5-2006

Copper(I) Chloride Carbonyl Polymers

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Recommended Citation

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SUMMARY: Addition of bridging diamine ligands to methanolic solutions of CuCl under CO purge produces polymeric complexes, $[(CuCl)_2(CO)_2(biL)]$, biL = diazabicyclo[2.2.2]octane (DABCO), piperazine (Pip), and N,N´-dimethylpiperazine (DMP). X-ray crystal structures of the three complexes reveal rhombic $OC–Cu(\mu\text{-}Cl)_2Cu–CO$ bridged by biL. Aromatic bridging ligands fail to produce carbonyl-bearing products.

Introduction

Metal-containing polymers have great potential as catalysts since they can combine the simplicity of use of insoluble heterogeneous catalysts with the chemical regularity and specificity of homogeneous catalysts.[1] In particular, metal-organic polymers are apt to preferentially coordinate small molecules, which can enter the pores in the network. In cases where coordination is reversible, catalytic delivery of

small molecules is possible. In contrast to their molecular analogs, networked catalysts are typically insoluble and therefore readily filterable, an advantage during product purification.

As part of our on-going studies of Cu(I) coordination polymers,[2] we are investigating the reactions of copper(I) halides with bridging ligands in the presence of carbon monoxide. Numerous Cu(I)-carbonyl complexes are known;[3–6] however, only a few polymeric crystal structures containing Cu–CO have been reported. These include that of CuCl(CO) itself, which forms a hexagonal honeycomb layer structure via triply bridging chloride.[4] The use of polydentate anions such as ethylsulfonate, hydrogen sulfonate, and trichloroacetate with $Cu(CO)^+$ produces chain structures.[5] Finally, [Cu(CO)(NCMe)(1,2-di-2-pyridylethylene)]$^+$ represents the only reported amine-bridged polymer of Cu(CO).[6]

Results and Discussion

Our group[2] and others[7] have previously characterized CO-free CuCl complexes of numerous diamine bridging ligands, biL = diazabicyclo[2.2.2]octane (DABCO), piperazine (Pip), N,N´-dimethylpiperazine (DMP), 4,4´-dipyridyl (Bpy), pyrazine (Pyz), quinoxaline (Quin), and phenazine (Phz).[2] The following complexes are recognized: [CuCl(biL)] (**1a** biL = Bpy, **1b** biL = Pyz) and [(CuCl)$_2$(biL)] (**2a** biL = DABCO, **2b** biL = Bpy, **2c** biL = Quin, **2d** biL = Phz).[2a] As illustrated in Chart 1, both product types form sheet structures, the principal difference residing in the bridging behavior of the halide (μ_2-Cl in **1** and μ_3-Cl in **2**). No complex of either type has yet been characterized for biL = Pip, DMP. When an additional monodentate ligand, L = $e.g.$ P(OPh)$_3$, PPh$_3$, is introduced into these reactions, the product invariably is [(CuCl)$_2$L$_2$(biL)] (**3**, biL = DABCO, DMP, Bpy, Pyz, Quin, Phz).[2a,2c,8] These materials are chain polymers composed of L–Cu(μ_2-Cl)$_2$Cu–L rhomboid dimers linked by biL units.

Copper(I) chloride dissolves in methanol under carbon monoxide purge; the resulting CuCl(CO) reacts with chelating amines to produce carbonyl-bearing products.[9] In the current work, the combination of methanolic solutions of biL and CuCl(CO) produced suspensions from which slightly to moderately air-sensitive white solids could be isolated by filtration. Elemental analysis of the products confirmed carbonyl-bearing formulations **3** (L = CO) for biL = DABCO (**3a**), Pip (**3b**), and DMP (**3c**).

Chart 1.

$\bigcirc$ = biL

1

2

3
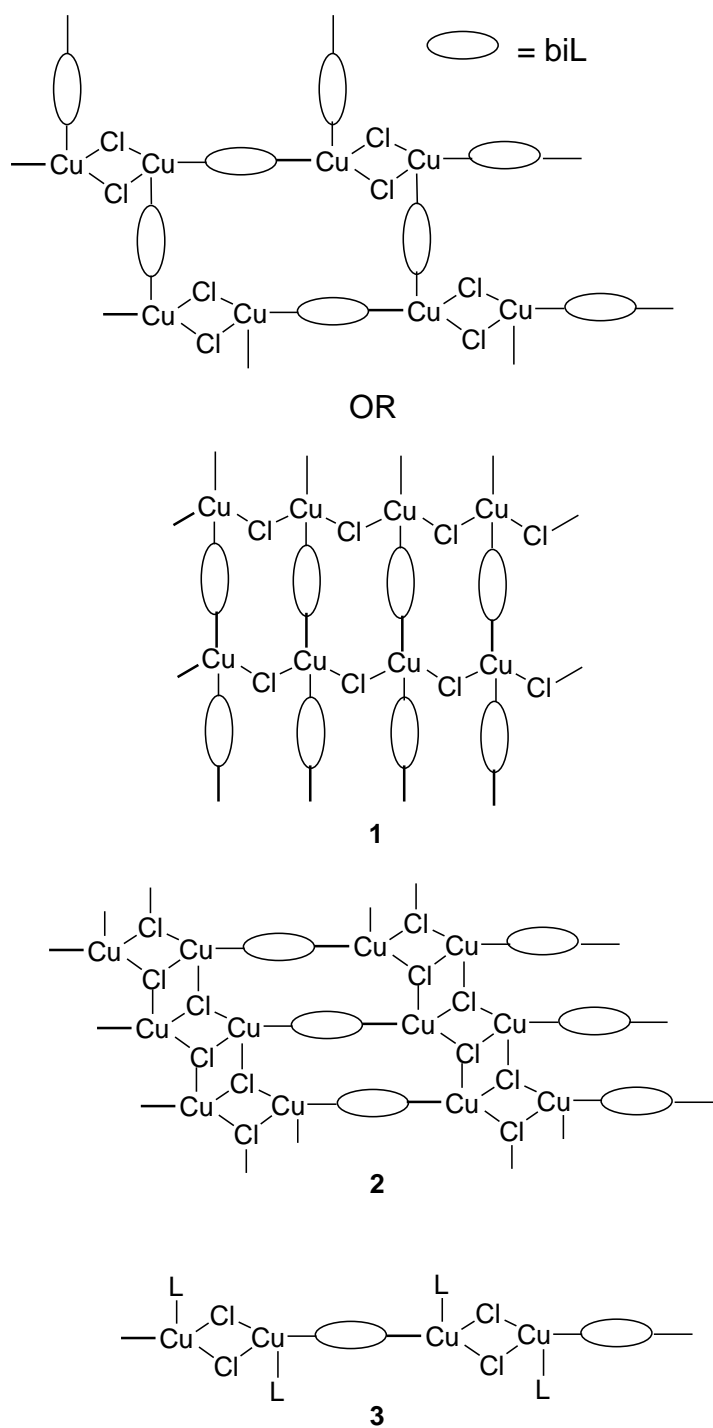
Solid state IR analysis of freshly prepared products revealed a strong carbonyl stretching band for each of these products. The relatively high frequency $\nu_{C\equiv O}$ values (2075–2084 cm^{-1}) observed for these neutral products is typical of Cu(I) carbonyl complexes[3–6] and is suggestive of limited Cu–C≡O π-backbonding.

3

When unsaturated biL = Bpy, Pyz, Quin, and Phz were reacted with CuCl(CO) as described above, red or yellow solids were produced. However, elemental and thermogravimetric analyses of these products showed them to be the well known carbonyl-free networks, **1a**, **1b**, **2c** and **2d**. Surprisingly, solid state IR analysis of these products revealed traces of carbonyl ($v_{C\equiv O} = 2084$–2097 cm^{-1}). However, quantitative IR analysis revealed these bands to be about ten times weaker than those of the saturated amine complexes, **3a**–**3c**. The origin of these bands is not yet known, but they are probably the result of trace impurities. The failure to form carbonyl complexes **3** with unsaturated diamine ligands points to a high electron demand on the part of the $(CuCl)_2(CO)_2$ fragment. It appears that saturated diamine ligands can satisfy this demand, whilst unsaturated diamine ligands cannot. This observation is consistent with the prevalence of saturated amine supporting ligands for known Cu(I) carbonyl complexes.[3]

Thermogravimetric analysis (TGA) was carried out under flowing nitrogen for the new carbonyl-bearing products. As shown in Figure 1, comparison of TGA data for complexes **2a** and **3a** reveals an additional feature in the **3a** trace. Occurring between about 35 and 155 ºC, with a sharp loss at 90–100 ºC, this new mass loss corresponds to about 15% CO by mass in **3a**. This value is in good agreement with the formula $[(CuCl)_2(CO)_2(DABCO)]$ (15.2% CO calculated). Complexes **3b** and **3c** show behavior similar to that of **3a**.
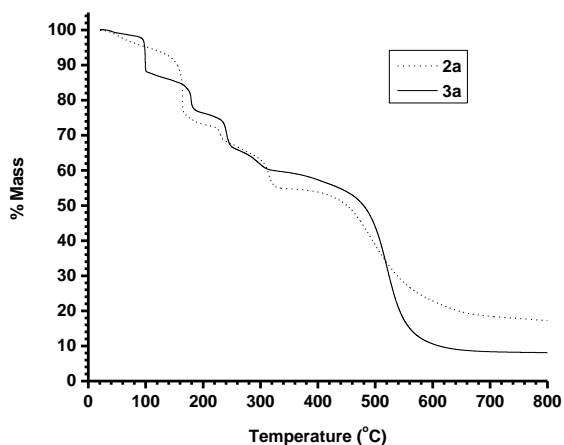

Figure 1. TGA traces for $[(CuCl)_2(DABCO)]$, **2a** and $[(CuCl)_2(CO)_2(DABCO)]$, **3a**.

Crystals of the insoluble complexes **3a**–**3c** were prepared by layering CO-saturated solutions of biL onto CO-saturated solutions of CuCl. X-ray structural analyses of the resulting colorless crystals yielded the results shown in Figures 2, 3 and 4. Crystallographic information is provided in Table 1. The polymeric structures of **3a**–**3c** are members of the series $[(CuCl)_2L_2(biL)]$ (see Chart 1, L = CO, PPh_3, $P(OPh)_3$),[2a,2c,8] being comprised of L–Cu(μ-Cl)$_2$Cu–L rhomboid units linked together by diamine ligands. In each of the new structures, only half of the polymer repeat unit is crystallographically independent. Crystallographic three-fold rotational disorder present in the DABCO ligand was modeled successfully. The **3a** and **3b** polymers are isostructural, with chains propagating perpendicularly to the crystallographic *b*-axis. The **3c** polymer propagates perpendicularly to the crystallographic *a*-axis. The carbonyl ligands are linear: Cu–C–O = 177.4(5)°, 178.5(3)°, and 175.8(4)° for **3a**–**3c**, respectively. Bond lengths for Cu–C are 1.811(5), 1.819(3), and 1.828(4) Å and for C≡O are 1.108(5), 1.120(4), and 1.126(5) Å for **3a**–**3c**, respectively. These values are well within the range of known copper carbonyl species (Cu–C–O range 169.2–180.0°, Cu–C range 1.660–1.968 Å, C≡O range 1.043–1.198 Å).[3–6] Dihedral angles (C–Cu···Cu–C) between carbonyls on either side of a DABCO are approximately 89.6° and on either side of a Pip are 68.6°, whilst those across a Cu_2Cl_2 dimer are exactly 180°. Since all non-hydrogen atoms in **3c** except chlorines and the ring carbons lie on the *ac* plane, all C–Cu···Cu–C dihedral angles for both carbonyls and DMP methyls are 180°. Thus, a line of sight along the polymer backbone reveals four CO positions for the **3a** and **3b**, but only two for **3c**. The larger cone angle of the DMP is reflected in the fairly wide C–Cu–N angle of 128.58(15)° in **3c** versus 122.49(12)° and 119.17(15)° for **3b** and **3a**. It is noteworthy that the metal centers coordinate to the axial positions of the DMP molecule. The carbonyls in **3a** and **3b** are somewhat folded back over kinks in the polymer backbone. In contrast, the carbonyls in **3c** project at nearly perpendicular angle to the backbone. The closest points of approach for adjacent chains are a distance of about 3.35 Å between adjacent DABCO ligands in **3a**, of about 3.00 Å between carbonyls in **3b**, and of about 3.24 Å between a carbonyl and a DMP methyl for **3c**. The only X-ray structures previously reported for Cu(I) with DABCO, Pip, and DMP analogs are the cyanide-containing polymers $[Cu_2(CN)_3(DABCO-H)]$, $[(CuCN)_2(Pip)]$,

Table 1. Crystallographic data.

	3a	3b	3c
Empirical formula	$C_8H_{12}Cl_2Cu_2N_2O_2$	$C_6H_{10}Cl_2Cu_2N_2O_2$	$C_8H_{14}Cl_2Cu_2N_2O_2$
Formula weight	366.18	340.14	368.19
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$C2/c$ (No. 15)	$C2/c$ (No. 15)	$C2/m$ (No. 12)
Unit cell dimensions	$a = 12.8912(4)$ Å	$a = 13.4585(4)$ Å	$a = 11.8093(9)$ Å
	$b = 13.3318(4)$ Å	$b = 13.4881(4)$ Å	$b = 8.7799(7)$ Å
	$c = 7.6987(2)$ Å	$c = 6.3617(2)$ Å	$c = 8.2075(11)$ Å
	$\beta = 102.668(2)°$	$\beta = 100.036(2)°$	$\beta = 131.624(3)°$
Volume	1290.91(7) Å^3	1137.17(6) Å^3	636.13(11) Å^3
Z	4	4	2
Radiation	Cu Kα, $\lambda = 1.54178$ Å	Cu Kα, $\lambda = 1.54178$ Å	Cu Kα, $\lambda = 1.54178$ Å
Temperature	296(2) K	100(2) K	100(2) K
Density (calculated)	1.884 Mg/m^3	1.987 Mg/m^3	1.922 Mg/m^3
Absorption coefficient	7.778 mm^{-1}	8.766 mm^{-1}	7.892 mm^{-1}
Crystal size	0.11 × 0.08 × 0.06 mm	0.33 × 0.11 × 0.07 mm	0.23 × 0.05 × 0.05 mm
θ range for data collection	7.01 to 68.95°	4.68 to 68.08°	7.11 to 68.26°
Reflections collected	7104	5801	3470
Independent reflections	1168 [R(int) = 0.0320]	1017 [R(int) = 0.0552]	606 [R(int) = 0.0607]
Parameters	103	84	60
Goodness-of-fit on F^2	1.074	1.045	1.051
Final R indices [I>2sigma(I)]	$R1 = 0.0357$, $wR2 = 0.0909$	$R1 = 0.0338$, $wR2 = 0.0890$	$R1 = 0.0284$, $wR2 = 0.0673$

[Cu$_2$(CN)$_3$(Pip-H)] and [(CuCN)$_2$(DMP)],[10] as well as dimeric [CuCl$_2$(DABCO-CH$_2$Cl)]$_2$ and zigzag polymeric [CuI(2-methylpiperazine)].[11,12] Numerous structures have been reported for Cu(II) with these ligands.[13]
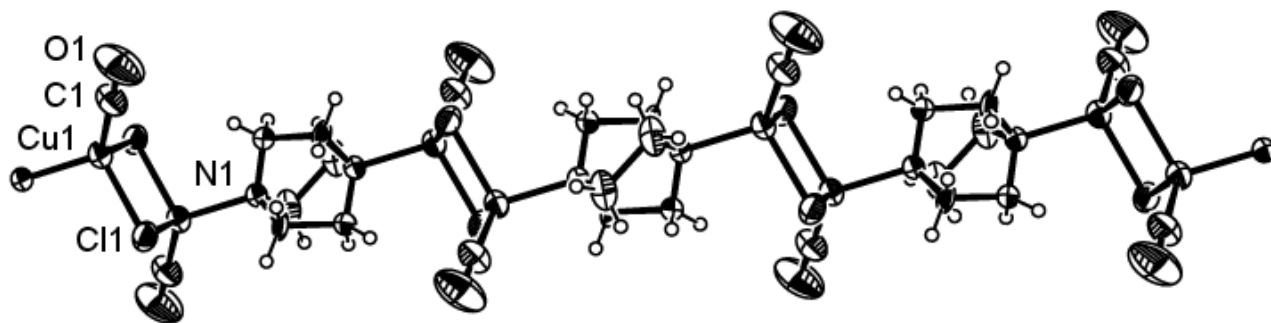

Figure 2. Polymeric structure of **3a**, 50% displacement ellipsoids, one of two rotational DABCO positions shown. Selected bond distances (Å) and angles (deg.): Cu(1)–C(1) = 1.811(5), Cu(1)–N(1) = 2.097(2), Cu(1)–Cl(1)#1 = 2.3613(10), Cu(1)–Cl(1) = 2.3656(10), O(1)–C(1) = 1.108(5); O(1)–C(1)–Cu(1) = 177.4(5) C(1)–Cu(1)–N(1) = 119.17(15), C(1)–Cu(1)–Cl(1)#1 = 115.27(16), N(1)–Cu(1)–Cl(1)#1 = 103.25(7), C(1)–Cu(1)–Cl(1) = 114.52(14), N(1)–Cu(1)–Cl(1) = 102.80(7), Cl(1)#1–Cu(1)–Cl(1) = 99.16(3), Cu(1)#1–Cl(1)–Cu(1) = 80.84(3).
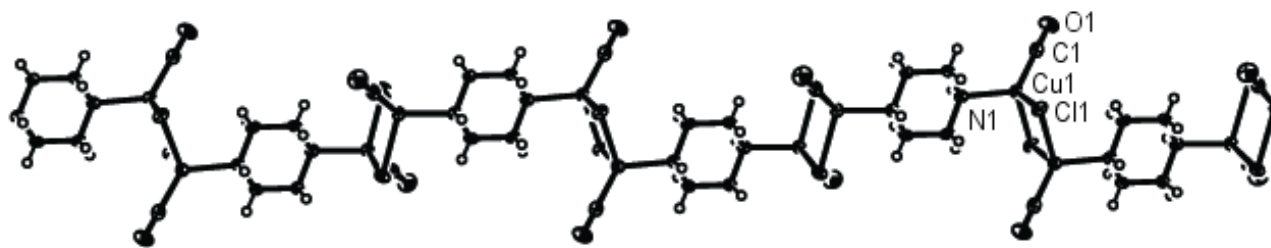

Figure 3. Polymeric structure of **3b**, 50% displacement ellipsoids. Selected bond distances (Å) and angles (deg.): Cu(1)–C(1) = 1.819(3), Cu(1)–N(1) = 2.044(3), Cu(1)–Cl(1) = 2.3766(8), O(1)–C(1) = 1.120(4); O(1)–C(1)–Cu(1) = 178.5(3) C(1)–Cu(1)–N(1) = 122.49(12), C(1)–Cu(1)–Cl(1) = 114.26(11), N(1)–Cu(1)–Cl(1) = 103.68(7), Cl(1)–Cu(1)–Cl(1)#1 = 98.84(3), Cu(1)–Cl(1)–Cu(1)#1 = 81.16(3)
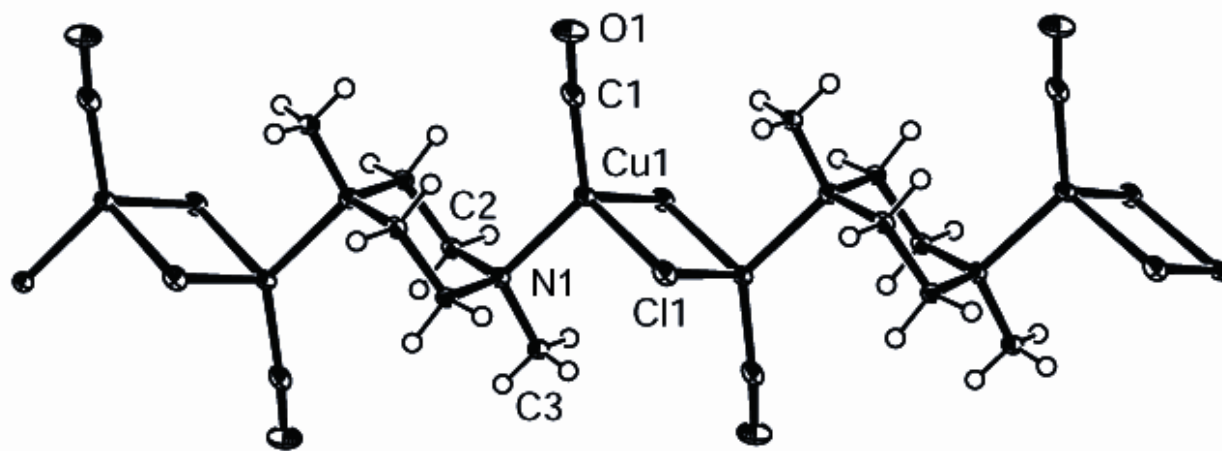
Figure 4. Polymeric structure of **3c**, 50% displacement ellipsoids. Selected bond distances (Å) and angles (deg.): Cu(1)–C(1) = 1.828(4), Cu(1)–N(1) = 2.096(3), Cu(1)–Cl(1) = 2.3781(8), O(1)–C(1) = 1.126(5); O(1)–C(1)–Cu(1) = 175.8(4) C(1)–Cu(1)–N(1) = 128.58(15), C(1)–Cu(1)–Cl(1) = 111.39(7), N(1)–Cu(1)–Cl(1) = 100.66(6), Cl(1)–Cu(1)–Cl(1)#1 = 100.20(4), Cu(1)–Cl(1)–Cu(1)#1 = 79.80(4)

Preliminary experiments in which CO was bubbled through ground solid or methanolic suspensions of **1a, 1b** or **2a–2d** yielded no evidence of CO incorporation by IR spectroscopy. However, the carbonyl ligand in **3** is readily replaced by MeCN. A sample of **3b** was stirred for five minutes suspended in MeCN. The solid state IR spectra before and after the experiment, which are shown in Figure 5, clearly demonstrate the rapid loss of CO under these conditions. In addition, the ability of carbon monoxide to diffuse out of solid **3** has been noted. This effect is most pronounced for DMP complex **3c**, for which the colorless crystals are stable only when sealed in methanol under CO atmosphere. When the CO atmosphere is removed, surface bubbles develop on the crystals even under methanol. The crystals soon become an opaque pale green.
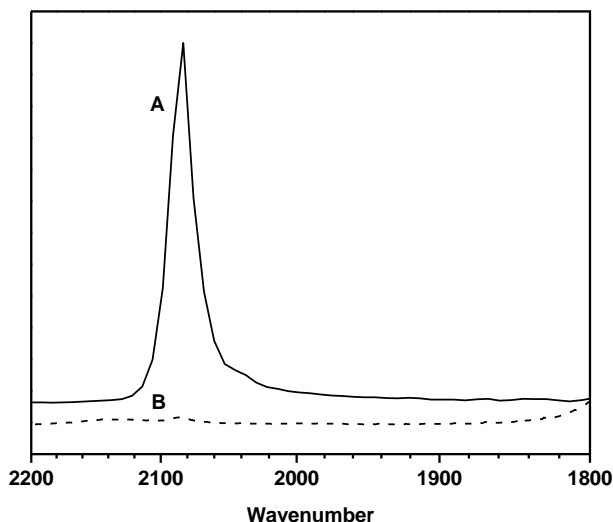
Figure 5. Solid state IR (KBr) spectra of **3b**, (A) initial, (B) after stirring for 5 min. suspended in MeCN.

Conclusion

We have demonstrated the first syntheses of carbonyl-bearing polymers of CuCl linked by diamine ligands. Although the saturated diamine ligands DABCO, Pip and DMP produce carbonyl complexes **3a–3c**, unsaturated ligands do not. This result suggests a high electron donation demand exerted by CuCl(CO). The CO ligand is highly labile, being rapidly and completely lost in coordinating solvent.

Experimental Section

Materials. The starting materials and solvents were purchased from commercial suppliers and were used without purification, except for CuCl which was recrystallized from HCl.

Synthesis of [(CuCl)₂(CO)₂(biL)] (3). In a typical experiment, freshly recrystallized CuCl (0.313 g, 3.16 mmol) in methanol (40 mL) was purged with carbon monoxide in a gas washing bottle for 30 min. The resulting solution was treated with DABCO (0.177 g, 1.58 mmol in 10 mL methanol). A white solid formed immediately. The solution was stirred for 30 min under continuing carbon monoxide purge. The white solid product, **3a**, was isolated by filtration and washed with ethyl ether. Yield: 0.443 g (79.5%). IR (KBr): 2075 cm^{-1}. Anal. Found: Cu, 35.55; C, 25.90; H, 3.35; N, 7.56. Calcd for C$_8$H$_{14}$Cl$_2$Cu$_2$N$_2$O$_2$:

Cu, 34.71; C, 26.24; H, 3.30; N, 7.65. Treatment of CuCl(CO) with Pip produced a white solid, **3b**. Yield: (43.2%). IR (KBr): 2084 cm^{-1}. Anal. Found: Cu, 36.88; C, 21.20; H, 3.03; N, 8.01. Calcd for $C_6H_{10}Cl_2Cu_2N_2O_2$: Cu, 37.36; C, 21.19; H, 2.96; N, 8.24. Treatment of CuCl(CO) with DMP produced a white solid, **3c**. Yield: (57.5%). IR (KBr): 2077 cm^{-1}. Anal. Found: Cu, 37.24; C, 23.31; H, 3.85; N, 7.30. Calcd for $C_8H_{14}Cl_2Cu_2N_2O_2$: Cu, 34.52; C, 26.10; H, 3.83; N, 7.61.

Thermogravimetric Analysis. Thermogravimetric analyses were run using a TA Instruments Q500 instrument in high resolution mode (heating rate dependent upon mass loss activity) under 60 mL/min N_2 flow.

Infrared Analysis. Quantitative solid state infrared spectra carried out by grinding together 4.1 mg of sample and 345.4 mg KBr. An 82.9 mg portion of this mixture was pressed into a pellet and analyzed using a Digilab FTS 7000 Series FTIR spectrophotometer.

X-ray Diffraction. Crystals suitable for X-ray diffraction were grown by layering a CO-saturated MeOH solution of biL (50 mM) onto a CO-saturated MeOH solution of CuCl (100 mM) in a 5 mm i.d. glass tube. After about 3 days, colorless crystals formed. X-ray structural determinations were carried out on a Bruker SMART Apex II diffractometer at either 296(2) K (**3a**) or 100(2) K (**3b**, **3c**) using graphite-monochromated Cu Kα radiation. The structures were solved by use of direct methods. Least squares refinement on F^2 was used for all reflections. Structure solution, refinement and the calculation of derived results were performed using the SHELXTL package of computer programs. The non-hydrogen atoms were refined anisotropically. For **3b** and **3c**, hydrogen atoms were located by standard difference Fourier techniques and were refined with isotropic thermal parameters. For **3a**, rotational disorder present in the DABCO was modeled with partial carbon occupancies. In this case hydrogen atoms were placed in theoretical positions and refined with a riding model.

Supporting Information Available. Full details of the crystal structure determinations of **3a**–**3c** (CCDC 297739, 297741, and 297740) in CIF format and Tables S1–S15. This material is available free of charge via the Internet at http://pubs.acs.org.

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Table of Contents Graphic.