_{40}{}^{65}CuN_6O^+$, respectively. IR (KBr, cm^{-1}): 3059, 2927, 2087, 1509, 840, 699, 558.

[(N_3CH)Cu^{II}(CH_3COCH_3)(H_2O)](PF_6)$_2$ (9). To compound **1c** (71.2 mg, 0.10 mmol) and [Cu(CH_3CN)$_4$]PF_6 (38 mg, 0.10 mmol) was added acetone (5 mL), and the resulting light greenish solution was stirred at room temperature for 0.5 h under argon. Then the solution was stirred under an O_2 atmosphere (balloon) at room temperature for 24 h to give a cloudy greenish solution. A white solid separated from the solution, which proved to be dimer **3c** (50%). Yellow crystals of **9** were obtained by slow diffusion of ether into the green solution (10%). LRMS(ESI): *m*/*z* 416.7, 417.6 (2.5%, 1.4%) for $C_{52}H_{46}{}^{63}CuN_6O^{2+}$ and $C_{52}H_{46}{}^{65}CuN_6O^{2+}$, respectively. IR (KBr, cm^{-1}): 3059, 2927, 1654, 1511, 1446, 1026, 841, 793, 700, 558. See Supporting Information for crystallographic data on **9**.

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Supporting Information Available: X-ray diffraction data and tables for **3b**, **3c**, **6**, **7**, **8**, and **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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