ligands, no hydroxylation of the arene occurs.

Studies on *m*-xylyl-bridged Schiff-base ligands also suggest that ligand basicity has little effect on the oxidation reaction (Scheme II),[9,15] since hydroxylation occurs despite changes in the nature of the heterocycle. Perhaps in those systems the geometry is optimal for correct orientation of the bound peroxo group and the arene ring. On the other hand, H^+ must be added in certain cases in order for hydroxylation to predominate over reduction of O_2 to water, so electronic effects undoubtedly play a role there, too.

Another factor that may influence the formation of a reactive peroxo adduct in complexes **8-14** is the potential of the Cu(I)/Cu(II) couple. From cyclic voltammetry studies, we find that $E_{1/2}$ for **10** is *between* that measured for **8** and **12**, which is incongruous with a simple correlation between ligand basicity and $E_{1/2}$. On the basis of the reactivity, we expected that $E_{1/2}$ for complex **10** might be at one end of the range of $E_{1/2}$ values. However, we do note that the conditions of the electrochemical measurements (CH_3CN) and the quasireversible nature of the scans may not reflect the true redox properties of the complexes in their reaction with dioxygen.

In contrast to the differences in dioxygen reactivity of the Cu(I) complexes, the Cu(II) species seem to react with H_2O_2 to hydroxylate the arene ring. Although a *solid* copper(II) complex could only be isolated for ligands **2** and **3**,[17] solutions of Cu(II) ions and the other ligands appear to react analogously with H_2O_2, as judged by absorption spectra. The difference in overall behavior of the Cu(I) vs the Cu(II) complexes is not surprising when one considers that their reactions occur via two different mechanisms. Through kinetic studies, Karlin has shown that the reaction of **10** with O_2 proceeds through a copper(II) peroxo adduct, but $Cu_2(L)^{4+}$ (L = **3**) reacts with hydrogen peroxide to give a hydroperoxide intermediate formed via association of two dimers.[17] Apparently the geometric and electronic effects are less important in the Cu(II) adducts than they are in the copper peroxo species formed from the analogous copper(I) complexes.

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Synthesis and Reactivity of Imidazolyl- and Benzimidazolyl-Containing Copper Complexes

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New polydentate ligands having (2-imidazolylethyl)amino and (2-benzimidazolylethyl)amino groups have been prepared via the imidate esters derived from *N*-(2-cyanoethyl)benzamides. These chelating ligands form stable copper(I) complexes that react with dioxygen at low temperature to give adducts presumed to be dinuclear peroxo complexes on the basis of the similarity of their electronic spectra with those for analogous pyridine-ligated species. A Schiff-base ligand derived from isophthalaldehyde and (aminoethyl)imidazole is hydroxylated when its copper(I) derivative is treated with dioxygen.

Hemocyanin is a copper protein responsible for transport of molecular oxygen in the hemolymph of many species of molluscs and arthropods. A crystal structure of deoxyhemocyanin[2] and extensive spectroscopic studies on the oxidized form of the protein[3] have contributed much to our knowledge about the *structure* of hemocyanin's dinuclear active site. Understanding how the active site reacts reversibly with O_2 has been a more difficult challenge and has relied on studies of inorganic model compounds that react with dioxygen.[4]

The active site of hemocyanin comprises a dinuclear unit in which each copper ion is ligated by three imidazole groups provided by histidine. One of the imidazole ligands is farther from the copper ions than the other two.[2] Since imidazole groups are relatively difficult to incorporate into synthetic ligands, many researchers have used nitrogen donors other than imidazole in designing copper chelates. Pyridine, pyrazole, and benzimidazole have been investigated extensively as donors in copper complexes, and both mononucleating and dinucleating ligands have been prepared.[5]

Karlin has developed a wealth of chemistry based on pyridyl-ligated copper compounds,[4] and he has been able to generate several dioxygen adducts with bis[2-(2'-pyridyl)ethyl]amine complexes. Although the peroxide complexes do not exhibit all of the spectroscopic properties of hemocyanin, those species constitute the best characterized systems that reversibly bind dioxygen.

The pyrazole derivatives of Karlin's ligands have markedly different reactivity toward oxygen, and many such complexes are inert to dioxygen in methylene chloride.[6] Because of its size, pyrazole is probably a better *structural* analogue for imidazole than is pyridine. However, pyrazole is significantly less basic than histidine, whereas pyridine has approximately the same basicity; so pyridine is possibly a better mimic for the *electronic* features of imidazole. It is noteworthy that incorporation of pyrazole into tris(pyrazolyl)borate ligands affects the electronic features significantly; and Thompson and Kitajima have used those ligands to prepare isolable copper(II) superoxide and peroxide complexes, respectively.[7,8]

The variation observed in the reactivity of copper complexes toward O_2 with respect to the heterocycle prompted us to prepare imidazole-containing ligands. Since imidazole is presumed to be the best model for histidine, we felt that studying the reactivity of the imidazole derivative would be a valuable complement to the work previously reported for the pyridyl and pyrazolyl complexes. The purpose of this work was to develop a general synthetic

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route toward tridentate ligands containing an amino group and two imidazole or benzimidazole groups as heterocyclic nitrogen donors. We report here the synthesis and reactivity of copper(I) complexes of several ligands containing bis[2-(2′-imidazolyl)-ethyl]amine, 2-(2′-imidazolyl)ethylamine, or the corresponding benzimidazole units.

Experimental Section

All reagents and solvents were purchased from commercial sources and used as received unless otherwise noted. The following solvents were distilled and stored under nitrogen: methanol, from $Mg(OMe)_2$; tetrahydrofuran (THF), from sodium benzophenone ketyl; acetonitrile, from CaH_2; methylene chloride, from CaH_2. Hydrogen chloride was dried by bubbling through concentrated H_2SO_4. Dioxygen was purified by passage through a column of calcium sulfate. All manipulations involving copper(I) complexes were performed in a Vacuum Atmosphere glovebox with less than 1 ppm of oxygen and water. Melting points were obtained with use of a Fisher-Johns apparatus and are uncorrected. Flash chromatography was performed by using the procedure of Still.[9] Thin-layer chromatography was performed by using Analtech precoated (0.25 mm) silica gel plates. Elemental analyses were determined by Desert Analytics, Tucson, AZ, or Atlantic Microlab, Norcross, GA. ^1H NMR and ^{13}C NMR spectra were recorded on an IBM AC 200 instrument at 200.132 MHz or on a Bruker WM 250 instrument at 250.13 MHz. Chemical shifts are reported in δ (parts per million) relative to an internal standard of tetramethylsilane. Infrared spectra were recorded on a Beckman IR 4250 spectrophotometer, and peaks are reported in cm^{-1}. Low-temperature absorption spectra were recorded on a Hewlett-Packard 8450A diode-array spectrometer or a Perkin-Elmer Model 552 double-beam scanning spectrometer as described previously.[10]

***N,N*-Bis(2-cyanoethyl)benzamide (1).** A magnetically stirred solution of 3,3′-iminodipropionitrile (25.0 g, 0.203 mol) in pyridine (120 mL) was cooled to 0 °C and treated dropwise with benzoyl chloride (28.5 g, 0.203 mol). When the addition was complete, the reaction mixture was allowed to stir at 25 °C for 1 h. Water was added to precipitate the product, which was collected by suction filtration, washed with water, and recrystallized from aqueous ethanol to give 38.2 g of white needles (83%), mp 106–108 °C. ^1H NMR (DMSO-d_6): δ 2.68 (br m, 4 H, CH_2–CN), 3.66 (br m, 4 H, OC–N–CH_2), 7.31–7.40 (m, 5 H, Ar H). ^{13}C NMR (DMSO-d_6/$CDCl_3$): δ 15.46 (br, t), 44.5 (br, t), 116.79 (s), 125.54 (d), 127.65 (d), 128.92 (d), 134.09 (s), 171.05 (s). IR (KBr): 1630 (C=O), 2235 (–CN).

***N,N*-Bis[2-(2′-imidazolyl)ethyl]benzamide (2a).** Anhydrous methanol (150 mL) was cooled to 0 °C and saturated with anhydrous hydrogen chloride. Solid compound **1** (20.0 g, 88.1 mmol) was added in small portions. When the amide had dissolved completely, the flask was sealed with a septum and stirred an additional 0.5 h at 0 °C. The solvent was evaporated under high vacuum while the water bath was maintained at 30 °C. The white foamy solid was dissolved in anhydrous methanol, and the mixture was cooled to 0 °C and treated with sodium methoxide in methanol (prepared by dissolving 4.0 g of sodium in 200 mL of methanol). Aminoacetaldehyde dimethyl acetal (18.5 g, 176.2 mmol) was added dropwise to this solution, and the mixture was allowed to stir at room temperature for 12–48 h until there was no imidate detectable by TLC (R_f = 0.75, methanol). The solvent was evaporated, and the residue was allowed to reflux vigorously in 6 N hydrochloric acid for 15 min. The solution was cooled, made basic with 10 N sodium hydroxide, and extracted thoroughly with chloroform. The combined extracts were dried over Na_2SO_4 and concentrated to a red oil, which was purified by flash chromatography with methanol as the eluent. The product (26.1 g, 96%) was isolated as pale yellow, hygroscopic crystals, mp 65–68 °C (R_f = 0.75, MeOH). ^1H NMR ($CDCl_3$): δ 2.44 (br m, 2 H, Im–CH_2–), 2.82 (br m, 2 H, Im–CH_2–), 3.50 (br m, 2 H, O=C–N–CH_2–), 3.75 (br m, 2 H, O=C–N–CH_2–), 6.79 (br s, 4 H, imidazolyl C–H), 7.00 (d, J = 2.5 Hz, 2 H, Ar H), 7.20–7.31 (m, 3 H, Ar H), 9.66 (br s, 2 H, N–H). ^{13}C NMR ($CDCl_3$): δ 27.36 (br t), 46.0 (br t), 49.3 (br t), 119.9 (br d), 121.7 (br d), 126.09 (d), 128.57 (d), 129.67 (d), 135.85 (s), 144.8 (br s), 173.00 (s). IR (KBr): 1615 (C=O).

***N,N*-Bis[2-(1′-methyl-2′-imidazolyl)ethyl]benzamide (2b).** This compound was prepared by the same procedure described for compound **2a**. Thus, the crude imidate made from benzamide **1** (20.0 g, 88.2 mmol) was treated with 2-((methylamino)methyl)-1,3-dioxolane (21.0 g, 179 mmol) to afford 19.4 g (66%) of the product as a viscous oil (R_f = 0.50, MeOH). ^1H NMR ($CDCl_3$): δ 2.80 (t, J = 7.0 Hz, 2 H, Im–CH_2), 3.15 (t, J = 7.0 Hz, 2 H, Im–CH_2), 3.26 (s, 6 H, imidazolyl N–Me), 3.64 (t, J = 7.0 Hz, 2 H, O=C–NCH_2), 3.89 (t, J = 7.0 Hz, 2 H, O=C–NCH_2), 6.72 (s, 1 H, imidazolyl C–H), 6.82 (s, 1 H, imidazolyl C–H), 6.86 (s, 1 H, imidazolyl C–H), 6.94 (s, 1 H, imidazolyl C–H), 7.1–7.2 (m, 2 H, Ar H), 7.3–7.4 (m, 3 H, Ar H). ^{13}C NMR ($CDCl_3$): δ 24.91 (t), 26.14 (t), 32.21 (q), 32.67 (q), 44.18 (t), 47.98 (t), 120.75 (d), 126.30 (d), 127.27 (d), 128.43 (d), 129.41 (d), 136.28 (s), 145.62 (s), 171.98 (s).

***N,N*-Bis[2-(1′-benzyl-2′-imidazolyl)ethyl]benzamide (2c).** A solution of compound **3a** (3.8 g, 12.3 mmol) in 100 mL of *N,N*-dimethylformamide (DMF) was added dropwise to a slurry of sodium hydride (0.6 g, 25 mmol) in DMF (30 mL). After gas evolution ceased, benzyl bromide (3 mL, 25 mmol) was added; the mixture was stirred at 25 °C for 1 day. Water (10 mL) was added, and the solvent was evaporated at reduced pressure. The residue was treated with water (20 mL) and extracted with chloroform. The combined extracts were dried over Na_2SO_4 and concentrated to a brown oil, which was purified by flash chromatography with chloroform–methanol (2:1) as the eluent (R_f = 0.97) to afford 3.4 g (57%) of a dark oil. ^1H NMR ($CDCl_3$): δ 2.78 (br t, 2 H, N–CH_2), 3.10 (br t, 2 H, N–CH_2), 3.65 (br t, 2 H, Im–CH_2), 3.80 (br t, 2 H, Im–CH_2), 4.70 (s, 2 H, Ph–CH_2), 5.20 (s, 2 H, Ph–CH_2), 6.8–7.2 (m, 19 H, Ar H and imidazolyl H).

***N,N*-Bis[2-(2′-imidazolyl)ethyl]amine (3a).** Benzamide **2a** (5.0 g, 16.2 mmol) was allowed to reflux in 6 N HCl for 8 h. The resultant mixture was washed with chloroform and then evaporated to dryness at reduced pressure. The residual solid was recrystallized from ethanol to afford 3.0 g (67%) of a light tan powder, mp 200–202 °C. ^1H NMR (DMSO-d_6): δ 3.51 (s, 8 H, CH_2CH_2), 6.59 (s, 4 H, imidazolyl C–H), 10.5 (br s, N–H). ^{13}C NMR (DMSO-d_6): 22.06 (t), 43.05 (t), 118.95 (d), 142.74 (d).

The free amine was isolated by treating a methanolic solution of the hydrochloride salt with anhydrous sodium bicarbonate until the mixture was basic. The sodium chloride was removed by filtration, and the filtrate was concentrated until a light tan powder precipitated, mp 189–190 °C. ^1H NMR ($CDCl_3$): δ 2.89 (t, J = 5.4 Hz, 4 H, N–CH_2), 2.97 (t, J = 5.4 Hz, 4 H, Im–CH_2), 6.93 (s, 4 H, imidazolyl C–H), 7.10 (br s, 3 H, N–H). ^{13}C NMR (DMSO-d_6): δ 24.11 (t), 44.87 (t), 120.36 (d), 143.78 (s).

***N,N*-Bis[2-(1′-methyl-2′-imidazolyl)ethyl]amine (3b).** Benzamide **2b** (2.5 g, 1.4 mmol) was treated as described for **3a** to afford 1.3 g (77%) of a pale yellow oil (R_f = 0.17, methanol). ^1H NMR ($CDCl_3$): δ 2.62 (t, J = 5.2 Hz, 4 H, N–CH_2), 2.98 (t, J = 5.2 Hz, 4 H, Im–CH_2), 3.48 (br s, 1 H, N–H), 3.50 (s, 6 H, imidazolyl N–Me), 6.71 (d, J = 1.2 Hz, 2 H, imidazolyl C–H), 6.81 (d, J = 1.2 Hz, 2 H, imidazolyl C–H). ^{13}C NMR ($CDCl_3$): δ 26.87 (t), 32.21 (q), 46.97 (t), 120.12 (d), 126.67 (d), 146.34 (s).

***N,N*-Bis[2-(1′-benzyl-2′-imidazolyl)ethyl]amine (3c).** This compound was prepared by the same procedure described for compound **3a**. Hydrolysis of amide **2c** (3.4 g, 6.9 mmol) afforded 1.0 g (37%) of the desired product as a pale yellow oil (R_f = 0.45, methanol). ^1H NMR ($CDCl_3$): δ 2.58 (br s, 1 H, N–H), 2.72 (t, J = 6.7 Hz, 4 H, N–CH_2), 2.95 (t, J = 6.7 Hz, 4 H, Im–CH_2), 5.01 (s, 4 H, ArCH_2), 6.79 (s, 2 H, imidazolyl C–H), 6.94 (s, 2 H, imidazolyl C–H), 6.97–7.01 (m, 4 H, Ar H), 7.19–7.32 (m, 6 H, Ar H). ^{13}C NMR ($CDCl_3$): δ 27.19 (t), 47.18 (t), 49.22 (t), 119.75 (d), 126.47 (d), 127.33 (d), 127.71 (d), 128.72 (d), 136.31 (s), 146.60 (s).

***N,N*-Bis[2-(1′-methyl-2′-imidazolyl)ethyl]-*N*-benzylamine (4b).** Benzyl bromide (0.800 g, 4.6 mmol) was added dropwise to a mixture of compound **3b** (1.0 g, 4.29 mmol), sodium iodide (250 mg), and potassium carbonate (1.0 g) in refluxing 2-propanol (100 mL). After 1.5 h, the solvent was evaporated at reduced pressure. The residue was made acidic with 10% HCl and washed with ether (200 mL). The aqueous layer was made basic with 10 N NaOH and extracted with three, 150-mL portions of chloroform. The extracts were dried over Na_2SO_4, concentrated, and purified by flash chromatography with methanol as the eluent (R_f = 0.60) to yield 0.85 g (61%) of a pale yellow oil. ^1H NMR ($CDCl_3$): δ 2.82 (t, J = 6.2 Hz, 4 H, N–CH_2), 2.96 (t, J = 6.2 Hz, 4 H, Im–CH_2), 3.46 (s, 6 H, Im–CH_3), 3.70 (s, 2 H, Ar–CH_2), 6.76 (d, J = 1.2 Hz, 2 H, imidazolyl C–H), 6.90 (d, J = 1.2 Hz, 2 H, imidazolyl C–H), 7.24 (s, 5 H, Ar H). ^{13}C NMR ($CDCl_3$): δ 24.99 (t), 32.5 (q), 51.93 (t), 58.86 (t), 120.37 (d), 126.60 (d), 126.89 (d), 128.14 (d), 128.56 (d), 139.32 (s), 146.56 (s).

***N,N*-Bis[2-(1′-benzyl-2′-imidazolyl)ethyl]-*N*-benzylamine (4c).** Compound **3a** (2.4 g, 8.6 mmol) was added in small portions to a slurry of sodium hydride (1.0 g, 42 mmol) in DMF (50 mL). When gas evolution had ceased, benzyl bromide (4.3 g, 25 mmol) was added; after being stirred at ambient temperature for 16 h, the solution was treated with water (5 mL) and evaporated to dryness under vacuum. The residue was treated with water (20 mL) and extracted with chloroform. The combined extracts were dried over Na_2SO_4 and concentrated to an oil, which was purified by flash chromatography with acetone as the eluent (R_f = 0.30) to afford 2.2 g (54%) of product. ^1H NMR ($CDCl_3$): δ 2.69 (t, J = 6.5 Hz, 4 H, N–CH_2), 2.82 (t, J = 6.5 Hz, 4 H, Im–CH_2), 3.52 (s,

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2 H, Ar-CH_2-N), 4.87 (s, 4 H, Ar-CH_2-Im), 6.72 (d, J = 1.3 Hz, 2 H, imidazolyl C-H), 6.90 (d, J = 1.3 Hz, 2 H, imidazolyl C-H), 6.95-7.29 (m, 19 H, Ar H). ^{13}C NMR ($CDCl_3$): δ 24.76 (t), 49.13 (t), 51.88 (t), 54.00 (t), 58.55 (t), 119.6 (d), 126.44 (d), 126.70 (d), 126.87 (d), 127.62 (d), 127.97 (d), 128.40 (d), 128.60 (d), 136.17 (s), 139.00 (s), 157.00 (s).

N,N-Bis[2-(2'-benzimidazolyl)ethyl]benzamide (5a). Anhydrous methanol (40 mL) was cooled to 0 °C and saturated with dry hydrogen chloride. Compound **1** (10.0 g, 0.44 mol) was then added in portions while the temperature was maintained below 20 °C. A steady stream of HCl was continued until solution of **1** was complete. After excess HCl was removed by purging dinitrogen through the solution, the reaction mixture was transferred to a beaker, washed with two, 800-mL portions of anhydrous ether, and dried in a vacuum desiccator over KOH pellets. The crude imidate salt was then dissolved in absolute methanol (200 mL) and treated with o-phenylenediamine (9.5 g, 0.088 mol). The reaction mixture was stirred overnight at 25 °C, neutralized with aqueous potassium carbonate, and thoroughly extracted with chloroform. The combined extracts were dried over Na_2SO_4 and subsequently evaporated to give a viscous brown oil, which was chromatographed with acetone as the eluent to give 14.2 g (79%) of the desired product (R_f = 0.45), mp 127-130 °C. ^{1}H NMR (DMSO-d_6): δ 3.19 (br m, 2 H, BIm-CH_2), 3.38 (br m, 2 H, BIm-CH_2), 3.75 (br m, 2 H, O=C-N-CH_2), 4.00 (br m, 2 H, O=C-N-CH_2), 6.30 (br s, 2 H, benzimidazolyl N-H), 6.97-7.22 (m, 9 H, benzimidazolyl C-H), 7.40-7.44 (m, 4 H, benzimidazolyl C-H). IR (KBr): 1612 (C=O).

N,N-Bis[2-(1'-methyl-2'-benzimidazolyl)ethyl]benzamide (5b). This compound was prepared in 39% yield by the same procedure as that described for **5a** by using N-methyl-o-phenylenediamine dihydrochloride. The product was purified by flash chromatography with methanol as the eluent (R_f = 0.74). ^{1}H NMR (DMSO-d_6): δ 2.96 (br m, 2 H, N-CH_2), 3.26 (br s, 3 H, N-Me), 3.37 (br m, 2 H, N-CH_2), 3.77 (br s, 3 H, N-Me), 4.06 (br m, 2 H, BIm-CH_2), 4.35 (br m, 2 H, BIm-CH_2), 7.10-7.25 (m, 11 H, Ar H and benzimidazolyl C-H), 7.63 (br d, 2 H, benzimidazolyl C-H).

N,N-Bis[2-(2'-benzimidazolyl)ethyl]amine (6a). Benzamide **5a** (4.0 g, 9.8 mmol) was allowed to reflux in 6 N HCl (20 mL) for 12 h. The resultant solution was cooled to 0 °C and basified with 10 N sodium hydroxide. The product was collected by suction filtration, washed thoroughly with water, and dried in a vacuum oven at 70 °C to afford 2.7 g (91%) of a white powder, mp 194-196 °C (R_f = 0.53, methanol). ^{1}H NMR (DMSO-d_6): δ 2.90-3.05 (m, 8 H, CH_2-CH_2), 3.38 (br s, 1 H, NH), 7.05-7.14 (m, 4 H, benzimidazolyl C-H), 7.04-7.45 (m, 4 H, benzimidazolyl C-H), 12.0 (br s, 2 H, benzimidazolyl N-H). ^{13}C NMR (DMSO-d_6): δ 29.17 (t), 47.16 (t), 115.0 (br s), 121.02 (d), 153.96 (s).

N,N-Bis[2-(1'-methyl-2'-benzimidazolyl)ethyl]amine (6b). Deprotection of benzamide **5b** (2.0 g, 4.5 mmol) was accomplished by the same procedure described for the synthesis of compound **6a** to afford 1.2 g (80%) of a light yellow powder, mp 75-77 °C (R_f = 0.30, methanol). ^{1}H NMR (DMSO-d_6): δ 3.09 (m, 8 H, Ch_2-CH_2), 3.71 (s, 6 H, N-Me), 4.77 (br s, N-H), 7.09-7.91 (m, 8 H benzimidazolyl C-H). ^{13}C NMR (DMSO-d_6): δ 26.18 (q), 29.48 (t), 50.62 (t), 109.70 (d), 182.22 (d), 121.11 (d), 121.45 (d), 135.67 (s), 142.09 (s), 153.33 (s).

N,N-Bis[2-(2'-benzimidazolyl)ethyl]-N-benzylamine (7a). A mixture of compound **6a** (1.2 g, 4.8 mmol), potassium carbonate (1.0 g), and sodium iodide (0.20 g) in 2-propanol (100 mL) was treated with benzyl bromide (0.82 g, 4.8 mmol). The mixture was stirred at ambient temperature for 14 h, and then the solvent was evaporated under vacuum. The residue was treated with water and extracted with chloroform. The combined extracts were dried over Na_2SO_4, concentrated, and purified by flash chromatography with 6:1 ethyl acetate-methanol as the eluent (R_f = 0.30). ^{1}H NMR ($CDCl_3$): δ 2.83 (t, J = 5.6 Hz, 2H, N-CH_2), 2.87 (t, J = 5.6 Hz, 2 H, BIm-CH_2), 3.50 (s, 2 H, Ar-CH_2), 6.75 (m, 5 H, Ar H), 7.18 (m, 4 H, benzimidazolyl C-H), 7.42 (m, 4 H, benzimidazolyl C-H). ^{13}C NMR ($CDCl_3$): δ 27.10 (t), 52.21 (t), 58.50 (t), 114.61 (s), 121.7 (2 d), 126.67 (d), 127.97 (d), 128.58 (d), 138.45 (s), 154.45 (s).

N,N-Bis[2-(1'-benzyl-2'-benzimidazolyl)ethyl]-N-benzylamine (7b). Compound **6a** (2.2 g, 7.2 mmol) was added in small portions to a slurry of NaH (1.5 g, 62 mmol) in DMF (50 mL) under dinitrogen. When gas evolution ceased, benzyl bromide (2.9 g, 16.8 mmol) was added dropwise; the reaction mixture was allowed to stir at room temperature for 12 h. The solvent was evaporated to dryness at reduced pressure, water (10 mL) was added to the residue, and the mixture was extracted with three, 100-mL portions of chloroform. The combined extracts were dried over Na_2SO_4 and concentrated. The crude product was purified by flash chromatography with ethyl acetate as the eluent to afford 2.7 g (65%) of an orange oil (R_f = 0.61). ^{1}H NMR ($CDCl_3$): δ 2.89 (t, J = 7.4 Hz, 4 H, CH_2), 3.08 (t, J = 7.4 Hz, 4 H, CH_2), 3.66 (s, 2 H, ArCH_2), 5.11 (s, 4 H, ArCH_2), 6.89-6.94 (m, 4 H, benzimidazolyl C-H), 7.14-7.27 (m, 17 H, Ar H, benzimidazolyl C-H), 7.71 (d of d, J = 6.0 Hz, J = 1.8 Hz, 2 H, benzimidazolyl C-H). ^{13}C NMR ($CDCl_3$): δ 25.69 (t), 46.59 (t), 51.96 (t), 58.83 (t), 109.05 (d), 119.05 (d), 121.05 (d), 122.16 (d), 126.01 (d), 126.90 (d), 127.65 (d), 128.12 (d), 128.55 (d), 128.78 (d), 135.19 (s), 135.88 (s), 138.94 (s), 142.58 (s), 153.65 (s).

2-(1'-Methyl-2'-imidazolyl)ethylamine (8). The hydrochloride salt was prepared by the literature method[11] except that 2-(methylamino)-methyl-1,3-dioxolane was used instead of N-methylaminoacetaldehyde diethyl acetal. ^{1}H NMR (D_2O): δ 3.23 (s, 4 H, CH_2-CH_2), 3.64 (s, 3 H, N-Me), 7.18 (s, 2 H, imidazolyl C-H). ^{13}C NMR (DMSO-d_6): δ 22.14 (t), 34.30 (q), 36.02 (t), 118.25 (d), 123.41 (d), 143.17 (s).

The free amine was obtained by dissolving the hydrochloride salt in methanol and adding anhydrous sodium bicarbonate until the solution was basic. Sodium chloride was removed by filtration, and the filtrate was concentrated. White needles were deposited when the solution was allowed to cool to room temperature, mp 196-198 °C. ^{1}H NMR ($CDCl_3$): δ 2.96 (t, J = 6.8 Hz, 2 H, N-CH_2), 3.14 (t, J = 6.8 Hz, 2 H, Im-CH_2), 3.30 (br s, 1 H, N-H), 3.48 (s, 3 H, N-Me), 6.79 (s, 1 H, imidazolyl C-H), 7.08 (s, 1 H, imidazolyl C-H). ^{13}C NMR (DMSO-d_6): δ 23.20 (t), 32.27 (q), 36.72 (t), 121.54 (d), 125.30 (d), 125.30 (d), 144.18 (s).

N-[2-(1'-methyl-2'-imidazolyl)ethyl]benzamide (9). 2-(1'-Methyl-2'-imidazolyl)ethylamine hydrochloride (3.0 g, 18.6 mmol) was dissolved in water (50 mL), and then sodium hydroxide (0.75 g, 18.8 mmol) was added. Excess benzoyl chloride was added, and the mixture was vigorously stirred. Aqueous sodium hydroxide (1.1 g in 20 mL) was added in small portions over a period of 1 h. The reaction mixture was thoroughly extracted with chloroform. The combined extracts were dried over Na_2SO_4 and evaporated, and the crude product was recrystallized from benzene to afford 3.0 g (71.4%) of white plates, mp 109-110 °C. ^{1}H NMR ($CDCl_3$): δ 2.91 (t, J = 6.0 Hz, 2 H, Im-CH_2), 3.51 (s, 3 H, N-Me), 3.89 (t, J = 6 Hz, 1 H, N-CH_2), 3.92 (t, J = 6 Hz, 1 H, N-CH_2), 6.68 (d, J = 1.2 Hz, 1 H, imidazolyl C-H), 6.77 (d, J = 1.2 Hz, 1 H, imidazolyl C-H), 7.29-7.44 (m, 3 H, Ar H), 7.80 (d, J = 3.2 Hz, 2 H, Ar H), 8.28 (br t, J = 5.2 Hz, 1 H, N-H). ^{13}C NMR ($CDCl_3$): δ 26.13 (t), 32.44 (q), 37.01 (t), 120.70 (d), 126.98 (d), 127.05 (d), 128.26 (s), 128.37 (d), 131.21 (d), 134.50 (s), 167.20 (s).

N-[2-(1'-methyl-2'-imidazolyl)ethyl]-N-benzylbenzamide (10). Benzamide **9** (2.6 g, 11.3 mmol) in DMF (20 mL) was added dropwise to a slurry of sodium hydride (0.5 g, 20.8 mmol) in DMF (20 mL). After the gas evolution had subsided, benzyl bromide (1.9 g, 11.3 mmol) was added, and the mixture was stirred at 25 °C for 2 days. The excess sodium hydride was destroyed by the addition of water (10 mL), and the resultant mixture was evaporated to dryness under reduced pressure. The residue was treated with water and extracted with chloroform. The combined extracts were dried over Na_2SO_4 and concentrated to give a pale yellow oil (3.0 g, 91%) (R_f = 0.75) (1:1 methanol-ethyl acetate). ^{1}H NMR ($CDCl_3$): δ 3.08 (t, J = 7.1 Hz, 2 H, Im-CH_2), 3.67 (s, 3 H, N-Me), 3.77 (t, J = 7.1 Hz, 2 H, N-CH_2), 4.52 (s, 2 H, N-CH_2), 6.84 (s, 1 H, imidazolyl C-H), 6.92 (s, 1 H, imidazolyl C-H), 7.10-7.40 (m, 10 H, Ar H).

[2-(1'-Methyl-2'-imidazolyl)ethyl]benzylamine (11). Amide **10** (3.0 g, 10.3 mmol) was deprotected by refluxing in 6 N hydrochloric acid (30 mL) for 12 h. The reaction mixture was washed with ether, made basic with 10 M NaOH, and extracted with chloroform. The chloroform extracts were dried over Na_2SO_4 and evaporated to give 1.2 g of a mobile oil (63%). ^{1}H NMR ($CDCl_3$): δ 2.83 (t, J = 6.3 Hz, 2 H, Im-CH_2), 3.00 (br s, 1 H, NH), 3.06 (t, J = 6.3 Hz, N-CH_2), 3.50 (s, 3 H, N-Me), 3.83 (s, 2 H, ArCH_2N), 6.75 (s, 1 H, imidazolyl C-H), 6.90 (s, 1 H, imidazolyl C-H), 7.24-7.38 (m, 5 H, Ar H). ^{13}C NMR ($CDCl_3$): δ 26.77 (t), 32.23 (q), 46.46 (t), 53.49 (t), 120.22 (d), 125.11 (d), 126.67 (d), 126.85 (d), 139.81 (s), 146.39 (s).

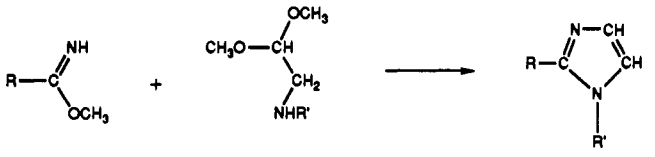
[2-(2'-Pyridyl)ethyl][2-(1'-methyl-2'-imidazolyl)ethyl]benzylamine (12) was prepared as described previously.[6b]

Synthesis of Copper(I) Complexes: General Procedure. A methanol or THF solution of the ligand was treated with 1 equiv of tetrakis(acetonitrile)copper(I) tetrafluoroborate under an inert atmosphere. The solution was stirred for at least 15 min, and then it was evaporated to dryness. Crystallization was accomplished in an inert-atmosphere box by the vapor diffusion method or by cooling a hot, filtered solution of the complex.

{N,N-Bis[2-(1'-methyl-2'-imidazolyl)ethyl]-N-benzylamine}copper(I) Tetrafluoroborate (13). The complex was crystallized from hot methanol. Anal. Calcd for $C_{19.5}H_{27}BCuF_4N_5O_{0.5}$: C, 47.82; H, 5.55; N, 14.29. Found: C, 47.54; H, 5.23; N, 14.60. A second crop obtained as needles by slow diffusion of benzene into the methanol solution did not contain the methanol solvate. Anal. Calcd for $C_{19}H_{25}BCuF_4N_5$: C, 48.17; H,

(11) Buschauer, A.; Schunak, W. *Arch. Pharm.* **1983**, *316*, 891-894.

Scheme I



5.32; N, 14.78. Found: C, 48.23; H, 5.31; N, 14.84. ^{1}H NMR (DMSO-d_6): δ 2.93 (br t, J = 5 Hz, 4 H, N–CH_2), 3.15 (br t, J = 5 Hz, 4 H, Im–CH_2), 3.61 (s, 6 H, N–Me), 3.86 (s, 2 H, ArCH_2N), 7.06 (d, J = 1.5 Hz, imidazolyl C–H), 7.26–7.39 (m, 5 H, Ar H), 7.29 (d, J = 1.5 Hz, 2 H, imidazolyl C–H).

{*N*,*N*-Bis[2-(1′-benzyl-2′-imidazolyl)ethyl]-*N*-benzylamine}copper(I) Tetrafluoroborate (14). Crystallization was accmplished by vapor diffusion of benzene into a THF solution of the complex. ^{1}H NMR (DMSO-d_6): δ 2.81 (br m, 4 H), 3.07 (br m, 4 H), 3.68 (s, 2 H, ArCH_2N), 5.26 (s, 4 H, ArCH_2–Im), 7.06–7.41 (m, 19 H, Ar H, imidazolyl C–H). Anal. Calcd for $C_{31}H_{33}N_5CuBF_4$: C, 59.48; H, 5.31; N, 11.18. Found: C, 59.43; H, 5.31; N, 11.13.

{*N*,*N*-Bis[2-(2′-benzimidazolyl)ethyl]amine}copper(I) Tetrafluoroborate (15). The white precipitate was collected and washed thoroughly with methanol. ^{1}H NMR (DMSO-d_6): δ 3.15 (m, 8 H, CH_2–CH_2), 3.39 (br s, 1 H, N–H), 7.37 (m, 4 H, benzimidazolyl C–H), 7.59 (m, 2 H, benzimidazolyl C–H), 7.92 (m, 2 H, benzimidazolyl C–H). Anal. Calcd for $C_{18}H_{15}BCuF_4N_5$: C, 47.55; H, 4.20; N, 15.36. Found: C, 47.22; H, 4.07; N, 15.52.

{*N*,*N*-Bis[2-(1′-methyl-2′-benzimidazolyl)ethyl]amine}copper(I) Tetrafluoroborate (16). The complex was crystallized from hot acetonitrile. Anal. Calcd for $C_{22}H_{25}BCuF_4N_6$: C, 50.44; H, 4.81; N, 16.04. Found: C, 50.04; H, 4.86; N, 15.74.

{*N*,*N*-Bis[2-(1′-benzyl-2′-benzimidazolyl)ethyl]-*N*-benzylamine}copper(I) Tetrafluoroborate (17). White needles were obtained by slow diffusion of THF into an acetone solution. ^{1}H NMR (DMSO-d_6): δ 3.07 (m, 4 H, N–CH_2), 3.46 (m, 4 H, BIm–CH_2), 3.97 (s, 2 H, ArCH_2N), 5.65 (s, 4 H, ArCH_2BIm), 7.12–7.21 (m, 7 H, Ar H), 7.30–7.52 (m, 12 H, Ar H, benzimidazolyl C–H), 7.70 (d, J = 8.0 Hz, 2 H, benzimidazolyl C–H), 8.01 (d, J = 8.0 Hz, 2 H, benzimidazolyl C–H). Anal. Calcd for $C_{39}H_{37}BCuF_4N_5$: C, 64.51; H, 5.14; N, 9.64. Found: C, 64.28; H, 4.93; N, 10.02.

{*N*-[2-(1′-Methyl-2′-imidazolyl)ethyl]-*N*-[2-(2′-pyridyl)ethyl]-*N*-benzylamine}copper(I) Hexafluorophosphate (18). The pale yellow product was precipitated and was collected by filtration. Anal. Calcd for $C_{20}H_{24}CuF_6N_4P$: C, 44.65; H, 4.50; N, 10.43. Found: C, 44.64; H, 4.44; N, 10.26. ^{1}H NMR (DMSO-d_6): δ 2.72 (m, 2 H, CH_2), 3.07 (m, 4 H, CH_2), 3.16 (m, 2 H, CH_2), 3.65 (s, 3 H, N–Me), 3.89 (s, 2 H, ArCH_2), 7.14–7.43 (m, 9 H, Ar H, pyridyl C–H, imidazolyl C–H), 7.87 (t, J = 7.5 Hz, 1 H, pyridyl C–H), 8.56 (d, J = 4.4 Hz, 1 H, pyridyl C–H).

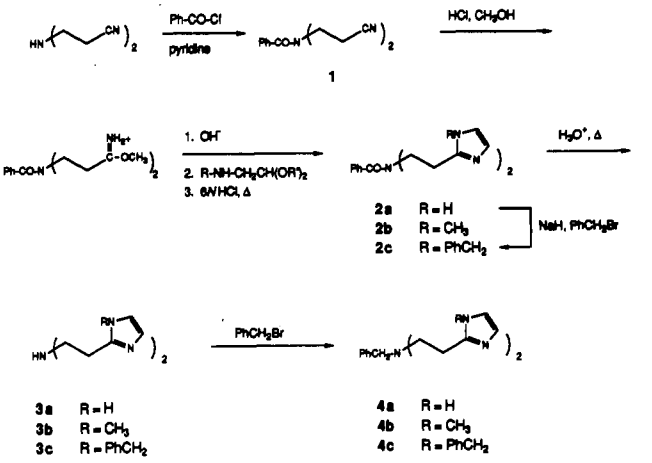
{1,3-Bis(*N*-(2-(1-methyl-2-imidazolyl)ethyl)formimidoyl)benzene}dicopper(I) Bis(tetrafluoroborate) (19). 2-(1′-Methyl-2′-imidazolyl)-ethylamine (**8**) (300 mg, 2.4 mmol) and isophthalaldehyde (162 mg, 1.2 mmol) were dissolved in methanol (25 mL) under an inert atmosphere. Tetrakis(acetonitrile)copper(I) tetrafluoroborate (780 mg, 2.5 mmol) was added, and the slurry was stirred at ambient temperature for 0.25 h. After being refluxed for 2 h, the reaction mixture was cooled to room temperature and the crude product was collected. Orange needles were obtained by slow diffusion of THF into an acetonitrile solution of the complex. ^{1}H NMR (DMSO-d_6): δ 3.08 (br t, 4 H, CH_2), 3.63 (s, 6 H, N–Me), 4.11 (br t, 4 H, CH_2), 6.93 (s, 2 H, imidazolyl C–H), 7.09 (s, 2 H, imidazolyl C–H), 7.56 (t, 1 H, Ar H), 7.85 (d, 2 H, Ar H), 8.57 (s, 2 H, HC=N), 9.25 (s, 1 H, Ar H).

Results

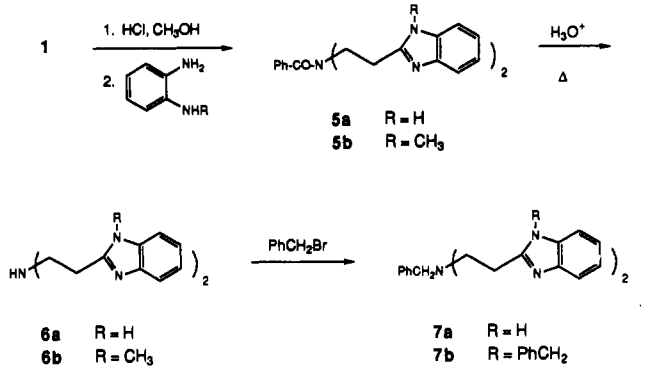
Synthesis. We have adapted a synthetic route for preparing the imidazole-containing tridentate ligands using a cyclization in which the heterocycle is formed by the condensation of an imidate ester with an α-aminoacetal (Scheme I).[12] This route should allow synthesis of imidazoles containing substituents on any atom of the ring, incorporating sterically bulky or hydrophobic groups on the subsequently prepared ligand.

The imidate esters can also be used to prepare benzimidazoles containing labile substituents that are not stable to the relatively harsh conditions of the Phillips synthesis.[13] Many workers have used benzimidazole ligands derived from aminoacetic acids, which result in five-membered chelate rings when coordinated to a metal ion. Since β-aminocarboxylic acids are prone to β-elimination, the benzimidazole ligands that coordinate copper ions with a six-membered chelate ring (e.g., **6** and **7**) are more difficult to prepare and have not been reported before.

Scheme II



Scheme III



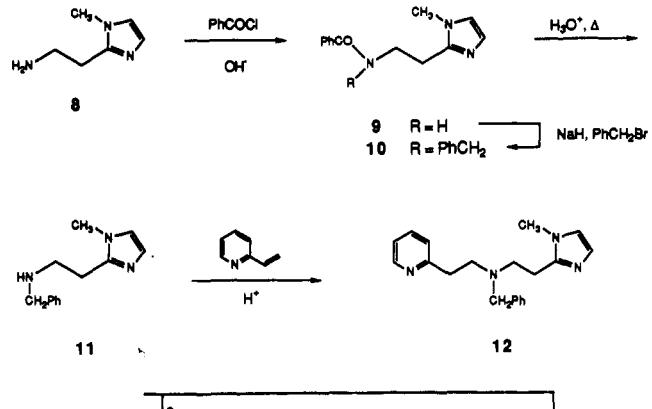
Our synthesis of these benzimidazole and imidazole ligands utilizes commercially available iminodipropionitrile. The amino group was protected as an amide to prevent β-elimination, and the synthetic steps used to prepare the tridentate imidazole ligands are shown in Scheme II. A Pinner reaction with anhydrous hydrogen chloride in methanol gave the extremely hygroscopic bis(imidate ester) as the hydrochloride salt, and it was used immediately without purification. The free bis(imidate ester) reacted with amino acetals at ambient temperature to generate amidine intermediates, which were not isolated but were cyclized to form the imidazole ring after briefly refluxing in 6 N hydrochloric acid. Acid hydrolysis of the amide afforded the tridentate ligands **3a** and **3b** in high yield. The unmethylated ligand **3a** was isolated as the hydrochloride salt because the free base is water soluble.

Alkylation of compound **2a** using sodium hydride and benzyl bromide gave compound **2c** in high yield. Acid hydrolysis afforded compound **3c**. The secondary amine group in **3** could be alkylated with benzyl bromide to give ligands **4**, although **4c** was prepared more efficiently from the dianion of compound **3a** and 3 equiv of benzyl bromide. Attempts to prepare these compounds by reduction of amides **2** failed, and no reaction was observed upon treatment with lithium aluminum hydride or borane-THF. Reductive amination of benzaldehyde with compound **3b** and sodium cyanoborohydride also failed to give a significant yield of compound **4b**, and 1-methyl-2-vinylimidazole was detected in the reaction mixture. We presume that the intermediate iminium ion eliminates vinylimidazole. An attempt to prepared the ethyl analogue by reaction of compound **3b** with acetic acid and sodium

(12) Sainsbury, M.; Theobald, R. S. In *Rodd's Chemistry of Carbon Compounds* Coffey, S., Ansell, M. F., Eds.; Elsevier: Amsterdam, 1986; Vol. IVc, p 122.

(13) (a) Phillips, M. A. *J. Chem. Soc.* **1928**, 2393. (b) *Ibid.* **1929**, 2820.

Scheme IV



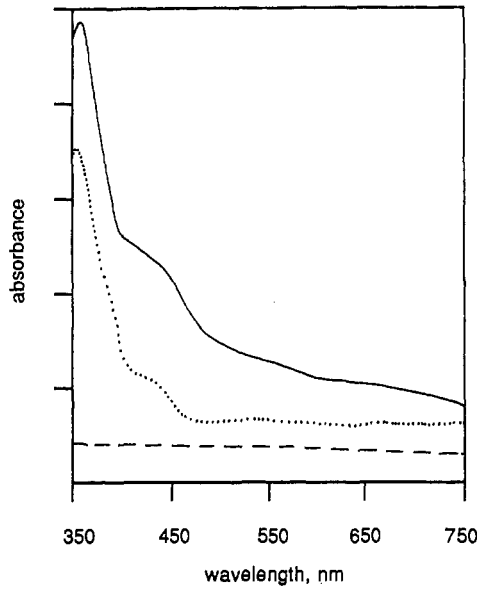


Figure 1. Absorption spectra for $Cu[Bz(NMI)_2N3]^+$ in CH_2Cl_2 at −78 °C under dinitrogen (- - -) and dioxygen (—) and for $Cu[Bz(Py)_2N3]^+$ under dioxygen (···). The absorbance scale is arbitrary.

borohydride[14] resulted in the formation of the acetamide even after vigorous refluxing for long periods of time.

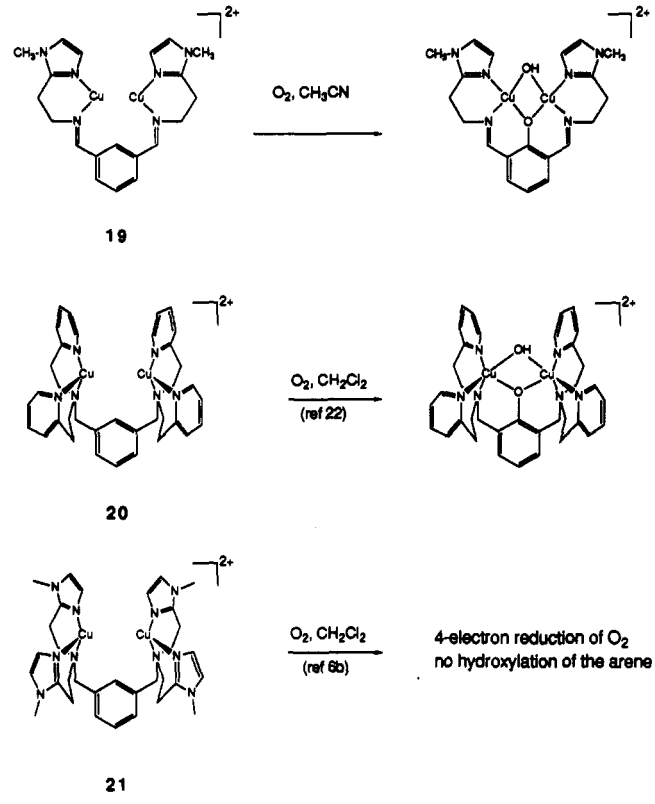
The bis(imidate ester) prepared from **1** was also used to prepare benzimidazole derivatives (Scheme III). Treatment with *o*-phenylenediamine or *N*-methyl-*o*-phenylenediamine produced the amino-protected benzimidazole or *N*-methylbenzimidazole compound, respectively. The ligands were again deprotected by refluxing in 6 N hydrochloric acid, and they were alkylated by using benzyl bromide.

The same procedures were used to prepare ligands with one imidazolylethyl "arm" (Scheme IV).[11] Alkylation was accomplished via the benzamide derivative **9**, and mixed pyridyl–imidazolyl ligands could be obtained by reaction of the amine with vinylpyridine.[6b] A dinucleating ligand could be prepared by the condensation of amine **8** with isophthalaldehyde in the presence of copper(I) ion to give the dinuclear complex **19**.

The copper(I) complexes, $Cu(L)^+$, were obtained by treating the ligand with tetrakis(acetonitrile)copper(I) tetrafluoroborate or hexafluorophosphate under an inert atmosphere and crystallization from an appropriate solvent. The complexes were characterized by IR and NMR spectroscopy and elemental analysis.

Spectroscopy and Reactivity. Of all of the mononuclear copper complexes prepared, only **13** (L = **4b**) and **14** (L = **4c**) react rapdily with O_2 at −80 °C in CH_2Cl_2 to generate brown species with multiple intense absorption bands (Figure 1). When the

Scheme V



brown solution was allowed to warm to room temperature, the solution turned green and then blue; attempts to remove the dioxygen under vacuum or with a stream of carbon monoxide led to generation of the same blue copper(II) complex.

Treatment of the Schiff-base complex **19** with dioxygen in methanol in the presence of acid led to formation of 2-hydroxy-1,3-benzenedicarbaldehyde after hydrolysis of the ligand (Scheme V).

Discussion

The imidazole- and benzimidazole-ligated copper(I) complexes reported here are only sparingly soluble in methylene chloride, limiting a complete study of their dioxygen chemistry. In more polar solvents, these compounds undergo simple oxidation to give copper(II) species. The exceptions are complexes **13** and **14**, which react with O_2 at low temperature to form an intermediate having spectroscopic properties different from those of their completely oxidized derivatives. On the basis of the observation of apparently intense bands in the region between 350 and 600 nm (Figure 1), which are similar to those reported for analogous pyridine-ligated complexes,[15] we believe that this brown complex is a peroxide adduct. Unfortunately, we were not able to obtain accurate extinction coefficients[16] for the absorption spectrum or to make precise gas uptake measurements because these compounds react with the solvent. Thus, stirring a solution of **13** with CH_2Cl_2 under nitrogen led to the production of a blue-green precipitate analyzing for $CuCl(BF_4)$ and having essentially no carbon, hydrogen, or nitrogen by elemental analysis. Reactivity toward methylene chloride has been observed with other copper(I) complexes,[17] so this is only a surprising result because analogous (pyridyl-

(14) Gribble, G. W.; Lord, P. D.; Skotnick, J.; Dietz, S. E.; Eaton, J. T.; Johnson, J. L. *J. Am. Chem. Soc.* **1974**, *96*, 7812–7814.

(15) Karlin, K. D.; Haka, M. S.; Cruse, R. W.; Meyer, G. J.; Farooq, Y.; Gultneh, Y.; Hayes, J. C.; Zubieta, J. *J. Am. Chem. Soc.* **1988**, *110*, 1196–1207.

(16) On the basis of the amount of material we use to prepare the samples for spectroscopy, we would estimate the extinction coefficient of the 360-nm peak to be between 5000 and 10000 M^{-1} cm^{-1}. It is possible that it is as low as 2000 or as high as 20000 M^{-1} cm^{-1}.

(17) For example, see: Jacobson, R. R.; Tyeklar, Z.; Farooq, A.; Karlin, K. D.; Liu, S.; Zubieta, J. *J. Am. Chem. Soc.* **1988**, *110*, 3690–3692.

ethyl)amine complexes are essentially inert toward dichloromethane.

Karlin has shown that several three-coordinate copper(I) complexes containing the bis[2-(2′-pyridyl)ethyl]amine moiety are capable of reversibly binding O_2 at low temperature in methylene chloride; detailed studies of the dinuclear complexes linked by alkyl chains or a fluorinated *m*-xylyl group have been reported.[18] The mononuclear complex $Cu(BzN_3Py_2)^+$ reacts similarly at low temperature,[19] and the dioxygen adduct $[(BzN_3Py_2)Cu]_2O_2^{2+}$ has a color and spectrum (Figure 1) very similar to that observed for the dinuclear complexes[15,18] and for **13**. When a solution of $(BzN_3Py_2)Cu^+$ is exposed to dioxygen at room temperature, a green bis(μ-oxo) species forms, followed by decomposition to a bis(μ-hydroxy) species.[20a] We therefore believe that similar chemistry occurs for **13** and **14**.

The reactivity of tyrosinase,[21] a copper-containing enzyme that is structurally similar to hemocyanin, has been mimicked by the reaction of molecular oxygen with the copper complex of *m*-xylyl-N_6Py_4 (**20**) in which one atom of dioxygen is inserted into the arene C–H bond of the ligand (Scheme V)[22] and which occurs through a copper(II) peroxide intermediate.[23] Since *N*-methylimidazole complexes apparently have the appropriate electronic properties to form the copper peroxide unit, on the basis of the reaction of **13** (Figure 1), it is surprising that the *m*-xylyl-$N_6(NMI)_4$ copper complex **21** does not react with oxygen to catalyze ligand hydroxylation, as reported earlier.[6b] Complex **21** does react rapidly with O_2 in a variety of solvents; but after the reaction, the copper ions were extracted with ammonium hydroxide and the ligand was reclaimed. Thin-layer chromatography and ^1H and ^{13}C NMR spectra established that the ligand had not been oxidized. Since **21** is virtually insoluble in CH_2Cl_2, the reaction with O_2 could not be monitored at low temperature to determine if a peroxide adduct formed.

It is unclear why the imidazole-ligated dimer **21** reacts differently from the pyridine analogue. In previous studies of Schiff-base ligands, Cu(I) adducts of pyridine and 4-substituted imidazole ligands showed similar reactivity patterns.[24-26] We prepared complex **19** to see if the lack of hydroxylation in **21** was related to the use of a 2-substituted imidazole instead of 4-substituted imidazole of histidine. Casella and co-workers have prepared Schiff-base complexes with histamine and histidine derivatives and found that hydroxylation occurred with the *N*-methyl derivative in acetonitrile.[24] With the N–H imidazole complexes, reaction with dioxygen results in ligand hydroxylation only in protic solvents, and the amount of hydroxylation can be increased by addition of a small amount of acetic acid. This dependence on proton concentration suggests that a hydroperoxide intermediate may be important in this reaction. An orange acetonitrile solution of complex **19** turns green upon exposure to O_2 (Scheme V), and an absorption band at 350 nm is observed, characteristic of ligand hydroxylation with this system. The acetonitrile was evaporated and the residue was treated with 10% HCl to hydrolyze the imine linkages. The solution was then extracted to obtain the aldehyde. Thin-layer chromatography of the extracts and an authentic sample of the phenol confirmed that hydroxylation had occurred. Thus, we conclude that the substitution of the imidazole ring has little effect on the reaction.

In summary, chelating imidazole- and benzimidazole-containing ligands form copper(I) complexes that react with dioxygen at low temperature according to previously described patterns. Compared with their pyridine analogues, the complexes have lower solubility and higher reactivity toward dichloromethane; these may limit broader application of their use. The solubility problem can be overcome by appropriate substitution of the imidazole ring, and we continue to explore complexes derived from such ligands.

Acknowledgment is made to the National Science Foundation and to the Alfred P. Sloan Foundation for their generous support of this work.

(18) Karlin, K. D.; Cruse, R. W.; Haka, M. S.; Gultneh, Y.; Cohen, B. I. *Inorg. Chim. Acta* **1986**, *125*, L43–L44.
(19) The ligand in this case is the pyridine analogue of **4**. We have prepared this complex,[20] and its low-temperature absorption spectrum and dioxygen uptake behavior (2:1 $Cu:O_2$) are the same as for the dinuclear analogues described in ref 15.
(20) (a) Karlin, K. D.; Gultneh, Y.; Hayes, J. C.; Zubieta, J. *Inorg. Chem.* **1984**, *23*, 519–521. (b) Blackburn, N. J.; Karlin, K. D.; Concannon, M.; Hayes, J. C.; Gultneh, Y.; Zubieta, J. *J. Chem. Soc., Chem. Commun.* **1984**, 939–940.
(21) Lerch, K. *Life Chem. Rep.* **1987**, *5*, 221–234.
(22) Karlin, K. D.; Hayes, J. C.; Gultneh, Y.; Cruse, R. W.; McKown, J. W.; Hutchinson, J. P.; Zubieta, J. *J. Am. Chem. Soc.* **1984**, *106*, 2121–2128.
(23) Cruse, R. W.; Kaderli, C. J.; Meyer, C. J.; Zuberbuhler, A. D.; Karlin, K. D. *J. Am. Chem. Soc.* **1988**, *110*, 5020–5024.
(24) Casella, L.; Rigoni, L. *J. Chem. Soc., Chem. Commun.* **1985**, 1668–1669.
(25) Gelling, O. J.; van Bolhuis, F.; Meetsma, A.; Feringa, B. L. *J. Chem. Soc., Chem. Commun.* **1988**, 552–554.
(26) Menif, R.; Martell, A. E. *J. Chem. Soc., Chem. Commun.* **1989**, 1521.