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# Sterically Hindered [Tris(imidazolyl)phosphine]copper Complexes: Formation and Reactivity of a Peroxo−Dicopper(II) Adduct and Structure of a Dinuclear Carbonate-Bridged Complex

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Copper(I) complexes of the new tripodal ligands tris[2-(1,4-diisopropylimidazolyl)]phosphine ($\mathrm{Pim}^{\mathrm{iPr2}}$) and tris-[2-(1-isopropyl-4-*tert*-butylimidazolyl)]phosphine ($\mathrm{Pim}^{\mathrm{iPr,tBu}}$) have been prepared and characterized by $^1$H NMR and elemental analysis. The dioxygen reactivity of the pseudotetrahedral complexes $[\mathrm{Cu(Pim^{iPr2})CH_3CN}]\mathrm{BF_4}$ and $[\mathrm{Cu(Pim^{iPr,tBu})CH_3CN}]\mathrm{BF_4}$ has been examined. The former complex forms a violet peroxo−dicopper(II) species upon reaction with dioxygen at low temperature; the electronic absorption spectrum ($\lambda$ = 343 nm, $\epsilon$ = 19 500 $\mathrm{M^{-1}\,cm^{-1}}$; $\lambda$ = 549 nm, $\epsilon$ = 790 $\mathrm{M^{-1}\,cm^{-1}}$) and O−O stretching frequency ($\nu$(O−O) = 750 $\mathrm{cm^{-1}}$) of this adduct approximate those of oxyhemocyanin. Warming a mixture of the peroxide complex and triphenylphosphine to room temperature affords $[\mathrm{Cu(Pim^{iPr2})PPh_3}]\mathrm{BF_4}$ and produces no $\mathrm{O{=}PPh_3}$. In methanol at −78 °C, the peroxide complex is unreactive toward acid, carbon dioxide, 1-hexene, and triphenylphosphine. Thermal decomposition of the dioxygen adduct in the presence of water yields a bis(hydroxide)-bridged dicopper(II) dimer, $[\mathrm{Cu(Pim^{iPr2})}]_2\mathrm{(OH)_2(BF_4)_2}$, which further reacts with atmospheric $\mathrm{CO_2}$ to produce the carbonate-bridged complex $[\mathrm{Cu(Pim^{iPr2})}]_2\mathrm{CO_3(BF_4)_2}$. X-ray crystallography has been used to characterize the carbonate complex. Crystal data: orthorhombic, space group *Pbca*, with $a$ = 16.8705(17) Å, $b$ = 17.4731(14) Å, $c$ = 51.358(4) Å, $V$ = 15139.4(22) Å$^3$, and $Z$ = 8. The structure of a prototypical mononuclear 5-coordinate complex, $[\mathrm{Cu(Pim^{iPr2})OAc}]\mathrm{BF_4}$, has also been determined. Crystal data: monoclinic, space group $P2_1/n$, with $a$ = 9.657(3) Å, $b$ = 17.001(5) Å, $c$ = 24.642(6) Å, $\beta$ = 100.987(23)°, $V$ = 3971.4(19) Å$^3$, and $Z$ = 4. The geometry about copper(II) in both structures is approximately square pyramidal, indicating that $\mathrm{Pim}^{\mathrm{iPr2}}$ can accommodate side-on binding of dioxygen to copper. The more sterically hindered copper(I) complex $[\mathrm{Cu(Pim^{iPr,tBu})CH_3CN}]\mathrm{BF_4}$ is inert to $\mathrm{O_2}$, but it reacts readily with CO to form the isolable adduct $[\mathrm{Cu(Pim^{iPr,tBu})CO}]\mathrm{BF_4}$ with $\nu$(CO) = 2086 $\mathrm{cm^{-1}}$. In accord with its lack of dioxygen reactivity, $[\mathrm{Cu(Pim^{iPr,tBu})CH_3CN}]\mathrm{BF_4}$ undergoes a quasi-reversible redox process at very high potential, with $E_{1/2}$ (in $\mathrm{CH_3CN}$) of +1.08 V vs Ag/AgCl.

## Introduction

Copper complexes of sterically demanding tris(pyrazolyl)hydroborate ligands have found application as synthetic analogs for cuproprotein active sites.[1] Placement of groups such as *tert*-butyl or isopropyl at the 3-position of the pyrazolyl rings is a key to the success of these systems, because the presence of the substituent inhibits formation of coordinatively saturated $(\mathrm{ligand})_2\mathrm{M}^{n+}$ complexes and allows for control over redox behavior.[2] The most effective model to date for the dioxygen transport protein hemocyanin (Hc)[3] utilizes the ligand tris[1-(3,5-diisopropylpyrazolyl)]hydroborate ($\mathrm{Tp}^{\mathrm{iPr2}}$), which forms a peroxo−dicopper(II) complex with spectroscopic and physicochemical properties that are strikingly similar to those of the protein.[4] In addition, the planar $\mu$-$\eta^2$:$\eta^2$ mode of dioxygen binding, determined by X-ray crystallography to be present in this complex, was subsequently demonstrated to be the same as that in Hc.[5]

While the importance of steric factors in Hc model systems has been established, it is less clear whether the electronic properties unique to the anionic tris(pyrazolyl)hydroborates are required to stabilize biomimetic copper−oxygen interactions. Copper(I) complexes of *m*-xylyl-supported ligands, for example, demonstrate marked differences in reactivity toward dioxygen when imidazole N donors are substituted for pyrazole, despite the similar geometries of those heterocycles.[6] Coupled with the ubiquity of histidinyl-imidazole ligation to metal ions *in vivo*, development of copper coordination compounds of imidazole-based, neutral ligands may lead to a better understanding of how hemocyanin and the related enzyme tyrosinase bind and/or activate $\mathrm{O_2}$. Because imidazoles are functionalized and incorporated into chelates with relative difficulty, there are few copper enzyme models in which imidazoles are the sole N donors[7] and fewer still with the steric properties necessary to enforce particular binding modes or create highly sheltered metal environments. The present paper describes the syntheses,

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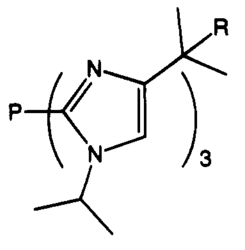
structures, and reactivities of copper complexes of the tridentate ligands Pim$^{iPr2}$ (1) and Pim$^{iPr,tBu}$ (2).[8]



**1** Pim$^{iPr2}$ (R = H)
**2** Pim$^{iPr,tBu}$ (R = $CH_3$)

## Experimental Section

**Materials and Methods.** The compounds 1,4-diisopropylimidazole,[9] 1-isopropyl-4-*tert*-butylimidazole,[9] and tetrakis(acetonitrile)copper(I) tetrafluoroborate[10] were synthesized according to the literature procedures. Syntheses and manipulations of copper(I) complexes were performed in a Vacuum Atmospheres drybox operating at less than 10 ppm of $O_2$ and $H_2O$, using commercially available anhydrous solvents that were degassed before use. Otherwise, all solvents and reagents were used without further purification. Unless otherwise indicated, spectral data were collected at room temperature. Proton and $^{31}P$ NMR spectra were recorded on Bruker AC200 and AMX300 instruments. Chemical shifts ($\delta$) of protons are reported in ppm relative to an internal standard of tetramethylsilane, and phosphorus shifts are reported in ppm relative to an external standard of 85% $H_3PO_4$. Infrared spectra were obtained using a Bio-Rad FTS-7 spectrophotometer, and peaks are reported in $cm^{-1}$. Electronic absorption spectra were recorded on a Perkin-Elmer Lambda 6 instrument; $\lambda$ values are in nm and $\epsilon$ values have units of $M^{-1}$ $cm^{-1}$. Low-temperature UV−vis spectroscopy[11] and manometric uptake experiments[12] were carried out using techniques similar to those previously reported. Elemental analyses were performed by Atlantic Microlab, Norcross, GA.

Resonance Raman experiments were conducted on frozen (77 K) methanol solutions that were approximately 0.05 M in metal complex. A 5-mm-diameter NMR tube containing the frozen sample was carefully flame-sealed to a length of approximately 3 cm, attached lengthwise to a concave cold finger, and lowered into a dewar with optical windows set 90° apart. The dewar was evacuated, and Raman scattering was excited by the 514.5 nm line of a Spectra-Physics Model 164 $Ar^+$ laser (40 mW incident power). The scattering was detected using an Instruments SA, Inc., Ramanor U1000 spectrophotometer equipped with a thermoelectrically cooled Hamamatsu R943-02 photomultiplier tube for photon counting via the ISA Spectra Link, controlled with ISA Enhanced Prism software. The spectral slit width was set at 5 $cm^{-1}$. Electrochemical measurements were made using a computer-driven EG&G PAR Model 273 potentiostat, on acetonitrile solutions that were 0.10 M in tetrabutylammonium tetrafluoroborate. The concentration of metal complexes was approximately 0.005 M. A three-electrode cell having a platinum disk working electrode, a platinum wire auxiliary electrode, and a silver/silver chloride reference electrode was utilized. A gentle flow of argon was passed over the solutions to exclude atmospheric $O_2$. Potentials are reported versus Ag/AgCl.

**Tris[2-(1,4-diisopropylimidazolyl)]phosphine, Pim$^{iPr2}$ (1).** A 250 mL three-necked flask containing a stir bar was dried at 120 °C, allowed to cool, and then fitted with an Ar inlet tube, a septum, and an addition funnel containing 1,4-diisopropylimidazole (6.0 g, 39 mmol) in diethyl ether (50 mL). A syringe was used to transfer a solution of 1.6 M *n*-butyllithium in hexanes (27 mL, 43 mmol) to the flask, and the flask was then lowered into a dry ice bath. Dropwise addition of the imidazole solution to the stirred solution of butyllithium was complete after 20 min, affording a yellow reaction mixture. After 1 h, the solution was allowed to warm to room temperature over 45 min, during which time the color darkened to orange-gold. The flask was again cooled to −78 °C, and another addition funnel containing $PCl_3$ (1.4 g, 10 mmol) in 10 mL of diethyl ether was quickly exchanged for the first. Very slow dropwise addition of the $PCl_3$ solution caused immediate precipitation of white solids. After the addition was complete, the mixture was allowed to stir for 2 h at −78 °C and then was warmed to room temperature over 1 h. Concentrated $NH_4OH$ (60 mL) was added, the biphasic mixture was stirred for 1 h, and the layers were separated. The organic layer was washed sequentially with water and saturated aqueous NaCl, dried over $MgSO_4$, filtered, and evaporated under vacuum to give an oily cream-colored residue. The solid was triturated with 20 mL of hexanes, collected by filtration, and washed with additional hexanes. Approximately 4% of the material was determined to be tris[2-(1,4-diisopropylimidazolyl)]phosphine oxide by $^1H$ NMR. Slow evaporation of an acetone solution under an inert atmosphere removed most of the phosphine oxide contaminant. Drying afforded 2.3 g (47%) of white solid product. $^1H$ NMR ($CDCl_3$): $\delta$ 1.14 (18H, d, $J$ = 6.6 Hz, 1-CH($CH_3$)$_2$), 1.20 (18H, d, $J$ = 6.9 Hz, 4-CH($CH_3$)$_2$), 2.87 (3H, sept, $J$ = 6.9 Hz, 4-$CH$($CH_3$)$_2$), 4.62−4.84 (3H, m, 1-$CH$($CH_3$)$_2$), 6.82 (3H, s, imidazolyl $C_5H$). $^{31}P$ NMR ($CDCl_3$): $\delta$ −62.62. The phosphine oxide is distinguished by a doublet in the $^1H$ NMR spectrum at 6.93 ppm and a resonance in the $^{31}P$ NMR spectrum at −3.98 ppm.

**Tris[2-(1-isopropyl-4-*tert*-butylimidazolyl)]phosphine, Pim$^{iPr,tBu}$ (2).** This compound was prepared according to the procedure described for Pim$^{iPr2}$, with 1-isopropyl-4-*tert*-butylimidazole (6.6 g, 40 mmol) as starting material. The yield of white solid was 2.0 g (38%). $^1H$ NMR ($CDCl_3$): $\delta$ 1.12 (18H, d, $J$ = 6.6 Hz, CH($CH_3$)$_2$), 1.23 (27H, s, C($CH_3$)$_3$), 4.69−4.90 (3H, m, $CH$($CH_3$)$_2$), 6.80 (3H, s, imidazolyl $C_5H$). $^{31}P$ NMR ($CDCl_3$): $\delta$ −64.08. The phosphine oxide is distinguished by a doublet in the $^1H$ NMR spectrum at 6.89 ppm and a resonance in the $^{31}P$ NMR spectrum at −4.90 ppm.

**{Tris[2-(1,4-diisopropylimidazolyl)]phosphine}(acetonitrile)copper(I) Tetrafluoroborate, [Cu(Pim$^{iPr2}$)$CH_3CN$]$BF_4$ (3-$BF_4$).** A solution of Pim$^{iPr2}$ (2.1 g, 4.3 mmol) in dichloromethane (10 mL) was treated with [Cu($CH_3CN$)$_4$]$BF_4$ (1.4 g, 4.3 mmol), and the resulting suspension was allowed to stir for 30 min. Sufficient diethyl ether was added to the colorless solution to precipitate the complex as a white powder, which was collected by filtration and washed with additional ether. Drying under vacuum afforded 2.8 g (94%) of the desired product. $^1H$ NMR ($CDCl_3$): $\delta$ 1.29 (18H, d, $J$ = 6.9 Hz, 4-CH($CH_3$)$_2$), 1.48 (18H, d, $J$ = 6.7 Hz, 1-CH($CH_3$)$_2$), 2.39 (3H, s, $CH_3$CN), 2.99 (3H, sept, $J$ = 6.9 Hz, 4-$CH$($CH_3$)$_2$), 4.98−5.21 (3H, m, 1-$CH$($CH_3$)$_2$), 6.80 (3H, d, $J$ = 4.1 Hz, imidazolyl $C_5H$). $^{31}P$ NMR ($CD_3OD$): $\delta$ −115.8. Anal. Calcd for $C_{29}H_{48}N_7BCuF_4P{\cdot}0.25CH_2Cl_2$: C, 50.38; H, 7.01; N, 14.06. Found: C, 50.43; H, 6.90; N, 14.05.

**{Tris[2-(1-isopropyl-4-*tert*-butylimidazolyl)]phosphine}(acetonitrile)copper(I) Tetrafluoroborate, [Cu(Pim$^{iPr,tBu}$)$CH_3CN$]$BF_4$ (4-$BF_4$).** Starting with 1.0 g (1.9 mmol) of Pim$^{iPr,tBu}$ in 5 mL of dichloromethane, we synthesized this complex according to the procedure described for [Cu(Pim$^{iPr2}$)$CH_3CN$]$BF_4$ (**3-$BF_4$**). Yield: 1.1 g (81%) of white powder. $^1H$ NMR ($CDCl_3$): $\delta$ 1.36 (27H, s, C($CH_3$)$_3$), 1.49 (18H, d, $J$ = 6.7 Hz, CH($CH_3$)$_2$), 2.40 (3H, s, $CH_3$CN), 5.04−5.25 (3H, m, $CH$($CH_3$)$_2$), 6.80 (3H, d, $J$ = 4.5 Hz, imidazolyl $C_5H$).

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Anal. Calcd for $C_{32}H_{54}N_7BCuF_4P$: C, 53.52; H, 7.58; N, 13.65. Found: C, 53.25; H, 7.66; N, 13.46.

**{Tris[2-(1,4-diisopropylimidazolyl)]phosphine}(triphenylphosphine)copper(I) Tetrafluoroborate, $[Cu(Pim^{iPr2})PPh_3]BF_4$ (5-BF$_4$).** Under an inert atmosphere, 100 mg (0.14 mmol) of $[Cu(Pim^{iPr2})CH_3CN]BF_4$ (**3-BF$_4$**) was dissolved in 1.5 mL of methanol in a test tube. A septum was affixed to the tube, and the solution was cooled in a dry ice–acetone bath to −78 °C. Dry dioxygen (1 atm) was introduced into the solution using a syringe needle. After 20 min, 47 mg (0.18 mmol) of triphenylphosphine was quickly added to the violet reaction mixture, the septum was replaced, and the tube was allowed to warm to room temperature with frequent agitation over the course of 1 h. During this time, the solution changed color to light green, and a white crystalline solid precipitated. The tube was returned to the inert-atmosphere box, and the supernatant was removed using a pipet. Dissolution of the precipitate in dichloromethane afforded a light yellow solution, which was filtered. Layering diethyl ether onto the filtrate produced a crop of fine colorless needles, which were dried under vacuum at 60 °C. Yield: 110 mg (88%). $^1$H NMR (CDCl$_3$): $\delta$ 0.74 (18H, d, $J$ = 6.9 Hz, 4-CH(C*H*$_3$)$_2$), 1.53 (18H, d, $J$ = 6.7 Hz, 1-CH(C*H*$_3$)$_2$), 2.61 (3H, sept, $J$ = 6.9 Hz, 4-C*H*(CH$_3$)$_2$), 5.15–5.38 (3H, m, 1-C*H*(CH$_3$)$_2$), 6.88 (3H, d, $J$ = 4.2 Hz, imidazolyl C$_5$*H*), 7.31–7.48 (9H, m, Ar*H*), 7.50–7.65 (6H, m, Ar*H*). Anal. Calcd for $C_{45}H_{60}N_6BCuF_4P_2$: C, 60.24; H, 6.74; N, 9.37. Found: C, 60.09; H, 6.73; N, 9.33.

**{Tris[2-(1-isopropyl-4-*tert*-butylimidazolyl)]phosphine}carbonylcopper(I) Tetrafluoroborate, $[Cu(Pim^{iPr,tBu})CO]BF_4$ (6-BF$_4$).** A solution of 20 mg (0.028 mmol) of $[Cu(Pim^{iPr,tBu})CH_3CN]BF_4$ (**4-BF$_4$**) in 1 mL of dichloromethane was saturated with carbon monoxide for 5 min. The reaction vessel was tightly stoppered and allowed to stand for 10 min, at which time diethyl ether was layered onto the colorless CH$_2$Cl$_2$ solution. Fine, colorless needles of the desired material appeared after a few hours. The supernatant was decanted, and the crystals were washed with ether. The product was dried under vacuum at 60 °C to give 18 mg (91%) of white powder. $^1$H NMR (CDCl$_3$): $\delta$ 1.43 (27H, s, C(C*H*$_3$)$_3$), 1.51 (18H, d, $J$ = 6.6 Hz, CH(C*H*$_3$)$_2$), 5.20–5.45 (3H, m, C*H*(CH$_3$)$_2$), 6.88 (3H, d, $J$ = 4.3 Hz, imidazolyl C$_5$*H*). IR (CH$_2$Cl$_2$): 3156, 2983, 2939, 2874, 2086 (CO), 1064 cm$^{-1}$ (BF$_4$). Anal. Calcd for $C_{31}H_{51}N_6BCuF_4OP$: C, 52.81; H, 7.29; N, 11.92. Found: C, 52.92; H, 7.30; N, 11.85.

**Bis{tris[2-(1,4-diisopropylimidazolyl)]phosphine}bis($\mu$-hydroxo)dicopper(II) Bis(tetrafluoroborate), $[Cu(Pim^{iPr2})]_2(OH)_2(BF_4)_2$ (7-(BF$_4$)$_2$).** Samples of this compound, independently prepared by oxidative and nonoxidative strategies, gave identical IR spectra.

**Method 1.** In an inert atmosphere box, 50 mg (0.072 mmol) of $[Cu(Pim^{iPr2})CH_3CN]BF_4$ (**3-BF$_4$**) was dissolved in 3 mL of methanol in a test tube. The tube was tightly stoppered with a septum, removed from the glovebox, and cooled to −78 °C. Dioxygen was bubbled into the solution through a syringe needle, causing the colorless solution to turn purple. After 20 min the needle was removed, a drop of water was added to the reaction, and the tube was allowed to stand at room temperature. Once the solution had turned green, the tube was flushed with argon and brought back into the glovebox. The solvent was evaporated to dryness under vacuum. Dichloromethane (1.5 mL) was added to the residue, and the solution was filtered through a plug of glass wool into a vial. Layering tetrahydrofuran (THF) onto the dichloromethane solution produced small blue-green needles of the desired complex after 2 days. Vacuum drying destroyed the crystallinity, leaving 12 mg (23%) of powder.

**Method 2.** In an inert-atmosphere box, 90 mg (0.19 mmol) of Pim$^{iPr2}$ was dissolved in 1 mL of methanol. With stirring, $Cu(BF_4)_2\cdot 5H_2O$ (62 mg, 0.19 mmol) was added, and the solution turned green. After 15 min, powdered NaOH (15 mg, 0.38 mmol) was placed in the flask, causing the reaction mixture to darken considerably. Dichloromethane (1 mL) was added after 1 h to partially dissolve precipitates which had formed, and the solution was filtered and evaporated to dryness under vacuum. The residue was dissolved in the minimal amount of CH$_2$Cl$_2$, and the compound was isolated as blue-green microcrystals by vapor diffusion of THF into the filtered solution. Yield: 47 mg (35%) after drying. IR (KBr): 3586, 3566, 3436 (br, H$_2$O), 3131, 2967, 2934, 2873, 1457, 1184, 1126, 1085 (BF$_4$), 1036 cm$^{-1}$. Anal. Calcd for $C_{54}H_{92}N_{12}B_2Cu_2F_8O_2P_2\cdot 5H_2O$: C, 46.52; H, 7.37; N, 12.06. Found: C, 46.19; H, 6.67; N, 11.69.[13]

**Bis{tris[2-(1,4-diisopropylimidazolyl)]phosphine}($\mu$-carbonato)dicopper(II) Bis(tetrafluoroborate), $[Cu(Pim^{iPr2})]_2CO_3(BF_4)_2$ (8-(BF$_4$)$_2$).** This compound was also independently prepared by oxidative and nonoxidative methods. The products gave identical $^1$H NMR, IR, and electronic absorption spectra.

**Method 1.** A colorless solution of $[Cu(Pim^{iPr2})CH_3CN]BF_4$ (**3-BF$_4$**) (0.50 g, 0.72 mmol) in 5 mL of dichloromethane was exposed to air for 3 d, leaving a deep green solid. The solid was dissolved in methanol, and the solution was filtered. X-ray quality crystals were grown by slow diffusion of THF into the green filtrate. Yield: 0.32 g (63%).

**Method 2.** To a stirred methanolic solution of Pim$^{iPr2}$ (88 mg, 0.18 mmol) was added $Cu(BF_4)_2\cdot 5H_2O$ (58 mg, 0.18 mmol), affording a light green solution. After 15 min, an excess of NaHCO$_3$ was added, causing the color of the mixture to deepen. Filtration and evaporation of the solvent left a green residue, which was dissolved in methanol. The complex was crystallized by slow diffusion of THF–diethyl ether into the methanol solution. Yield: 97 mg (76%). $^1$H NMR (CDCl$_3$): $\delta$ 1.27 (36H, br s, 4-CH(C*H*$_3$)$_2$), 1.51 (36H, d, $J$ = 6.5 Hz, 1-CH(C*H*$_3$)$_2$), 3.04 (6H, br s, 4-C*H*(CH$_3$)$_2$), 5.33 (6H, m, 1-C*H*(CH$_3$)$_2$), 7.07 (6H, s, imidazolyl C$_5$*H*). IR (KBr): 3140, 2969, 2934, 2875, 1595 (CO$_3$), 1435, 1352, 1201, 1057 cm$^{-1}$ (BF$_4$). UV–vis (CH$_2$Cl$_2$): 347 nm ($\epsilon$ 11 000), 665 (290). Anal. Calcd for $C_{55}H_{90}N_{12}B_2Cu_2F_8O_3P_2\cdot C_4H_8O$: C, 50.54; H, 7.04; N, 11.99. Found: C, 50.56; H, 7.17; N, 11.81.

**{Tris[2-(1,4-diisopropylimidazolyl)]phosphine}(acetato)copper(II) Tetrafluoroborate, $[Cu(Pim^{iPr2})OAc]BF_4$ (9-BF$_4$).** To a stirring solution of Pim$^{iPr2}$ (0.10 g, 0.21 mmol) in methanol (5 mL) was added $Cu(BF_4)_2\cdot 5H_2O$ (0.068 g, 0.21 mmol). After 30 min, 3 equiv of sodium acetate was added to the light green solution, and the mixture was stirred for several hours. The suspension was filtered to remove excess salts, and the filtrate was evaporated to dryness. A residue remained, which was dissolved in a small amount of 2-butanone. Crystals suitable for X-ray diffraction studies were grown by slow diffusion of ether into the butanone solution at −20 °C. The yield of green needles was 0.14 g (87%). The crystals rapidly became opaque in air from loss of solvate molecules. IR (KBr): 3136, 2972, 2935, 2874, 1476, 1056 cm$^{-1}$ (BF$_4$). UV–vis (CH$_2$Cl$_2$): 763 nm ($\epsilon$ 130). Anal. Calcd for $C_{29}H_{48}N_6BCuF_4O_2P\cdot 0.5C_4H_8O\cdot H_2O$: C, 49.77; H, 7.28; N, 11.23. Found: C, 49.79; H, 7.09; N, 11.28.

**Low-Temperature Oxygenation of $[Cu(Pim^{iPr2})CH_3CN]BF_4$ (3-BF$_4$).** The putative complex $[Cu(Pim^{iPr2})]_2O_2(BF_4)_2$ (**10-(BF$_4$)$_2$**) was isolated as a thermally unstable solid in the following manner. In a glovebox, 190 mg of **3-BF$_4$** was placed in a test tube. Methanol (1.5 mL) dissolved the complex to give a colorless solution. The tube was tightly sealed with a septum, removed from the inert atmosphere, and cooled in a dewar containing dry ice–acetone. Dioxygen, dried by successive passage through a column of Drierite and a cold trap held at −78 °C, was bubbled directly into the solution through a syringe needle. The methanol solution immediately turned purple. Three h later, the needle was removed and 8 mL of chilled (−78 °C) dioxygen-saturated diethyl ether was poured into the tube all at once, causing a fluffy purple solid to precipitate. The tube was allowed to stand for 2 d at −78 °C, during which time the color of the supernatant was discharged, indicating that precipitation was complete. The solvents were removed with a pipet, and the tube was allowed to warm to −50 °C. Cold, oxygenated dichloromethane was slowly added until the solid just dissolved. After recooling to −78 °C, THF was layered onto the purple solution. Very small crystals formed over several days. Spectroscopic characterization of **10-(BF$_4$)$_2$** was carried out upon samples prepared *in situ* by oxygenating methanol or acetone solutions of **3-BF$_4$**. $^1$H NMR (CD$_3$OD, −43 °C): $\delta$ 1.22 (36H, d, $J$ = 6.0 Hz,

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(13) If dichloromethane is chosen as the solvate instead of water, the experimentally determined C, H, and N values for **7-(BF$_4$)$_2$** all fall within 0.4% of the calculated values (calcd for $C_{54}H_{92}N_{12}B_2Cu_2F_8O_2P_2\cdot 1.5CH_2Cl_2$: C, 46.57; H, 6.69; N, 11.74). This formulation does not account for the broad band in the IR spectrum at 3436 cm$^{-1}$, however. The analytical and IR data do not exclude the possibility that the hydroxide complex is mononuclear, of general formula $[Cu(Pim^{iPr2})OH]BF_4\cdot$solvent. We have not been able to obtain well-resolved $^1$H or $^{31}$P NMR spectra for **7-(BF$_4$)$_2$**.

**Table 1.** Crystallographic Data for $[Cu(Pim^{iPr2})]_2CO_3(BF_4)_2$ (**8-(BF$_4$)$_2$**) and $[Cu(Pim^{iPr2})OAc]BF_4$ (**9-BF$_4$**)

| | **8-(BF$_4$)$_2$** | **9-BF$_4$** |
|---|---|---|
| formula | $C_{59}H_{100}B_2Cu_2$<br>$F_8N_{12}O_5P_2$ | $C_{33}H_{56}BCu$<br>$F_4N_6O_3P$ |
| fw | 1420.15 | 766.16 |
| cryst size, mm | 0.15 × 0.28 × 0.30 | 0.35 × 0.25 × 0.20 |
| cryst system | orthorhombic | monoclinic |
| space group | *Pbca* | $P2_1/n$ |
| $a$, Å | 16.8705(17) | 9.657(3) |
| $b$, Å | 17.4731(14) | 17.001(5) |
| $c$, Å | 51.358(4) | 24.642(6) |
| $\beta$, deg | 90 | 100.987(23) |
| $V$, Å$^3$ | 15139.4(22) | 3971.4(19) |
| Z | 8 | 4 |
| $\varrho_{calc}$, g cm$^{-3}$ | 1.246 | 1.281 |
| $\mu$, mm$^{-1}$ | 1.61 | 0.65 |
| radiation | Cu Kα | Mo Kα |
| $\lambda$, Å | 1.541 84 | 0.710 73 |
| temp, °C | 23 | −160 |
| $R$,[a] $R_w$[b] | 0.088, 0.092 | 0.069, 0.079 |

[a] $R = \sum(F_o - F_c)/\sum F_o$. [b] $R_w = [\sum w(F_o - F_c)^2/\sum(wF_o^2)]^{1/2}$.

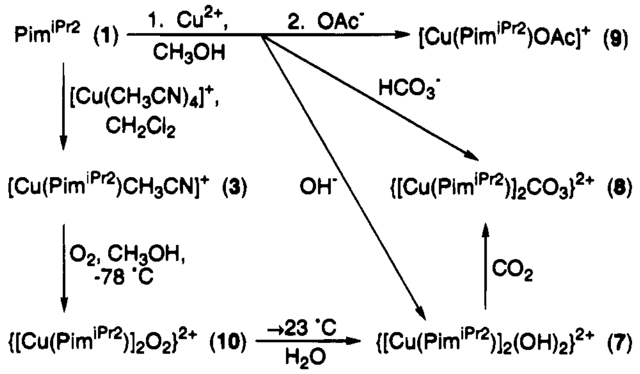
$CH(CH_3)_2$), 1.47 (d, partially obscured by **3-BF$_4$**, $CH(CH_3)_2$), 3.31 (6H, br s, $CH(CH_3)_2$), 5.18 (6H, br s, $CH(CH_3)_2$), 7.46 (6H, d, $J$ = 4.0 Hz, imidazolyl $C_5H$). $^{31}P$ NMR ($CD_3OD$, −78 °C): $\delta$ −120.4. UV−vis ($CH_3OH$, −45 °C): 343 nm ($\epsilon$ 19 500), 549 (790). Resonance Raman ($CH_3OH$, 77 K): 750 cm$^{-1}$ ($\nu$(O−O)). EPR ($CH_3COCH_3$, −45 °C): silent. The thermal instability of the $O_2$ adduct precluded an elemental analysis.

**Crystallographic Structure Determinations.** For both $[Cu(Pim^{iPr2})]CO_3(BF_4)_2$ (**8-(BF$_4$)$_2$**) and $[Cu(Pim^{iPr2})OAc]BF_4$ (**9-BF$_4$**), data collection was carried out using a Rigaku AFC6S diffractometer, with graphite-monochromatized radiation. The $\theta-2\theta$ scan mode was used to record intensities. A stationary count for one-tenth of the scan time at each end of the peak was used to correct for background counts. Peaks were subjected to profile analysis, and any portions of the scan not included in the peak were used to improve background estimates. The structures were refined using full-matrix least-squares techniques. Calculations were performed using the NRCVAX system.[14] No corrections were made for absorption. Crystal data for **8-(BF$_4$)$_2$** and **9-BF$_4$** are summarized in Table 1.

X-ray quality deep green plates of **8-(BF$_4$)$_2$** were grown by vapor diffusion of THF into a methanol solution. A crystal of dimensions 0.15 × 0.28 × 0.30 mm was selected and mounted on the diffractometer, and data collection proceeded at 23 °C using Cu Kα radiation ($\lambda$ = 1.541 84 Å). Unit cell constants were derived from least-squares refinement of 80 reflections in the range $40 < 2\theta < 60°$. Of the 11 254 unique reflections collected, 4758 with $I > 2\sigma(I)$ were used for structure solution and refinement. All non-hydrogen atoms were refined anisotropically, except for the $BF_4$ counterions. The function minimized was $[\sum w(F_o - F_c)^2]^{1/2}$ using unit weights. There are single solvate molecules of tetrahydrofuran and water which are included with 100% occupancy. In the final difference Fourier map, the deepest hole was −0.640 e/Å$^3$, and the highest peak was 1.070 e/Å$^3$.

For **9-BF$_4$**, light green needles suitable for X-ray study were grown by vapor diffusion of diethyl ether into a 2-butanone solution at −20 °C. A crystal of dimensions 0.35 × 0.25 × 0.20 mm was mounted on the diffractometer, and data collection proceeded at −160 °C using Mo Kα radiation ($\lambda$ = 0.710 73 Å). Unit cell constants were derived from least-squares refinement of 54 reflections in the range $30° < 2\theta < 40°$. Of the 5169 unique reflections collected, 2690 with $I > 2.5\sigma(I)$ were used for structure solution and refinement. Only the copper, phosphorus, and fluorine atoms of $BF_4$ were refined anisotropically. The function minimized was $[\sum w(F_o - F_c)^2]^{1/2}$ with weights based on counting statistics. There is a molecule of 2-butanone of solvation which is included with 100% occupancy. In the final difference Fourier map, the deepest hole was −0.580 e/Å$^3$, and the highest peak was 1.330 e/Å$^3$.

**Scheme 1**



## Results and Discussion

**Synthesis.** The copper(I) complexes $[Cu(Pim^{iPr2})CH_3CN]BF_4$ (**3-BF$_4$**) and $[Cu(Pim^{iPr,tBu})CH_3CN]BF_4$ (**4-BF$_4$**) were prepared by stirring the appropriate tris(imidazolyl)phosphine ligand[15] with $[Cu(CH_3CN)_4]BF_4$ followed by precipitation of the respective products with diethyl ether. The triphenylphosphine adduct $[Cu(Pim^{iPr2})PPh_3]BF_4$ (**5-BF$_4$**) was synthesized indirectly by treating a cold, oxygenated methanol solution of $[Cu(Pim^{iPr2})CH_3CN]BF_4$ with $PPh_3$ and allowing the resultant mixture to warm to room temperature, whereupon the desired complex was deposited. The carbonyl complex $[Cu(Pim^{iPr,tBu})CO]BF_4$ (**6-BF$_4$**) was obtained by saturating a dichloromethane solution of $[Cu(Pim^{iPr,tBu})CH_3CN]BF_4$ with CO. All of the copper(I) complexes could be recrystallized from $CH_2Cl_2$−ether, although the acetonitrile adducts were isolated as analytically pure crystalline solids without this step. All of these complexes have simple $^1H$ NMR spectra consistent with $C_{3v}$ symmetry. For $[Cu(Pim^{iPr2})CH_3CN]BF_4$ and $[Cu(Pim^{iPr,tBu})CH_3CN]BF_4$ the appearance of a singlet which integrates for three hydrogen atoms and appears somewhat downfield from uncoordinated acetonitrile is characteristic of the acetonitrile methyl group in copper(I) complexes with a pseudotetrahedral geometry about the Cu(I) ion.[16] Analytical data are also consistent with formulating the complexes as four-coordinate monomers, as we have found no evidence for loss of $CH_3CN$, $PPh_3$, or CO coligands, which presumably would be necessary for dimerization to $[Cu^IL]_2^{2+}$ species.

Preparation of copper(II) complexes can be carried out by several routes, which are outlined in Scheme 1. Oxidative synthesis of the dinuclear complex $[Cu(Pim^{iPr2})]_2(OH)_2(BF_4)_2$ (**7-(BF$_4$)$_2$**) is effected by oxygenating the copper(I) complex $[Cu(Pim^{iPr2})CH_3CN]BF_4$ (**3-BF$_4$**) at low temperature and then allowing the solution to warm in the presence of water. The initial decomposition product is presumed to be a $\mu$-oxo-bridged dimer,[17] which through a rapid reaction with water forms the isolable hydroxide complex. Formation of similar dimers from dioxygen complexes has been observed in other systems, having

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(14) Gabe, E. J.; Le Page, Y.; Charland, J.-P.; Lee, F. L.; White, P. S. *J. Appl. Crystallogr.* **1989**, *22*, 384.

(15) Examples of other tris(imidazolyl)phosphines: (a) Curtis, N. J.; Brown, R. S. *J. Org. Chem.* **1980**, *45*, 4038. (b) Moore, S. S.; Whitesides, G. M. *J. Org. Chem.* **1982**, *47*, 1489. (c) Slebocka-Tilk, H.; Cocho, J. L.; Frakman, Z.; Brown, R. S. *J. Am. Chem. Soc.* **1984**, *106*, 2421. (d) Brown, R. S.; Zamkanei, M.; Cocho, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 5222. (e) Wu, F.-J.; Kurtz, D. M.; Hagen, K. S.; Nyman, P. D.; Debrunner, P. G.; Vankai, V. A. *Inorg. Chem.* **1990**, *29*, 5174.

(16) Kurtz and co-workers have described a structurally characterized monomeric copper(I) complex of tris[2-(1-ethyl-4-isopropylimidazolyl)]phosphine, in which the fourth ligand on Cu(I) is acetonitrile. See refs 7f and 7g.

(17) (a) Kitajima, N.; Koda, T.; Iwata, Y.; Moro-oka, Y. *J. Am. Chem. Soc.* **1990**, *112*, 8833. (b) Sanyal, I.; Mahroof-Tahir, M.; Nasir, M. S.; Ghosh, P.; Cohen, B. I.; Gultneh, Y.; Cruse, R. W.; Farooq, A.; Karlin, K. D.; Liu, S.; Zubieta, J. *Inorg. Chem.* **1992**, *31*, 4322.

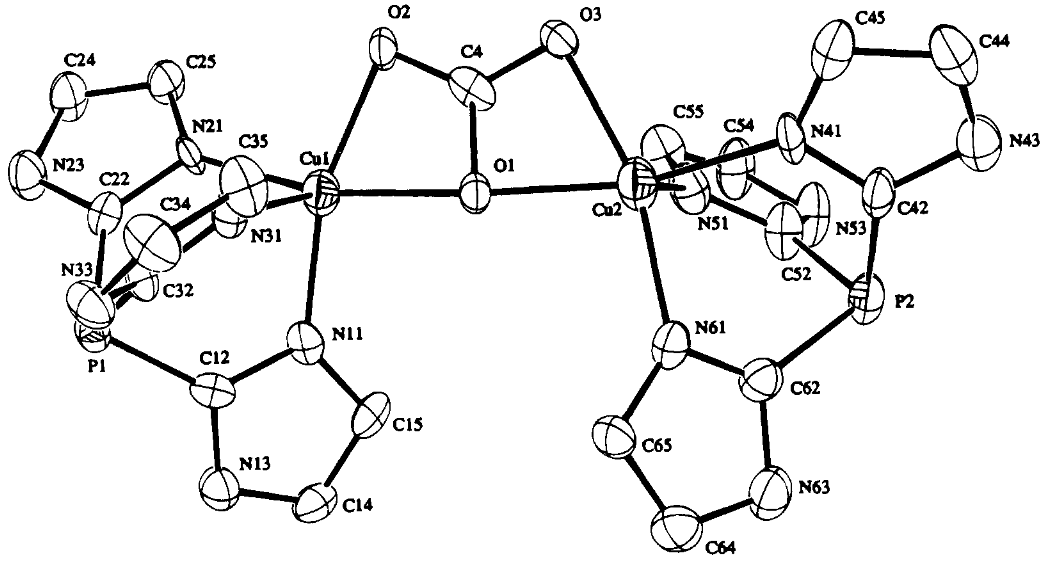

**Figure 1.** ORTEP drawing of $\{[\mathrm{Cu(Pim^{iPr2})}]_2\mathrm{CO_3}\}^{2+}$ (**8**). Thermal ellipsoids are at the 30% probability level. Isopropyl groups on the 1- and 4-positions of the imidazolyl rings have been omitted for clarity.

both pyrazole[6,18] and pyridine[19] ligands. To confirm that fluoride ion abstraction from $\mathrm{BF_4}^-$ was not taking place during the oxidation of **3-BF$_4$**,[20] the hydroxide-bridged complex was also synthesized by a metathesis reaction, in which a solution of $\mathrm{Pim^{iPr2}}$ and $\mathrm{Cu(BF_4)_2{\cdot}5H_2O}$ was treated with NaOH. Complex **7-(BF$_4$)$_2$** is highly efficient in fixing atmospheric carbon dioxide and is therefore handled under an inert atmosphere when in solution.

Synthesis of $[\mathrm{Cu(Pim^{iPr2})}]_2\mathrm{CO_3(BF_4)_2}$ (**8-(BF$_4$)$_2$**) is accomplished in a single step from $[\mathrm{Cu(Pim^{iPr2})CH_3CN}]\mathrm{BF_4}$ (**3-BF$_4$**) or $[\mathrm{Cu(Pim^{iPr2})}]_2\mathrm{(OH)_2(BF_4)_2}$ (**7-(BF$_4$)$_2$**), by removing a solution of either complex from an inert atmosphere and allowing it to stand. The reaction of the hydroxide-bridged dimer with carbon dioxide was followed spectroscopically. A dilute dichloromethane solution of $[\mathrm{Cu(Pim^{iPr2})}]_2\mathrm{(OH)_2(BF_4)_2}$ was sealed under dinitrogen in a cuvette, and its absorption spectrum was recorded ($\lambda_{\max} \approx 640$ nm). The atmosphere above the solution was replaced with $\mathrm{CO_2}$, and the cuvette was gently shaken. Absorption bands attributable to the carbonate complex ($\lambda_{\max}$ = 347, 665 nm) are the only ones observed after approximately 30 min. Nonoxidative syntheses of **8-(BF$_4$)$_2$** and the acetate complex $[\mathrm{Cu(Pim^{iPr2})OAc}]\mathrm{BF_4}$ (**9-BF$_4$**) proceeded in good yields by adding $\mathrm{NaHCO_3}$ and NaOAc, respectively, to methanolic solutions of $\mathrm{Pim^{iPr2}}$ and $\mathrm{Cu(BF_4)_2{\cdot}5H_2O}$. X-ray quality crystals of these compounds were obtained by the vapor diffusion method.

**Table 2.** Selected Bond Distances (Å) and Angles (deg) for $[\mathrm{Cu(Pim^{iPr2})}]_2\mathrm{CO_3(BF_4)_2}$ (**8-(BF$_4$)$_2$**) and $[\mathrm{Cu(Pim^{iPr2})OAc}]\mathrm{BF_4}$ (**9-BF$_4$**)

| | | | |
|---|---|---|---|
| $[\mathrm{Cu(Pim^{iPr2})}]_2\mathrm{CO_3(BF_4)_2}$ (**8-(BF$_4$)$_2$**) | | | |
| Cu(1)−N(11) | 1.973(11) | O(1)−C(4) | 1.310(19) |
| Cu(1)−N(21) | 1.975(9) | O(2)−C(4) | 1.263(17) |
| Cu(1)−N(31) | 2.293(10) | O(3)−C(4) | 1.277(17) |
| Cu(1)−O(1) | 2.013(8) | P(1)−C(12) | 1.802(14) |
| Cu(1)−O(2) | 1.979(9) | P(1)−C(22) | 1.805(15) |
| Cu(2)−N(41) | 1.981(10) | P(1)−C(32) | 1.784(13) |
| Cu(2)−N(51) | 2.322(10) | P(2)−C(42) | 1.789(18) |
| Cu(2)−N(61) | 1.972(12) | P(2)−C(52) | 1.792(14) |
| Cu(2)−O(1) | 2.036(8) | P(2)−C(62) | 1.839(15) |
| Cu(2)−O(3) | 2.011(9) | Cu(1)−Cu(2) | 4.045(8) |
| N(11)−Cu(1)−N(21) | 91.7(4) | N(61)−Cu(2)−O(3) | 161.4(4) |
| N(11)−Cu(1)−N(31) | 93.3(4) | Cu(1)−O(1)−C(4) | 87.7(8) |
| N(21)−Cu(1)−N(31) | 91.3(4) | Cu(1)−O(2)−C(4) | 90.5(8) |
| N(11)−Cu(1)−O(1) | 99.5(4) | O(1)−Cu(1)−O(2) | 66.1(4) |
| N(11)−Cu(1)−O(2) | 161.5(4) | Cu(2)−O(1)−C(4) | 88.2(8) |
| N(21)−Cu(1)−O(1) | 163.2(4) | Cu(2)−O(3)−C(4) | 90.2(9) |
| N(21)−Cu(1)−O(2) | 100.1(4) | O(1)−Cu(2)−O(3) | 65.5(4) |
| N(31)−Cu(1)−O(1) | 100.5(4) | Cu(1)−O(1)−Cu(2) | 175.3(5) |
| N(31)−Cu(1)−O(2) | 100.6(4) | O(1)−C(4)−O(2) | 115.6(12) |
| N(41)−Cu(2)−N(51) | 92.0(5) | O(1)−C(4)−O(3) | 115.6(13) |
| N(41)−Cu(2)−N(61) | 92.9(5) | O(2)−C(4)−O(3) | 128.8(14) |
| N(51)−Cu(2)−N(61) | 92.1(5) | C(12)−P(1)−C(22) | 96.3(6) |
| N(41)−Cu(2)−O(1) | 164.4(5) | C(12)−P(1)−C(32) | 98.1(6) |
| N(41)−Cu(2)−O(3) | 101.0(5) | C(22)−P(1)−C(32) | 99.6(6) |
| N(51)−Cu(2)−O(1) | 97.8(4) | C(42)−P(2)−C(52) | 98.8(7) |
| N(51)−Cu(2)−O(3) | 99.6(4) | C(42)−P(2)−C(62) | 96.4(7) |
| N(61)−Cu(2)−O(1) | 98.8(4) | C(52)−P(2)−C(62) | 99.5(7) |
| $[\mathrm{Cu(Pim^{iPr2})OAc}]\mathrm{BF_4}$ (**9-BF$_4$**) | | | |
| Cu(1)−N(11) | 2.003(8) | O(2)−C(4) | 1.265(12) |
| Cu(1)−N(21) | 2.212(8) | C(3)−C(4) | 1.491(14) |
| Cu(1)−N(31) | 1.990(7) | P(1)−C(12) | 1.835(10) |
| Cu(1)−O(1) | 2.034(6) | P(1)−C(22) | 1.815(10) |
| Cu(1)−O(2) | 2.021(6) | P(1)−C(32) | 1.808(9) |
| O(1)−C(4) | 1.304(13) | | |
| N(11)−Cu(1)−N(21) | 91.8(3) | Cu(1)−O(1)−C(4) | 87.3(5) |
| N(11)−Cu(1)−N(31) | 92.1(3) | Cu(1)−O(2)−C(4) | 88.9(6) |
| N(21)−Cu(1)−N(31) | 92.6(3) | O(1)−Cu(1)−O(2) | 65.8(3) |
| N(11)−Cu(1)−O(1) | 99.1(3) | O(1)−C(4)−O(2) | 118.0(8) |
| N(11)−Cu(1)−O(2) | 162.5(3) | O(1)−C(4)−C(3) | 120.1(9) |
| N(21)−Cu(1)−O(1) | 103.8(3) | O(2)−C(4)−C(3) | 121.9(9) |
| N(21)−Cu(1)−O(2) | 100.2(3) | C(12)−P(1)−C(22) | 98.9(4) |
| N(31)−Cu(1)−O(1) | 159.7(3) | C(12)−P(1)−C(32) | 96.3(4) |
| N(31)−Cu(1)−O(2) | 100.0(3) | C(22)−P(1)−C(32) | 97.3(4) |

**Molecular Structure of $[\mathrm{Cu(Pim^{iPr2})}]_2\mathrm{CO_3(BF_4)_2}$ (8-(BF$_4$)$_2$).** Thin plates of this complex crystallize from methanol−THF in the orthorhombic space group *Pbca*. The solid-state structure of $\{[\mathrm{Cu(Pim^{iPr2})}]_2\mathrm{CO_3}\}^{2+}$ (**8**) is presented in Figure 1, and important bond distances and angles are given at the top of Table 2. Final positional parameters for significant atoms can be found in Table 3. Each $\mathrm{Pim^{iPr2}}$ ligand provides three nitrogen atoms to a single copper ion, with the carbonate moiety bridging the metals in a symmetrical bis(bidentate) fashion, completing the $\mathrm{N_3O_2}$ donor set. While this mode of carbonate binding is also found in $[\mathrm{Cu(Tp^{iPr2})}]_2\mathrm{CO_3}$,[21] it is unlike that found in

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(18) (a) Sorrell, T. N.; Jameson, D. L.; Malachowski, M. R. *Inorg. Chem.* **1982**, *21*, 3250. (b) 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.

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

(20) Lee, S. C.; Holm, R. H. *Inorg. Chem.* **1993**, *32*, 4745.

**Table 3.** Atomic Positional Parameters for $[Cu(Pim^{iPr2})]_2CO_3(BF_4)_2$ (**8-BF$_4$)$_2$**)

| | $x$ | $y$ | $z$ | $B_{iso}$,[a] Å$^2$ | | $x$ | $y$ | $z$ | $B_{iso}$,[a] Å$^2$ |
|---|---|---|---|---|---|---|---|---|---|
| Cu(1) | 0.06950(12) | 0.22183(10) | 0.08647(3) | 3.61(8) | C(45) | 0.2020(11) | 0.0298(8) | 0.1931(3) | 4.8(9) |
| Cu(2) | 0.08486(14) | 0.09734(11) | 0.15267(3) | 4.16(9) | C(46) | 0.0784(12) | −0.0946(10) | 0.2347(3) | 7.2(10) |
| P(1) | 0.01383(24) | 0.39405(20) | 0.06391(7) | 4.03(18) | C(47) | 0.0970(19) | −0.0740(18) | 0.2610(4) | 15.7(21) |
| P(2) | −0.0291(3) | −0.01284(22) | 0.19097(7) | 5.01(21) | C(48) | 0.0992(15) | −0.1735(13) | 0.2277(5) | 11.5(16) |
| O(1) | 0.0747(6) | 0.1634(5) | 0.12019(15) | 3.8(4) | C(49) | 0.2728(11) | 0.0690(9) | 0.1831(3) | 5.3(9) |
| O(2) | 0.1626(6) | 0.1535(5) | 0.08934(16) | 4.2(4) | C(50) | 0.2682(12) | 0.1536(10) | 0.1875(3) | 7.2(11) |
| O(3) | 0.1777(6) | 0.0909(5) | 0.12823(17) | 4.5(5) | C(51) | 0.3483(13) | 0.0351(11) | 0.1942(4) | 8.4(12) |
| C(4) | 0.1418(9) | 0.1342(7) | 0.1120(3) | 3.8(7) | N(51) | 0.0120(8) | −0.0070(6) | 0.13811(22) | 5.0(7) |
| N(11) | −0.0399(7) | 0.2612(5) | 0.08881(19) | 3.7(6) | C(52) | −0.0238(11) | −0.0440(8) | 0.1578(3) | 5.4(8) |
| C(12) | −0.0552(8) | 0.3313(8) | 0.0801(3) | 3.7(7) | N(53) | −0.0544(9) | −0.1113(7) | 0.14906(23) | 6.4(7) |
| N(13) | −0.1310(8) | 0.3493(7) | 0.08403(21) | 4.4(6) | C(54) | −0.0407(12) | −0.1157(10) | 0.1227(3) | 6.3(10) |
| C(14) | −0.1674(9) | 0.2870(9) | 0.0951(3) | 4.8(8) | C(55) | 0.0011(11) | −0.0526(9) | 0.1162(3) | 5.4(9) |
| C(15) | −0.1119(10) | 0.2315(9) | 0.09873(21) | 4.1(7) | C(56) | −0.0966(15) | −0.1688(11) | 0.1647(3) | 7.8(12) |
| C(16) | −0.1723(11) | 0.4228(9) | 0.0791(3) | 6.2(9) | C(57) | −0.1815(14) | −0.1716(15) | 0.1573(4) | 10.8(15) |
| C(17) | −0.2342(18) | 0.4129(14) | 0.0599(5) | 13.6(18) | C(58) | −0.0585(19) | −0.2456(11) | 0.1629(5) | 13.3(20) |
| C(18) | −0.1905(19) | 0.4627(13) | 0.1021(5) | 14.9(22) | C(59) | 0.0324(12) | −0.0309(10) | 0.0901(3) | 5.9(9) |
| C(19) | −0.1183(10) | 0.1510(9) | 0.1070(3) | 5.5(9) | C(60) | 0.1181(13) | −0.0449(11) | 0.0874(3) | 7.9(12) |
| C(20) | −0.1866(12) | 0.1410(10) | 0.1262(3) | 7.0(10) | C(61) | −0.0131(14) | −0.0726(10) | 0.0683(3) | 8.7(12) |
| C(21) | −0.1313(12) | 0.0980(10) | 0.0845(4) | 7.9(11) | N(61) | −0.0061(7) | 0.1379(7) | 0.17246(20) | 4.5(6) |
| N(21) | 0.0770(7) | 0.2509(5) | 0.04939(18) | 3.3(5) | C(62) | −0.0491(9) | 0.0894(8) | 0.1857(3) | 4.3(7) |
| C(22) | 0.0551(9) | 0.3226(7) | 0.04245(24) | 4.1(7) | N(63) | −0.1132(9) | 0.1245(7) | 0.19707(22) | 5.5(7) |
| N(23) | 0.0652(8) | 0.3323(6) | 0.01657(20) | 5.0(6) | C(64) | −0.1069(10) | 0.2011(9) | 0.1900(3) | 5.3(8) |
| C(24) | 0.0937(11) | 0.2643(8) | 0.00644(24) | 5.9(9) | C(65) | −0.0416(10) | 0.2098(8) | 0.1752(3) | 4.7(8) |
| C(25) | 0.1012(9) | 0.2131(8) | 0.02667(24) | 4.4(7) | C(66) | −0.1766(13) | 0.0892(11) | 0.2117(4) | 7.5(11) |
| C(26) | 0.0476(12) | 0.4014(9) | 0.0013(3) | 6.2(10) | C(67) | −0.1946(19) | 0.1314(15) | 0.2355(5) | 16.1(22) |
| C(27) | −0.0168(16) | 0.3848(11) | −0.0183(4) | 10.4(15) | C(68) | −0.2471(18) | 0.0762(21) | 0.1961(5) | 16.7(24) |
| C(28) | 0.1203(16) | 0.4335(10) | −0.0098(4) | 9.9(14) | C(69) | −0.0034(12) | 0.2818(9) | 0.1648(3) | 6.1(9) |
| C(29) | 0.1271(14) | 0.1306(8) | 0.0269(3) | 6.3(10) | C(70) | −0.0643(13) | 0.3441(10) | 0.1612(4) | 8.1(12) |
| C(30) | 0.0699(20) | 0.0840(13) | 0.0153(10) | 23.1(38) | C(71) | 0.0648(13) | 0.3078(10) | 0.1818(4) | 8.5(12) |
| C(31) | 0.1948(21) | 0.1191(14) | 0.0118(10) | 27.5(39) | B(1) | 0.8284(6) | 0.8369(5) | 0.23930(17) | 18.1(3) |
| N(31) | 0.1244(7) | 0.3361(6) | 0.09906(19) | 3.9(6) | F(11) | 0.9048(6) | 0.8115(8) | 0.2320(3) | 18.1(3) |
| C(32) | 0.0887(8) | 0.3956(7) | 0.08841(24) | 3.5(6) | F(12) | 0.8062(8) | 0.8016(8) | 0.26297(21) | 18.1(3) |
| N(33) | 0.1176(7) | 0.4612(6) | 0.09898(23) | 4.5(6) | F(13) | 0.7734(8) | 0.8172(8) | 0.21965(24) | 18.1(3) |
| C(34) | 0.1767(10) | 0.4405(8) | 0.1159(3) | 5.2(8) | F(14) | 0.8293(9) | 0.9172(5) | 0.2426(3) | 18.1(3) |
| C(35) | 0.1786(10) | 0.3621(8) | 0.1167(3) | 4.7(8) | B(2) | 0.6107(5) | 0.2044(5) | 0.07641(16) | 16.5(3) |
| C(36) | 0.0930(12) | 0.5402(8) | 0.0929(4) | 6.8(10) | F(21) | 0.5277(5) | 0.2150(8) | 0.0776(3) | 16.5(3) |
| C(37) | 0.0715(17) | 0.5814(10) | 0.1174(4) | 12.0(16) | F(22) | 0.6282(8) | 0.1253(5) | 0.0773(3) | 16.5(3) |
| C(38) | 0.1502(14) | 0.5805(12) | 0.0771(5) | 10.7(14) | F(23) | 0.6400(8) | 0.2357(7) | 0.05292(19) | 16.5(3) |
| C(39) | 0.2313(11) | 0.3117(8) | 0.1325(3) | 5.6(8) | F(24) | 0.6469(8) | 0.2417(7) | 0.09777(21) | 16.5(3) |
| C(40) | 0.2725(13) | 0.3568(9) | 0.1546(4) | 8.7(11) | O(81) | 0.860(3) | 0.230(3) | 0.0192(9) | 33.3(19) |
| C(41) | 0.2934(11) | 0.2711(11) | 0.1165(4) | 8.0(12) | C(82) | 0.837(4) | 0.157(5) | 0.0097(15) | 30.3(28) |
| N(41) | 0.1257(8) | 0.0393(6) | 0.18297(19) | 4.1(6) | C(83) | 0.823(4) | 0.135(4) | −0.0148(17) | 30.1(27) |
| C(42) | 0.0747(10) | −0.0028(8) | 0.19729(25) | 4.6(8) | C(84) | 0.788(4) | 0.171(5) | −0.0426(14) | 40.9(38) |
| N(43) | 0.1154(10) | −0.0406(7) | 0.21582(23) | 5.3(7) | C(85) | 0.856(4) | 0.219(4) | −0.0166(15) | 30.6(25) |
| C(44) | 0.1923(13) | −0.0209(9) | 0.2132(3) | 5.8(9) | Ow(1) | 0.9422(16) | 0.6521(15) | 0.2536(5) | 23.1(10) |

[a] $B_{iso}$ is the mean of the principal axes of the thermal ellipsoid.

$[Cu(TMPA)]_2CO_3(ClO_4)_2$,[22] in which $CO_3^{2-}$ bridges the copper(II) ions in a μ-O,O′ fashion. The use of tetradentate ligands like tris[(2-pyridyl)methyl]amine (TMPA) or tripodal ligands such as tris[1-(3-*tert*-butylpyrazolyl)]hydroborate[23] forces the carbonate ion to coordinate to each metal center in a unidentate manner.

Bond distances from the metal ions to the equatorial ligand atoms of **8** are all close to the expected 2.0 Å, and the distances to the axial imidazole nitrogen atoms are approximately 0.3 Å longer. Because these apical nitrogens lie away from the perpendicular to the basal planes defined by O(1)−O(2)−N(11)−N(21) and O(1)−O(3)−N(41)−N(61), the environments about copper deviate from ideal square pyramids. The Cu(1)−O(1)−Cu(2) angle is 175.3(5)°,[24] and the Cu(1)−Cu(2) distance is 4.045(8) Å. For comparison, the Cu(1)−O(1)−Cu(2) angle of $[Cu(Tp^{iPr2})]_2CO_3$ is 175.7(2)°, and the Cu(1)−Cu(2) distance is 4.044(2) Å.[21] The only significant differences in the coordination spheres of $\{[Cu(Pim^{iPr2})]_2CO_3\}^{2+}$ and $[Cu(Tp^{iPr2})]_2CO_3$ are found in the distances to the axial heterocyclic donors, which are less elongated in the tris(pyrazolyl)hydroborate complex. This effect is not unexpected in view of the smaller "bite" of $Tp^{iPr2}$ (i.e. P−C$_{im}$ ≈ 1.8 Å; B−N$_{pz}$ ≈ 1.55 Å).

**Molecular Structure of $[Cu(Pim^{iPr2})OAc]BF_4$ (9-BF$_4$).** Needles grown from 2-butanone−diethyl ether form in the monoclinic space group $P2_1/n$. The structure of the cation $[Cu(Pim^{iPr2})OAc]^+$ (**9**) is shown in Figure 2, with significant bond distances and angles summarized at the bottom of Table 2. Final positional parameters for selected atoms of this complex are listed in Table 4. The square pyramidal geometry about copper is very similar to that determined for $\{[Cu(Pim^{iPr2})]_2CO_3\}^{2+}$ (**8**). Bond distances and angles are unexceptional for this coordination mode, as can be seen by comparison with a copper(II)−benzoato complex of $Tp^{iPr2}$.[25]

**Dioxygen Reactivity.** Colorless methanol, acetone, and dichloromethane solutions of $[Cu(Pim^{iPr2})CH_3CN]BF_4$ (**3-BF$_4$**) react rapidly with dioxygen at room temperature, turning green

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[21] Kitajima, N.; Hikichi, S.; Tanaka, M.; Moro-oka, Y. *J. Am. Chem. Soc.* **1993**, *115*, 5496.

[22] Tyeklár, Z.; Paul, P. P.; Jacobson, R. R.; Farooq, A.; Karlin, K. D.; Zubieta, J. *J. Am. Chem. Soc.* **1989**, *111*, 388.

[23] Han, R.; Looney, A.; McNeill, K.; Parkin, G.; Rheingold, A. L.; Haggerty, B. S. *J. Inorg. Biochem.* **1993**, *49*, 105.

[24] Preliminary magnetic measurements show strong antiferromagnetic coupling between the Cu(II) ions of $[Cu(Pim^{iPr2})]_2CO_3(BF_4)_2$ (**8-(BF$_4$)$_2$**), mediated by the nearly linear Cu−O−Cu array.

[25] Kitajima, N.; Fujisawa, K.; Moro-oka, Y. *Inorg. Chem.* **1990**, *29*, 357.

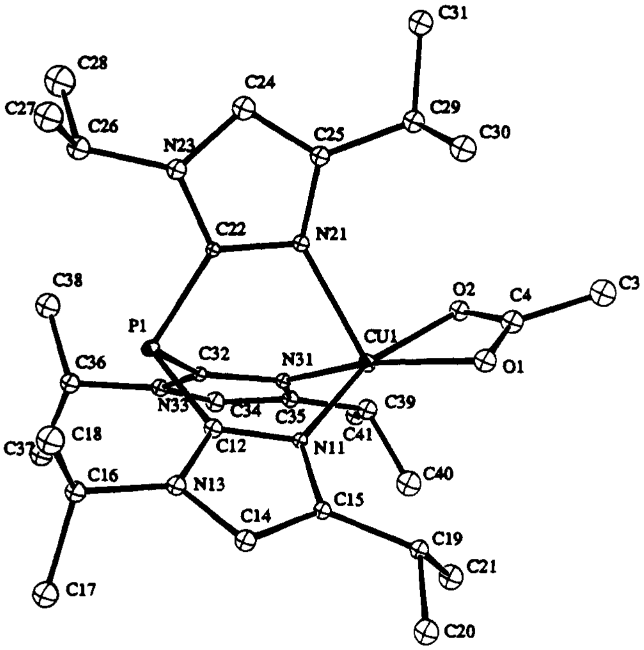

**Figure 2.** ORTEP drawing of $[Cu(Pim^{iPr2})OAc]^+$ (**9**). Thermal ellipsoids are at the 30% probability level.

within seconds after being exposed to air. Treatment of methanol or acetone solutions of **3-BF$_4$** with dioxygen at $<-40$ °C, however, causes an intensely violet-colored species (**10-(BF$_4$)$_2$**) to form, which is stable for at least 5 days at −78 °C. Vigorously bubbling argon through the cold violet-colored solutions for ≈ 2 h regenerates the colorless copper(I) complex **3-BF$_4$**, if the reaction vessels are occasionally and briefly removed from the cooling source. Using a similar [tris(imidazolyl)phosphine]copper(I) complex, Kurtz *et al.* have also demonstrated facile removal of bound dioxygen.[7f,g] The diamagnetic nature of dioxygen adduct **10-(BF$_4$)$_2$** is inferred from its variable-temperature $^1H$ and $^{31}P$ NMR spectra, which consist of sharp peaks, and from its EPR silence. During the course of low-temperature NMR experiments, using $CD_3OD$ or $CD_3COCD_3$ solutions that were $>0.02$ M in **3-BF$_4$**, we found that *even after up to 8 h of oxygenation at −78 °C, approximately one-half of the* $[Cu(Pim^{iPr2})CH_3CN]BF_4$ *remains uncomplexed to* $O_2$ (Figures 3 and 4). This result is corroborated by manometric gas uptake measurements, wherein less than 1 mol of $O_2$ is consumed for every 2 mol of **3-BF$_4$**. Lowering the temperature of the NMR samples to −93 °C shifts the equilibrium to the right, as would be expected for an entropically-driven process, but even at this temperature about 45% of **3-BF$_4$** is unreacted in methanol. Whether this equilibrium affects the accuracy of extinction coefficients is difficult to assess, because the analyte concentrations typically used in NMR and UV−vis experiments differ by several orders of magnitude. The relatively higher concentration of dissolved dioxygen in samples used for electronic absorption measurements would tend to favor formation of **10-(BF$_4$)$_2$**, however.

**Table 4.** Atomic Positional Parameters for $[Cu(Pim^{iPr2})OAc]BF_4$ (**9-BF$_4$**)

| | $x$ | $y$ | $z$ | $B_{iso}$,[a] Å$^2$ |
|---|---|---|---|---|
| Cu(1) | 0.07582(14) | 0.22678(7) | 0.04360(5) | 0.97(5) |
| P(1) | 0.0393(3) | 0.15053(15) | 0.16700(10) | 0.88(12) |
| O(1) | 0.1306(7) | 0.1992(4) | −0.0298(3) | 1.56(14) |
| O(2) | 0.1744(7) | 0.3145(4) | 0.0106(3) | 1.30(14) |
| C(3) | 0.2602(13) | 0.2942(6) | −0.0740(4) | 2.29(24) |
| C(4) | 0.1856(11) | 0.2694(6) | −0.0291(4) | 1.63(21) |
| N(11) | −0.0432(8) | 0.1327(4) | 0.0518(3) | 0.67(15) |
| C(12) | −0.0476(11) | 0.1055(6) | 0.1016(4) | 1.02(20) |
| N(13) | −0.1241(9) | 0.0391(4) | 0.0986(3) | 1.07(16) |
| C(14) | −0.1740(11) | 0.0237(6) | 0.0441(4) | 1.26(20) |
| C(15) | −0.1233(11) | 0.0810(5) | 0.0154(4) | 0.88(19) |
| C(16) | −0.1518(11) | −0.0095(6) | 0.1464(4) | 1.20(20) |
| C(17) | −0.3060(12) | −0.0326(6) | 0.1361(4) | 1.80(22) |
| C(18) | −0.0569(12) | −0.0803(6) | 0.1569(4) | 2.04(23) |
| C(19) | −0.1513(11) | 0.0943(6) | −0.0474(4) | 1.05(20) |
| C(20) | −0.2437(12) | 0.0290(6) | −0.0764(4) | 1.76(22) |
| C(21) | −0.2146(12) | 0.1741(6) | −0.0651(4) | 1.87(22) |
| N(21) | 0.2531(9) | 0.1810(4) | 0.1059(3) | 0.85(15) |
| C(22) | 0.2171(10) | 0.1575(5) | 0.1534(4) | 0.62(18) |
| N(23) | 0.3334(9) | 0.1405(5) | 0.1913(3) | 1.21(16) |
| C(24) | 0.4495(12) | 0.1536(6) | 0.1675(4) | 1.63(21) |
| C(25) | 0.3974(11) | 0.1783(6) | 0.1151(4) | 1.15(20) |
| C(26) | 0.3374(11) | 0.1112(6) | 0.2496(4) | 1.63(22) |
| C(27) | 0.3881(13) | 0.0267(6) | 0.2540(5) | 2.43(24) |
| C(28) | 0.4294(14) | 0.1650(7) | 0.2906(5) | 3.1(3) |
| C(29) | 0.4800(11) | 0.1989(6) | 0.0705(4) | 1.48(21) |
| C(30) | 0.4608(12) | 0.1341(6) | 0.0258(4) | 1.90(22) |
| C(31) | 0.6350(12) | 0.2133(6) | 0.0923(4) | 1.89(22) |
| N(31) | −0.0032(8) | 0.2870(4) | 0.0999(3) | 0.75(15) |
| C(32) | −0.0142(11) | 0.2505(5) | 0.1485(4) | 0.67(19) |
| N(33) | −0.0700(9) | 0.3009(4) | 0.1805(3) | 1.02(16) |
| C(34) | −0.0946(11) | 0.3716(6) | 0.1530(4) | 1.42(21) |
| C(35) | −0.0550(11) | 0.3622(6) | 0.1026(4) | 1.00(20) |
| C(36) | −0.0936(11) | 0.2832(6) | 0.2377(4) | 1.35(20) |
| C(37) | −0.2394(12) | 0.3094(6) | 0.2446(4) | 1.91(22) |
| C(38) | 0.0200(13) | 0.3175(6) | 0.2809(4) | 2.22(23) |
| C(39) | −0.0597(12) | 0.4201(6) | 0.0571(4) | 1.51(22) |
| C(40) | −0.1624(13) | 0.3926(6) | 0.0062(5) | 2.31(24) |
| C(41) | −0.1010(11) | 0.5018(6) | 0.0739(4) | 1.46(21) |
| B(1) | 0.6756(15) | 0.5742(8) | 0.2148(5) | 1.8(3) |
| F(1) | 0.7480(6) | 0.6059(3) | 0.26456(22) | 2.0(3) |
| F(2) | 0.5648(9) | 0.5306(5) | 0.2217(3) | 6.0(5) |
| F(3) | 0.6298(11) | 0.6340(5) | 0.1790(3) | 6.5(5) |
| F(4) | 0.7636(9) | 0.5287(5) | 0.1906(4) | 7.9(5) |
| C(51) | 0.3218(14) | 0.3666(7) | 0.1905(5) | 3.2(3) |
| C(52) | 0.3909(16) | 0.3920(8) | 0.1427(6) | 4.6(3) |
| C(53) | 0.3550(17) | 0.4677(8) | 0.1203(6) | 4.6(3) |
| O(54) | 0.2623(10) | 0.5044(5) | 0.1307(4) | 4.75(22) |
| C(55) | 0.4544(20) | 0.4983(10) | 0.0816(7) | 7.3(5) |

[a] $B_{iso}$ is the mean of the principal axes of the thermal ellipsoid.

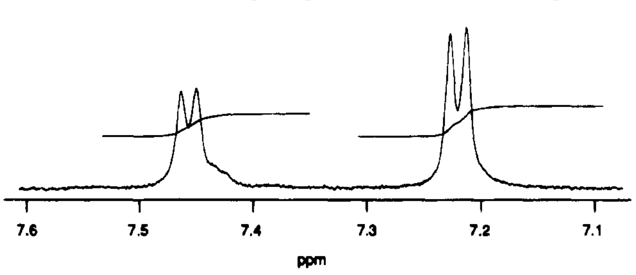

**Figure 3.** Imidazolyl $C_5H$ region of the $^1H$ NMR spectrum of **3-BF$_4$** ($CD_3OD$, −43 °C) after 8 h of oxygenation at −78 °C. The doublet at 7.46 ppm is assigned to **10-(BF$_4$)$_2$**. The initial concentration of **3-BF$_4$** was 0.025 M.

Because $\{[Cu(Pim^{iPr2})]_2O_2\}^{2+}$ (**10**) is cationic and thus conceivably more electrophilic than the analogous tris(pyrazolyl)hydroborate-ligated system, we believed that **10-(BF$_4$)$_2$** might prove to be an effective oxidant toward substrates such as olefins and triphenylphosphine, which are *not* oxidized by $[Cu(Tp^{Me2})]_2O_2$ under anaerobic conditions.[17a] To determine whether the electron density at copper (and by extension of the bound peroxide) is lower for complexes of $Pim^{iPr2}$ relative to $Tp^{iPr2}$, the labile carbonyl adduct $[Cu(Pim^{iPr2})CO]^+$ (**11**) was prepared by saturating a dichloromethane solution of $[Cu(Pim^{iPr2})CH_3CN]BF_4$ with CO, and its $\nu$(CO) was observed at 2083 cm$^{-1}$. The value of $\nu$(CO) for copper(I)−carbonyl complexes is known to vary with the amount of back-bonding into $\pi^*$ orbitals of CO; hence the measurement of this stretching frequency is a rough probe of electron density at the metal ion. In comparison with $Cu(Tp^{iPr2})CO$, which has $\nu$(CO) = 2056 cm$^{-1}$,[4b] the cuprous ion of **11** *is* relatively electron deficient.

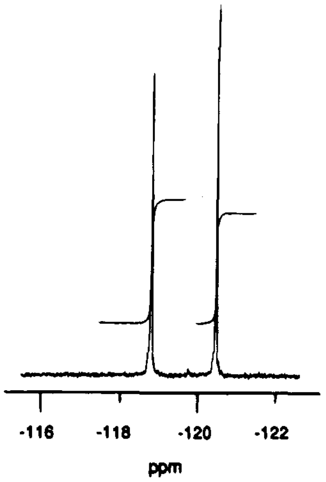

**Figure 4.** $^{31}P$ NMR spectrum of **3-BF$_4$** ($CD_3OD$, −78 °C) after 3 h of oxygenation at −78 °C. The singlet at −120.4 ppm is assigned to **10-(BF$_4$)$_2$**. The initial concentration of **3-BF$_4$** was 0.052 M.

The reaction of the peroxide complex with 1-hexene and $PPh_3$ was therefore explored by replacing the atmosphere above the violet-colored methanol solutions of **10-(BF$_4$)$_2$** (prepared by oxygenating 0.03 M solutions of $[Cu(Pim^{iPr2})CH_3CN]BF_4$ for 20 min) with argon and introducing a slight excess of these reagents. After 3 h at −78 °C, neither of the reaction mixtures showed a discernible loss of color.[26] The sample containing 1-hexene was warmed to room temperature, and no 1-hexene oxide or allylic oxidation products were detected by $^1H$ NMR. The reaction mixture containing triphenylphosphine turned light green after 5−10 min at −40 °C, and then was allowed to further warm to 23 °C, during which time a white solid precipitated. Analysis of the white solid and light green supernatant by $^1H$ NMR and IR spectroscopy showed no $O{=}PPh_3$ to be present. Thus, the oxo-transfer capability of $[Cu(II)L]_2O_2^{n+}$ species does not appear to improve when neutral ligands with imidazolyl N-donors are used in place of tris(pyrazolyl)hydroborates.[27]

The more highly hindered complex $[Cu(Pim^{iPr,tBu})CH_3CN]BF_4$ (**4-BF$_4$**) is inert to dioxygen in methanol or dichloromethane. Bubbling $O_2$ directly into colorless solutions of the material for several minutes causes no visible color change, and solutions allowed to stand in air for 1 week become only very faintly yellow. The lack of reactivity toward dioxygen cannot be wholly ascribed to steric blocking of the metal center, because this complex readily forms an isolable carbonyl adduct, $[Cu(Pim^{iPr,tBu})CO]BF_4$ (**6-BF$_4$**), distinguished by $\nu(CO) = 2086$ cm$^{-1}$. The redox potential of **4-BF$_4$** was determined by cyclic voltammetry, to assess if its $E_{1/2}$ is sufficiently high as to make its oxidation by dioxygen unfavorable. The scans were carried out upon acetonitrile solutions of **4-BF$_4$** containing 0.10 M tetrabutylammonium tetrafluoroborate as the supporting electrolyte. At a scan rate of 200 mV/s, a quasi-reversible process takes place with $E_{1/2}$ at +1.08 V vs Ag/AgCl. The peak separation is 170 mV, and does not decrease with slower scan rates. The complex $[Cu(Pim^{iPr2})CH_3CN]BF_4$ (**3-BF$_4$**) did not give reproducible scans, but a *less* positive $E_{1/2}$ is indicated by its rapid reaction with dioxygen in solution. The trend of increasing $E_{1/2}$ with increasing steric bulk near copper(I) is well established for complexes of tris[2-(1-pyrazolyl)ethyl]amines[28] and poly(pyridylmethyl)- and (quinolylmethyl)amines.[29] By analogy to those systems, the high potential assigned to the $[Cu(Pim^{iPr,tBu})CH_3CN]^+/[Cu(Pim^{iPr,tBu})CH_3CN]^{2+}$ couple is believed to arise in part from stabilization of the lower-charged Cu(I) valence by the hydrophobic pocket created by the *tert*-butyl groups of $Pim^{iPr,tBu}$. Also, an examination of space-filling models shows that the *tert*-butyl groups prevent approach of a fifth ligand such as $CH_3CN$ to the copper ion, preventing it from becoming 5-coordinate upon oxidation. Since copper(II) tends to adopt a square-pyramidal ligand environment when bound to rigid tridentate ligands, this effect would inhibit formation of Cu(II).

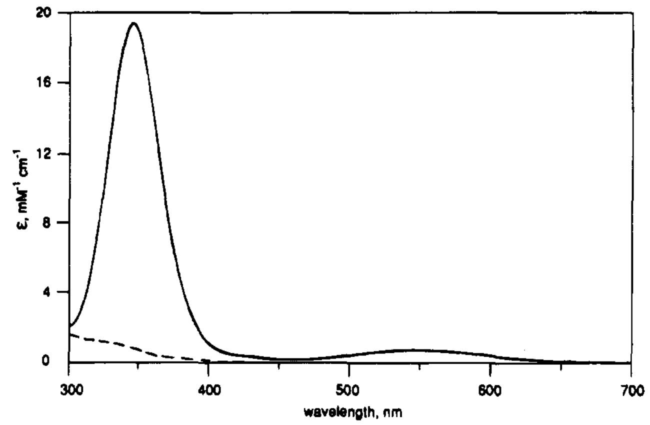

**Figure 5.** Electronic absorption spectra of **3-BF$_4$** ($CH_3OH$, −45 °C) before (− − −) and after (—) oxygenation at −45 °C. The initial concentration of **3-BF$_4$** was $5.04 \times 10^{-5}$ M.

**Spectroscopy.** The absorption spectrum of the dioxygen adduct **10-(BF$_4$)$_2$** (Figure 5) has maxima at 343 nm ($\epsilon$ = 19 500) and 549 nm ($\epsilon$ = 790). The positions and intensities of the bands are analogous to those observed for oxyhemocyanin [$\lambda_{max} \approx 340$ nm ($\epsilon$ = 20 000), ≈ 570 nm ($\epsilon$ = 1000)] and the $\mu$-$\eta^2$:$\eta^2$ peroxo−dicopper(II) complex of $Tp^{iPr2}$ [$\lambda_{max}$ = 349 nm ($\epsilon$ = 21 000), 551 nm ($\epsilon$ = 790)] characterized by Kitajima and co-workers.[4] The broad peak centered about 549 nm is assigned to $O_2^{2-} \rightarrow Cu(II)$ LMCT, because its large extinction coefficient precludes its arising from d−d transitions and because the other copper(II) complexes reported here show no analogous absorptions. The high-energy band cannot be definitively attributed to peroxide → copper(II) charge transfer, since the complex $[Cu(Pim^{iPr2})]_2CO_3(BF_4)_2$ (**8-(BF$_4$)$_2$**) reported herein displays a relatively intense absorbance at approximately the same energy. More copper(II) complexes of tris(imidazolyl)phosphine ligands will have to be examined before this feature of the dioxygen adduct can be assigned unambiguously.

At an excitation wavelength of 514.5 nm, the resonance Raman spectrum of the dioxygen adduct **10-(BF$_4$)$_2$** at 77 K shows an enhancement at 750 cm$^{-1}$, which is not found in the spectrum of $[Cu(Pim^{iPr2})CH_3CN]BF_4$ (**3-BF$_4$**). This peak disappears when the violet-colored sample is allowed to warm until it turns green. The green decomposition product also lacks any bands near 750 cm$^{-1}$ when the excitation wavelength is changed to 647.1 nm. In complexes known to have a $Cu_2O_2$ chromophore, peaks appearing at 740−760 cm$^{-1}$ have been shown by isotopic substitution experiments to arise from O−O stretching,[4,7g] and calculations by Solomon have led to the proposal that $\nu$(O−O) frequencies in this region are characteristic of planar $\mu$-$\eta^2$:$\eta^2$ binding of dioxygen.[30] This value for $\nu$(O−O) is significantly lower than that found for a structurally

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(26) Under similar conditions, **10-(BF$_4$)$_2$** was also inert to $HBF_4$ and $CO_2$.

(27) It cannot be ruled out that the lack of oxo-transfer activity of **10-(BF$_4$)$_2$** results from steric effects, whereby the 4-isopropyl groups create a "cage" around the bound peroxide ion, making it inaccessible to substrates.

(28) Sorrell, T. N.; Jameson, D. L. *Inorg. Chem.* **1982**, *21*, 1014.

(29) Wei, N.; Murthy, N. N.; Chen, Q.; Zubieta, J.; Karlin, K. D. *Inorg. Chem.* **1994**, *33*, 1953.

(30) Solomon, E. I.; Baldwin, M. J.; Lowery, M. D. *Chem. Rev.* **1992**, *92*, 521.

characterized dicopper(II) complex in which $O_2$ bridges the metal centers in a *trans*-$\mu$-1,2 fashion.[31]

## Summary and Conclusions

A neutral tris(imidazolyl) ligand, Pim$^{iPr2}$, designed to be a mimic for histidinyl coordination in hemocyanin, has been incorporated into a copper(I) complex that binds dioxygen at low temperature. The peroxo–dicopper(II) adduct has spectroscopic and magnetic properties that have been ascribed to planar side-on coordination of $O_2$. Unlike the reaction of [Cu(Tp$^{iPr2}$)]$_n$ with dioxygen, which quantitatively and irreversibly yields [Cu(Tp$^{iPr2}$)]$_2$O$_2$,[4b] the reaction of [Cu(Pim$^{iPr2}$)CH$_3$CN]$^+$ and $O_2$ does not go to completion at relatively high concentrations of Cu(I) complex. The peroxide complex is ineffective as an oxidant toward 1-hexene and triphenylphosphine. Thermal decomposition of the peroxide adduct leads to a hydroxide–copper(II) complex, which rapidly (and often unavoidably) fixes atmospheric $CO_2$. An examination of structurally characterized copper(II) complexes of Pim$^{iPr2}$ shows that this ligand readily accommodates square pyramidal geometry about Cu(II), which would be required for $\mu$-$\eta^2$:$\eta^2$ dioxygen binding. A Cu(I) complex of a homologous ligand with *tert*-butyl groups proximal to the cuprous ion does not react with $O_2$, demonstrating that steric effects are important in defining Cu(I)–$O_2$ interactions for this ligand class.

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**Supplementary Material Available:** A figure showing all non-hydrogen atoms of **8**, full listings of the details of crystallographic data acquisition, and complete tables of bond lengths and angles, atomic coordinates, and thermal parameters for **8-(BF$_4$)$_2$** and **9-BF$_4$** (12 pages). Ordering information is given on any current masthead page.

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(31) Baldwin, M. J.; Ross, P. K.; Pate, J. E.; Tyeklár, Z.; Karlin, K. D.; Solomon, E. I. *J. Am. Chem. Soc.* **1991**, *113*, 8671.