

# Mononuclear and Binuclear Copper(I) Complexes Ligated by Bis(3,5-diisopropyl-1-pyrazolyl)methane: Insight into the Fundamental Coordination Chemistry of Three-Coordinate Copper(I) Complexes with a Neutral Coligand†

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By using the neutral bidentate nitrogen-containing ligand, bis(3,5-diisopropyl-1-pyrazolyl)methane ( $L1''$ ), the copper(I) complexes  $[Cu(L1'')_2](CuCl_2)$  (**1CuCl<sub>2</sub>**),  $[Cu(L1'')_2](ClO_4)$  (**1ClO<sub>4</sub>**),  $[Cu(L1'')_2](ClO_4)_2$  (**2ClO<sub>4</sub>**),  $[Cu(L1'')_2](BF_4)_2$  (**2BF<sub>4</sub>**),  $[Cu(L1'')(NCMe)](PF_6)$  (**3PF<sub>6</sub>**),  $[Cu(L1'')(PPh_3)](ClO_4)$  (**4ClO<sub>4</sub>**),  $[Cu(L1'')(PPh_3)](PF_6)$  (**4PF<sub>6</sub>**),  $[Cu(L1'')(CO)]_2(\mu-ClO_4)(ClO_4)$  (**5ClO<sub>4</sub>**), and the copper(II) complexes  $[Cu(L1'')_2(\mu-OH)(\mu-ClO_4)_2]$  (**6**), and  $[Cu(L1'')Cl_2]$  (**7**) were systematically synthesized and fully characterized by X-ray crystallography and by IR and  $^1H$  NMR spectroscopy. In the case of copper(II), ESR spectroscopy was also applied. In comparison with the related neutral tridentate ligand  $L1'$ , bis-chelated copper(I) complexes and binuclear linear-coordinated copper(I) complexes are easy to obtain with  $L1''$ , like **1CuCl<sub>2</sub>**, **1ClO<sub>4</sub>**, **2ClO<sub>4</sub>**, and **2BF<sub>4</sub>**. Importantly, stronger and bulkier ligands such as acetonitrile (**3PF<sub>6</sub>**) and especially triphenylphosphine (**4ClO<sub>4</sub>** and **4PF<sub>6</sub>**) generate three-coordinate structures with a trigonal-planar geometry. Surprisingly, for the smaller ligand carbon monoxide, a mononuclear three-coordinate structure is very unstable, leading to the formation of a binuclear complex (**5ClO<sub>4</sub>**) with one bridging perchlorate anion, such that the copper(I) centers are four-coordinate. The same tendency is observed for the copper(II) bis- $(\mu$ -hydroxo) compounds **6**, which is additionally bridged by two perchlorate anions. Both copper(II) complexes **6** and **7** were obtained by molecular  $O_2$  oxidation of the corresponding copper(I) complexes. A comparison of the new copper(I) triphenylphosphine complexes **4ClO<sub>4</sub>** and **4PF<sub>6</sub>** with corresponding species obtained with the related tridentate ligands  $L1'$  and  $L1$  (**8ClO<sub>4</sub>** and **9**, respectively) reveals surprisingly small differences in their spectroscopic properties. Density functional theory (DFT) calculations are used to shed light on the differences in bonding in these compounds and the spectral assignments. Finally, the reactivity of the different bis(pyrazolyl)methane complexes obtained here toward  $PPh_3$ , CO, and  $O_2$  is discussed.

## Introduction

Since Trofimenko's first report in 1970, poly(pyrazolyl)-alkanes, especially bis(pyrazolyl)methane, have been popular polydentate nitrogen donor ligands.<sup>1</sup> Their coordination behavior can easily be adjusted by changing the electronic and steric characteristics of the substituents on the pyrazolyl

rings, using straightforward synthetic procedures.<sup>1,2</sup> Therefore, the transition-metal complexes with these ligands have raised interest among many researchers, and they continue to be the subject of many studies, especially in organometallic chemistry.<sup>3</sup> In particular, the coordination chemistry of copper(I) complexes with low coordination numbers is of increasing interest, for example two-coordinate structures.<sup>4</sup>

† Dedicated to Professor O. Yamauchi on the occasion of his 70th birthday.

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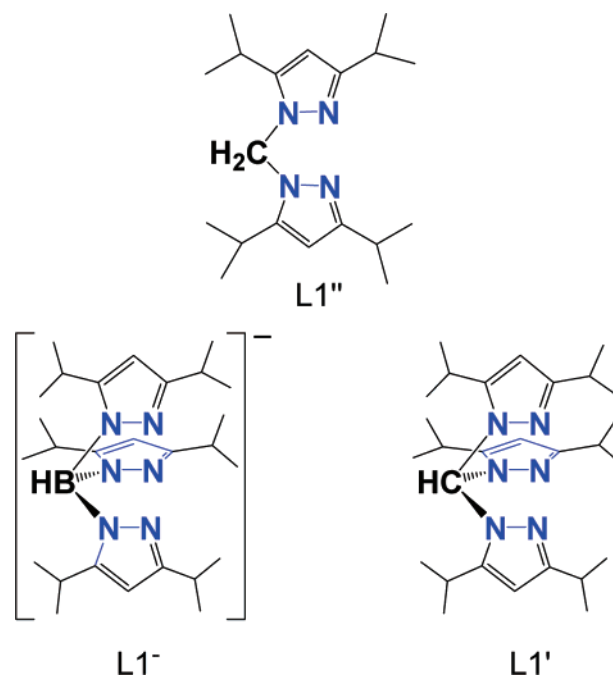
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Recently, a number of investigations of copper complexes with neutral bidentate nitrogen-containing ligands using pyrazolyl donors have been carried out. Chou and co-workers structurally characterized the 2:1 co-crystal of the mixed copper(I)/copper(II) complexes  $[\text{Cu}^{\text{I}}(\text{H}_2\text{Cpz}_2)(\text{NCMe})_2](\text{ClO}_4)$  and  $[\text{Cu}^{\text{II}}(\text{H}_2\text{Cpz}_2)_2(\text{OCIO}_3)_2]$ , the perchlorate bridged bis- $(\mu\text{-hydroxo})$  dicopper(II) complex  $[\{\text{Cu}^{\text{II}}(\text{H}_2\text{Cpz}_2)_2(\mu\text{-OH})_2(\mu\text{-ClO}_4)\}](\text{ClO}_4)$ , and the bis-chelated copper(I) complex  $[\text{Cu}^{\text{I}}(\text{H}_2\text{Cpz}_2)_2](\text{ClO}_4)$ , using bis(pyrazolyl)methane ( $\text{H}_2\text{Cpz}_2$ ) as a ligand.<sup>5</sup> They also determined the crystal structures of the related mononuclear copper(I) complexes,  $[\text{Cu}^{\text{I}}\{\text{H}_2\text{C}(3,5\text{-Me}_2\text{pz})_2\}(\text{NCMe})](\text{ClO}_4)$ ,  $[\text{Cu}^{\text{I}}\{\text{H}_2\text{C}(3,5\text{-Me}_2\text{pz})_2\}(\text{CO})(\text{OCIO}_3)]$ , and  $[\text{Cu}^{\text{I}}\{\text{H}_2\text{C}(3,5\text{-Me}_2\text{pz})_2\}(\text{PPh}_3)](\text{ClO}_4)$  with the methyl-substituted ligand bis(3,5-dimethyl-1-pyrazolyl)methane ( $\text{H}_2\text{C}(3,5\text{-Me}_2\text{pz})_2$ ) and investigated the reactivity of these compounds.<sup>6</sup> A few other substituted N2 ligands with pyrazolyl rings have also been applied, such as diphenylbis(pyrazolyl)methane ( $\text{Ph}_2\text{Cpz}_2$ ), 1,3-bis(5-methylpyrazolyl)propane (bmpp), and 1,3-bis(3,5-dimethylpyrazolyl)propane (bdpp), and the corresponding copper(II) complexes  $[\text{Cu}^{\text{II}}(\text{Ph}_2\text{Cpz}_2)(\text{NO}_3)_2(\text{H}_2\text{O})]$ ,  $[\text{Cu}^{\text{II}}(\text{Ph}_2\text{Cpz}_2)\text{Cl}_2]$ ,  $[\text{Cu}^{\text{II}}(\text{bmpp})(\text{NO}_3)_2]$ , and  $[\text{Cu}^{\text{II}}(\text{bdpp})\text{Cl}_2]$  were structurally characterized.<sup>7,8</sup>

In our previous studies, we have focused on tridentate nitrogen-containing ligands such as the neutral ligand tris(3,5-diisopropyl-1-pyrazolyl)methane ( $\text{L1}'$ ) and the corresponding anionic ligand hydrotris(3,5-diisopropyl-1-pyrazolyl)borate anion ( $\text{L1}^-$ , Figure 1). Four-coordinate copper(I) complexes were prepared with these ligands and characterized.<sup>9</sup> These results provide insight into second coordination sphere effects caused by the different ligands employed; that is, the influence of the total charge, the steric hindrance, and electronic effects of the ligands on the structures, properties, and the reactivity of the complexes. These findings prompted us to attempt the comparison of the structures, spectroscopic properties, and reactivities of these copper(I) complexes with corresponding compounds containing the bidentate ligand bis(3,5-diisopropyl-1-pyrazolyl)methane  $\text{H}_2\text{C}(3,5\text{-iPr}_2\text{pz})_2$  ( $\text{L1}''$ , Figure 1). It can be expected that the change in coordination number of the supporting coligand from tridentate to biden-



**Figure 1.** Structures of the ligands discussed in this work: bis(3,5-diisopropyl-1-pyrazolyl)methane ( $\text{L1}''$ ), hydrotris(3,5-diisopropyl-1-pyrazolyl)borate anion ( $\text{L1}^-$ ), and tris(3,5-diisopropyl-1-pyrazolyl)methane ( $\text{L1}'$ ).

tate will have a great influence on the properties and reactivities. In this work, the syntheses of the copper(I) complexes  $[\text{Cu}(\text{L1}'')_2](\text{CuCl}_2)$  (**1CuCl<sub>2</sub>**),  $[\text{Cu}(\text{L1}'')_2](\text{ClO}_4)$  (**1ClO<sub>4</sub>**),  $[\text{Cu}(\text{L1}'')_2](\text{ClO}_4)_2$  (**2ClO<sub>4</sub>**),  $[\text{Cu}(\text{L1}'')_2](\text{BF}_4)_2$  (**2BF<sub>4</sub>**),  $[\text{Cu}(\text{L1}'')(\text{NCMe})](\text{PF}_6)$  (**3PF<sub>6</sub>**),  $[\text{Cu}(\text{L1}'')(\text{PPh}_3)](\text{ClO}_4)$  (**4ClO<sub>4</sub>**),  $[\text{Cu}(\text{L1}'')(\text{PPh}_3)](\text{PF}_6)$  (**4PF<sub>6</sub>**), and  $[\{\text{Cu}(\text{L1}'')(\text{CO})_2(\mu\text{-ClO}_4)\}](\text{ClO}_4)$  (**5ClO<sub>4</sub>**) with  $\text{H}_2\text{C}(3,5\text{-iPr}_2\text{pz})_2$  as a bidentate nitrogen-containing ligand and the reactivity of the obtained copper(I) complexes toward  $\text{PPh}_3$ , CO, and  $\text{O}_2$  are investigated. A special focus is put on the preparation of low-coordinate copper(I) complexes, that is, three-coordinate compounds with acetonitrile, phosphine, and CO as the third ligands. For this purpose, we have investigated the factors that favor or disfavor the formation of three-coordinate copper(I) and how the metal avoids this unfavorable coordination number with a neutral bidentate N2 coligand. The copper(II) complexes  $[\{\text{Cu}(\text{L1}'')_2(\mu\text{-OH})_2(\mu\text{-ClO}_4)_2\}]$  (**6**) and  $[\text{Cu}(\text{L1}'')\text{Cl}_2]$  (**7**)<sup>10</sup> have been obtained by the reaction of copper(I) precursors with molecular  $\text{O}_2$ . All of the complexes were characterized by IR, far-IR, and NMR/ESR spectroscopy, and by X-ray crystallography. The properties of the copper(I) triphenylphosphine complexes **4ClO<sub>4</sub>** and **4PF<sub>6</sub>** are compared to those of  $[\text{Cu}(\text{L1}')(\text{PPh}_3)](\text{ClO}_4)$  (**8ClO<sub>4</sub>**) and  $[\text{Cu}(\text{L1}')(\text{PPh}_3)]$  (**9**),<sup>11b</sup> which contain the tridentate ligands  $\text{L1}'$  and  $\text{L1}^-$  (vide supra). Density functional theory (DFT) calculations were performed to shed light on the spectroscopic properties and assignments of these phosphine

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complexes. The systematic comparison of copper(I) complexes with the related coligands  $L1''$ ,  $L1'$ , and  $L1^-$  that have identical isopropyl-substituted pyrazolyl rings leads to detailed insight into the structural favors and reactivities of these compounds, as a function of the applied coligand.

## Experimental Section

**Materials.** Preparation and handling of all of the complexes were performed under an argon atmosphere using standard Schlenk tube techniques or in a VAC inert atmosphere glovebox containing argon gas. Dichloromethane and acetonitrile were distilled from phosphorus pentoxide and calcium hydride prior to use, respectively. Diethyl ether and heptane were carefully purified by refluxing/distilling under an argon atmosphere over sodium benzophenone ketyl.<sup>12</sup> Chloroform and octane were spectroscopic grade and were used after bubbling with argon gas. Anhydrous solvents,  $[Cu(MeCN)_4](PF_6)$ ,  $AgClO_4$ , and  $AgPF_6$  were purchased from Aldrich Chemical Co., Inc. and stored in a glovebox.  $CuCl$  was purified according to a published method.<sup>11</sup>  $^{13}C$ -enriched carbon monoxide and NMR solvents were obtained from Cambridge Isotope Laboratories, Inc. An autoclave (TVS-1, 300 cm<sup>3</sup>) was used for ligand syntheses. Silica gel was obtained from Merck KGaA. Other reagents were purchased from Wako Pure Chemical Ind. Ltd. and used without further purification. The copper(I) perchlorate complex  $[Cu\{HC(3,5-iPr_2pz)_3\}(OCIO_3)]$  ( $[Cu(L1')(OCIO_3)]$ )<sup>9</sup> and the copper(I) acetonitrile complex  $[Cu\{HB(3,5-iPr_2pz)_3\}(NCMe)]$  ( $[Cu(L1)(NCMe)]$ )<sup>9</sup> were prepared by published methods. Although the synthetic procedure for  $[Cu\{HB(3,5-iPr_2pz)_3\}(PPh_3)]$  ( $[Cu(L1)(PPh_3)]$ ) (**9**)<sup>11b</sup> has already been reported, this complex was prepared here by a modified method. The synthesis of  $H_2C(3,5-iPr_2pz)_2$  ( $L1''$ ) has been reported before by us<sup>10</sup> and Tang.<sup>3f</sup> *Caution! Perchlorate salts are potentially explosive and should be handled with care.*

**Instrumentation.** IR and far-IR spectra were recorded on KBr pellets in the 4000–400 cm<sup>-1</sup> region and on CsI pellets in the 650–150 cm<sup>-1</sup> region, respectively, using a JASCO FT/IR-550 spectrophotometer. Abbreviations used in the description of vibrational data are as follows: vs, very strong; s, strong; m, medium; w, weak. <sup>1</sup>H NMR (600 MHz), <sup>13</sup>C NMR (150 MHz), and <sup>31</sup>P NMR (242 MHz) spectra were obtained on a Bruker AVANCE-600 NMR spectrometer at room temperature (296 K) unless stated otherwise. <sup>1</sup>H and <sup>13</sup>C chemical shifts were reported as  $\delta$  values downfield from the internal standard tetramethylsilane. <sup>31</sup>P chemical shifts were referenced relative to an external standard of  $PPh_3$ . ESR spectra were recorded on a Bruker EMXT ESR spectrometer as frozen solutions at  $\sim -135$  °C in quartz tubes (diameter 5 mm) using the liquid-nitrogen temperature controller BVT 3000. UV–vis absorption spectra at room temperature in the 240–1100 nm range were recorded on a JASCO V-570 spectrophotometer. The elemental analyses (C, H, and N) were performed by the Department of Chemistry at the University of Tsukuba.

**Calculations.** Spin-restricted density functional theory calculations using Becke's three-parameter hybrid functional with the correlation functional of Lee, Yang, and Parr (B3LYP<sup>13</sup>) were performed using the program package Gaussian 03.<sup>14</sup> The structures of the three complexes,  $[Cu(L1'')(PPh_3)]^+$ ,  $[Cu(L1')(PPh_3)]^+$ , and  $[Cu(L1)(PPh_3)]$ , were fully optimized without any simplifications using B3LYP/LanL2DZ. This is necessary to ensure that all of the

steric interactions between the bulky ligands  $L1''$ ,  $L1'$ ,  $L1^-$ , and the large ligand  $PPh_3$  are taken into account. To handle molecules of this size ( $\sim 100$  atoms), application of the LanL2DZ basis set is necessary for the geometry optimizations and frequency calculations. The calculated structures show good overall agreement with experiment. The obtained vibrational frequencies exhibit no imaginary modes. The LanL2DZ basis set applies Dunning/Huzinaga full double- $\zeta$  (D95)<sup>15</sup> basis functions on first-row and Los Alamos effective core potentials plus DZ functions on all of the other atoms.<sup>16</sup> In addition, the structures of the species  $[Cu(L1'')]^+$ ,  $[Cu(L1')]^+$ , and  $[Cu(L1)]$  as well as free  $PPh_3$  were also fully optimized using B3LYP/LanL2DZ for the calculation of complex formation energies. For this purpose, single point calculations using B3LYP/TZVP on the LanL2DZ structures were also performed. The TZVP basis set<sup>17</sup> has been applied as implemented in G03.

**Preparation of Complexes.**  $[Cu\{H_2C(3,5-iPr_2pz)_2\}_2](CuCl_2)$ ,  $[Cu(L1'')_2](CuCl_2)$  (**1** $CuCl_2$ ). Acetone (60 cm<sup>3</sup>) was added to a mixture of  $L1''$  (588 mg, 1.86 mmol)<sup>10</sup> and  $CuCl$  (202 mg, 2.04 mmol) in a glovebox. After stirring for 24 h, the solution was filtered, and the filtrate was evaporated under vacuum. A yellowish-white powder was obtained. Recrystallization from acetonitrile at  $-30$  °C afforded colorless crystals. Yield: 65% (501 mg, 0.603 mmol). Anal. Calcd for  $C_{38}H_{64}N_8Cl_2Cu_2$ : C, 54.92; H, 7.76; N, 13.48. Found: C, 54.83; H, 7.65; N, 13.45. IR (cm<sup>-1</sup>): 3199w, 2965vs, 1545s, 1469s, 1383s, 1271vs, 1183m, 1068m, 1058m, 807s. Far-IR (cm<sup>-1</sup>): 583m, 536s, 516w, 470m, 408vs, 399vs, 367w, 323w, 302w, 253w, 226w, 179w, 170w. <sup>1</sup>H NMR ( $CD_2Cl_2$ ): 1.04 (d,  $J_{HH} = 6.2$  Hz, 24H,  $CH(CH_3)_2$ ), 1.23 (d,  $J_{HH} = 6.8$  Hz, 24H,  $CH(CH_3)_2$ ), 2.74 (br, 4H,  $CH(CH_3)_2$ ), 3.02 (sept,  $J_{HH} = 6.8$  Hz, 4H,  $CH(CH_3)_2$ ), 6.03 (s, 4H, 4-H(pz)), 6.05 (s, 4H,  $H_2C$ ). <sup>13</sup>C NMR ( $CD_2Cl_2$ ): 22.79 ( $CH(CH_3)_2$ ), 23.23 ( $CH(CH_3)_2$ ), 26.28 ( $CH(CH_3)_2$ ), 28.32 ( $CH(CH_3)_2$ ), 57.00 ( $H_2C$ ), 101.7 (pz-4C), 153.3 (pz-3C), 165.3 (pz-5C).

$[Cu\{H_2C(3,5-iPr_2pz)_2\}_2](ClO_4)$ ,  $[Cu(L1'')_2](ClO_4)$  (**1** $ClO_4$ ).  $[Cu(L1'')_2](ClO_4)_2$  (**2** $ClO_4$ ) (133 mg, 0.139 mmol) was dissolved in acetonitrile (15 cm<sup>3</sup>) in a glovebox. After stirring for 24 h, the solvent was evaporated under vacuum. Recrystallization from chloroform/heptane (1:2) at  $-50$  °C yielded colorless crystals. Yield: 45% (50.2 mg, 0.0631 mmol). Anal. Calcd for  $C_{38}H_{64}N_8ClCuO_4 \cdot 0.1CHCl_3$ : C, 56.64; H, 8.00; N, 13.87. Found: C, 56.37; H, 7.86; N, 13.77. IR (cm<sup>-1</sup>): 2965vs, 2930s, 2869m, 1546s, 1461s, 1382m, 1274s, 1144s, 1113vs, 1090vs, 796m, 625m. Far-IR (cm<sup>-1</sup>): 623vs, 584m, 536w, 472m, 406m, 325w, 248w, 226w,

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169w, 154w.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): 0.967 (d,  $J_{\text{HH}} = 6.9$  Hz, 24H,  $\text{CH}(\text{CH}_3)_2$ ), 1.32 (d,  $J_{\text{HH}} = 6.8$  Hz, 24H,  $\text{CH}(\text{CH}_3)_2$ ), 2.29 (br, 4H,  $\text{CH}(\text{CH}_3)_2$ ), 3.24 (sept,  $J_{\text{HH}} = 6.8$  Hz, 4H,  $\text{CH}(\text{CH}_3)_2$ ), 5.94 (s, 4H, 4-*H*(pz)), 6.25 (s, 4H,  $H_2\text{C}$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ): 22.38 ( $\text{CH}(\text{CH}_3)_2$ ), 23.16 ( $\text{CH}(\text{CH}_3)_2$ ), 25.58 ( $\text{CH}(\text{CH}_3)_2$ ), 27.63 ( $\text{CH}(\text{CH}_3)_2$ ), 57.00 ( $H_2\text{C}$ ), 99.28 (pz-4C), 152.1 (pz-3C), 160.6 (pz-5C).

**[Cu{H<sub>2</sub>C(3,5-*i*Pr<sub>2</sub>p<sub>z</sub>)<sub>2</sub>]<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub>, [Cu(L1'')]<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub> (2ClO<sub>4</sub>).** A solution of AgClO<sub>4</sub> (110 mg, 0.532 mmol) in tetrahydrofuran (10 cm<sup>3</sup>) was added to a solution of [Cu(L1'')<sub>2</sub>](CuCl<sub>2</sub>) (**1CuCl<sub>2</sub>**) (221 mg, 0.266 mmol) in dichloromethane (15 cm<sup>3</sup>) in a glovebox. After stirring for 1.5 h, the solution was filtered, and the filtrate was concentrated under reduced pressure. Recrystallization from dichloromethane/tetrahydrofuran/heptane (1:2:3) at  $-50^\circ\text{C}$  gave colorless crystals. Yield: 98% (250 mg, 0.261 mmol). Anal. Calcd for  $\text{C}_{38}\text{H}_{64}\text{N}_8\text{Cl}_2\text{Cu}_2\text{O}_8 \cdot 0.25\text{CH}_2\text{Cl}_2$ : C, 46.87; H, 6.63; N, 11.43. Found: C, 46.68; H, 6.76; N, 11.59. IR ( $\text{cm}^{-1}$ ): 3129w, 2968vs, 2933s, 2872s, 1546s, 1481m, 1461m, 1290m, 1267m, 1091vs, 622s. Far-IR ( $\text{cm}^{-1}$ ): 623vs, 552w, 536w, 464w, 418w, 336w, 298w, 211w, 197w, 186w, 168w, 160w.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ): 1.15 (d,  $J_{\text{HH}} = 6.9$  Hz, 24H,  $\text{CH}(\text{CH}_3)_2$ ), 1.18 (d,  $J_{\text{HH}} = 6.9$  Hz, 24H,  $\text{CH}(\text{CH}_3)_2$ ), 2.82 (sept,  $J_{\text{HH}} = 6.9$  Hz, 4H,  $\text{CH}(\text{CH}_3)_2$ ), 2.91 (sept,  $J_{\text{HH}} = 6.9$  Hz, 4H,  $\text{CH}(\text{CH}_3)_2$ ), 6.21 (s, 4H, 4-*H*(pz)), 6.70 (br, 4H,  $H_2\text{C}$ ).  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ ): 22.52 ( $\text{CH}(\text{CH}_3)_2$ ), 23.14 ( $\text{CH}(\text{CH}_3)_2$ ), 26.83 ( $\text{CH}(\text{CH}_3)_2$ ), 30.01 ( $\text{CH}(\text{CH}_3)_2$ ), 61.08 ( $H_2\text{C}$ ), 102.6 (pz-4C), 156.5 (pz-3C), 164.0 (pz-5C).

**[Cu{H<sub>2</sub>C(3,5-*i*Pr<sub>2</sub>p<sub>z</sub>)<sub>2</sub>]<sub>2</sub>(BF<sub>4</sub>)<sub>2</sub>, [Cu(L1'')]<sub>2</sub>(BF<sub>4</sub>)<sub>2</sub> (2BF<sub>4</sub>).** The preparation was carried out by the same method as applied for **2ClO<sub>4</sub>** using [Cu(L1'')<sub>2</sub>](CuCl<sub>2</sub>) (**1CuCl<sub>2</sub>**) (205 mg, 0.247 mmol) in dichloromethane (15 cm<sup>3</sup>) and AgBF<sub>4</sub> (96 mg, 0.493 mmol) in tetrahydrofuran (10 cm<sup>3</sup>) in a glovebox. Recrystallization from dichloromethane/tetrahydrofuran/heptane (1:2:3) at  $-50^\circ\text{C}$  gave colorless crystals. Yield: 67% (154 mg, 0.165 mmol). Anal. Calcd for  $\text{C}_{38}\text{H}_{64}\text{N}_8\text{B}_2\text{Cu}_2\text{F}_8 \cdot 0.25\text{CH}_2\text{Cl}_2$ : C, 48.11; H, 6.81; N, 11.73. Found: C, 47.99; H, 6.84; N, 11.86. IR ( $\text{cm}^{-1}$ ): 3136w, 2967vs, 2934s, 2872s, 1546s, 1478m, 1463m, 1290m, 1275m, 1057vs, 806m. Far-IR ( $\text{cm}^{-1}$ ): 641s, 628w, 583w, 550w, 520vs, 471w, 413w, 253w, 171w, 156s.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): 1.22 (br, 24H,  $\text{CH}(\text{CH}_3)_2$ ), 1.26 (br, 24H,  $\text{CH}(\text{CH}_3)_2$ ), 2.93 (br, 4H,  $\text{CH}(\text{CH}_3)_2$ ), 3.06 (br, 4H,  $\text{CH}(\text{CH}_3)_2$ ), 6.22 (s, 4H, 4-*H*(pz)), 6.79 (s, 4H,  $H_2\text{C}$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ): 22.37 ( $\text{CH}(\text{CH}_3)_2$ ), 22.91 ( $\text{CH}(\text{CH}_3)_2$ ), 26.25 ( $\text{CH}(\text{CH}_3)_2$ ), 29.30 ( $\text{CH}(\text{CH}_3)_2$ ), 61.37 ( $H_2\text{C}$ ), 102.0 (pz-4C), 156.3 (pz-3C), 163.5 (pz-5C).

**[Cu{H<sub>2</sub>C(3,5-*i*Pr<sub>2</sub>p<sub>z</sub>)<sub>2</sub>](NCMe)](PF<sub>6</sub>), [Cu(L1'')](NCMe)](PF<sub>6</sub>) (3PF<sub>6</sub>).** A solution of L1'' (212 mg, 0.669 mmol) in dichloromethane (10 cm<sup>3</sup>) was added to a solution of [Cu(MeCN)<sub>4</sub>](PF<sub>6</sub>) (274 mg, 0.736 mmol) in acetonitrile (20 cm<sup>3</sup>). After stirring for 1 h, the solvent was evaporated under vacuum. The resulting solid was extracted with dichloromethane (25 cm<sup>3</sup>). The obtained solution was evaporated under vacuum, and a yellowish white powder was obtained. Recrystallization from dichloromethane/diethyl ether (1:2) at  $-30^\circ\text{C}$  afforded colorless crystals. Yield: 72% (272 mg, 0.481 mmol). Anal. Calcd for  $\text{C}_{21}\text{H}_{35}\text{N}_5\text{CuF}_6\text{P}$ : C, 44.56; H, 6.23; N, 12.37. Found: C, 44.53; H, 6.26; N, 12.45. IR ( $\text{cm}^{-1}$ ): 2966s, 2933m, 2872m, 1545m, 1465m, 1384m, 1274s, 1183w, 1108w, 843vs, 558s. Far-IR ( $\text{cm}^{-1}$ ): 645s, 559vs, 536w, 503w, 477m, 411w, 377w, 281w, 214w, 205w, 161m.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ): 1.20 (d,  $J_{\text{HH}} = 7.0$  Hz, 12H,  $\text{CH}(\text{CH}_3)_2$ ), 1.22 (d,  $J_{\text{HH}} = 6.8$  Hz, 12H,  $\text{CH}(\text{CH}_3)_2$ ), 2.31 (s, 3H,  $\text{CH}_3\text{CN}$ ), 2.96 (sept,  $J_{\text{HH}} = 6.8$  Hz, 4H,  $\text{CH}(\text{CH}_3)_2$ ), 5.94 (s, 2H, 4-*H*(pz)), 5.99 (s, 2H,  $H_2\text{C}$ ).  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ ): 23.14 ( $\text{CH}(\text{CH}_3)_2$ ), 26.27 ( $\text{CH}(\text{CH}_3)_2$ ), 28.83 ( $\text{CH}(\text{CH}_3)_2$ ), 57.08 ( $H_2\text{C}$ ), 100.4 (pz-4C), 153.2 (pz-3C), 162.7 (pz-5C).

**[Cu{H<sub>2</sub>C(3,5-*i*Pr<sub>2</sub>p<sub>z</sub>)<sub>2</sub>](PPh<sub>3</sub>)](ClO<sub>4</sub>), [Cu(L1'')](PPh<sub>3</sub>)](ClO<sub>4</sub>) (4ClO<sub>4</sub>).** Method a: Dichloromethane (15 cm<sup>3</sup>) was added to a

mixture of [Cu(L1'')]<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub> (**2ClO<sub>4</sub>**) (134 mg, 0.140 mmol) and PPh<sub>3</sub> (77 mg, 0.293 mmol) in a glovebox. After stirring for 2 h, the solution was filtered and the filtrate was evaporated under vacuum, yielding a white powder. Recrystallization from chloroform/diethyl ether (1:2) at  $-50^\circ\text{C}$  gave colorless crystals. Yield: 56% (121 mg, 0.163 mmol). Method b: **4ClO<sub>4</sub>** could also be obtained by the reaction between [Cu(L1'')](CO)]<sub>2</sub>( $\mu$ -ClO<sub>4</sub>)](ClO<sub>4</sub>) (**5ClO<sub>4</sub>**) (103 mg, 0.101 mmol) and PPh<sub>3</sub> (55.6 mg, 0.212 mmol) in dichloromethane (10 cm<sup>3</sup>). Recrystallization from dichloromethane/octane (1:2) at  $-50^\circ\text{C}$  gave a white powder. Yield: 39% (58.9 mg, 0.0794 mmol). Anal. Calcd for  $\text{C}_{37}\text{H}_{47}\text{N}_4\text{ClCuO}_4\text{P}$ : C, 59.91; H, 6.39; N, 7.55. Found: C, 59.49; H, 6.34; N, 7.43. IR ( $\text{cm}^{-1}$ ): 3126w, 3055w, 2970vs, 2933m, 2872m, 1547s, 1479s, 1435s, 1272s, 1094vs, 747s, 696s, 622s, 528s, 507m. Far-IR ( $\text{cm}^{-1}$ ): 623vs, 583w, 529vs, 506vs, 499s, 444m, 425m, 404w, 376w, 256w, 188m, 167w, 158m.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): 0.856 (d,  $J_{\text{HH}} = 6.9$  Hz, 12H,  $\text{CH}(\text{CH}_3)_2$ ), 1.33 (d,  $J_{\text{HH}} = 6.8$  Hz, 12H,  $\text{CH}(\text{CH}_3)_2$ ), 2.56 (sept,  $J_{\text{HH}} = 6.9$  Hz, 2H,  $\text{CH}(\text{CH}_3)_2$ ), 3.29 (sept,  $J_{\text{HH}} = 6.9$  Hz, 2H,  $\text{CH}(\text{CH}_3)_2$ ), 5.96 (s, 2H, 4-*H*(pz)), 6.51 (s, 2H,  $H_2\text{C}$ ), 7.46–7.53 (m, 15H, PPh<sub>3</sub>).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ): 23.02 ( $\text{CH}(\text{CH}_3)_2$ ), 23.11 ( $\text{CH}(\text{CH}_3)_2$ ), 25.49 ( $\text{CH}(\text{CH}_3)_2$ ), 28.59 ( $\text{CH}(\text{CH}_3)_2$ ), 57.44 ( $H_2\text{C}$ ), 99.14 (pz-4C), 129.2 (PPh<sub>3</sub>), 129.3 (PPh<sub>3</sub>), 130.9 (PPh<sub>3</sub>), 131.0 (PPh<sub>3</sub>), 131.2 (PPh<sub>3</sub>), 133.6 (PPh<sub>3</sub>), 133.7 (PPh<sub>3</sub>), 153.9 (pz-3C), 161.9 (pz-5C).  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ): 12.11 (s, PPh<sub>3</sub>).

**[Cu{H<sub>2</sub>C(3,5-*i*Pr<sub>2</sub>p<sub>z</sub>)<sub>2</sub>](PPh<sub>3</sub>)](PF<sub>6</sub>), [Cu(L1'')](PPh<sub>3</sub>)](PF<sub>6</sub>) (4PF<sub>6</sub>).** The preparation was carried out by the same method as applied for **4ClO<sub>4</sub>** using [Cu(L1'')](NCMe)](PF<sub>6</sub>) (**3PF<sub>6</sub>**) (120 mg, 0.212 mmol) and PPh<sub>3</sub> (58 mg, 0.222 mmol) in dichloromethane (15 cm<sup>3</sup>). Recrystallization from dichloromethane/diethyl ether (1:2) at  $-50^\circ\text{C}$  gave colorless crystals. Yield: 38% (63.5 mg, 0.0807 mmol). Anal. Calcd for  $\text{C}_{37}\text{H}_{47}\text{N}_4\text{CuF}_6\text{P}_2$ : C, 56.45; H, 6.02; N, 7.12. Found: C, 56.23; H, 5.99; N, 7.00. IR ( $\text{cm}^{-1}$ ): 3135w, 3054w, 2969s, 2934m, 2874m, 1548m, 1480s, 1436s, 1273s, 1097m, 1058m, 842vs, 746s, 695s, 558s, 531s. Far-IR ( $\text{cm}^{-1}$ ): 643s, 620w, 558vs, 530s, 506s, 494s, 445m, 427w, 401w, 303w, 258w, 247w, 176w, 161m.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): 0.873 (d,  $J_{\text{HH}} = 6.9$  Hz, 12H,  $\text{CH}(\text{CH}_3)_2$ ), 1.33 (d,  $J_{\text{HH}} = 6.8$  Hz, 12H,  $\text{CH}(\text{CH}_3)_2$ ), 2.56 (sept,  $J_{\text{HH}} = 6.8$  Hz, 2H,  $\text{CH}(\text{CH}_3)_2$ ), 3.22 (sept,  $J_{\text{HH}} = 6.7$  Hz, 2H,  $\text{CH}(\text{CH}_3)_2$ ), 5.98 (s, 2H, 4-*H*(pz)), 6.35 (s, 2H,  $H_2\text{C}$ ), 7.47–7.52 (m, 15H, PPh<sub>3</sub>).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ): 22.99 ( $\text{CH}(\text{CH}_3)_2$ ), 25.49 ( $\text{CH}(\text{CH}_3)_2$ ), 28.61 ( $\text{CH}(\text{CH}_3)_2$ ), 57.10 ( $H_2\text{C}$ ), 99.28 (pz-4C), 129.3 (PPh<sub>3</sub>), 129.4 (PPh<sub>3</sub>), 130.8 (PPh<sub>3</sub>), 131.0 (PPh<sub>3</sub>), 133.5 (PPh<sub>3</sub>), 133.6 (PPh<sub>3</sub>), 153.9 (pz-3C), 162.0 (pz-5C).  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ): 12.20 (s, PPh<sub>3</sub>), –138.9 (sept, PF<sub>6</sub>).

**[{Cu{H<sub>2</sub>C(3,5-*i*Pr<sub>2</sub>p<sub>z</sub>)<sub>2</sub>}(CO)]<sub>2</sub>( $\mu$ -ClO<sub>4</sub>)](ClO<sub>4</sub>), [{Cu(L1'')}(CO)]<sub>2</sub>( $\mu$ -ClO<sub>4</sub>)](ClO<sub>4</sub>) (**5ClO<sub>4</sub>**).** [Cu(L1'')]<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub> (**2ClO<sub>4</sub>**) (150 mg, 0.156 mmol) was dissolved in dichloromethane (15 cm<sup>3</sup>) in a glovebox. The solution was cooled to  $-78^\circ\text{C}$  in an argon atmosphere, and the argon gas was then replaced by a CO atmosphere. The solution was allowed to warm up to room temperature. After stirring for 3 days, the solution was filtered and the filtrate was concentrated under reduced pressure. Recrystallization from dichloromethane/heptane (1:2) at  $-50^\circ\text{C}$  under a CO atmosphere gave colorless crystals. Yield: 41% (64.8 mg, 0.0638 mmol). Anal. Calcd for  $\text{C}_{40}\text{H}_{64}\text{N}_8\text{Cl}_2\text{Cu}_2\text{O}_{10} \cdot 2\text{CH}_2\text{Cl}_2$ : C, 42.58; H, 5.78; N, 9.46. Found: C, 42.61; H, 5.97; N, 9.47. IR ( $\text{cm}^{-1}$ ): 3135w, 3071w, 2970vs, 2934s, 2872m, 2104vs, 1545s, 1462s, 1397s, 1385s, 1278vs, 1095vs, 1029s, 808m, 728s, 623s. Far-IR ( $\text{cm}^{-1}$ ): 624vs, 587w, 542m, 516m, 473w, 415m, 376w, 324w, 301w, 201m, 188m.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ): 1.26 (d,  $J_{\text{HH}} = 6.8$  Hz, 24H,  $\text{CH}(\text{CH}_3)_2$ ), 1.27 (d,  $J_{\text{HH}} = 6.8$  Hz, 24H,  $\text{CH}(\text{CH}_3)_2$ ), 2.97 (sept,  $J_{\text{HH}} = 6.8$  Hz, 4H,  $\text{CH}(\text{CH}_3)_2$ ), 3.05 (sept,  $J_{\text{HH}} = 6.9$  Hz, 4H,  $\text{CH}(\text{CH}_3)_2$ ), 6.00 (s, 4H, 4-*H*(pz)), 6.06 (s, 4H,  $H_2\text{C}$ ).  $^{13}\text{C}$  NMR

(CD<sub>2</sub>Cl<sub>2</sub>): 22.90 (CH(CH<sub>3</sub>)<sub>2</sub>), 22.93 (CH(CH<sub>3</sub>)<sub>2</sub>), 26.03 (CH(CH<sub>3</sub>)<sub>2</sub>), 28.96 (CH(CH<sub>3</sub>)<sub>2</sub>), 55.98 (H<sub>2</sub>C), 99.96 (pz-4C), 152.8 (pz-3C), 162.3 (pz-5C), 172.9 (CO).

[{Cu{H<sub>2</sub>C(3,5-*i*Pr<sub>2</sub>p<sub>z</sub>)<sub>2</sub>}<sub>2</sub>(μ-OH)<sub>2</sub>(μ-ClO<sub>4</sub>)<sub>2</sub>}, [Cu(L1'')]<sub>2</sub>(μ-OH)<sub>2</sub>(μ-ClO<sub>4</sub>)<sub>2</sub>] (6). [Cu(L1'')]<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub> (2ClO<sub>4</sub>) (95.5 mg, 0.0996 mmol) was dissolved in dichloromethane in a Schlenk tube and cooled to -78 °C in an argon atmosphere. The argon gas was then replaced by an O<sub>2</sub> atmosphere, and the solution was allowed to warm up to room temperature. After stirring for 24 h, the solvent was concentrated under reduced pressure. Recrystallization from dichloromethane/heptane (1:2) at -30 °C gave two kinds of crystals. The main product was **6** obtained as blue crystals, which were manually separated. A small amount of green crystals remained, the nature of which is not known. Yield: 24% (24.0 mg, 0.0242 mmol). Anal. Calcd for C<sub>38</sub>H<sub>66</sub>N<sub>8</sub>Cl<sub>2</sub>Cu<sub>2</sub>O<sub>10</sub>: C, 45.96; H, 6.70; N, 11.28. Found: C, 45.82; H, 6.54; N, 11.12. IR (cm<sup>-1</sup>): 3536s, 2969vs, 2932s, 2871m, 1549s, 1484s, 1467s, 1404m, 1386m, 1275s, 1183m, 1096vs, 812m, 623m. Far-IR (cm<sup>-1</sup>): 624vs, 548w, 519m, 460w, 422w, 306w, 213w. UV-vis absorption (CH<sub>2</sub>Cl<sub>2</sub>, λ<sub>max</sub>, nm) (ε/M<sup>-1</sup> cm<sup>-1</sup>) 256 (8950), 355 (1360), 563 (100). ESR (CH<sub>2</sub>Cl<sub>2</sub>) silent.

[Cu{H<sub>2</sub>C(3,5-*i*Pr<sub>2</sub>p<sub>z</sub>)<sub>2</sub>}Cl<sub>2</sub>], [Cu(L1'')Cl<sub>2</sub>] (7).<sup>10</sup> Method a: [Cu(L1'')]<sub>2</sub>(CuCl<sub>2</sub>) (1CuCl<sub>2</sub>) (110 mg, 0.132 mmol) was dissolved in dichloromethane in a Schlenk tube and stirred in air. The clear solution of **1CuCl<sub>2</sub>** turned dark yellow over 24 h. The solution was filtered, and the filtrate was concentrated under reduced pressure. Recrystallization from dichloromethane/heptane (1:2) at -30 °C gave orange crystals. Yield: 51% (30.5 mg, 0.0676 mmol). Method b: **7** could also be obtained as follows: L1'' (202 mg, 0.639 mmol) dissolved in dichloromethane (15 cm<sup>3</sup>) was added to a solution of CuCl<sub>2</sub>·2H<sub>2</sub>O (122 mg, 0.716 mmol) in acetone (20 cm<sup>3</sup>). The color of the solution gradually turned to dark yellow. After stirring for 1 h, the solvent was removed under vacuum. The residue was extracted with dichloromethane, and the obtained organic solution was filtered. The organic solvent was then concentrated under reduced pressure. Recrystallization from dichloromethane/heptane (1:2) at -30 °C gave orange crystals. Yield: 72% (208 mg, 0.461 mmol). Anal. Calcd for C<sub>19</sub>H<sub>32</sub>N<sub>4</sub>Cl<sub>2</sub>Cu: C, 50.61; H, 7.15; N, 12.42. Found: C, 50.36; H, 7.17; N, 12.24. IR (cm<sup>-1</sup>): 3123w, 2967vs, 2931s, 2870m, 1547s, 1462s, 1441s, 1398s, 1384s, 1279s, 1184m, 1062m, 810s, 657w. Far-IR (cm<sup>-1</sup>): 645m, 629m, 590w, 545s, 470w, 315vs, 181m, 171m. UV-vis absorption (CH<sub>2</sub>Cl<sub>2</sub>, λ<sub>max</sub>, nm) (ε/M<sup>-1</sup> cm<sup>-1</sup>) 289 (3720), 375 (1330), 911 (140). ESR (CH<sub>2</sub>Cl<sub>2</sub>:CH<sub>2</sub>ClCH<sub>2</sub>Cl = 1:1) g<sub>av</sub> = 2.14.

[Cu{HC(3,5-*i*Pr<sub>2</sub>p<sub>z</sub>)<sub>3</sub>}(PPh<sub>3</sub>)](ClO<sub>4</sub>), [Cu(L1')(PPh<sub>3</sub>)](ClO<sub>4</sub>) (8ClO<sub>4</sub>). The preparation was carried out by the same method as applied for **4ClO<sub>4</sub>** using [Cu(L1')(OCIO<sub>3</sub>)]<sup>9</sup> (173 mg, 0.275 mmol) and PPh<sub>3</sub> (75.6 mg, 0.288 mmol) in dichloromethane (15 cm<sup>3</sup>) in a glovebox. Recrystallization from dichloromethane/diethyl ether (1:2) at -50 °C gave colorless crystals. Yield: 47% (116 mg, 0.130 mmol). Anal. Calcd for C<sub>46</sub>H<sub>61</sub>N<sub>6</sub>ClCuO<sub>4</sub>P: C, 61.94; H, 6.89; N, 9.42. Found: C, 61.75; H, 6.93; N, 9.30. IR (cm<sup>-1</sup>): 3130w, 3055w, 2965vs, 2931s, 2869m, 1556s, 1469s, 1435s, 1397s, 1385s, 1291s, 1233s, 1094vs, 825s, 697s, 622m, 530m. Far-IR (cm<sup>-1</sup>): 623vs, 531vs, 505vs, 497s, 444w, 425w, 395w, 366w, 305w, 273w, 258w. <sup>1</sup>H NMR (CDCl<sub>3</sub>): 0.83 (d, J<sub>HH</sub> = 6.8 Hz, 18H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.38 (d, J<sub>HH</sub> = 6.9 Hz, 18H, CH(CH<sub>3</sub>)<sub>2</sub>), 2.62 (sept, J<sub>HH</sub> = 6.7 Hz, 3H, CH(CH<sub>3</sub>)<sub>2</sub>), 3.49 (sept, J<sub>HH</sub> = 6.6 Hz, 3H, CH(CH<sub>3</sub>)<sub>2</sub>), 5.98 (s, 3H, 4-H(pz)), 7.44–7.54 (m, 15H, PPh<sub>3</sub>), 8.27 (s, 1H, HC). <sup>13</sup>C NMR (CDCl<sub>3</sub>): 22.78 (CH(CH<sub>3</sub>)<sub>2</sub>), 23.34 (CH(CH<sub>3</sub>)<sub>2</sub>), 25.88 (CH(CH<sub>3</sub>)<sub>2</sub>), 28.51 (CH(CH<sub>3</sub>)<sub>2</sub>), 66.93 (HC), 99.25 (pz-4C), 129.0 (PPh<sub>3</sub>), 129.1 (PPh<sub>3</sub>), 130.6 (PPh<sub>3</sub>), 132.8 (PPh<sub>3</sub>), 133.1 (PPh<sub>3</sub>), 133.7 (PPh<sub>3</sub>),

133.8 (PPh<sub>3</sub>), 153.1 (pz-3C), 161.5 (pz-5C). <sup>31</sup>P NMR (CDCl<sub>3</sub>): 13.79 (br, s, PPh<sub>3</sub>).

[Cu{HB(3,5-*i*Pr<sub>2</sub>p<sub>z</sub>)<sub>3</sub>}(PPh<sub>3</sub>)], [Cu(L1)(PPh<sub>3</sub>)] (9). The preparation was carried out by the same method<sup>10</sup> as applied for **4ClO<sub>4</sub>** using [Cu(L1)(NCMe)]<sup>9</sup> (123 mg, 0.215 mmol) and PPh<sub>3</sub> (59.2 mg, 0.226 mmol) in dichloromethane (15 cm<sup>3</sup>) in a glovebox. Recrystallization from dichloromethane/acetonitrile (1:2) at -30 °C gave colorless crystals. Yield: 36% (61.0 mg, 0.0771 mmol). Anal. Calcd for C<sub>45</sub>H<sub>61</sub>N<sub>6</sub>BCuP: C, 68.30; H, 7.77; N, 10.62. Found: C, 67.97; H, 7.78; N, 10.37. IR (cm<sup>-1</sup>): 3071w, 3055w, 2962vs, 2927s, 2865s, 2531m, 1536s, 1469s, 1458s, 1434s, 1392s, 1379s, 1295s, 1172vs, 1041s, 783s, 698s, 527s. Far-IR (cm<sup>-1</sup>): 528vs, 512vs, 489s, 437m, 413m, 403m, 395m, 305w, 261w. <sup>1</sup>H NMR (CDCl<sub>3</sub>): 0.72 (d, J<sub>HH</sub> = 6.8 Hz, 18H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.24 (d, J<sub>HH</sub> = 6.9 Hz, 18H, CH(CH<sub>3</sub>)<sub>2</sub>), 2.69 (sept, J<sub>HH</sub> = 6.8 Hz, 3H, CH(CH<sub>3</sub>)<sub>2</sub>), 3.53 (sept, J<sub>HH</sub> = 6.7 Hz, 3H, CH(CH<sub>3</sub>)<sub>2</sub>), 5.67 (s, 3H, 4-H(pz)), 7.25–7.36, 7.61–7.64 (m, 15H, PPh<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>): 23.77 (CH(CH<sub>3</sub>)<sub>2</sub>), 23.88 (CH(CH<sub>3</sub>)<sub>2</sub>), 26.17 (CH(CH<sub>3</sub>)<sub>2</sub>), 28.42 (CH(CH<sub>3</sub>)<sub>2</sub>), 95.09 (pz-4C), 128.39 (PPh<sub>3</sub>), 128.45 (PPh<sub>3</sub>), 129.38 (PPh<sub>3</sub>), 134.23 (PPh<sub>3</sub>), 134.33 (PPh<sub>3</sub>), 135.34 (PPh<sub>3</sub>), 135.55 (PPh<sub>3</sub>), 154.48 (pz-3C), 157.99 (pz-5C). <sup>31</sup>P NMR (CDCl<sub>3</sub>): 10.73 (br, s, PPh<sub>3</sub>).

**Reaction of [Cu(L1'')]<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub> (2ClO<sub>4</sub>) with <sup>13</sup>CO.** The <sup>13</sup>CO-labeled complex was prepared by the same method as the corresponding unlabeled complex **5ClO<sub>4</sub>** using **2ClO<sub>4</sub>** and <sup>13</sup>CO.

**Reaction of [Cu(L1'')(NCMe)](PF<sub>6</sub>) (3PF<sub>6</sub>) with O<sub>2</sub>.** In a Schlenk tube, **3PF<sub>6</sub>** was dissolved in dichloromethane and cooled to -78 °C under an argon atmosphere. The argon was then replaced by dioxygen, and the solution was allowed to warm up to room temperature. After stirring for 24 h, the solvent was removed under vacuum.

**X-ray Data Collection and Structural Determination.** Crystal data and refinement parameters for the investigated ligand (L1'') and the copper complexes are given in Tables 1 and 2. The diffraction data for all of the complexes were measured on a Rigaku/MSM Mercury CCD system with graphite monochromated Mo Kα (λ = 0.71069 Å) radiation at low temperatures (-69 to -90 °C). Each crystal was mounted on the tip of a glass fiber using a heavy-weight oil. The unit cell parameters of each crystal from six image frames were retrieved using the Rigaku *Daemon* software and refined with *CrystalClear* on all of the observed reflections.<sup>18</sup> Data using 0.5° intervals in φ and ω for 20–45 s/frame were collected with a maximum resolution of 0.77 Å (55°, 744 oscillation images). The data were corrected for Lorentz and polarization effects. An empirical absorption correction was applied for each complex.<sup>18–20</sup> Structures were solved by direct methods (*SIR* 92<sup>21</sup> or *SIR* 97<sup>22</sup>). The positions of the metal atoms and their first coordination sphere were located from the E-map; other non-hydrogen atoms were found in alternating difference Fourier syntheses.<sup>23</sup> Least-squares refinement was carried out anisotropically during the final cycles

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**Table 1.** Crystallographic Data of Ligand L1'' and of the Complexes **1CuCl<sub>2</sub>**, **1ClO<sub>4</sub>**, **2ClO<sub>4</sub>**, **2BF<sub>4</sub>**, and **3PF<sub>6</sub>**

complex	L1''	<b>1CuCl<sub>2</sub></b>	<b>1ClO<sub>4</sub></b> ·5CHCl <sub>3</sub>	<b>2ClO<sub>4</sub></b> ·2CH <sub>2</sub> Cl <sub>2</sub> ·C <sub>4</sub> H <sub>8</sub> O	<b>2BF<sub>4</sub></b> ·2CH <sub>2</sub> Cl <sub>2</sub> ·C <sub>4</sub> H <sub>8</sub> O·2H <sub>2</sub> O	<b>3PF<sub>6</sub></b>
formula	C <sub>19</sub> H <sub>32</sub> N <sub>4</sub>	C <sub>38</sub> H <sub>64</sub> Cl <sub>2</sub> Cu <sub>2</sub> N <sub>8</sub>	C <sub>43</sub> H <sub>69</sub> Cl <sub>16</sub> Cu <sub>2</sub> N <sub>8</sub> O <sub>4</sub>	C <sub>44</sub> H <sub>76</sub> Cl <sub>16</sub> Cu <sub>2</sub> N <sub>8</sub> O <sub>9</sub>	C <sub>44</sub> H <sub>80</sub> B <sub>2</sub> Cl <sub>4</sub> Cu <sub>2</sub> F <sub>8</sub> N <sub>8</sub> O <sub>3</sub>	C <sub>21</sub> H <sub>32</sub> CuF <sub>6</sub> N <sub>3</sub> P
fw	316.49	830.98	1392.86	1200.94	1211.68	563.03
space group	<i>P</i> 2 <sub>1</sub> / <i>c</i> (no. 14)	<i>P</i> 1̄ (no. 2)	<i>P</i> 2 <sub>1</sub> / <i>n</i> (no. 14)	<i>C</i> 2/ <i>c</i> (no. 15)	<i>C</i> 2/ <i>c</i> (no. 15)	<i>Pna</i> 2 <sub>1</sub> (no. 33)
<i>a</i> (Å)	8.8156(10)	8.9380(2)	14.1946(4)	20.5140(17)	20.4617(14)	20.370(10)
<i>b</i> (Å)	19.959(2)	9.2290(2)	23.0068(5)	13.6093(9)	13.6674(7)	13.493(7)
<i>c</i> (Å)	10.9411(15)	26.3640(9)	20.3309(5)	21.0771(18)	20.8773(10)	9.657(5)
α (deg)	90	80.693(5)	90	90	90	90
β (deg)	96.308(7)	81.471(5)	97.0640(4)	100.4450(14)	99.7430(10)	90
γ (deg)	90	84.762(5)	90	90	90	90
<i>V</i> (Å <sup>3</sup> )	1913.4(4)	2117.32(10)	6589.1(3)	5786.8(8)	5754.3(6)	2654(2)
<i>Z</i>	4	2	4	4	4	4
reflns collected/unique	15 365/4362	16 297/9179	51 519/15 039	19 083/6468	22 359/6564	20 336/3156
obsd reflns	3240 ( <i>I</i> > 3σ( <i>I</i> ))	4920 ( <i>I</i> > 3σ( <i>I</i> ))	4533 ( <i>I</i> > 5σ( <i>I</i> ))	4263 ( <i>I</i> > 3σ( <i>I</i> ))	4618 ( <i>I</i> > 3σ( <i>I</i> ))	2442 ( <i>I</i> > 3σ( <i>I</i> ))
reflns params	240	518	744	359	359	339
final <i>R</i> , <i>R</i> <sub>w</sub> <sup>a</sup>	0.054, 0.051	0.069, 0.082	0.058, 0.068	0.095, 0.107	0.076, 0.094	0.055, 0.054

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|; R_w = [(\sum w(|F_o| - |F_c|)^2) / \sum w F_o^2]^{1/2}, w = 1/\sigma^2(|F_o|).$$

**Table 2.** Crystallographic Data of the Complexes **4ClO<sub>4</sub>**, **4PF<sub>6</sub>**, **5ClO<sub>4</sub>**, **6**, **7**, and **8ClO<sub>4</sub>**

complex	<b>4ClO<sub>4</sub></b>	<b>4PF<sub>6</sub></b>	<b>5ClO<sub>4</sub></b> ·2CH <sub>2</sub> Cl <sub>2</sub>	<b>6</b> ·6CH <sub>2</sub> Cl <sub>2</sub>	<b>7</b> ·2CH <sub>2</sub> Cl <sub>2</sub>	<b>8ClO<sub>4</sub></b> ·1.5CH <sub>2</sub> Cl <sub>2</sub>
formula	C <sub>37</sub> H <sub>47</sub> ClCuN <sub>4</sub> O <sub>4</sub> P	C <sub>37</sub> H <sub>47</sub> CuF <sub>6</sub> N <sub>4</sub> P <sub>2</sub>	C <sub>42</sub> H <sub>68</sub> Cl <sub>6</sub> Cu <sub>2</sub> N <sub>8</sub> O <sub>10</sub>	C <sub>44</sub> H <sub>78</sub> Cl <sub>14</sub> Cu <sub>2</sub> N <sub>8</sub> O <sub>10</sub>	C <sub>21</sub> H <sub>36</sub> Cl <sub>6</sub> CuN <sub>4</sub>	C <sub>47.5</sub> H <sub>64</sub> Cl <sub>4</sub> CuN <sub>6</sub> O <sub>4</sub> P
fw	741.78	787.29	1184.86	1502.58	620.81	1019.40
space group	<i>P</i> 1̄ (no. 2)	<i>P</i> 1̄ (no. 2)	<i>P</i> 2 <sub>1</sub> / <i>c</i> (no. 14)	<i>P</i> 1̄ (no. 2)	<i>P</i> 1̄ (no. 2)	<i>Pbca</i> (no. 61)
<i>a</i> (Å)	10.3789(4)	10.49370(10)	12.6250(2)	9.76550(10)	12.931(5)	19.3853(4)
<i>b</i> (Å)	18.1638(7)	13.2790(2)	19.2085(4)	12.83230(10)	13.192(5)	20.7432(4)
<i>c</i> (Å)	20.1690(7)	14.9003(2)	24.0421(5)	15.41210(10)	20.405(9)	25.8555(5)
α (deg)	98.9760(17)	82.208(5)	90	68.413(8)	78.57(2)	90
β (deg)	99.6730(17)	76.009(5)	105.0230(2)	78.870(9)	77.268(2)	90
γ (deg)	90.6630(15)	71.340(4)	90	71.475(8)	64.711(16)	90
<i>V</i> (Å <sup>3</sup> )	3699.5(2)	1904.96(4)	5631.11(19)	1696.47(2)	3048.4(20)	10 396.8(4)
<i>Z</i>	4	2	4	1	4	8
reflns collected/unique	29 531/16 422	15 440/8426	43 053/12 713	13 166/7509	24 687/13 686	78 630/11 886
obsd reflns	8300 ( <i>I</i> > 3σ( <i>I</i> ))	5389 ( <i>I</i> > 3σ( <i>I</i> ))	4139 ( <i>I</i> > 5σ( <i>I</i> ))	4355 ( <i>I</i> > 5σ( <i>I</i> ))	15 216 ( <i>I</i> > 5σ( <i>I</i> ))	5186 ( <i>I</i> > 5σ( <i>I</i> ))
reflns params	959	498	681	391	649	660
final <i>R</i> , <i>R</i> <sub>w</sub> <sup>a</sup>	0.068, 0.075	0.057, 0.068	0.042, 0.053	0.068, 0.072	0.085, 0.105	0.1656, 0.1995

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|; R_w = [(\sum w(|F_o| - |F_c|)^2) / \sum w F_o^2]^{1/2}, w = 1/\sigma^2(|F_o|).$$

(*CrystalStructure*).<sup>19,20</sup> Hydrogen atoms were placed in calculated positions but not refined anisotropically. Strong remaining peaks in **1ClO<sub>4</sub>**, **2ClO<sub>4</sub>**, **2BF<sub>4</sub>**, **6**, **7**, and **8ClO<sub>4</sub>** are due to disordered solvent molecules. Hydrogen atoms of solvent water molecules in **2BF<sub>4</sub>** were not placed. Chlorine atoms of one of the solvent molecules CHCl<sub>3</sub> in **1ClO<sub>4</sub>** and CH<sub>2</sub>Cl<sub>2</sub> in **2ClO<sub>4</sub>** were highly disordered; therefore, sets of them have equal occupancy. The structure of **8ClO<sub>4</sub>** could not be determined at a very good quality because of a high degree of disorder even at low temperature (−90 °C). The absolute configuration of **3PF<sub>6</sub>** was confirmed from the values of the Flack parameters.<sup>24</sup>

## Results and Discussion

**A. Syntheses and Structures. General Synthetic Procedures.** The coordination chemistry of bis(pyrazolyl)-methanes toward transition-metal ions has received increasing attention, and many transition-metal complexes containing bis(pyrazolyl)methanes have been synthesized and characterized in recent years.<sup>3–7,10,25,26</sup> These ligands are especially valuable for the preparation of two- and three-coordinate transition-metal complexes, which are active in catalysis due to their unsaturated coordination environment.<sup>4</sup> In addition, a number of heteroscorpionate ligands based on bis(pyra-

zoly)methane have been prepared,<sup>26</sup> which further underlines the fundamental importance of the coordination chemistry of these ligands. The synthesis of H<sub>2</sub>C(3,5-*i*Pr<sub>2</sub>pz)<sub>2</sub> (L1'') was reported previously in ref 3f. We have prepared this ligand by an alternative method using an autoclave, and, this way we were able to obtain crystals for X-ray analysis. This method can lead to higher yields and substantially less darkening of the reaction mixture, compared to the procedure reported before.<sup>3f</sup>

To avoid the reaction of the copper(I) complexes with dioxygen, all of the compounds were prepared in a glovebox. Schematic drawings of all of the transformations performed in this work are presented in Scheme 1. Details are available from the Experimental Section and Section C. Complexes [Cu(L1'')<sub>2</sub>](CuCl<sub>2</sub>) (**1CuCl<sub>2</sub>**) and [Cu(L1'')(NCMe)](PF<sub>6</sub>) (**3PF<sub>6</sub>**) were obtained from L1'' and the corresponding copper(I) salts. [Cu(L1'')<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> (**2ClO<sub>4</sub>**) and [Cu(L1'')<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> (**2BF<sub>4</sub>**) were synthesized by the reaction of **1CuCl<sub>2</sub>** with AgClO<sub>4</sub> and AgBF<sub>4</sub>, respectively. [Cu(L1'')(PPh<sub>3</sub>)](ClO<sub>4</sub>) (**4ClO<sub>4</sub>**) and [Cu(L1'')(PPh<sub>3</sub>)](PF<sub>6</sub>) (**4PF<sub>6</sub>**) were

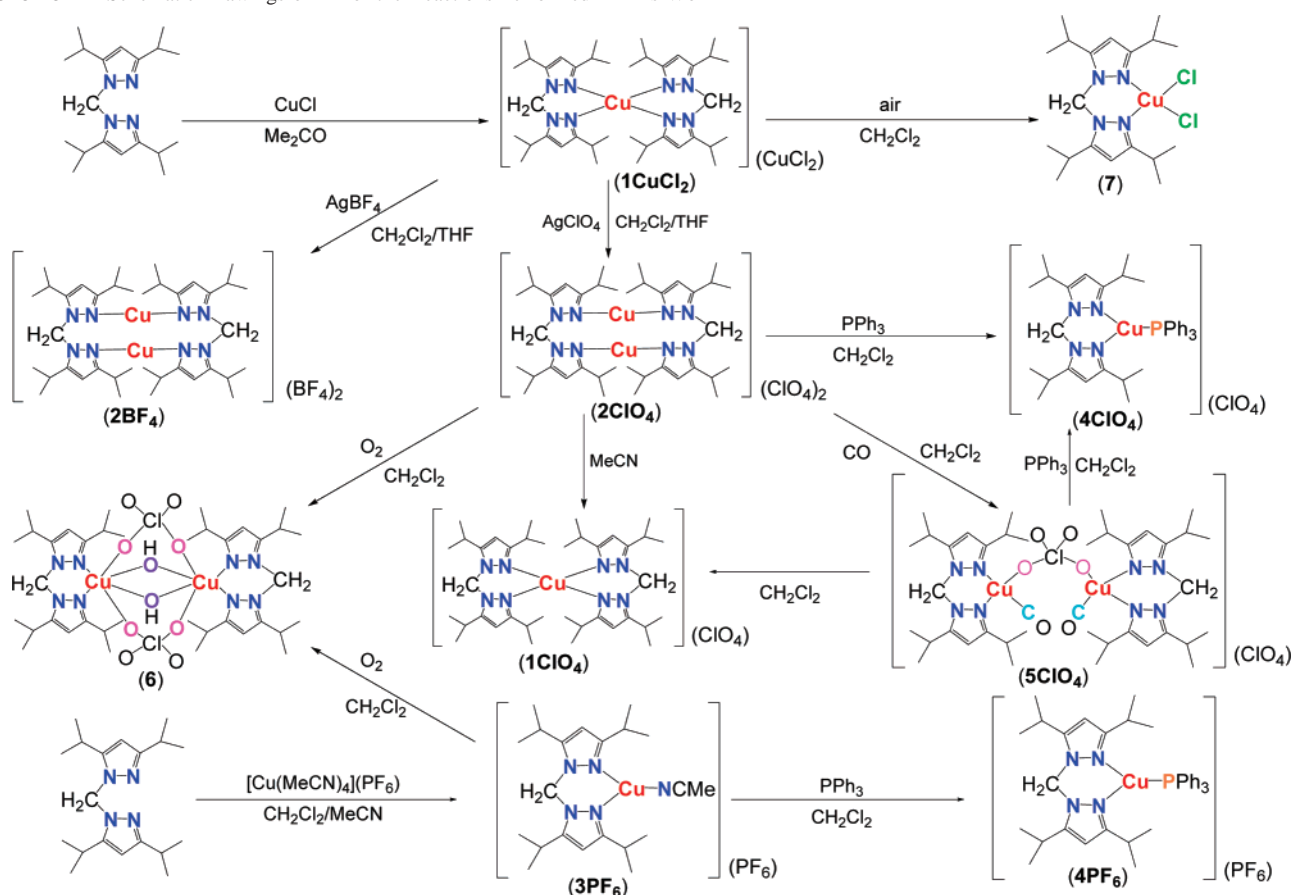
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**Scheme 1.** Schematic Drawings of All of the Reactions Performed in This Work



obtained from the reaction of **2ClO<sub>4</sub>** and **3PF<sub>6</sub>** with PPh<sub>3</sub>, respectively. [{Cu(LI')(CO)}<sub>2</sub>(μ-ClO<sub>4</sub>)](ClO<sub>4</sub>) (**5ClO<sub>4</sub>**), [Cu-(LI'')<sub>2</sub>](ClO<sub>4</sub>) (**1ClO<sub>4</sub>**), and [{Cu(LI'')<sub>2</sub>(μ-OH)<sub>2</sub>(μ-ClO<sub>4</sub>)<sub>2</sub>] (**6**) were synthesized by the reaction of **2ClO<sub>4</sub>** with CO, MeCN, and O<sub>2</sub>, respectively. The copper(II) chloro complex [Cu(LI')Cl<sub>2</sub>] (**7**) was synthesized by stirring **1CuCl<sub>2</sub>** in dichloromethane in air. [Cu(LI')(PPh<sub>3</sub>)](ClO<sub>4</sub>) (**8ClO<sub>4</sub>**) and [Cu(LI)(PPh<sub>3</sub>)] (**9**) were generated by the reaction of PPh<sub>3</sub> with [Cu(LI')(OCIO<sub>3</sub>)]<sup>9</sup> and [Cu(LI)(NCMe)]<sup>9</sup>, respectively.

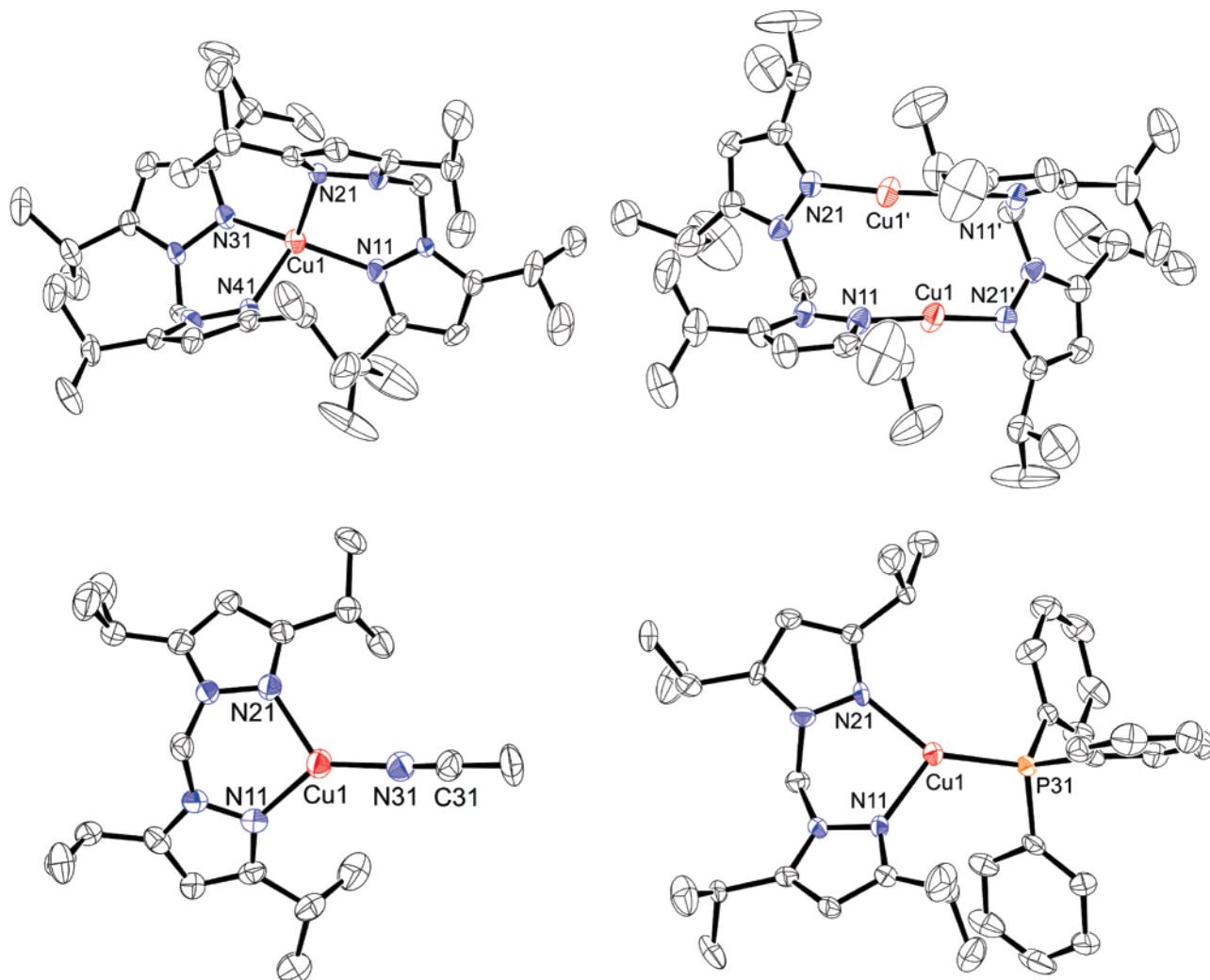
**Structures and Insight from Complex Syntheses.** An ORTEP drawing of the crystal structure of ligand L1'' is shown in Figure S1 in the Supporting Information (structural parameters: see Table S1 in the Supporting Information). The averaged C(methylene)–N distance and N–C(methylene)–N angle are 1.450 Å and 113.7°, respectively. These values are almost identical to those of the corresponding neutral tridentate ligand L1' (1.447 Å and 112.7°).

The copper complexes **1CuCl<sub>2</sub>**, **1ClO<sub>4</sub>**, **2ClO<sub>4</sub>**, **2BF<sub>4</sub>**, **3PF<sub>6</sub>**, **4ClO<sub>4</sub>**, **4PF<sub>6</sub>**, **5ClO<sub>4</sub>**, **6**, and **7** with L1'' were also obtained as crystals suitable for X-ray crystallography. The ORTEP drawings of these complexes are shown in Figures 2 and 3, with exception of **1ClO<sub>4</sub>**, **2BF<sub>4</sub>**, and **4PF<sub>6</sub>**, which are presented in Figure S2 in the Supporting Information. Selected bond distances and angles are listed in Table 3. The preliminary structure of **8ClO<sub>4</sub>** is shown in Figure S3 in the Supporting Information (structural parameters: see Table S2 in the Supporting Information).

In complex  $[\text{Cu}(\text{L}'')_2](\text{CuCl}_2)$  (**1CuCl<sub>2</sub>**) containing the unusual counterion  $(\text{Cu}^+\text{Cl}_2)^-$ , the copper(I) ion is in a distorted tetrahedral environment with two bidentate ligands  $\text{L}''$  bound, showing Cu–N distances ranging from 1.993(5) to 2.120(6) Å and N–Cu–N angles ranging from 95.6(2) to 134.6(2)° (Figure 2, top left). The overall structure is similar to that of the previously reported complex  $[\text{Cu}\{\text{H}_2\text{C}(\text{pz})_2\}_2](\text{ClO}_4)$ .<sup>5</sup> The dihedral angle between the two chelating planes (N11–Cu1–N21 and N31–Cu1–N41) is 94.1°, which is somewhat larger than the 90.0° expected for a tetrahedral geometry. Importantly, a three-coordinate complex of type  $[\text{Cu}(\text{L}'')(\text{Cl})]$  is therefore avoided by copper(I) in this case by undergoing a *ligand disproportionation reaction*:



Correspondingly, treatment of the tridentate ligand L1' with CuCl results in the clean formation of [Cu(L1')(Cl)].<sup>9</sup> A similar ligand disproportionation process is observed during the formation of [Cu(L1'')<sub>2</sub>](ClO<sub>4</sub>) (**1ClO<sub>4</sub>**), is shown in Figure S2, top in the Supporting Information. In this case, the formation of [Cu(L1'')(NCMe)]<sup>+</sup> is avoided (cf. Scheme 1) by the generation of [Cu(L1'')<sub>2</sub>]<sup>+</sup> and [Cu(NCMe)<sub>4</sub>]<sup>+</sup> (not isolated). **1ClO<sub>4</sub>** with ClO<sub>4</sub><sup>-</sup> as a counterion has a very similar structure to that of **1CuCl<sub>2</sub>** (cf. Table 3). The dihedral angle of the two chelating planes (N11–Cu1–N21 and N31–Cu1–N41) is only 91.3° in this case. The difference



**Figure 2.** Crystal structures of the cationic parts of  $[\text{Cu}(\text{L1}'')_2](\text{CuCl}_2)$  (**1CuCl<sub>2</sub>**) (top left),  $[\text{Cu}(\text{L1}'')_2](\text{ClO}_4)_2$  (**2ClO<sub>4</sub>**) (top right),  $[\text{Cu}(\text{L1}'')(\text{NCMe})](\text{PF}_6)$  (bottom left), and  $[\text{Cu}(\text{L1}'')(\text{PPh}_3)](\text{ClO}_4)$  (**4ClO<sub>4</sub>**) (bottom right). The hydrogen atoms are omitted for clarity. All of the ellipsoids are drawn at the 50% probability level. In the case of **4ClO<sub>4</sub>**, two crystallographically independent molecules are present, whose structural features are essentially identical. Molecule 1 is presented here.

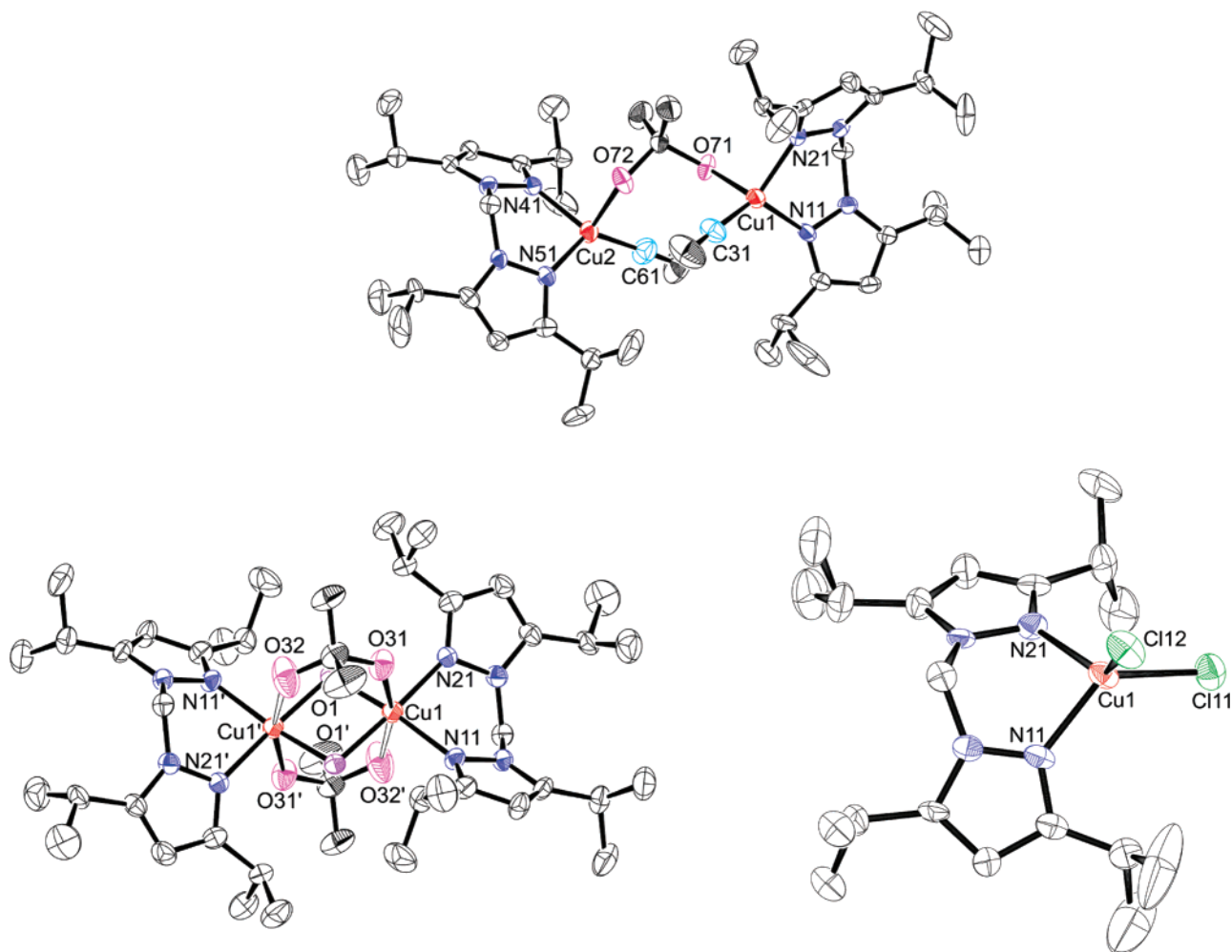
between **1CuCl<sub>2</sub>** and **1ClO<sub>4</sub>** relates to somewhat stronger interactions between the copper(I) center and the counterion in **1ClO<sub>4</sub>**.

Interestingly, the molecular structures of  $[\text{Cu}(\text{L1}'')_2](\text{ClO}_4)_2$  (**2ClO<sub>4</sub>**) and  $[\text{Cu}(\text{L1}'')_2](\text{BF}_4)_2$  (**2BF<sub>4</sub>**) correspond to binuclear linear-coordinated copper(I) complexes with two bridging L1'' ligands and two  $\text{ClO}_4^-$  or two  $\text{BF}_4^-$  counterions, respectively (Figure 2, top right; and Figure S2, center in the Supporting Information). Importantly, the N–Cu–N angles are close to  $180^\circ$  in **2ClO<sub>4</sub>** and **2BF<sub>4</sub>**. In this case, the formation of the three-coordinate complex  $[\text{Cu}(\text{L1}'')(\text{ClO}_4)]$  is avoided by dimerization (ligand disproportionation does not happen here because  $[\text{Cu}(\text{ClO}_4)_2]^-$  with the weak ligand perchlorate is unstable). The same situation leading to the formation of  $[\text{Cu}(\text{L1}'')_2]^{2+}$  is encountered with the non-coordinating counterion  $\text{BF}_4^-$ . Iber and co-workers previously reported the structures of binuclear linear-coordinated copper(I) complexes such as  $[\text{Cu}(\text{HBpz}_3)]_2$  and  $[\text{Cu}\{\text{HB}(3,5\text{-Me}_2\text{pz})_3\}]_2$ .<sup>27</sup> In these cases, monoanionic tridentate ligands such as  $\text{HBpz}_3^-$  and  $\text{HB}(3,5\text{-Me}_2\text{pz})_3^-$  have been applied.

Because the N–Cu–N angles of  $[\text{Cu}(\text{HBpz}_3)]_2$  and  $[\text{Cu}\{\text{HB}(3,5\text{-Me}_2\text{pz})_3\}]_2$  are not linear (N–Cu–N =  $\sim 140^\circ$ ), the Cu⋯Cu distances are distinctively shorter in these cases compared to **2ClO<sub>4</sub>** and **2BF<sub>4</sub>** (Cu⋯Cu distance: 2.66 Å in  $[\text{Cu}(\text{HBpz}_3)]_2$ , 2.51 Å in  $[\text{Cu}\{\text{HB}(3,5\text{-Me}_2\text{pz})_3\}]_2$ , 2.97 Å in **2ClO<sub>4</sub>**, and 2.91 Å in **2BF<sub>4</sub>**). These differences again relate to the different coordination number (bidentate vs tridentate) and charge (neutral vs anionic) of L1'' and these hydrotris-(pyrazolyl)borate ligands. Correspondingly, using the neutral tridentate ligand L1', treatment of  $[\text{Cu}(\text{L1}')(\text{Cl})]$  with  $\text{AgClO}_4$  results in the straightforward formation of the tetrahedral complex  $[\text{Cu}(\text{L1}')(\text{OCIO}_3)]$ .<sup>9</sup> Therefore, to obtain the desired three-coordinate complexes of type  $[\text{Cu}(\text{L1}'')(\text{X})\text{Z}]$  with a neutral bidentate ligand, stronger ligands such as acetonitrile or triphenylphosphine are needed to prevent this dimer formation. Note that related complexes with less-hindered bis(pyrazolyl)methanes ( $\text{H}_2\text{Cpz}_2$  or  $\text{H}_2\text{C}(3,5\text{-Me}_2\text{pz})_2$ ) have

(27) (a) Arcus, C. S.; Wilkinson, J. L.; Mealli, C.; Marks, T. J.; Iber, J. A. *J. Am. Chem. Soc.* **1974**, *96*, 7564–7565. (b) Mealli, C.; Arcus, C. S.; Wilkinson, J. L.; Marks, T. J.; Iber, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 711–718.





**Figure 3.** Crystal structures of the cationic parts of  $[\{\text{Cu}(\text{L1}'')(\text{CO})\}_2(\mu\text{-ClO}_4)](\text{ClO}_4)$  (**5ClO<sub>4</sub>**) (top),  $[\{\text{Cu}(\text{L1}')\}_2(\mu\text{-OH})_2(\mu\text{-ClO}_4)_2]$  (**6**) (bottom left), and  $[\text{Cu}(\text{L1}')\text{Cl}_2]$  (**7**) (bottom right). The hydrogen atoms are omitted for clarity. All of the ellipsoids are drawn at the 50% probability level. In the case of **7**, two crystallographically independent molecules are present, whose structural features are essentially identical. Molecule 1 is presented here.

not been obtained, indicating that the alkyl substitution of  $\text{L1}'$  is also critical for the nature of the complexes formed.<sup>5,6</sup>

The copper(I) acetonitrile complex **3PF<sub>6</sub>** finally has the desired trigonal-planar structure (total angle around the copper(I) ion:  $360^\circ$ ) as shown in Figure 2, bottom left. As mentioned above, the formation of this complex is enabled by the strong ligand acetonitrile combined with the strictly non-coordinating counterion  $\text{PF}_6^-$ . The geometry of this complex is very similar to  $[\text{Cu}\{\text{H}_2\text{C}(3,5\text{-Me}_2\text{pz})_2\}(\text{NCMe})](\text{ClO}_4)$  published before with a less-hindered bidentate ligand.<sup>6</sup> The deviation of the copper(I) ion from the  $\text{N11-N21-N31}$  plane in **3PF<sub>6</sub>** is only  $0.008 \text{ \AA}$ , which is smaller than the value of  $0.078 \text{ \AA}$  observed for  $[\text{Cu}\{\text{H}_2\text{C}(3,5\text{-Me}_2\text{pz})_2\}(\text{NCMe})](\text{ClO}_4)$ . This might relate to the stronger interaction of copper(I) with perchlorate ( $\text{Cu}\cdots\text{O}(\text{ClO}_4^-) = 3.181 \text{ \AA}$ ) in the latter case compared to the  $\text{Cu}(\text{I})\cdots\text{F}$  interaction in **3PF<sub>6</sub>** ( $\text{Cu1}\cdots\text{F45}(\text{PF}_6^-) = 4.939(4) \text{ \AA}$ ). Furthermore, the difference in alkyl substituents of these ligands seems to contribute to this difference. The  $\text{Cu}^{\text{I}}\text{-N}(\text{MeCN})$  distance of  $1.870(5) \text{ \AA}$  in **3PF<sub>6</sub>** is similar to the reported values for  $[\text{Cu}(\text{L1}')(\text{NCMe})](\text{PF}_6)$ <sup>9</sup> ( $1.887(5) \text{ \AA}$ ) and  $[\text{Cu}\{\text{H}_2\text{C}(3,5\text{-Me}_2\text{pz})_2\}(\text{NCMe})](\text{ClO}_4)$ <sup>6</sup> ( $1.879(5) \text{ \AA}$ ). Because of the small size of MeCN, this ligand does not experience

much steric repulsion, which leads to similar  $\text{Cu}^{\text{I}}\text{-N}(\text{MeCN})$  distances in all of these complexes.

The molecular structures of  $[\text{Cu}(\text{L1}'')(\text{PPh}_3)](\text{ClO}_4)$  (**4ClO<sub>4</sub>**) and  $[\text{Cu}(\text{L1}'')(\text{PPh}_3)](\text{PF}_6)$  (**4PF<sub>6</sub>**) with the strong ligand triphenylphosphine are both trigonal planar (total angles around the copper(I) ion:  $357.2^\circ$  in **4ClO<sub>4</sub>** and  $358.2^\circ$  in **4PF<sub>6</sub>**) as shown in Figure 2, bottom right and in Figure S2, bottom in the Supporting Information. Note that, in the case of **4ClO<sub>4</sub>**, two crystallographically independent complex molecules exist. The copper(I) ion is slightly deviated from the  $\text{N-N-P}(\text{PPh}_3)$  plane by  $0.170$  and  $0.208 \text{ \AA}$  in **4ClO<sub>4</sub>**, and by  $0.155 \text{ \AA}$  in **4PF<sub>6</sub>** toward the counterion ( $\text{Cu}\cdots\text{O}(\text{ClO}_4^-)$ :  $4.83$  and  $5.25 \text{ \AA}$  in **4ClO<sub>4</sub>**,  $\text{Cu}\cdots\text{F}(\text{PF}_6^-)$ :  $4.45 \text{ \AA}$  in **4PF<sub>6</sub>**). The steric hindrance between the *i*Pr groups of  $\text{L1}''$  and the bulky  $\text{PPh}_3$  ligand leads to a slight lengthening of the average  $\text{Cu-N}$  distance ( $2.008 \text{ \AA}$  in **4ClO<sub>4</sub>** and  $2.006 \text{ \AA}$  in **4PF<sub>6</sub>**) and asymmetric bidentate coordination of  $\text{L1}''$  ( $\Delta = 0.042$  (Cu1) and  $0.028 \text{ \AA}$  (Cu2) in **4ClO<sub>4</sub>** and  $0.035 \text{ \AA}$  in **4PF<sub>6</sub>**) as compared to the three-coordinate acetonitrile complex **3PF<sub>6</sub>** ( $\text{Cu-N} = 1.997 \text{ \AA}$  and  $\Delta = 0.004 \text{ \AA}$ ). Interestingly, the bulky *i*Pr groups of  $\text{L1}''$  seem to keep the counteranion away from copper, and, this way, play an important role in achieving three-coordinate copper com-

**Table 3.** Selected Bond Distances (Å) and Angles (Degrees) for Complexes Characterized by X-ray Crystallography<sup>a</sup>

[Cu(L1'') <sub>2</sub> ](CuCl <sub>2</sub> ) ( <b>1CuCl<sub>2</sub></b> )			
Cu1–N11	1.999(5)	Cu1–N21	2.209(5)
Cu1–N41	2.120(6)	N11–Cu1–N21	98.6(2)
N11–Cu1–N41	107.6(2)	N21–Cu1–N31	112.3(2)
N31–Cu1–N41	95.6(2)		
[Cu(L1'') <sub>2</sub> ](ClO <sub>4</sub> ) ( <b>1ClO<sub>4</sub></b> ) <sup>b</sup>			
Cu1–N11	2.186(7)	Cu1–N21	1.972(5)
Cu1–N41	2.001(6)	N11–Cu1–N21	96.1(2)
N11–Cu1–N41	109.9(2)	N21–Cu1–N31	111.5(2)
N31–Cu1–N41	97.2(2)		
[Cu(L1'') <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub> ( <b>2ClO<sub>4</sub></b> ) <sup>c</sup>			
Cu1–N11	1.868(5)	Cu1–N21'	1.874(5)
N11–Cu1–N21'	176.0(2)		
[Cu(L1'') <sub>2</sub> ](BF <sub>4</sub> ) <sub>2</sub> ( <b>2BF<sub>4</sub></b> ) <sup>b,c</sup>			
Cu1–N11	1.878(3)	Cu1–N21'	1.874(3)
N11–Cu1–N21	174.58(18)		
[Cu(L1'')](NCMe)](PF <sub>6</sub> ) ( <b>3PF<sub>6</sub></b> )			
Cu1–N11	1.999(5)	Cu1–N21	1.995(5)
N11–Cu1–N21	96.1(2)	N11–Cu1–N31	138.0(2)
Cu1–N31–C31	175.3(6)		
[Cu(L1'')](PPh <sub>3</sub> )](ClO <sub>4</sub> ) ( <b>4ClO<sub>4</sub></b> )			
Cu1–N11	2.024(5)	Cu1–N21	1.982(6)
Cu2–N51	1.998(6)	Cu2–N61	2.026(5)
N11–Cu1–N21	93.3(2)	N11–Cu1–P31	122.87(18)
N51–Cu2–N61	93.4(2)	N51–Cu2–P61	139.60(16)
[Cu(L1'')](PPh <sub>3</sub> )](PF <sub>6</sub> ) ( <b>4PF<sub>6</sub></b> ) <sup>b</sup>			
Cu1–N11	1.988(3)	Cu1–N21	2.023(4)
N11–Cu1–N21	93.60(15)	N11–Cu1–P31	140.67(13)
[{Cu(L1'')}(CO)] <sub>2</sub> (μ-ClO <sub>4</sub> )](ClO <sub>4</sub> ) ( <b>5ClO<sub>4</sub></b> )			
Cu1–N11	2.017(6)	Cu1–N21	2.030(7)
Cu1–O71	2.252(5)	Cu2–N41	1.989(6)
Cu2–C61	1.802(10)	Cu2–O72	2.311(5)
C61–O62	1.115(13)	N11–Cu1–N21	97.3(3)
N21–Cu1–C31	126.5(3)	N11–Cu1–O71	95.8(2)
O71–Cu1–C31	105.6(3)	Cu1–C31–O31	178.3(9)
N41–Cu2–C61	128.6(3)	N51–Cu2–C61	125.8(3)
N51–Cu2–O72	98.7(2)	O72–Cu2–C61	102.9(3)
[{Cu(L1'')}(μ-OH)] <sub>2</sub> (μ-ClO <sub>4</sub> ) <sub>2</sub> ( <b>6</b> ) <sup>d</sup>			
Cu1–N11	2.018(6)	Cu1–N21	1.995(4)
Cu1–O1'	1.921(3)	Cu1–O31	2.428(4)
Cu1···Cu1'	2.9466(10)	N11–Cu1–N21	90.3(2)
N11–Cu1–O1'	95.80(19)	N21–Cu1–O1	93.3(2)
O1–Cu1–O1'	79.89(18)	Cu1–O1–Cu1'	100.1(2)
N11–Cu1–O32'	99.84(19)	N21–Cu1–O31	92.96(18)
O1–Cu1–O31	94.54(19)	O1–Cu1–O32'	72.97(19)
O1'–Cu1–O32'	81.19(15)		
[Cu(L1'')Cl <sub>2</sub> ] ( <b>7</b> )			
Cu1–N11	1.971(4)	Cu1–N21	1.999(5)
Cu1–Cl12	2.234(2)	Cu2–N31	1.967(4)
Cu2–Cl22	2.2157(14)	Cu2–Cl21	2.228(2)
N11–Cu1–Cl11	127.81(13)	N11–Cu1–Cl12	101.35(16)
N21–Cu1–Cl12	125.30(14)	Cl11–Cu1–Cl12	103.67(6)
N31–Cu2–Cl21	131.38(15)	N31–Cu2–Cl22	97.82(16)
N41–Cu2–Cl22	128.16(14)	Cl21–Cu2–Cl22	102.77(6)
		Cu1–Cl11	2.2214(14)
		Cu2–N41	2.023(5)
		N11–Cu1–N21	90.2(2)
		N21–Cu1–Cl11	110.45(15)
		N31–Cu2–N41	90.3(2)
		N41–Cu2–Cl21	109.41(13)

<sup>a</sup> Estimated standard deviations indicated in parentheses. <sup>b</sup> Structures are presented in the Supporting Information. <sup>c</sup> Symmetry code:  $-x + 1, y, -z + 1/2 + 1$ . <sup>d</sup> Symmetry code:  $-x + 1, -y, -z + 1$ .

plexes. This can be seen by comparison with [Cu{H<sub>2</sub>C(3,5-Me<sub>2</sub>pz)<sub>2</sub>}(PPh<sub>3</sub>)](ClO<sub>4</sub>), where the Cu···O(ClO<sub>4</sub><sup>−</sup>) distance is only 2.574 Å. The Cu–P(PPh<sub>3</sub>) distances of 2.171(2) and 2.177(2) Å in **4ClO<sub>4</sub>**, 2.174(2) Å in **4PF<sub>6</sub>**, and 2.173(1) Å in [Cu{H<sub>2</sub>C(3,5-Me<sub>2</sub>pz)<sub>2</sub>}(PPh<sub>3</sub>)](ClO<sub>4</sub>)<sup>6</sup> are extremely similar. Selected bond distances and angles of these compounds are summarized in Table 4, which also provides a comparison with other PPh<sub>3</sub> complexes with related nitrogen-containing ligands.<sup>28</sup>

The molecular structure of **5ClO<sub>4</sub>** consists of a binuclear [{Cu(L1'')(CO)]<sub>2</sub>(μ-ClO<sub>4</sub>)]<sup>+</sup> unit, where two {Cu(L1'')(CO)}<sup>+</sup> subunits are bridged by ClO<sub>4</sub><sup>−</sup> (Figure 3, top). This way, the formation of the three-coordinate complex [Cu(L1'')(CO)]<sup>+</sup> is avoided. This is possible as a result of the small size of CO, which allows a direct dimerization of the subunits, and the presence of a coordinating counterion, which functions as a bridge. Nevertheless, it is surprising to find a dimeric species in this case, because coordination of

**Table 4.** Selected Structural Parameters for Copper(I) Triphenylphosphine Complexes with Bidentate or Tridentate Coligands

	Cu–N (av) (Å)	N–Cu–N (av) (deg)	Cu–P (Å)	$\delta$ ( $^{31}\text{P}$ ) (ppm)	ref
neutral Nn (n = 2 or 3) coligands					
[Cu(L1'')(PPh <sub>3</sub> )](ClO <sub>4</sub> ) ( <b>4ClO<sub>4</sub></b> )	2.008(6)	93.4(2)	2.174(2) <sup>a</sup>	12.11	this work
[Cu(L1'')(PPh <sub>3</sub> )](PF <sub>6</sub> ) ( <b>4PF<sub>6</sub></b> )	2.006(4)	93.6(1)	2.1726(12)	12.20	this work
[Cu{H <sub>2</sub> C(3,5-Me <sub>2</sub> pz) <sub>2</sub> }(PPh <sub>3</sub> )](ClO <sub>4</sub> )	2.019(6)	95.0(2)	2.171(2)	<sup>c</sup>	6
[Cu(L1')(PPh <sub>3</sub> )](ClO <sub>4</sub> ) ( <b>8ClO<sub>4</sub></b> )	2.085(10)	89.0(4)	2.159(4)	13.79 <sup>b</sup>	this work
anionic N3 coligand					
[Cu{HB(3,5-Me <sub>2</sub> pz) <sub>3</sub> }(PPh <sub>3</sub> )]	2.098(14)	90.6(5)	2.166(6)	11.87 <sup>b</sup>	28

<sup>a</sup> Average distance. <sup>b</sup> Broad. <sup>c</sup> Not reported.**Table 5.** Selected Structural Parameters and Properties of Copper(I)–Carbonyl Complexes with Bidentate and Tridentate Coligands

	Cu–N (av) (Å) <sup>a</sup>	Cu–C (Å)	C–O (Å)	Cu–C–O (deg)	$\nu$ (C–O) (cm <sup>−1</sup> )	$\delta$ ( $^{13}\text{C}$ ) (ppm)	ref
neutral Nn (n = 2 or 3) coligands							
[{Cu(L1'')(CO)} <sub>2</sub> ( $\mu$ -ClO <sub>4</sub> )](ClO <sub>4</sub> ) ( <b>5ClO<sub>4</sub></b> )	2.010(7)	1.809(10) <sup>a</sup>	1.110(13) <sup>a</sup>	178.5(10) <sup>a</sup>	2104	172.9	this work
[Cu{H <sub>2</sub> C(3,5-Me <sub>2</sub> pz) <sub>2</sub> }(CO)(OCIO <sub>3</sub> )]	2.004(3)	1.806(5)	1.124(6)	176.8(4)	2108	173.9	6
[Cu(NH(py) <sub>2</sub> )(CO)(OCIO <sub>3</sub> )]	1.991(1)	1.808(2)	<sup>b</sup>	<sup>b</sup>	2110	<sup>b</sup>	29
[Cu(en)(CO)(PhBPh <sub>3</sub> )]	2.041(4)	1.806(6)	1.110(7)	178.3(5)	2117	<sup>b</sup>	32
[Cu(L1')(CO)](ClO <sub>4</sub> )	2.041(4)	1.777(5)	1.127(6)	176.7(5)	2107	173.7	9
[Cu{HC(3- <i>r</i> Bupz) <sub>3</sub> }(CO)](PF <sub>6</sub> )	2.080(6)	1.778(10)	1.133(9)	176.8(9)	2100	<sup>b</sup>	34
anionic Nn (n = 2 or 3) coligands							
[Cu{N[(C <sub>3</sub> F <sub>7</sub> )C(Dipp)N] <sub>2</sub> }(CO)]	1.9401(15)	1.782(2)	1.138(2)	178.3(2)	2109	172.9	30a
[Cu{N[(C <sub>3</sub> F <sub>7</sub> )C(Ftfmp)N] <sub>2</sub> }(CO)]	1.957(3)	1.816(5) <sup>a</sup>	1.115(5) <sup>a</sup>	178.4(4)	2128	<sup>b</sup>	30b
[Cu{N[(C <sub>3</sub> F <sub>7</sub> )C(C <sub>6</sub> F <sub>5</sub> )N] <sub>2</sub> }(CO)(NCMe)]	2.0366(12)	1.8333(17)	1.124(2)	176.68(12)	2108	<sup>b</sup>	30b
[{Cu(CO)} <sub>2</sub> (TC-5,5)]	1.934(6)	1.760(9) <sup>a</sup>	1.124(10) <sup>a</sup>	177.1(8) <sup>a</sup>	2071	<sup>b</sup>	31
[Cu(L1)(CO)]	2.018(6)	1.769(8)	1.118(10)	178.6(9)	2056	169.9, 174.1 178.7, 183.0	9,11,35
[Cu{HB(pz) <sub>3</sub> }(CO)]	2.046(4)	1.765(11)	1.120(13)	178.3(5)	2083	<sup>b</sup>	36

<sup>a</sup> Averaged value. <sup>b</sup> Not reported.

perchlorate and CO at the same time indicates that the simple four-coordinate monomer [Cu(L1'')(CO)(OCIO<sub>3</sub>)] should also be able to form. In fact, corresponding four-coordinate complexes have been isolated for other ligands (see below). Somehow, the bridged dimer is energetically favored under the synthetic conditions of **5ClO<sub>4</sub>**, but the exact reason for this dimerization is not known. Cu(I)–O(ClO<sub>4</sub><sup>−</sup>) distances are 2.252 (Cu1) and 2.311 Å (Cu2). By using other bidentate nitrogen-containing ligands, the copper(I) carbonyl complexes [Cu{H<sub>2</sub>C(3,5-Me<sub>2</sub>pz)<sub>2</sub>}(CO)(OCIO<sub>3</sub>)],<sup>6</sup> [Cu(NH(py)<sub>2</sub>)(CO)(OCIO<sub>3</sub>)] (py = 2-pyridyl),<sup>29</sup> [Cu{N[(C<sub>3</sub>F<sub>7</sub>)C(Dipp)N]<sub>2</sub>}(CO)] (Dipp = 2,6-diisopropylphenyl),<sup>30a</sup> [Cu{N[(C<sub>3</sub>F<sub>7</sub>)C(Ftfmp)N]<sub>2</sub>}(CO)] (Ftfmp = 2-fluoro-6-trifluoromethylphenyl),<sup>30b</sup> [Cu{N[(C<sub>3</sub>F<sub>7</sub>)C(C<sub>6</sub>F<sub>5</sub>)N]<sub>2</sub>}(CO)(NCMe)],<sup>30b</sup> [{Cu(CO)}<sub>2</sub>(TC-5,5')] (TC = tropocoronand),<sup>31</sup> and [Cu(en)(CO)(PhBPh<sub>3</sub>)]<sup>32</sup> were structurally characterized. Importantly, *three-coordinate complexes are only obtained with anionic coligands*. All of these complexes show linear Cu–C–O units (cf. Table 5), which is the normal case. The Cu–C(CO) distances in the compounds with neutral coligands are similar: 1.816(10) Å (Cu1) and 1.802(10) Å (Cu2) in **5ClO<sub>4</sub>**, 1.806(5) Å in [Cu{H<sub>2</sub>C(3,5-Me<sub>2</sub>pz)<sub>2</sub>}(CO)(OCIO<sub>3</sub>)],<sup>6</sup> 1.808(2) Å in [Cu(NH(py)<sub>2</sub>)(CO)(OCIO<sub>3</sub>)],<sup>29</sup> and 1.806(6) Å in [Cu-

(en)(CO)(PhBPh<sub>3</sub>)]<sup>32</sup> (the structure of this latter complex indicates a weak interaction between copper(I) and the counterion, where the metal is displaced by 0.26 Å from the N<sub>2</sub>C plane). In contrast, the Cu–C(CO) distances of the three-coordinate complexes with anionic coligands tend to be shorter: 1.782(2) Å in [Cu{N[(C<sub>3</sub>F<sub>7</sub>)C(Dipp)N]<sub>2</sub>}(CO)],<sup>30a</sup> 1.813(5) and 1.818(5) Å in [Cu{N[(C<sub>3</sub>F<sub>7</sub>)C(Ftfmp)N]<sub>2</sub>}(CO)],<sup>30b</sup> and 1.771(7) and 1.749(9) Å in [{Cu(CO)}<sub>2</sub>(TC-5,5')].<sup>31</sup> Thus, real three-coordinate carbonyl complexes are very rare.<sup>33</sup> Selected bond distances and angles of copper(I)–carbonyl complexes are summarized in Table 5, including species with neutral and anionic tridentate nitrogen-containing ligands.<sup>9,11b,34–36</sup> Interestingly, the Cu–C(CO) distances of the complexes with tridentate ligands are slightly shorter, indicating a somewhat stronger  $\pi$ -backbond in these cases.

In the copper(II) complex [{Cu(L1'')}( $\mu$ -OH)<sub>2</sub>( $\mu$ -ClO<sub>4</sub>)<sub>2</sub>] (**6**), two [Cu(L1'')] <sup>2+</sup> units are bridged by two OH<sup>−</sup> and two ClO<sub>4</sub><sup>−</sup> anions to form a binuclear structure (Figure 3, bottom left). The copper(II) ions are symmetry-equivalent and exhibit a square pyramidal coordination ( $\tau$  = 0.02),<sup>37</sup> with two

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(33) To our knowledge, no three-coordinate Cu(I)–carbonyl complex with a neutral bidentate coligand has been characterized by X-ray crystallography to this date.

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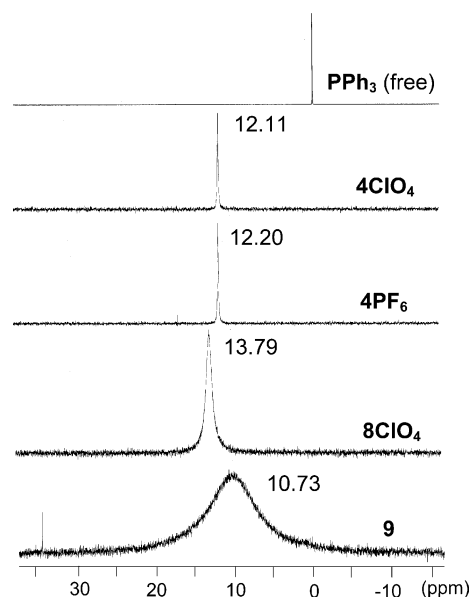
nitrogen atoms of L1'', two oxygen atoms of OH<sup>-</sup>, and one oxygen atom of ClO<sub>4</sub><sup>-</sup> bound. The interaction between copper and the second bridging perchlorate is very weak (Cu–O(ClO<sub>4</sub><sup>-</sup>) distance: 3.137(5) Å), leading to the square pyramidal geometry. The Cu1–O1–Cu1' angle is 100.1–(2)° and the Cu1...Cu1' distance is 2.9466(10) Å. The molecular structure of **6** is different from [{Cu(H<sub>2</sub>Cpz<sub>2</sub>)}<sub>2</sub>–(μ-OH)<sub>2</sub>(μ-ClO<sub>4</sub>)](ClO<sub>4</sub>) reported before.<sup>5</sup> Whereas this complex has a butterfly {Cu<sub>2</sub>(OH)<sub>2</sub>}<sup>2+</sup> core with a dihedral angle of 153.1°, **6** possesses a planar {Cu<sub>2</sub>(OH)<sub>2</sub>}<sup>2+</sup> structure (dihedral angle: 180°). These differences relate to the steric hindrance of the *i*Pr substituents of the pyrazolyl rings: if the {Cu<sub>2</sub>(OH)<sub>2</sub>}<sup>2+</sup> core in **6** would have a butterfly structure, the *i*Pr groups would get too close to each other. Using a neutral tridentate ligand like in [{Cu(L1')<sub>2</sub>(μ-OH)<sub>2</sub>](CF<sub>3</sub>–SO<sub>3</sub>)<sub>2</sub>},<sup>38</sup> no coordination of the counterion is observed due to the additional nitrogen donor present. Here, a planar {Cu<sub>2</sub>(OH)<sub>2</sub>}<sup>2+</sup> core is again observed.

In [Cu(L1'')Cl<sub>2</sub>] (**7**), the copper(II) ion is four-coordinate with L1'' and two chloride ions bound (Figure 3, bottom right). The average Cu–Cl bond distance of 2.225(2) Å in **7** is slightly shorter than that of 2.258 Å in the five-coordinate complex [Cu(L1')Cl<sub>2</sub>] with a neutral tridentate ligand.<sup>39</sup>

In the copper(I) triphenylphosphine complex [Cu(L1')–(PPh<sub>3</sub>)](ClO<sub>4</sub>) (**8ClO<sub>4</sub>**), the copper(I) ion is distorted tetrahedrally coordinated by three nitrogen atoms of L1' and one phosphorus atom of PPh<sub>3</sub> (Figure S3 and Table S2 in the Supporting Information). Interestingly, the Cu–P distance of 2.159(4) Å in **8ClO<sub>4</sub>** is shorter than that of **4ClO<sub>4</sub>** (2.174(2) Å) and **4PF<sub>6</sub>** (2.1726(12) Å), and also the value of 2.166(6) Å reported for [Cu{HB(3,5-Me<sub>2</sub>pz)<sub>3</sub>}(PPh<sub>3</sub>)],<sup>28</sup> which contains an anionic hydrotris(pyrazolyl)borate ligand (Table 4). This is further discussed in the next section. In the case of [Cu(L1)(PPh<sub>3</sub>)] (**9**), crystals suitable for high-quality X-ray analysis could not be obtained.

**B. Properties. NMR Spectroscopy.** <sup>1</sup>H and <sup>13</sup>C NMR spectra were measured for the ligand L1'' and for all the obtained copper(I) complexes. In all cases, the appropriate signals of the protons and carbon atoms of the bidentate or tridentate nitrogen-containing ligands are observed (see Experimental Section).

The <sup>31</sup>P NMR spectra of the copper(I) triphenylphosphine complexes **4ClO<sub>4</sub>**, **4PF<sub>6</sub>**, **8ClO<sub>4</sub>**, and **9** show a single resonance for PPh<sub>3</sub> (cf. Figure 4). <sup>31</sup>P chemical shifts of PPh<sub>3</sub> in these complexes appear downfield compared to free triphenylphosphine, indicating a decrease in shielding due to the presence of the metal, which is the expected case for a σ-donor ligand like phosphine. As mentioned before, the complexes **4ClO<sub>4</sub>** and **4PF<sub>6</sub>** are trigonal planar with similar structures, which is consistent with their almost identical <sup>31</sup>P chemical shifts of 12.11 ppm (**4ClO<sub>4</sub>**) and 12.20 ppm (**4PF<sub>6</sub>**). In comparison, the <sup>31</sup>P chemical shift of PPh<sub>3</sub> in **8ClO<sub>4</sub>** with



**Figure 4.** <sup>31</sup>P NMR spectra of copper(I) triphenylphosphine complexes in the PPh<sub>3</sub> resonance region: [Cu(L1'')(PPh<sub>3</sub>)](ClO<sub>4</sub>) (**4ClO<sub>4</sub>**), [Cu(L1'')(PPh<sub>3</sub>)](PF<sub>6</sub>) (**4PF<sub>6</sub>**), [Cu(L1')(PPh<sub>3</sub>)](ClO<sub>4</sub>) (**8ClO<sub>4</sub>**), and [Cu(L1)(PPh<sub>3</sub>)] (**9**). <sup>31</sup>P NMR shifts are referenced relative to an external standard of PPh<sub>3</sub> (0 ppm, top).

the neutral tridentate ligand L1' appears at 13.79 ppm. These differences in the <sup>31</sup>P NMR properties of **4ClO<sub>4</sub>** (or **4PF<sub>6</sub>**) and **8ClO<sub>4</sub>** are related to the difference in coordination number of these complexes. The somewhat larger chemical shift for **8ClO<sub>4</sub>** indicates that PPh<sub>3</sub> is a stronger donor to the metal in this complex, which is surprising on the basis of the larger coordination number of copper in this case. This finding is in agreement with the DFT calculations, which show an increase in the atomic charge on phosphorus in [Cu–(L1')(PPh<sub>3</sub>)]<sup>+</sup> compared to [Cu(L1'')(PPh<sub>3</sub>)]<sup>+</sup> (cf. Table 6). <sup>31</sup>P NMR spectra of **9** with the anionic tridentate ligand L1<sup>-</sup> show a broad resonance at 10.73 ppm. The broad nature of this signal is likely due to an instability of this complex in solution. In contrast, the relatively sharp signals of **4ClO<sub>4</sub>** and **4PF<sub>6</sub>** indicate more stable Cu–P bonds with ligand L1''. Correspondingly, **9** has the smallest calculated formation energy of all of the PPh<sub>3</sub> complexes investigated here (cf. Table 6). A similar behavior is also observed for [Cu{HB(3,5-Me<sub>2</sub>pz)<sub>3</sub>}(PPh<sub>3</sub>)].<sup>28</sup>

In general, <sup>13</sup>C chemical shifts for terminal CO ligands in classical metal carbonyls appear in the range of 184–223 ppm.<sup>9,40</sup> In comparison, terminal CO ligands in nonclassical metal carbonyls show smaller chemical shifts in the range of 140–189 ppm.<sup>9,40</sup> In **5ClO<sub>4</sub>**, the signal of the carbonyl carbon is observed at 172.9 ppm. <sup>13</sup>C chemical shifts of other copper(I) carbonyl complexes ligated by either bidentate or tridentate nitrogen-containing ligands are listed in Table 5, which also lists the C–O stretching frequencies of these complexes. The <sup>13</sup>C chemical shift obtained for **5ClO<sub>4</sub>** is

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similar to that of the mononuclear copper(I) carbonyl complex  $[\text{Cu}\{\text{H}_2\text{C}(3,5\text{-Me}_2\text{pz})_2\}(\text{CO})(\text{OCIO}_3)]$  (173.9 ppm).<sup>6</sup> The reason for this similarity is that, in these two complexes, copper(I) is coordinated by two nitrogen donors, one carbon atom of CO, and one oxygen atom of  $\text{ClO}_4^-$ , in a distorted tetrahedral geometry. However, the  $^{13}\text{C}$  chemical shifts of these compounds are also unexpectedly close to that of the related complex  $[\text{Cu}(\text{L}1')(\text{CO})](\text{ClO}_4)$  (173.7 ppm), which contains a tridentate ligand. Therefore,  $^{13}\text{C}$  chemical shifts simply do not seem to be very sensitive to the structures of the complexes and the nature of the coligands applied (see also ref 9).

**Vibrational Spectroscopy.** IR and far-IR spectra of all of the complexes prepared here were measured. In the case of the acetonitrile complex **3PF<sub>6</sub>**, the C–N stretching mode of the coordinated acetonitrile ligand could not be observed. This seems surprising, but a similar observation was made in the case of  $[\text{Cu}(\text{L}1')(\text{NCMe})](\text{PF}_6)$ . In comparison,  $\nu(\text{C–N})$  is observed at  $2255\text{ cm}^{-1}$  for  $[\text{Cu}(\text{L}1)(\text{NCMe})]$  with the anionic N3 ligand  $\text{L}1^-$ .<sup>9</sup> The reason for this difference is not clear.

The far-IR spectra of the triphenylphosphine complexes **4ClO<sub>4</sub>** and **4PF<sub>6</sub>** show three strong bands near  $500\text{ cm}^{-1}$  (Figure S4 in the Supporting Information), which are assigned to Whiffen's  $\gamma$  vibrations (out-of-plane bending of the phenyl rings).<sup>41</sup> A second group of three medium-intense bands appears near  $450\text{--}400\text{ cm}^{-1}$ , which most likely correspond to Whiffen's  $t$  vibrations. The so-called  $u$  and  $x$  vibrations of  $\text{PPh}_3$  appear as weak bands around  $250\text{--}270\text{ cm}^{-1}$ . Unfortunately, the  $\nu(\text{Cu–P})$  vibration could not be identified from the spectra. The reason for this finding is discussed in the DFT section below. The far-IR spectra of **8ClO<sub>4</sub>** and **9** show spectral features similar to  $\text{PPh}_3$ , as discussed above (cf. Figure S5 in the Supporting Information).

Copper(I) carbonyl complexes are stabilized by back-donation of copper(I) d electrons into the antibonding  $\pi^*$  orbitals of CO. Correspondingly, the C–O stretching vibration  $\nu(\text{C–O})$  is a sensitive indicator of the extent of back-donation, or vice versa, the electron density available at the metal center.<sup>9,42</sup> In general, copper(I) carbonyl complexes show intense IR bands around  $2100\text{ cm}^{-1}$  assignable to  $\nu(\text{C–O})$ . The carbonyl complex **5ClO<sub>4</sub>** exhibits the C–O stretch at  $2104\text{ cm}^{-1}$ . Upon  $^{13}\text{C}$  isotope labeling, this band shifts to  $2050\text{ cm}^{-1}$  (Figure S6 in the Supporting Information), which confirms this assignment. A comparison of C–O stretching frequencies in **5ClO<sub>4</sub>** and other carbonyl complexes with neutral bidentate nitrogen-containing ligands, such as  $[\text{Cu}\{\text{H}_2\text{C}(3,5\text{-Me}_2\text{pz})_2\}(\text{CO})(\text{OCIO}_3)]$ ,<sup>6</sup>  $[\text{Cu}\{\text{NH}(\text{py})_2\}(\text{CO})(\text{OCIO}_3)]$ ,<sup>29</sup> and  $[\text{Cu}(\text{en})(\text{CO})(\text{PhBPPh}_3)]$ ,<sup>32</sup> is given in Table 5. Surprisingly, in these three cases,  $\nu(\text{C–O})$  is also observed at  $2108\text{--}2117\text{ cm}^{-1}$ . This result indicates that the nature of the pyrazolyl alkyl substituents ( $\text{L}1''$ :  $i\text{Pr}$  and

$\text{H}_2\text{C}(3,5\text{-Me}_2\text{pz})_2$ : Me) and the different types of nitrogen-donor groups in these ligands only play a minor role for the properties of the copper(I) centers. Furthermore, the value of  $\nu(\text{C–O})$  in **5ClO<sub>4</sub>** is unexpectedly close to those of the related copper(I) carbonyl complexes  $[\text{Cu}(\text{L}1')(\text{CO})](\text{ClO}_4)$ <sup>9</sup> at  $2107\text{ cm}^{-1}$  and  $[\text{Cu}\{\text{HC}(3\text{-}t\text{Bupz})_3\}(\text{CO})](\text{PF}_6)$ <sup>34</sup> at  $2100\text{ cm}^{-1}$ . This means that the electron density at the copper(I) center in **5ClO<sub>4</sub>**, with two nitrogen and one oxygen donors (from perchlorate) coordinated, is comparable to that of  $[\text{Cu}(\text{L}1')(\text{CO})](\text{ClO}_4)$  with three nitrogen donors instead. These results are consistent with the obtained  $^{13}\text{C}$  chemical shifts of these compounds described above, which are also similar. The Cu–CO stretching frequency in **5ClO<sub>4</sub>** is observed at  $415\text{ cm}^{-1}$ , as identified by  $^{13}\text{CO}$  labeling, in the case of which this band shifts to  $399\text{ cm}^{-1}$ .

The far-IR and UV–vis absorption spectra of the copper(II) chloro complex **7** are shown in Figures S7 and S8 in the Supporting Information, respectively. The chloride-to-copper(II) CT transition of **7** is assigned to the absorption band at  $375\text{ nm}$ , whereas the feature at  $911\text{ nm}$  corresponds to a d–d transition. The UV–vis spectrum of  $[\{\text{Cu}(\text{L}1'')\}_2(\mu\text{-OH})_2(\mu\text{-ClO}_4)_2]$  (**6**) shows two bands at  $355$  and  $563\text{ nm}$  (Figure S9 in the Supporting Information), which are assigned to a hydroxide-to-copper(II) CT transition and a d–d transition, respectively, on the basis of a comparison with  $[\{\text{Cu}(\text{L}1)\}_2(\mu\text{-OH})_2]$ .<sup>43</sup> Interestingly, whereas **6** and  $[\{\text{Cu}(\text{L}1)\}_2(\mu\text{-OH})_2]$ <sup>10</sup> have planar  $\{\text{Cu}_2(\text{OH})_2\}^{2+}$  cores and diamagnetic ground states ( $S = 0$ , from ESR),  $[\{\text{Cu}(\text{H}_2\text{-Cpz})_2\}_2(\mu\text{-OH})_2(\mu\text{-ClO}_4)](\text{ClO}_4)$  with a butterfly  $\{\text{Cu}_2(\text{OH})_2\}^{2+}$  core has a ferromagnetic ground state ( $S = 1$ , from ESR).<sup>5</sup>

**C. Reactivity.** In this work, the reactivity of **2ClO<sub>4</sub>** and **3PF<sub>6</sub>** toward  $\text{PPh}_3$ , CO, and  $\text{O}_2$  is the main focus of the investigation, because these complexes show unusual geometric structures, binuclear linear and trigonal planar, respectively. The reactivity of each complex is described in Scheme 1.

First, the reactivity of **2ClO<sub>4</sub>** and **3PF<sub>6</sub>** with  $\text{PPh}_3$  is discussed. The reaction between **2ClO<sub>4</sub>** and 2 equiv of  $\text{PPh}_3$  results in the rapid formation of the triphenylphosphine complex **4ClO<sub>4</sub>**. Similarly, **4PF<sub>6</sub>** is generated by the reaction of **3PF<sub>6</sub>** with 1 equiv of  $\text{PPh}_3$ . Because phosphines are strong ligands to copper(I) and  $\text{PPh}_3$  is also quite bulky, three-coordinate copper(I) complexes are easily obtained with this ligand. Interestingly, as shown in Figure S10 in the Supporting Information, the additive IR spectrum of the starting complex **2ClO<sub>4</sub>** and  $\text{PPh}_3$  is similar to the IR data of the generated triphenylphosphine complex **4ClO<sub>4</sub>**. This behavior is also observed for **4PF<sub>6</sub>** (Figure S11 in the Supporting Information). Importantly, this means that from the IR spectra, it is not clear whether  $\text{PPh}_3$  coordinates or not. This problem is solved by  $^{31}\text{P}$  NMR spectroscopy (cf. Figure 3), which shows distinct  $^{31}\text{P}$  chemical shifts for **4ClO<sub>4</sub>** and **4PF<sub>6</sub>**.

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**Table 6.** Calculated Properties and Formation Energies of Cu(I)–Phosphine Complexes

complex	bond distances (Å)		$\nu(\text{Cu}–\text{P})/\text{PPh}_3$ (Inv.) <sup>a</sup>	charge <sup>b</sup> P(PPh <sub>3</sub> )	complex formation energy <sup>c</sup>	
	Cu–N (av.)	Cu–P			LanL2DZ	TZVP
[Cu(L1'')(PPh <sub>3</sub> )] <sup>+</sup>	2.052	2.323	537	+0.56	–35.3	–38.3
[Cu(L1')(PPh <sub>3</sub> )] <sup>+</sup>	2.148	2.329	534	+0.57	–29.8	–32.8
[Cu(L1)(PPh <sub>3</sub> )]	2.122	2.343	531	+0.60	–19.2	–21.5

<sup>a</sup> In cm<sup>–1</sup>. <sup>b</sup> Calculated Mulliken charge on phosphorus. <sup>c</sup> Calculated using the equation: [Cu(L)]<sup>0/+</sup> + PPh<sub>3</sub> → [Cu(L)(PPh<sub>3</sub>)]<sup>0/+</sup>. In kcal/mol.

compared to free PPh<sub>3</sub>. From NMR, PPh<sub>3</sub> certainly coordinates to copper(I), consistent with the X-ray structural analyses.

Second, the reaction of **2ClO<sub>4</sub>** with CO is evaluated. After the reaction of **2ClO<sub>4</sub>** with CO, the solvent was removed under vacuum, and an IR spectrum of the crude product was measured. The IR data show  $\nu(\text{C}–\text{O})$  as a broad band at 2104 cm<sup>–1</sup> (Figure S12, middle in the Supporting Information). Recrystallization of this material led to colorless crystals, which, however, did not exhibit  $\nu(\text{C}–\text{O})$  in the IR spectrum anymore (Figure S12, bottom in the Supporting Information). X-ray crystallography then showed that the final product corresponds to **1ClO<sub>4</sub>**, where two bidentate ligands L1'' are bound to copper, but CO is not present. This result indicates a surprising instability of the Cu(I)–CO bond in these systems, whereas this bond is usually quite strong. Correspondingly, if the solvent was not removed after the reaction of **2ClO<sub>4</sub>** with CO, and the recrystallization was performed under a CO atmosphere, colorless crystals were obtained that show the intense  $\nu(\text{C}–\text{O})$  band at 2104 cm<sup>–1</sup>. X-ray crystallography then confirmed that the obtained material was the binuclear copper(I) carbonyl complex **5ClO<sub>4</sub>**. From these results, **5ClO<sub>4</sub>** seems to be very unstable toward the loss of CO in solution. In the same way, if **5ClO<sub>4</sub>** was dissolved in acetonitrile and stirred under an argon atmosphere,  $\nu(\text{C}–\text{O})$  disappeared in the IR spectrum (Figure S13, bottom in the Supporting Information), which means that CO was removed. This behavior is also observed for [Cu(L1')(CO)]<sup>+</sup> with a neutral tridentate ligand but not for [Cu(L1)(CO)].<sup>9</sup> CO in **5ClO<sub>4</sub>** was also readily displaced by PPh<sub>3</sub> (Figure S14 in the Supporting Information). To further investigate this, the reaction of **3PF<sub>6</sub>** with CO was performed. After the reaction, the solvent was removed under vacuum, and the IR spectrum of the resulting crude product was measured, showing a very small band for  $\nu(\text{C}–\text{O})$  around 2090 cm<sup>–1</sup> (Figure S15, middle in the Supporting Information). Importantly, this frequency is somewhat different from **5ClO<sub>4</sub>**. Because PF<sub>6</sub><sup>–</sup> is a non-coordinating, this band could belong to the elusive, three-coordinate species [Cu(L1')–(CO)]<sup>+</sup> or the corresponding four-coordinate acetonitrile complex. From the literature, the latter possibility is much more likely (see ref 29). If recrystallization of this material was performed under argon, CO was removed as a ligand, as indicated in the IR spectrum in Figure S15, bottom in the Supporting Information. From these results, it becomes clear that the reactivity of **3PF<sub>6</sub>** toward CO is even lower than that of **2ClO<sub>4</sub>**. The reason for this is again the apparent instability of [Cu(L1'')(CO)]<sup>+</sup>: whereas perchlorate in **2ClO<sub>4</sub>** serves as an additional ligand to copper, preventing the formation of a three-coordinate complex, this is not possible

with PF<sub>6</sub><sup>–</sup>. Additionally, acetonitrile is a strong ligand for copper(I) and, therefore, competes with CO and is harder to replace. To synthesize a mononuclear copper(I) carbonyl complex, [Cu(L1'')(CO)]X, **2BF<sub>4</sub>** was then utilized. After reaction of this compound with CO, the solvent was removed and the IR spectrum was measured showing  $\nu(\text{C}–\text{O})$  at 2104 cm<sup>–1</sup> (Figure S16 in the Supporting Information). Recrystallization was carried out under a CO atmosphere, but no crystals exhibiting  $\nu(\text{C}–\text{O})$  in the IR spectrum could be obtained. This again shows that the coordinated perchlorate anion in **5ClO<sub>4</sub>** plays an important role in stabilizing the CO complex. As mentioned above, the <sup>13</sup>C chemical shift of CO and  $\nu(\text{C}–\text{O})$  in **5ClO<sub>4</sub>** are both similar to those of [Cu(L1')(CO)](ClO<sub>4</sub>) (cf. Table 5), but the latter complex with the tridentate ligand is clearly more stable in solution.<sup>9</sup> The reason for this difference is that the structural integrity of **5ClO<sub>4</sub>** depends on the labile perchlorate bridge, which is most likely easily lost in solution, leading to an equilibrium with different mononuclear species. Our main hypothesis is that the three-coordinate complex [Cu(L1'')(CO)]<sup>+</sup> is formed in this process, which is very labile toward the loss of CO. This way, CO leaks out of the system, and only CO-free compounds are finally obtained. In comparison, four-coordinate [Cu(L1')(CO)]<sup>+</sup> constitutes a stable unit in solution.

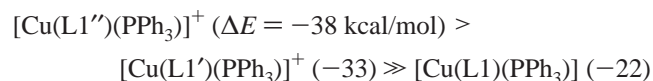
Next, the reactivity of **2ClO<sub>4</sub>** and **3PF<sub>6</sub>** toward O<sub>2</sub> is discussed. **2ClO<sub>4</sub>** was dissolved in dichloromethane and cooled to –78 °C under an argon atmosphere. The argon gas was then replaced by O<sub>2</sub>, and the solution was allowed to warm up to room temperature. During this time, the color of the solution turned gradually from colorless to deep green. From the reaction mixture, **6** was obtained and characterized by X-ray crystallography as well as by ESR and UV–vis absorption spectroscopy. The reaction of **3PF<sub>6</sub>** with O<sub>2</sub> has also been performed, but surprisingly, only very small amounts of oxidative products were obtained. *This means that three-coordinate 3PF<sub>6</sub> is basically stable toward O<sub>2</sub>.* In comparison, the cationic complex [Cu(L1')(NCMe)]PF<sub>6</sub> with the neutral tridentate ligand L1' reacts slowly with O<sub>2</sub> to give the  $\mu\text{-}\eta^2\text{-}\eta^2$  peroxo complex {[Cu(L1')]<sub>2</sub>( $\mu\text{-}\eta^2\text{-}\eta^2\text{-O}_2$ )](PF<sub>6</sub>)<sub>2</sub> (ca. ~10% conversion),<sup>9</sup> whereas the neutral complex [Cu(L1)(NCMe)] with the anionic tridentate ligand L1 reacts readily with O<sub>2</sub> to give the  $\mu\text{-}\eta^2\text{-}\eta^2$  peroxo complex {[Cu(L1)]<sub>2</sub>( $\mu\text{-}\eta^2\text{-}\eta^2\text{-O}_2$ )]}.<sup>9,11</sup> On the basis of these findings, part of the lack of reactivity of **3PF<sub>6</sub>** relates to the charge of the complex, which shifts the redox potential. Two-coordinate **2ClO<sub>4</sub>** still reacts much slower with O<sub>2</sub> than [Cu(L1')(NCMe)]X, which is in agreement with the literature.<sup>4a,4c</sup> Unfortunately, no oxygenated intermediate could be obtained in the reaction of the Cu(I)–L1'' complexes with O<sub>2</sub>. The



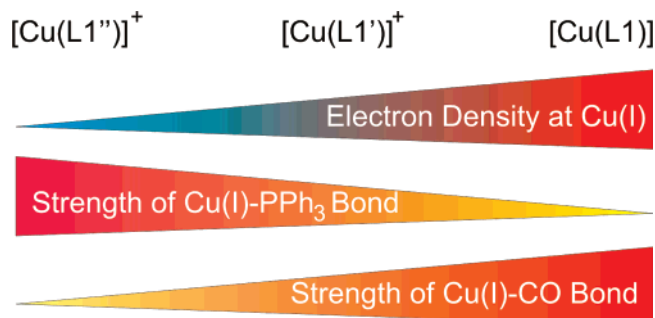
reason for this is not clear, especially because corresponding side-on peroxo complexes could be obtained easily with  $L1'$  as mentioned above, but also with simple bidentate amine ligands.<sup>44,45</sup> One possibility is that the dioxygen complex with  $L1''$  is too unstable, such that the decomposition of this species yielding simple copper(II) complexes is always faster than its generation. In this case, the intermediate would never appear at a significant concentration. We also tried to generate an oxygen intermediate by the reaction of  $[Cu(L1'')_2(\mu-OH)_2(\mu-ClO_4)_2]$  (**6**) with hydrogen peroxide at low temperature. However, no intermediates were observed. Recently, exactly this observation has been reported for  $[Cu_2(H3m)(CO)_2]^{2+}$  ( $H3m$  = dinucleating hexaaza macrocyclic derivatives)<sup>46</sup> and  $[Cu(baib)]_2^{2+}$  ( $baib$  = Schiff base derivatives)<sup>47</sup> upon reaction with  $O_2$ . Finally, we explored the reaction of  $[Cu(L1'')_2](CuCl_2)$  (**1CuCl<sub>2</sub>**) with  $O_2$ . Recrystallization gave orange crystals of  $[Cu(L1'')Cl_2]$  (**7**).<sup>10</sup> A similar behavior was reported before for  $[Cu\{Ph_2C(pz)_2\}_2](CuCl_2)$ .<sup>7</sup>

The reaction of **2ClO<sub>4</sub>** with acetonitrile surprisingly did not yield the three-coordinate complex  $[Cu(L1'')(NCMe)](ClO_4)$ , but **1ClO<sub>4</sub>**. In contrast, this reaction proceeds readily with the analogous complex  $[Cu(L1')(OCIO_3)]$ . As described above, this is due to a ligand disproportionation reaction in the case of  $L1''$  to avoid the formation of a three-coordinate complex (cf. Section A).

**D. DFT Calculations on Cu(I)–PPh<sub>3</sub> Complexes.** To gain further insight into the properties of the PPh<sub>3</sub> complexes and the vibrational assignments, DFT calculations on the three complexes  $[Cu(L1'')(PPh_3)]^+$ ,  $[Cu(L1')(PPh_3)]^+$ , and  $[Cu(L1)(PPh_3)]$  were applied without any structural simplifications. The obtained optimized structures show very good overall agreement with experiment. Table 6 shows that the average Cu–N distances are also reproduced reasonably well. In contrast, the Cu–P distances are obtained too long (consistently about 0.15 Å longer compared to experiment), which is due to the lack of polarization functions in the LanL2DZ basis set, as observed before.<sup>48</sup> As shown in Table 6, the calculated formation energies for these three PPh<sub>3</sub> complexes show an interesting trend where,



indicating that the complex with bidentate  $L1''$  has the most electron-poor copper(I), which therefore binds to the phosphine donor the strongest, whereas anionic  $L1^-$  leads to the most electron-rich copper(I), which has the lowest affinity



**Figure 5.** Overview of the properties of copper(I) complexes with the ligands  $L1''$ ,  $L1'$ , and  $L1^-$ .

for PPh<sub>3</sub>. The latter result is in agreement with the instability of **9** in solution as observed by <sup>31</sup>P NMR. This trend is strikingly confirmed by the properties of the corresponding carbonyl complexes, where (based on the observed C–O stretching frequencies), the electron-rich complex with  $L1^-$  shows a stronger Cu(I)–CO bond than the compound with  $L1'$ .<sup>9</sup> This inverse trend in bond stabilities compared to PPh<sub>3</sub> is due to the fact that phosphines are strong donors, whereas CO is an acceptor that prefers electron-rich metals. On the basis of the results obtained here,  $L1''$  leads to the most unstable CO complex, again in agreement with this trend. Figure 5 summarizes these findings.

Another interesting problem is the lack of a distinct Cu–P stretching mode in the vibrational spectra of the PPh<sub>3</sub> complexes, which would be expected to occur as a new, additional band compared to the additive spectra of the precursor  $[Cu(L)]^{0/+}$  and PPh<sub>3</sub>. However, no such band is observed experimentally. Surprisingly, this finding is actually confirmed by the DFT calculations on the three PPh<sub>3</sub> complexes investigated here. Triphenylphosphine shows three bands in the 500 cm<sup>−1</sup> region, which belong to C–P–C bending vibrations. In ideal  $C_3$  symmetry, these would actually lead to an  $A_1$  and an E component. The  $A_1$  vibration is special, because it corresponds to the PR<sub>3</sub> inversion mode, where the phosphorus atom moves perpendicular to the plane formed by the three attached carbons. Hence, this mode actually corresponds to a Cu–P stretch in the resulting Cu(I)–PPh<sub>3</sub> complex, where the phosphorus atom then moves along the Cu–P vector. Importantly, this  $A_1$  vibration occurs at higher energy than the E components (in the calculations), which indicates that the bands at 529/530 cm<sup>−1</sup> in **4ClO<sub>4</sub>/4PF<sub>6</sub>** (Calcd: 537 cm<sup>−1</sup>), at 531 cm<sup>−1</sup> in **8ClO<sub>4</sub>** (Calcd: 534 cm<sup>−1</sup>), and at 528 cm<sup>−1</sup> in **9** (Calcd: 531 cm<sup>−1</sup>) have to be assigned to this mode. Other PPh<sub>3</sub> vibrations (especially the  $A_1$ -symmetric P–C stretch) also contain a Cu–P stretching component. Importantly, this also implies that the mode around 530 cm<sup>−1</sup> is not very diagnostic for the strength of the Cu–P bond.

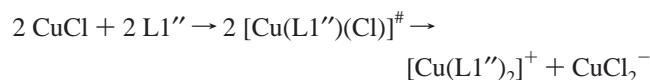
## Conclusions

In this work, eight copper(I) complexes and two copper(II) complexes with the neutral bidentate nitrogen-containing coligand  $L1''$  were systematically synthesized and characterized, and their reactivity was evaluated in comparison to analogous complexes with the related neutral tridentate

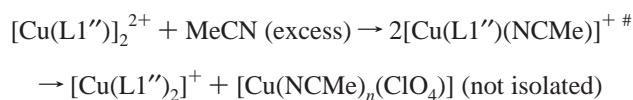
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ligand L1' published before.<sup>9</sup> The second focus of this article is the synthesis of mononuclear three-coordinate copper(I) complexes of the type  $[\text{Cu}(\text{L1}'')(X)](\text{Z})$ , where  $X = \text{MeCN}$ ,  $\text{CO}$ , and  $\text{PPh}_3$ ;  $\text{Z} =$  counterion.

Importantly, our results demonstrate how the structures and reactivities of copper(I) complexes are affected by changing the coordination number of the coligand from neutral tridentate (L1') to neutral bidentate (L1''). Whereas the treatment of L1' with  $\text{CuCl}$  results in the formation of  $[\text{Cu}(\text{L1}')(\text{Cl})]$ ,<sup>9</sup> the same reaction with L1'' yields the complex  $[\text{Cu}(\text{L1}'')_2](\text{CuCl}_2)$  (**1CuCl<sub>2</sub>**), which corresponds to a disproportionation of type,



which we have designated as *ligand disproportionation reaction*. This is our first example where a coordination number of 3 is avoided by copper(I). Obviously, if a reasonably strong ligating counterion Z is present, the formation of a four-coordinate complex and a two-coordinate anion of type  $\text{CuZ}_2^-$  is in fact energetically favored over the three-coordinate species. A similar process is observed for the reaction of  $[\text{Cu}(\text{L1}'')_2](\text{ClO}_4)_2$  (**2ClO<sub>4</sub>**) with acetonitrile. Here, the formation of the three-coordinate species  $[\text{Cu}(\text{L1}'')(\text{NCMe})]^\#$  is avoided:



This complex can only be obtained with the non-coordinating counterion  $\text{PF}_6^-$  (**3PF<sub>6</sub>**; vide infra). The synthesis of the starting complex of this reaction,  $[\text{Cu}(\text{L1}'')_2](\text{ClO}_4)_2$ , is yet another example for this general reaction scheme. The three-coordinate complex  $[\text{Cu}(\text{L1}'')(\text{OCIO}_3)]$  presumably formed as an intermediate in the synthetic procedure is unstable, and instead, the two-coordinate complex  $[\text{Cu}(\text{L1}'')_2](\text{ClO}_4)_2$  is isolated from the reaction mixtures. With CO as a ligand, a perchlorate-bridged dimer is formed, where each copper(I) is four-coordinate. Correspondingly, when a non-coordinating counterion is used, no stable CO complex can be isolated. These results present strong evidence that three-coordinate copper(I) with L1'' as a neutral coligand is energetically unstable, and hence, does not willingly form in contrast to complexes that contain monoanionic bidentate nitrogen-donor ligands such as  $\{\text{N}[(\text{C}_3\text{F}_7)\text{C}(\text{Dipp})\text{N}]_2\}^-$ <sup>30a</sup> and  $\{\text{N}[(\text{C}_3\text{F}_7)\text{C}(\text{Ftfmp})\text{N}]_2\}^-$ <sup>30b</sup>. Even these complexes easily form four-coordinate species with coordinated acetonitrile.

As mentioned above, a three-coordinate copper(I) complex could only be obtained with acetonitrile in the presence of the non-coordinating counterion  $\text{PF}_6^-$ . However, this picture completely changes when phosphines are used: the strong and bulky ligand  $\text{PPh}_3$  forms three-coordinate copper(I) complexes very easily. The resulting compounds can be characterized best by <sup>31</sup>P NMR spectroscopy. Complexes  $[\text{Cu}(\text{L1}'')(\text{PPh}_3)](\text{ClO}_4)$  (**4ClO<sub>4</sub>**) and  $[\text{Cu}(\text{L1}'')(\text{PPh}_3)](\text{PF}_6)$  (**4PF<sub>6</sub>**) with L1'' show <sup>31</sup>P chemical shifts that are charac-

teristically different from those obtained for  $[\text{Cu}(\text{L1}')(\text{PPh}_3)](\text{ClO}_4)$  (**8ClO<sub>4</sub>**) and  $[\text{Cu}(\text{L1})(\text{PPh}_3)]$  (**9**), which both contain N3 tridentate ligands. Other three-coordinate structures such as  $[\text{Cu}(\text{PPh}_3)_3]^+$ <sup>49</sup> and  $[\text{Cu}(\text{SPh}_3)_3]^{2-}$ <sup>50</sup> are observed in the case of phosphine or hindered anionic ligands. In addition, three-coordinate structures were recently reported using hindered *tert*-butyl isocyanide as a ligand<sup>51</sup> and hindered anionic  $\beta$ -diketoiminate  $\{\text{Ph}[\text{CCH}_2(\text{Dipp})\text{N}]_2\}^-$ <sup>52</sup> and fluorinated bis(pyrazolyl)borate  $\{\text{H}_2\text{B}(3,5-(\text{CF}_3)_2\text{pz})\}^-$ <sup>53</sup> ligands. These examples are also consistent with our finding that three-coordinate copper(I) complexes are easily obtained with bidentate anionic ligands or phosphines, whereas neutral bidentate nitrogen-donor ligands require steric hindrance, and the obtained complexes are still unstable.

As indicated above, the reaction of **2ClO<sub>4</sub>** with CO leads to the generation of the binuclear carbonyl complex  $\{[\text{Cu}(\text{L1}'')(\text{CO})]_2(\mu\text{-ClO}_4)\}(\text{ClO}_4)$  (**5ClO<sub>4</sub>**), and no three-coordinate carbonyl complex of type  $[\text{Cu}(\text{L1}'')(\text{CO})]^\#$  could have been obtained.<sup>33</sup> On the other hand,  $[\text{Cu}(\text{L1}')(\text{CO})](\text{ClO}_4)$ <sup>9</sup> is readily generated by using the tridentate ligand L1'. These experimental results show that the stability of **5ClO<sub>4</sub>** is much lower than that of  $[\text{Cu}(\text{L1}')(\text{CO})](\text{ClO}_4)$ , although the electronic structure of the Cu(I)–CO bond is very similar in these compounds, as indicated by the C–O stretching frequencies and the <sup>13</sup>C chemical shifts. The reason for the low stability of **5ClO<sub>4</sub>** in solution is that the integrity of this complex depends on the presence of the weak perchlorate bridge. Loss of this bridge, which should be easily possible in solution, leads to the generation of free  $[\text{Cu}(\text{L1}'')(\text{CO})]^\#$ , which readily loses CO to form two-coordinate  $[\text{Cu}(\text{L1}'')_2]^{2+}$  or other four-coordinate complexes.

The trends observed in the stabilities and spectroscopic properties of the copper(I) complexes with L1'', L1', and L1<sup>–</sup>, and the donor and acceptor ligands  $\text{PPh}_3$  and CO are nicely reproduced by the DFT calculations. Taken together, these results show that the electron density at the copper center increases in the order:  $\text{L1}'' < \text{L1}' < \text{L1}^-$  (cf. Figure 5). Hence, L1'' should give rise to the strongest Cu(I)–phosphine interaction, whereas L1<sup>–</sup> leads to the strongest Cu(I)–CO bond. The DFT calculations also explain the absence of a discrete Cu–P stretching band in the IR spectra. In fact, several internal  $\text{PPh}_3$  vibrations of idealized  $A_1$  symmetry (especially the C–P–C bend, but also the P–C stretch) obtain Cu–P stretching contributions in the corresponding complexes, which means that the Cu–P stretching coordinate is extremely delocalized over a number of  $\text{PPh}_3$  modes.

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Finally, whereas  $[\text{Cu}(\text{L1}')(\text{NCMe})](\text{ClO}_4)$  and  $[\text{Cu}(\text{L1}')(\text{OClO}_3)]$  with the tridentate nitrogen-containing ligand  $\text{L1}'$  react readily with  $\text{O}_2$  to give oxygen intermediates such as the  $\mu\text{-}\eta^2\text{:}\eta^2$  peroxo complex,<sup>9</sup> no corresponding oxygen intermediate could be obtained in the presence of the bidentate ligand  $\text{L1}''$ . Presumably, the stability of these intermediates is too low with  $\text{L1}''$ , which facilitates fast decomposition even at low temperature. In addition, three-coordinate  $\mathbf{3PF}_6$  is quite stable toward  $\text{O}_2$  at room temperature, which is completely unexpected.

All of these surprising differences originate from the change in the coordination number of the supporting ligand from three to two. On the basis of all of these results combined with the previous findings, it is now possible to efficiently control the structures and reactivities of copper(I) complexes by changing the coordination number, the charge, and the steric demand of the supporting coligand. We are currently pursuing studies to investigate the effect of different pyrazolyl side chains in bis(pyrazolyl)methane

type ligands on the structures and reactivities of the resulting copper(I) and copper(II) complexes.

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**Supporting Information Available:** Crystal structures of  $\text{L1}''$ ,  $\mathbf{1ClO}_4$ ,  $\mathbf{2BF}_4$ ,  $\mathbf{4PF}_6$ , and **9** (Figures S1–S3), selected structural parameters (Tables S1–S2), IR, far-IR, and UV–vis spectra (Figures S4–S16), and the Cartesian coordinates of fully optimized  $[\text{Cu}(\text{L1}'')(\text{PPh}_3)]^+$ ,  $[\text{Cu}(\text{L1}')(\text{PPh}_3)]^+$ , and  $[\text{Cu}(\text{L1})(\text{PPh}_3)]$  (Tables S3–S5). Crystallographic data is available in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K., and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition numbers (620276–620287).

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