Rational Synthesis of Dinuclear Mixed-Valence Cu(I)/Cu(II) Carboxylate Derivatives. Steric Influence of Phosphine Ligands on the Structures of the Complexes

Donald J. Darensbourg,* Matthew W. Holtcamp, Bandana Khandelwal, Kevin K. Klausmeyer, and Joseph H. Reibenspies

Department of Chemistry, Texas A&M University, College Station, Texas 77843

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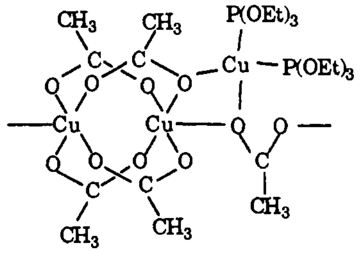
The mixed-valence Cu(I)/Cu(II) complexes $(Ph_3P)_4Cu^I_2Cu^{II}(O_2CCH_2CO_2)_2$ (**1**) and $(Cy_3P)_4Cu^I_2Cu^{II}(O_2CCH_2CO_2)_2$ (**2**), have been prepared from the acid–base reaction of $Cu^{II}(acac)_2$ or $Cu^{II}(butyrate)_2$ with the respective copper(I) hydrogen dicarboxylate derivative and their solid-state structures determined crystallographically. The Cu(II) center in both derivatives is chelated by two malonate dianions in a square-planar geometry. In complex 1 the two bis(triphenylphosphine)copper(I) moieties are coordinated to the internal oxygen atoms of the Cu(II) malonate core at an average distance of 2.177[4] Å, resulting in a Cu(I)···Cu(II) separation of 3.132(1) Å. On the other hand in complex 2 the two bis(tricyclohexylphosphine)copper(I) groups are appended asymmetrically to opposite ketonic oxygens of the malonate ligands, hence affording a larger Cu(I)···Cu(II) separation of 4.600(1) Å. That is, the Cu(I) center in complex 1 is four-coordinate and a distorted tetrahedron, whereas in complex 2 the Cu(I) center is three-coordinate and trigonal planar. These structural differences, which persist in dichloromethane solution, are ascribed to the steric requirements of the phosphine ligands. Crystal data for **1**: space group $P2_1/n$, $a = 9.978(2)$ Å, $b = 23.365(5)$ Å, $c = 16.703(10)$ Å, $\beta = 103.840(0)°$, $Z = 2$, $R = 6.04\%$. Crystal data for 2: space group $P\bar{1}$, $a = 9.7280(10)$ Å, $b = 15.084(2)$ Å, $c = 17.198(2)$ Å, $\alpha = 103.910(10)°$, $\beta = 98.680(10)°$, $\gamma = 102.890(10)°$, $Z = 1$, $R = 5.89\%$.

Introduction

The probing of electron exchange between copper centers in mixed-valence Cu(I)/Cu(II) complexes remains a subject of intense interest.[1] These studies require data obtained from complexes possessing a wide range of internuclear separations of the metals. Pertinent to this matter, mixed-valence copper(I,II) complexes containing the ubiquitous carboxylate ligands are rare. Indeed the current literature contains only a few structurally characterized derivatives. These have been prepared by the partial reduction of Cu(II) carboxylates or the one-electron oxidation of Cu(I) carboxylates. Specifically, Beddoes *et al.* partially reduced copper(II) acetate with triethylphosphine and characterized a polymeric chain of repeating $Cu^{II}_2Cu^I$ units as shown in **A**.[2,3] In an analogous manner, Valigura *et al.* have synthesized and characterized a tetrameric complex using triphenylphosphine as depicted in **B**.[4,5] These interesting complexes contain discrete $Cu_2(O_2CCH_3)_4$ units, with the Cu(I) phosphine moieties serving as ligands on the dimeric Cu(II) unit. The influence of the phosphine ligands is noted as seen in the two different solid-state structures.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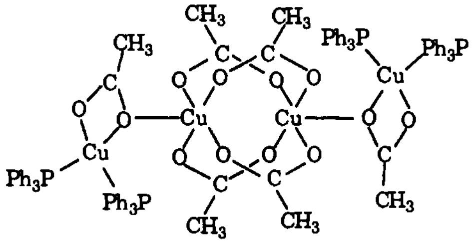
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Alternatively, Wrobleski *et al.* have synthesized two dimeric Cu(I)/Cu(II) carboxylates, $Cu_2(acacP)_2(3\text{-}CH_3OC_6H_4CO_2)$ and $Cu(acacP)_2(PhCO_2)$, where the acacP represents [*o*-(diphenylphosphino)benzoyl]pinacolonate.[6,7] The complexes were prepared by the one-electron oxidation by oxygen of the corresponding $[Cu^I(acacP)]_2$ dimer. The combination of "hard" and "soft" electron donors, namely bis(β-diketonate) and phosphine ligands, respectively, allows for the stabilization of mixed-valence copper complexes.

Although a large variety of phosphine derivatives of Cu(I)/Cu(II) carboxylates with interesting chemical and structural properties could potentially be prepared, as evident by the array of phosphines and carboxylic acids that are available, to date this chemistry is relatively unexplored. This is in part due to a need

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for improved, more systematic, synthetic routes to mixed-valence Cu(I)/Cu(II) carboxylates. During the course of our studies involving phosphine derivatives of copper(I) hydrogen dicarboxylates as possible intermediates in the catalytic decarboxylation of dicarboxylic acids,[8] it became apparent that these complexes provide a rational route to a variety of Cu(I)/Cu(II) mixed-valence carboxylates. A new class of Cu(I)/Cu(II) species of the general formula $(R_3P)_4Cu^I{}_2Cu^{II}(O_2CCH_2CO_2)_2$ have been synthesized and their structures determined by X-ray crystallography, where R = Ph (**1**) and cyclohexyl (**2**). The solid-state structures of complexes **1** and **2** were shown to be governed by the steric influences of the phosphine ligands.

Experimental Section

Methods and Materials. All manipulations were carried out under an inert atmosphere unless otherwise stated. The solvents were freshly distilled prior to use. Triphenylphosphine was purchased from Aldrich Chemical Co. and used as received. Copper(II) acetylacetonate and copper(II) butyrate were purchased from Strem Chemicals. The (triphenylphosphine)cuprous malonate half salt and (tricyclohexylphosphine)cuprous malonate half salt were prepared by published procedures.[8] Infrared spectra were recorded on a Mattson 6021 spectrometer with DTGS and MCT detectors.

Synthesis of 1, $(Ph_3P)_4Cu^I{}_2Cu^{II}(O_2CCH_2CO_2)_2$. (Triphenylphosphine)cuprous hydrogen malonate (0.800 g) and copper(II) acetylacetonate (0.158 g) were loaded into a 50-mL Schlenk flask. Dichloromethane (20 mL) was cannulated into the mixture, forming a purple solution. The mixture was stirred for 1 h under argon. Diethyl ether was slowly added via cannula, resulting in a color change to light green with concomitant precipitation. The light green precipitate was filtered off, washed with approximately 30 mL of diethyl ether, and dried under vacuum. The green powder was recrystallized from dichloromethane, yielding 0.610 g (73.0%) of product. Anal. Calcd for $C_{78}H_{64}Cu_3O_8P_4 \cdot CH_2Cl_2$: C, 64.95: H, 4.48. Found: C, 65.15; H, 5.22. IR (CH_2Cl_2; $\upsilon(CO_2)$, cm^{-1}): 1653 (s), 1344 (m).

Recrystallization by slow diffusion of diethyl ether into a dichloromethane solution produced single, light green crystals suitable for an X-ray structure determination.

Synthesis of 2, $(Cy_3P)_4Cu^I{}_2Cu^{II}(O_2CCH_2CO_2)_2$. (Tricyclohexylphosphine)cuprous hydrogen malonate (0.514 g) and copper(II) butyrate (0.084 g) were loaded into a 50-mL Schlenk flask. A mixture of dichloromethane (10 mL) and methanol (20 mL) was cannulated into the first mixture to afford a blue-green solution. The mixture was stirred for 1 h under argon. The solvent was removed under vacuum during which time a color change to light purple with concomitant precipitation resulted. The complex was redissolved and the solution dried under vacuum four times to completely remove butyric acid impurities. The light purple precipitate was filtered off, washed with approximately 30 mL of diethyl ether, and dried under vacuum. The purple powder was recrystallized from dichloromethane, yielding 0.445 g (72.0%) of product. Anal. Calcd for $C_{78}H_{136}Cu_3O_8P_4$: C, 61.78; H, 9.04. Found: C, 60.25; H, 9.50. IR (CH_2Cl_2; $\upsilon(CO_2)$, cm^{-1}): 1628 (s), 1576 (s), 1413 (m).

Recrystallization by slow diffusion of diethyl ether into a dichloromethane solution produced single, light purple crystals suitable for an X-ray structure determination.

X-ray Crystallographic Study of 1 and 2. Crystal data and details of data collection are given in Table 1. A pale green plate (0.5 mm × 0.25 mm × 0.32 mm) of **1** and a light violet needle (0.1 mm × 0.1 mm × 0.3 mm) of **2** were each mounted on a glass fiber, at room temperature. Preliminary examination and data collection were performed on a Rigaku AFC5R X-ray diffractometer (oriented graphite monochromator). Cell parameters were calculated from the least-squares fitting of the setting angles for 25 reflections. ω scans for several intense reflections indicated acceptable crystal quality. Data were collected for $5.0° \leq 2\theta \leq 50.0°$, at 296 °K. For both **1** and **2**, three control reflections, collected every 150 reflections, showed no significant trends. Background measurements were performed by stationary-crystal and stationary-counter techniques at the beginning and end of each scan for half of the total scan time. Lorentz and polarization corrections were applied to 7303 reflections for **1** and 7217 for **2**. A semiempirical absorption correction was applied. Totals of 3119 unique reflections ($R_{int} = 0.02$), with $|I| \geq 2.0\sigma_I$, for **1** and 3941 ($R_{int} = 0.04$) for **2** were used in further calculations. The structures were solved by direct methods [SHELXS, SHELXTL-PLUS program package, Sheldrick (1990)]. Full-matrix least-squares anisotropic refinement for all non-hydrogen atoms yielded $R = 0.060$, $R_w = 0.056$, and $S = 1.37$ for **1** and provided $R = 0.059$, $R_w = 0.072$, and $S = 2.04$ for **2** at convergence. Hydrogen atoms were placed in idealized positions with isotropic thermal parameters fixed at 0.08 Å^2. Neutral-atom scattering factors and anomalous scattering correction terms were taken from the *International Tables for X-ray Crystallography*.

Table 1. Crystallographic Data and Data Collection Parameters

	1	**2**
formula	$C_{80}H_{68}O_8P_4Cl_4Cu_3$	$C_{81}H_{131}O_9P_4Cu_3Cl_6$
fw	1613.6	1763.5
space group	monoclinic $P2_1/n$	triclinic $P\bar{1}$
a, Å	9.978(2)	9.7280(10)
b, Å	23.365(5)	15.084(2)
c, Å	16.703(10)	17.198(2)
α, deg		103.910(10)
β, deg	103.840(0)	98.680(10)
γ, deg		102.890(10)
V, Å^3	3781.060(0)	2331.5(6)
Z	2	1
d(calcd), g/cm^3	1.417	1.256
abs coeff, mm^{-1}	1.117	3.392
λ, Å	0.710 73	1.541 78
T, K	296	293
transm coeff	0.9109–0.9999	0.6887–0.9999
R,[a] %	6.04	5.89
wR_w,[a] %	5.60	7.19

[a] $R = \sum|F_o - F_c|/\sum F_o$. $R_w = \{[\sum w(F_o - F_c)^2]/[\sum w(F_o)^2]\}^{1/2}$. GOF = 1.37 and 2.04 for **1** and **2**, respectively.

A molecule of CH_2Cl_2 for **1** and two molecules of CH_2Cl_2 and one molecule of water for **2** were included in the structure refinement. One of the two CH_2Cl_2 molecules and the water molecule for **2** appeared to only partially fill their occupation sites (50% for CH_2Cl_2 and 33% for H_2O).

Results

Synthesis. The new complex $(Ph_3P)_4Cu^I{}_2Cu^{II}(O_2CCH_2CO_2)_2$ (**1**) was prepared by the acid–base reaction of $Cu^{II}(acac)_2$ (where acac = acetylacetonate) with the respective copper(I) hydrogen dicarboxylate derivative (eq 1). It was interesting to note that

$$2(Ph_3P)_2Cu^IO_2CCH_2COOH + Cu^{II}(acac)_2 \rightarrow \{(Ph_3P)_2Cu^IO_2CCH_2CO_2\}_2Cu^{II} + 2Hacac \quad (1)$$

a homogeneous solution of the copper(I) and copper(II) complexes did not react, as evident by infrared spectroscopy, until the introduction of diethyl ether. That is, the addition of ether to a dichloromethane solution of the two complexes resulted in a color change from bluish-purple to light green with concomitant precipitation of product. This enhanced reactivity of $(Ph_3P)_2Cu^I(O_2CCH_2CO_2H)$ upon introducing ether might be explained by the mode of hydrogen bonding in the monomeric complex. We recently determined that the appended carboxylic acid in $(Ph_3P)_2Cu^I(O_2CCH_2CO_2H)$ forms a strong intramolecular hydrogen bond with the distal oxygen atom of the carboxylate group bound to copper in the solid state and in non-hydrogen-bonding solvents.[8] The addition of ether, a hydrogen-bonding solvent, would be expected to disrupt the intramolecular hydrogen bonding in the complex, allowing for more facile proton transfer. Alternatively, this may simply be ascribed to a reaction driven by product insolubility.

Complex **2** was similarly prepared from $Cu^{II}(butyrate)_2$ and $(Cy_3P)_2Cu^IO_2CCH_2COOH$, where Cy = cyclohexyl (eq 2).

$$2(Cy_3P)_2Cu^IO_2CCH_2COOH + Cu^{II}(butyrate)_2 \rightarrow \{(Cy_3P)_2Cu^IO_2CCH_2CO_2\}_2Cu^{II} + 2 \text{ butyric acid} \quad (2)$$

Attempts to synthesize the tricyclohexylphosphine analog using

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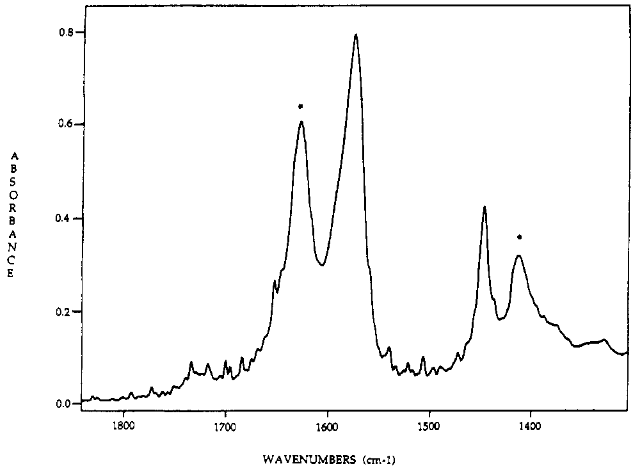

Figure 1. Infrared spectrum of complex **2** in CH_2Cl_2 in $\upsilon(CO_2^-)$ region. The peaks marked by asterisks at 1628 and 1413 cm^{-1} represent the asymmetric and symmetric modes for the monodentately bound carboxylate, whereas the peak at 1576 cm^{-1} corresponds to the asymmetric $\upsilon(CO_2^-)$ vibration of the bridging carboxylate. The symmetric band of the bridging carboxylate is coincident with either the $\upsilon(CO_2^-)_{sym}$ of the monodentate carboxylate or the peak due to tricyclohexylphosphine at 1448 cm^{-1}.

$Cu^{II}(acac)_2$ as a source of proton acceptor, and otherwise identical reaction conditions, failed even though acac⁻ is a much stronger base than butyrate. It thus appears to be a steric factor involved in inhibiting proton transfer, since Cy_3P has a much larger cone angle than Ph_3P.[9,10]

Both complexes **1** and **2** are air-sensitive in solution and in the solid state but may be handled in air in the solid state for short periods. The infrared spectra in the $\upsilon(CO_2^-)$ regions of the two complexes are quite different, suggesting alternative carboxylate binding modes in the two phosphine derivatives. That is, complex **1** exhibits an asymmetric and symmetric $\upsilon(CO_2^-)$ band pattern of 1653 and 1344 cm^{-1} in CH_2Cl_2 and 1653 and 1340 cm^{-1} in KBr, indicative of a symmetrically bound monodentate carboxylate.[11] On the other hand, complex **2** displays at least three vibrational modes in the $\upsilon(CO_2^-)$ region at 1628, 1576, and 1413 cm^{-1} (CH_2Cl_2) and 1636, 1588, and 1418 cm^{-1} (KBr). Figure 1 illustrates the solution spectrum of **2**, which is suggestive of both monodentate and bidentate or bridging carboxylate binding.[12]

Structures. Definitive solid-state structures were assigned to the two Cu(I)/Cu(II) derivatives by X-ray crystallography. Crystals suitable for an X-ray investigation were obtained by slow diffusion of diethyl ether into a concentrated dichloromethane solution of the respective complex at −20 °C. The final atomic positional and equivalent isotropic displacement parameters for complex **1** are listed in Table 2. Figure 2 shows an ORTEP drawing of the molecule, and selected bond distances and angles are provided in Table 3. The two malonate dianions chelate around the square-planar Cu(II) center, forming highly distorted six-membered rings. The chelated malonate ions bind almost symmetrically, (Cu(2)–O(3a) and Cu(2)–O(2) bond distances are 1.906 and 1.892 Å, respectively.) The Cu(II) malonate core is similar to that previously reported in $CH_2(COO)_2Cu{\cdot}4H_2O$, which contains symmetric Cu–O bond distances, 1.96 and 1.97 Å.[13] The Cu(I) atoms coordinate to the internal oxygen atoms of the malonate ligands at an average distance of 2.177[4] Å, forming a bridge between the Cu(I) atoms and the Cu(II) atom *via* an oxygen atom. The Cu(I)···Cu(II) separation is 3.132(1) Å. The Cu(1)–P bond distances are 2.259(2) and 2.216(2) Å

Table 2. Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å² × 10³) for **1**[a]

	x	*y*	*z*	*U*(eq)[b]
Cu(1)	4936(1)	343(1)	1803(1)	37(1)
Cu(2)	5000	0	0	42(1)
Cl(1)	9300(11)	1522(5)	−356(4)	424(8)
Cl(2)	10935(7)	2489(4)	510(5)	292(5)
P(1)	5015(2)	1179(1)	2439(1)	34(1)
P(2)	5078(2)	−527(1)	2405(1)	36(1)
O(1)	1586(6)	364(4)	725(4)	98(4)
O(2)	3652(5)	219(2)	568(3)	45(2)
O(3)	3706(5)	−263(2)	−962(3)	42(2)
O(4)	1702(5)	−340(3)	−1829(3)	62(3)
C(1)	3408(8)	−756(4)	2541(5)	38(3)
C(2)	2488(9)	−344(4)	2633(5)	59(4)
C(3)	1145(10)	−477(5)	2675(6)	72(5)
C(4)	767(11)	−1037(6)	2625(6)	73(5)
C(5)	1653(13)	−1449(5)	2527(7)	95(6)
C(6)	2986(10)	−1325(4)	2495(5)	63(4)
C(7)	7575(8)	−361(4)	3501(5)	51(3)
C(8)	8549(9)	−432(5)	4237(6)	68(5)
C(9)	8238(11)	−716(5)	4883(6)	7(65)
C(10)	6968(11)	−947(5)	4801(6)	70(5)
C(11)	5983(9)	−898(4)	4063(5)	52(4)
C(12)	6290(8)	−604(3)	3406(5)	39(3)
C(13)	5591(8)	−1106(3)	1814(5)	37(3)
C(14)	6673(9)	−1473(4)	2114(5)	59(4)
C(15)	4890(9)	−1170(4)	1001(5)	54(4)
C(16)	7032(11)	−1884(5)	1622(7)	82(5)
C(17)	5263(12)	−1574(5)	501(6)	74(5)
C(18)	6330(12)	−1937(4)	825(7)	79(5)
C(19)	6196(8)	1153(3)	3463(5)	35(3)
C(20)	8220(10)	1398(5)	4488(6)	75(5)
C(21)	7862(12)	1041(5)	5040(6)	70(5)
C(22)	6673(10)	731(4)	4812(5)	58(4)
C(23)	7394(9)	1463(4)	3699(5)	58(4)
C(24)	5843(9)	792(4)	403(5)	49(4)
C(25)	3448(8)	1454(3)	2672(5)	38(3)
C(26)	3484(9)	1891(4)	3249(5)	48(4)
C(27)	2298(11)	2079(4)	3435(6)	63(4)
C(28)	1077(11)	1844(5)	3054(7)	79(6)
C(29)	991(10)	1408(5)	2511(7)	75(5)
C(30)	2181(8)	1213(4)	2311(5)	48(4)
C(31)	5660(9)	1765(3)	1916(4)	36(3)
C(32)	6925(9)	1698(4)	1722(5)	51(4)
C(33)	7445(11)	2127(5)	1322(6)	73(5)
C(34)	6698(12)	2617(5)	1090(6)	71(5)
C(35)	5451(11)	2682(4)	1266(6)	61(4)
C(36)	4921(9)	2263(4)	1684(5)	49(4)
C(37)	2345(9)	252(4)	296(5)	52(4)
C(38)	1746(9)	181(5)	−623(5)	90(5)
C(39)	2394(8)	−174(3)	−1183(5)	42(4)
C(40)	10153(22)	1891(10)	135(11)	265(18)

[a] Estimated standard deviations are given in parentheses. [b] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

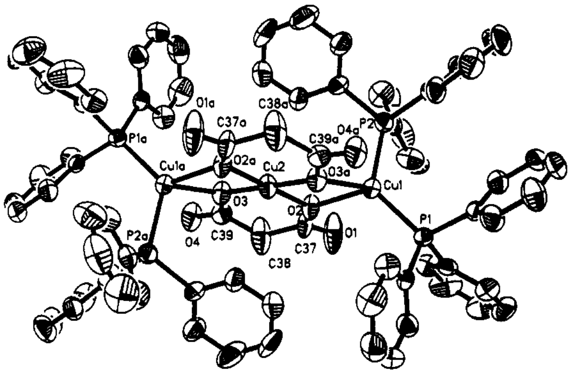

Figure 2. ORTEP drawing of **1** showing the atom-numbering scheme. Thermal ellipsoids are drawn at the 50% probability level.

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Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) for 1[a]

Cu(1)–Cu(2)	3.132(1)	Cu(1)–P(1)	2.216(2)
Cu(1)–P(2)	2.259(2)	Cu(1)–O(2)	2.172(4)
Cu(1)–O(3a)	2.181(5)	Cu(2)–O(2)	1.892(5)
Cu(2)–O(3)	1.906(4)	Cu(2)–Cu(1a)	3.132(1)
Cu(2)–O(2a)	1.892(5)	Cu(2)–O(3a)	1.906(4)
O(1)–C(37)	1.19(1)	O(2)–C(37)	1.277(9)
O(3)–C(39)	1.290(9)	O(3)–Cu(1a)	2.181(5)
O(4)–C(39)	1.198(9)	C(37)–C(38)	1.52(1)
C(38)–C(39)	1.51(1)		
Cu(2)–Cu(1)–P(1)	132.9(1)	Cu(2)–Cu(1)–P(2)	100.6(1)
P(1)–Cu(1)–P(2)	126.1(1)	P(1)–Cu(1)–O(2)	121.3(2)
P(2)–Cu(1)–O(2)	105.2(2)	Cu(2)–Cu(1)–O(3a)	36.8(1)
P(1)–Cu(1)–O(3a)	115.3(2)	P(2)–Cu(1)–O(3a)	103.1(2)
O(2)–Cu(1)–O(3a)	72.1(2)	Cu(1)–Cu(2)–O(3)	136.7(2)
O(2)–Cu(2)–O(3)	95.2(2)	Cu(1)–Cu(2)–Cu(1a)	180.0(1)
O(2)–Cu(2)–Cu(1a)	137.0(1)	O(3)–Cu(2)–Cu(1a)	43.3(2)
Cu(1)–Cu(2)–O(2a)	137.0(1)	O(2)–Cu(2)–O(2a)	180.0(1)
O(3)–Cu(2)–O(2a)	84.8(2)	Cu(1a)–Cu(2)–O(2a)	43.0(1)
Cu(1)–Cu(2)–O(3a)	43.3(2)	O(2)–Cu(2)–O(3a)	84.8(2)
O(3)–Cu(2)–O(3a)	180.0(1)	C(31)–C(36)–C(35)	119.7(9)
O(1)–C(37)–O(2)	122.8(7)	O(1)–C(37)–C(38)	118.7(7)
O(2)–C(37)–C(38)	118.4(8)	C(37)–C(38)–C(39)	124.4(7)
O(3)–C(39)–O(4)	122.2(8)	O(3)–C(39)–C(38)	117.9(7)
O(4)–C(39)–C(38)	119.8(7)		

[a] Estimated standard deviations are given in parentheses.

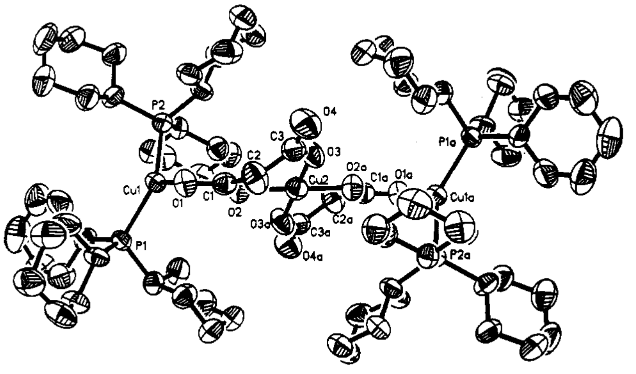

Figure 3. ORTEP drawing of **2** showing the atom-numbering scheme. Thermal ellipsoids are drawn at the 50% probability level.

and are similar to the Cu(1)–P distances previously reported for bis(triphenylphosphine)copper(I) hydrogen malonate and related derivatives.[8,12] On the other hand, the P(2)–Cu(1)–P(1) bond angle is 126.1(1)°, smaller than that found in the monomeric complex, where the P(2)–Cu(1)–P(1) bond angle is 131.1°. The smaller angle for complex **1** is expected since $(Ph_3P)_2CuO_2CH_2CO_2H$ has a three-coordinate trigonal-planar geometry whereas complex **1** was determined to be a four-coordinate distorted-tetrahedral complex.

Positional and thermal parameters for complex **2** are given in Table 4, and selected bond distances and angles are listed in Table 5. Figure 3 shows the coordination environments about the copper centers and the numbering scheme used in the tables. Complex **2** consists of a square planar Cu(II) malonate core similar to that of complex **1**; however, the Cu(2)–O bond distances (Cu(2)–O(2) = 1.931 Å, Cu(2)–O(3) = 1.895 Å) indicate asymmetrical chelation of the malonate ions around the Cu(II) center. This asymmetrical behavior is a result of the two $(Cy_3P)_2Cu^I$ moieties binding in a monodentate fashion through opposite ketonic oxygens of the malonate dianions, as depicted in Figure 3. The steric bulk of the tricyclohexylphosphine induces formation of a monodentate distorted trigonal planar Cu(I) center; furthermore, it appears that steric effects cause the Cu(I) to coordinate to the ketonic malonate oxygens rather than the internal oxygens as seen in complex **1**. This in turn causes an elongation of the Cu(I)···Cu(II) distance in 2 compared to that in **1** at 4.600(1) Å. On the other hand, the Cu(1)–O(1) distance at 2.079 Å is shorter than the observed average Cu(I)–O distance in **1**. The Cu(1)–P bond distances of 2.241(2) and 2.236(2) Å are very similar to those of the analogous triphenylphosphine complex. The P(1)–Cu(1)–P(2) bond angle at 140.7°, indicative of a large distortion from the expected 120° for ideal trigonal-planar geometry, is further evidence of the large steric requirement of the Cy_3P ligand.

Table 4. Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å² × 10³) for 2[a]

	x	*y*	*z*	*U*(eq)[b]
Cu(1)	–194(1)	2927(1)	–2487(1)	49(1)
Cu(2)	0	5000	0	59(1)
Cl(1)	6682(5)	2980(3)	959(2)	160(3)
Cl(2)	5372(7)	2992(6)	2307(4)	286(6)
Cl(3)	5852(14)	310(10)	1023(5)	626(9)
Cl(4)	6411(18)	474(12)	1487(9)	405(8)
P(1)	–462(2)	3450(1)	–3597(1)	48(1)
P(2)	–1218(2)	1743(1)	–2009(1)	49(1)
O(1)	1803(5)	3710(4)	–1736(3)	63(2)
O(2)	406(6)	4301(4)	–997(3)	64(2)
O(3)	1618(7)	4841(4)	663(3)	78(3)
O(4)	3752(7)	4604(5)	913(4)	87(3)
O(5)	4115(19)	4630(13)	–2293(10)	97(10)
C(1)	1622(9)	4205(6)	–1093(5)	56(4)
C(2)	2934(9)	4717(7)	–395(5)	79(4)
C(3)	2763(10)	4714(6)	455(5)	60(4)
C(4)	–1964(11)	1636(6)	–4632(5)	91(5)
C(5)	–3322(11)	970(7)	–5222(6)	104(5)
C(6)	–3670(12)	1251(8)	–5972(7)	114(6)
C(7)	–3588(13)	2276(8)	–5835(7)	137(7)
C(8)	–2249(11)	2937(6)	–5229(5)	89(5)
C(9)	–1934(9)	2654(5)	–4453(5)	66(4)
C(10)	–2354(9)	4491(6)	–3071(6)	78(4)
C(11)	–2807(10)	5398(7)	–2929(6)	92(5)
C(12)	–1628(12)	6224(6)	–2355(6)	92(5)
C(13)	–248(10)	6321(6)	–2668(6)	82(5)
C(14)	210(9)	5402(5)	–2805(5)	69(4)
C(15)	–986(8)	4574(5)	–3430(4)	53(3)
C(16)	1884(9)	2880(6)	–4091(6)	77(5)
C(17)	3451(10)	3130(7)	–4213(6)	91(5)
C(18)	3608(10)	3701(7)	–4808(6)	85(5)
C(19)	3001(9)	4513(7)	–4633(6)	85(5)
C(20)	1440(9)	4241(6)	–4559(5)	72(4)
C(21)	1298(8)	3722(5)	–3900(5)	53(3)
C(22)	–1832(10)	–307(5)	–2416(5)	76(4)
C(23)	–1957(12)	–1212(6)	–3082(6)	94(5)
C(24)	–587(13)	–1217(7)	–3374(7)	105(6)
C(25)	–87(11)	–364(7)	–3650(6)	96(5)
C(26)	66(9)	552(6)	–2997(5)	73(4)
C(27)	–1325(9)	563(5)	–2711(5)	59(4)
C(28)	–1122(10)	1299(6)	–454(4)	71(4)
C(29)	–251(12)	1581(7)	440(5)	91(5)
C(30)	1268(11)	1491(7)	484(5)	88(5)
C(31)	2031(10)	2046(6)	–10(6)	85(5)
C(32)	1210(9)	1758(6)	–882(5)	64(4)
C(33)	–305(8)	1894(5)	–934(4)	55(3)
C(34)	–4057(8)	1516(6)	–2806(5)	67(4)
C(35)	–5587(9)	1535(7)	–2768(6)	80(5)
C(36)	–5680(10)	2450(7)	–2216(6)	81(5)
C(37)	–4735(10)	2638(6)	–1361(6)	80(5)
C(38)	–3203(8)	2618(6)	–1394(5)	66(4)
C(39)	–3123(8)	1681(5)	–1957(5)	55(3)
C(40)	5721(15)	3472(12)	1603(8)	163(10)
C(41)	5000	0	0	232(12)

[a] Estimated standard deviations are given in parentheses. [b] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Discussion

A systematic synthesis of Cu(I)/Cu(II) derivatives has been developed employing the acid–base reaction of phosphine derivatives of a Cu(I) hydrogen dicarboxylate, in particular dimalonate, with $Cu^{II}(acac)_2$ or $Cu^{II}(butyrate)_2$. The structures of these complexes were shown to contain a square-planar Cu(II) center, with the binding and coordination number of the appended bis(phosphine)copper(I) moiety being determined by the steric

Table 5. Selected Bond Lengths (Å) and Bond Angles (deg) for **2**[a]

Cu(1)–Cu(2)	4.600(1)	Cu(1)–P(1)	2.236(2)
Cu(1)–P(2)	2.241(2)	Cu(1)–O(1)	2.079(4)
Cu(2)–O(2)	1.931(5)	Cu(2)–O(3)	1.895(6)
O(1)–C(1)	1.24(1)	O(2)–C(1)	1.25(1)
O(3)–C(3)	1.26(1)	O(4)–C(3)	1.22(1)
C(1)–C(2)	1.52(1)	C(2)–C(3)	1.50(1)
P(1)–Cu(1)–P(2)	140.7(1)	P(1)–Cu(1)–O(1)	107.6(2)
P(2)–Cu(1)–O(1)	111.0(2)	O(2)–Cu(2)–O(3)	92.5(2)
O(2)–Cu(2)–O(2a)	180.0(1)	O(3)–Cu(2)–O(2a)	87.5(2)
Cu(1)–P(1)–C(9)	113.9(3)	Cu(1)–P(1)–C(15)	114.3(3)
C(9)–P(1)–C(15)	101.7(4)	Cu(1)–P(1)–C(21)	109.1(3)
C(9)–P(1)–C(21)	112.8(4)	C(15)–P(1)–C(21)	104.5(4)
Cu(1)–P(2)–C(27)	111.3(3)	Cu(1)–P(2)–C(33)	111.8(2)
C(27)–P(2)–C(33)	112.4(4)	Cu(1)–P(2)–C(39)	113.0(3)
C(27)–P(2)–C(39)	103.6(3)	C(33)–P(2)–C(39)	104.3(4)
Cu(1)–O(1)–C(1)	109.4(5)	Cu(2)–O(2)–C(1)	125.6(4)
Cu(2)–O(3)–C(3)	127.3(6)	O(1)–C(1)–O(2)	122.6(6)
O(1)–C(1)–C(2)	118.3(8)	O(2)–C(1)–C(2)	119.1(7)
C(1)–C(2)–C(3)	117.3(7)	O(3)–C(3)–O(4)	123.5(8)
O(3)–C(3)–C(2)	118.5(8)	O(4)–C(3)–C(2)	118.0(9)

[a] Estimated standard deviations are given in parentheses.

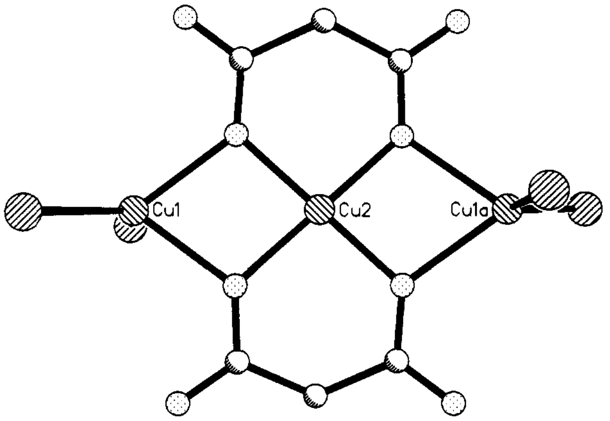

Figure 4. Perspective view of **1** where the phosphine's phenyl rings are omitted for clarity.

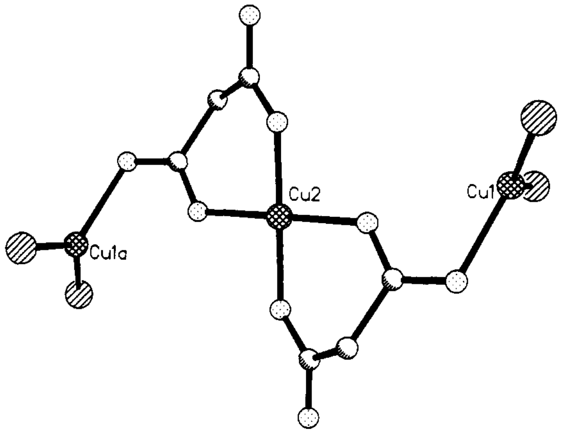

Figure 5. Perspective view of **2** where the phosphine's cyclohexyl rings are omitted for clarity.

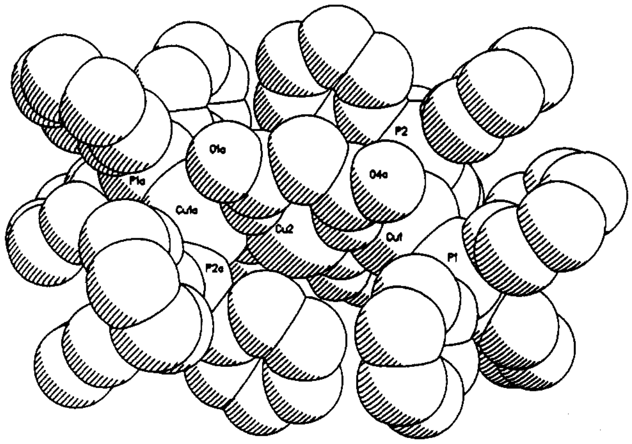

Figure 6. Space-filling model of complex **1**.

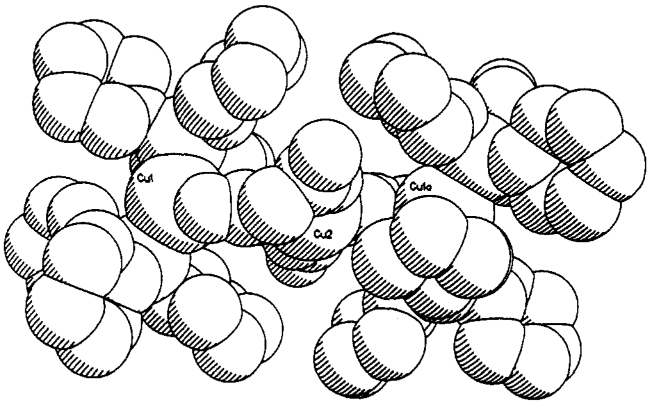

Figure 7. Space-filling model of complex **2**.

requirements of the phosphine ligands. Figures 4 and 5 depict skeletal views of the structures observed herein, where the Cu(I)···Cu(II) separation is greatly affected by the steric requirements of the donor ligands on the copper(I) center. The steric encumberance of triphenylphosphine *vs* tricyclohexylphosphine is best seen in the space-filling models of the two derivatives (Figures 6 and 7). Notwithstanding the uncertainties in describing definitive structures for the two complexes, in particular complex **2**, on the basis of infrared spectroscopy in the $\nu(CO_2^-)$ region, what is apparent from their infrared spectra is that each complex has the same solution and solid-state structure.

In conclusion, the methodology presented here for preparing Cu(I)/Cu(II) derivatives should be readily augmented to include a wide variety of phosphorus donor or other donor ligands and dicarboxylate groups. The availability of mixed-valence copper derivatives exemplified by complex **1** may provide a rich chemistry associated with their reactions with dioxygen.[7,14] Indeed copper(I)/copper(II) dimers bridged by oxygen atoms play an important role in copper-catalyzed substrate oxygenation in biochemical processes.[14-17]

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Supplementary Material Available: ORTEP views of molecules **1** and **2** with all atoms labeled, including molecules of solvation, and tables providing complete bond lengths, bond angles, and anisotropic thermal parameters for complexes **1** and **2** (11 pages). Ordering information is given on any current masthead page.

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(14) See for example the excellent contribution in this area by: Mahroof-Tahir, M.; Karlin, K. D. *J. Am. Chem. Soc.* **1992**, *114*, 7599 and references therein.

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