

Structural characterization of bidentate carboxylate derivatives of copper(I) bistriphenylphosphine [☆]

Donald J. Darensbourg ^{*}, Matthew W. Holtcamp, Elisabeth M. Longridge,
Kevin K. Klausmeyer, Joseph H. Reibenspies

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

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Abstract

The complexes $(\text{Ph}_3\text{P})_2\text{Cu}(\text{carboxylate})$ (carboxylate = acetate (**1**), hippurate (**2**), vinyl acetate (**3**), fluorene (**4**)) have been prepared and their solid-state structures determined crystallographically. The copper(I) center in all four structures exhibits a distorted tetrahedral geometry, with varying degrees of asymmetric bidentate binding of the carboxylate ligand. For example, in complex **2** the hippurate ligand displays the greatest extent of asymmetry with the two Cu–O bond distances differing by 0.234(6) Å. The structures of all four derivatives were each shown to be the same both in the solid-state and in dichloromethane solution based on infrared spectroscopy. The magnitude of $\Delta(\nu_{\text{as}}(\text{CO}_2^-) - \nu_{\text{s}}(\text{CO}_2^-))$ in these copper(I) derivatives, determined to be quite similar to the corresponding ionic values, is used as constituting a diagnosis for asymmetric bidentate binding of the carboxylate ligand. Although all four complexes are structurally quite similar, only the fluorene derivative which affords a resonance-stabilized carbanion upon carbon dioxide extrusion undergoes the decarboxylation reaction. Crystal data for **1**: space group $P2_1/c$, $a = 18.085(5)$, $b = 10.977(2)$, $c = 17.979(5)$ Å, $\beta = 115.62(2)^\circ$, $Z = 4$, $R = 3.91\%$. Crystal data for **2**: space group $P\bar{1}$, $a = 9.96(2)$, $b = 14.68(3)$, $c = 14.96(3)$ Å, $\alpha = 115.46(14)$, $\beta = 97.54(16)$, $\gamma = 102.31(15)^\circ$, $Z = 2$, $R = 5.84\%$. Crystal data for **3**: space group $P\bar{1}$, $a = 12.755(3)$, $b = 13.125(2)$, $c = 12.572(2)$ Å, $\alpha = 118.85(1)$, $\beta = 105.85(1)$, $\gamma = 97.65(1)^\circ$, $Z = 2$, $R = 4.08\%$. Crystal data for **4**: space group $P\bar{1}$, $a = 11.554(1)$, $b = 15.217(2)$, $c = 15.285(2)$ Å, $\alpha = 63.71(1)$, $\beta = 79.08(1)$, $\gamma = 75.20(1)^\circ$, $Z = 2$, $R = 7.6\%$.

Keywords: Crystal structures; Copper complexes; Bidentate carboxylate complexes

1. Introduction

Dinuclear copper(I) carboxylate derivatives can be prepared from the reactions of copper(I) carboxylates, which are tetrameric or polymeric in the solid-state [1], with a variety of ligands while maintaining the dimetallic unit [2]. For example, the reaction of $[\text{Cu}(\text{PhCO}_2)]_4$ with isocyanides or carbon monoxide provides dimeric complexes with rather close Cu...Cu distances [3]. Similarly, copper(I) acetate reacts with 1,2-bis(diphenylphosphino)ethane to provide $\text{dpe}(\text{CuO}_2\text{CCH}_3)_2$ which exists in the solid-state as a polymeric chain of dimeric copper(I) units containing bridging dpe and acetate ligands, with the dimers being linked together via weaker Cu–O interactions [4]. Alternatively, it is possible to prepare monomeric copper(I) carboxylates with trialkyl- or triarylphosphine

ligands [2a,5]. An additional route to derivatives of this latter type specifically containing fluoro-substituted acetate and triphenylphosphine ligands, involves the electrochemical oxidation of copper metal in acetonitrile solution in the presence of PPh_3 and the appropriate acid [6]. The importance of phosphine derivatives of copper(I) cyanoacetate as a CO_2 carrier [7], and as a catalyst for the decarboxylation of cyanoacetic acid [8], have been firmly established. In addition phosphine derivatives of several copper(I) carboxylates are involved in the decarboxylation of select carboxylic and dicarboxylic acids [9,10]. A condition precedent to an understanding of the mechanistic aspects of the role of copper(I) in these processes is a detailed description of the solution and solid-state structures of these phosphine copper(I) carboxylate derivatives.

The present report concerns the reactivity of several copper(I) carboxylates with triphenylphosphine which afford monomeric bis-triphenylphosphine copper(I) carboxylate derivatives. These complexes have been isolated and structurally characterized in both the solid-state

[☆] This paper is dedicated to Professor György Bor on the occasion of his 70th birthday.

^{*} Corresponding author.

and in solution. Particular note has been taken of the asymmetry of the bidentate bonding of the carboxylates to the copper(I) center.

2. Experimental

2.1. Methods and materials

All manipulations were carried out under argon in a dry box or a double-manifold Schlenk vacuum line, using freshly distilled solvents. Triphenylphosphine, acetic acid, acetic anhydride, butyric acid, butyric anhydride, hippuric acid, fluorene and vinyl-acetic acid were purchased from Aldrich Chemical Company and used without further purification. IR spectra were recorded on a Mattson 6021 spectrometer with DTGS and MCT detectors.

2.2. $\text{Cu(I)O}_2\text{CCH}_3$ [1c]

Anhydrous acetonitrile (100 ml) was added to anhydrous copper(II) acetate (4.0 g) and copper turnings (10 g). Acetic acid–acetic anhydride (4:1, 25 ml) was then added and the reactants were stirred for 48 h under N_2 . After solvent volume reduction to ~50 ml the product was obtained by adding the solution to stirred, anhydrous, degassed diethyl ether (300 ml). The product was washed with diethyl ether and dried under vacuum (yield 85%).

2.3. Cu(I)n-butylate

This compound was prepared by an analogous method to that described above for the acetate derivative (yield 80%).

2.4. $\text{Cu(I)O}_2\text{Cfluorene}$

Cu(I) n-butylate (1.02 mmol) and 9-fluorenicarboxylic acid (1.16 mmol) were loaded into separate 50 ml flasks in the dry box. 25 ml of triethylorthoformate were used to dissolve the 9-fluorenicarboxylic acid, and this solution was transferred to the Cu(I) n-butylate. The solution turned a pale blue initially. After 30 min a fine white precipitate formed with a pale blue supernatant. The solid was isolated by filtration and washed with triethylorthoformate and diethyl ether, and was dried under vacuum (yield 62%). IR (CH_2Cl_2 , cm^{-1}): $\nu(\text{CO}_2)$ 1566(s), 1406(s).

2.5. $(\text{Ph}_3\text{P})_2\text{CuO}_2\text{CCH}_3$ (1)

$\text{Cu(I)O}_2\text{CCH}_3$ (2.47 mmol) was loaded into a 100 ml flask in the dry box. PPh_3 (9.93 mmol), dissolved in 30 ml toluene, was added to the flask and the

resulting clear solution was stirred. A fine white precipitate began to form after 1 h. After further stirring for 2 h, the solid was isolated and washed with toluene and diethyl ether. The white solid was dried under vacuum (yield 80%). IR (CH_2Cl_2 , cm^{-1}): $\nu(\text{CO}_2)$ 1558(s), 1415(ms).

2.6. $(\text{Ph}_3\text{P})_2\text{Cu(hippurate)}$ (2)

This synthesis was accomplished by the above described procedure using cuprous butyrate (0.400 g), hippuric acid (0.475 g) and 1.40 g of triphenylphosphine. 1.70 g (83.0%) of fine white powder were obtained. *Anal.* Calc. for $\text{C}_{45}\text{H}_{38}\text{CuO}_3\text{P}_2\text{N}\cdot\text{H}_2\text{O}$: C, 70.53; H, 5.00. Found: C, 68.88; H, 4.24%. IR (CH_2Cl_2 , cm^{-1}): $\nu(\text{CO}_2)$ 1581.2(s), 1409.8(s); $\nu(\text{CO})$ 1666.4(vs); $\nu(\text{triphenylphosphine})$ 1481.2(s), 1436.9(vs). IR (KBr, cm^{-1}): $\nu(\text{CO}_2)$ 1579.8(s), 1406.2(s).

Recrystallization from slow diffusion of diethyl ether into a dichloromethane solution produced single, colorless crystals suitable for X-ray structure determination.

2.7. $(\text{Ph}_3\text{P})_2\text{Cu(vinyl acetate)}$ (3)

Cuprous butyrate (0.40 g) was loaded into a 50 ml flask, and 20 ml of diethyl ether were added via cannula. Approximately 1 ml (excess) of degassed vinyl acetate was added with a syringe and the resulting slurry was stirred for 1 h. The white slurry was allowed to settle and the solvent was removed by cannulation, and washed twice with 20 ml of diethyl ether to remove excess carboxylic acids. A diethyl ether solution of triphenylphosphine (1.40 g in 20 ml) was added to the flask containing the cuprous vinyl acetate, and the slurry was stirred for 4 h during which there was an increase in white precipitate. The precipitate was filtered, washed with 20 ml of diethyl ether and dried by vacuum. After recrystallization from dichloromethane and diethyl ether, 1.48 g (81.6%) of product were obtained. *Anal.* Calc. for $\text{C}_{40}\text{H}_{35}\text{O}_2\text{P}_2\text{Cu}$: C, 71.37; H, 5.24. Found: C, 71.61; H, 5.10%. IR (CH_2Cl_2 , cm^{-1}): $\nu(\text{CO}_2)$ 1559.4(s), 1395(s) (1481.2(m), 1435.9(vs) characteristic of triphenylphosphine). IR (KBr cm^{-1}): $\nu(\text{CO}_2)$ 1564.4(s), 1394.6(s).

Recrystallization from slow diffusion of diethyl ether into a dichloromethane solution produced single, colorless crystals suitable for X-ray structure determination.

2.8. $(\text{PPh}_3)_2\text{CuO}_2\text{Cfluorene}\cdot\text{Et}_2\text{O}$ (4)

$\text{CuO}_2\text{Cfluorene}$ (1.31 mmol) was loaded into a 50 ml flask in the dry box. PPh_3 (2.63 mmol), dissolved in 30 ml benzene was added to the flask. The resulting clear solution was stirred for 2.5 h, after which a fine white precipitate began to form. The suspension was stirred overnight and the product was isolated (yield 80%). The white solid was washed with diethyl ether

and dried under vacuum. *Anal. Calc.* for $C_{54}H_{48}P_2O_3Cu$: C, 74.51; H, 5.56. *Found*: C, 74.25; H, 5.37%. IR (CH_2Cl_2 , cm^{-1}): $\nu(CO_2)$ 1568(s), 1377(s).

2.9. X-ray crystallographic study 1 and 2

Crystal data and details of data collection are given in Table 1. Colorless parallelepipeds for **1** and **2** were mounted on a glass fiber with epoxy cement, at room temperature and cooled to 193 K in a nitrogen cold stream (Siemens LT-2). Preliminary examination and data collection was performed on a Siemens R3m/V X-ray diffractometer (oriented graphite monochromator; Mo $K\alpha$ ($\lambda = 0.71073 \text{ \AA}$) radiation). 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 $4.0 \leq 2\theta \leq 50.0^\circ$ [ω (Wyckoff)] scans at 193 K. A 5.0% decay in the intensity of three control reflections collected every 97 reflections was observed for **2**. The intensities of the data set were corrected by employing a correction curve based on the intensity decay of the control reflections. Lorentz and polarization corrections were applied to 6189 reflections for **1** and 5731 for **2**. A semi-empirical absorption correction was applied (ellipsoid approximation; $\mu \times r = 0.04$, $T_{max} = 0.9690$, $T_{min} = 0.9353$ for **1**; $\mu \times r = 0.05$, $T_{max} = 0.9505$, $T_{min} = 0.7812$ for **2**). A total of 4366 unique reflections for **1** and 3784 for **2**, with $|I| \geq 2.0\sigma I$, was used in further calculations. Structure **1** was solved by Patterson synthesis and structure **2** was solved by direct methods [11]. Full-matrix least-squares anisotropic refinement for all non-hydrogen atoms yielded $R = 0.039$, $R_w = 0.044$ and $S = 1.87$ for **1** and $R = 0.058$, $R_w = 0.044$ and $S = 2.01$ for **2** at con-

vergence (largest $\Delta/\sigma = 0.002$ for **1** and 0.026 for **2**; largest positive peak in the Fourier difference map = $0.35 e \text{ \AA}^{-3}$ for **1** and $0.61 e \text{ \AA}^{-3}$ for **2**). Hydrogen atoms were placed in idealized positions with isotropic thermal parameters fixed at 0.08 \AA^2 . Neutral atom scattering factors and anomalous scattering correction terms were taken from the International Tables for X-ray Crystallography [12].

2.10. X-ray crystallographic study of 3 and 4

Crystal data and details of data collection are given in Table 1. A colorless plate was mounted in a capillary tube for **3**, and a colorless crystal for **4** was mounted on a glass fiber with epoxy cement at room temperature. Preliminary examination and data collection were performed on a Rigaku AFC5R X-ray diffractometer (oriented graphite monochromator; Cu $K\alpha$ ($\lambda = 1.54178 \text{ \AA}$) radiation). 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 $5.0 \leq 2\theta \leq 120.0^\circ$ at 296 K. Three control reflections, collected every 150 reflections, showed no significant trends. Lorentz and polarization corrections were applied to 5285 reflections for **3** and 7164 for **4**. A semi-empirical absorption correction was applied ($T_{max} = 0.9990$, $T_{min} = 0.883$ for **3** and $T_{max} = 0.9990$, $T_{min} = 0.9010$ for **4**). A total of 4140 unique reflections ($R_{int} = 0.06$) for **3** and 3183 unique reflections ($R_{int} = 0.02$) for **4** with $|I| \geq 2.0\sigma I$, was used in further calculations. Both structures were solved by direct methods [11]. Full-matrix least-squares anisotropic refinement for all non-hydrogen atoms yielded $R = 0.041$, $R_w = 0.051$ and $S = 1.91$ at convergence for **3** (largest

Table 1
Crystallographic data for complexes 1–4

	1	2	3	4
Empirical formula	$C_{38}H_{33}O_2P_2Cu$	$C_{45}H_{38}NO_3P_2Cu$	$C_{40}H_{35}O_2P_2Cu$	$C_{54}H_{48}O_3P_2Cu$
Formula weight	647.1	766.2	673.2	870.4
Space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
V (\AA^3)	3218.3(14)	1866(6)	1683.410(1)	2320.5(6)
Z	4	2	2	2
D_{calc} ($g \text{ cm}^{-3}$)	1.336	1.364	1.328	1.246
a (\AA)	18.085(5)	9.96(2)	12.755(3)	11.554(1)
b (\AA)	10.977(2)	14.68(3)	13.125(2)	15.217(2)
c (\AA)	17.979(5)	14.96(3)	12.572(2)	15.285(2)
α ($^\circ$)		115.46(14)	118.85(1)	63.71(1)
β ($^\circ$)	115.62(2)	97.54(16)	105.85(1)	79.08(1)
γ ($^\circ$)		102.31(15)	97.65(1)	75.20(1)
T (K)	193	193	298	298
μ (Mo $K\alpha$) (mm^{-1})	0.808	0.710	2.063 (Cu $K\alpha$)	1.624 (Cu $K\alpha$)
Wavelength (\AA)	0.71073	0.71073	1.54178	1.54178
R_F^a (%)	3.91	5.84	4.08	7.6
R_{wF}^a (%)	4.40	4.43	5.12	7.7

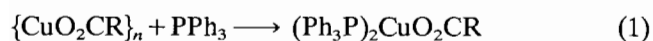
^a $R_F = \sum |F_o - F_c| / \sum F_o$; $R_{wF} = \{[\sum w(F_o - F_c)^2] / [\sum w F_o^2]\}^{1/2}$.

$\Delta/\sigma=0.040$ for **3** and 0.113 for **4**; largest positive peak in the Fourier difference map = $0.57 \text{ e } \text{\AA}^{-3}$ for **3** and $0.43 \text{ e } \text{\AA}^{-3}$ for **4**). Full-matrix least-squares isotropic refinement for O3, C51, C52 and C53, and anisotropic refinement for all remaining non-hydrogen atoms yielded $R=0.076$, $R_w=0.077$ and $S=2.46$ at convergence for **4**. Hydrogen atoms were placed in idealized positions with isotropic thermal parameters fixed at 0.08 \AA^2 . Neutral atom scattering factors and anomalous scattering correction terms were taken from the International Tables for X-ray Crystallography [12]. The atomic distances were restrained for the following atoms for **4**. The distance between the atoms in the pairs (C51, C52; C53, C54) was restrained to 1.54 (0.01). The distance between the atoms in the pairs (C52, O3; C53, O3) was restrained to 1.43 (0.01). The distance between the atoms in the pairs (C51, O3; C52, C53; C54, O3) was restrained to 2.90 (0.01). The restrained model was allowed to refine to convergence.

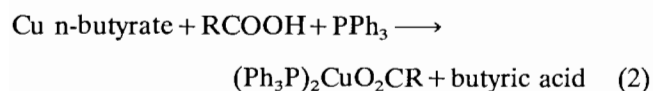
3. Results

3.1. Synthesis and characterization

The complexes (**1–4**) were prepared by either the reaction of the corresponding copper(I) carboxylate with PPh_3 (Eq. (1)) or by the reaction of Cu(I) *n*-butyrate with the appropriate carboxylic acid in the presence of PPh_3 (Eq. (2)). The complexes were shown to possess bidentate carboxylate functionality both in solution and in the solid-state via IR spectroscopy in the $\nu(\text{CO}_2^-)$ region, coupled with X-ray crystallography (vice infra). Table 2 lists the $\nu(\text{CO}_2^-)$ bands in both dichloromethane and KBr. As indicated in Table 2 the separation of the asymmetric and symmetric $\nu(\text{CO}_2^-)$



$\text{RCO}_2^- = \text{acetate (1), fluoreneate (4)}$



$\text{RCO}_2^- = \text{hippurate (2), vinyl acetate (3)}$

vibrational modes of the carboxylate ligands in the $(\text{Ph}_3\text{P})_2\text{CuO}_2\text{CR}$ derivatives support a bidentate formulation in both media. That is, the difference ($\Delta = \nu_a(\text{CO}_2^-) - \nu_s(\text{CO}_2^-)$) in each instance is smaller than the Δ value exhibited for the corresponding ionic salt. For example, in complex **2**, Δ is observed to be 171 and 174 cm^{-1} in CH_2Cl_2 solution and KBr, respectively, as compared to the ionic value of 205 cm^{-1} . Nevertheless, these Δ values are still large, i.e. generally the Δ values determined for metal complexes containing symmetrically chelating carboxylates are significantly less than the ionic values (about a factor of 0.5) [13].

3.2. Structures

The asymmetric bidentate binding of the acetate ligand in $(\text{Ph}_3\text{P})_2\text{Cu}(\text{O}_2\text{CCH}_3)$ (**1**) has been previously reported based on an X-ray structure determination at ambient temperature [5a]. However, in a low-temperature ($-120 \text{ }^\circ\text{C}$) structural determination of **1** the inequivalency of the two Cu–O bonds was found to be much less than that earlier determined, 0.034(4) versus 0.095(12) \AA [14]. For comparative purposes with the other structures contained herein we have further examined the solid-state structure of **1** at 193 K. Colorless crystals of **1** were obtained after several days by slow diffusion of diethyl ether into a CH_2Cl_2 solution of the complex at room temperature. The final atomic positional and equivalent isotropic displacement parameters are listed in Table 3. Table 4 contains a comparison of the pertinent structural parameters determined in this study and the two previous determination, with the Cu–O distances boxed. It is clear from Table 4 that these structural parameters are quite similar in all three determinations with the greatest disparity being in the Cu–O bond lengths. Fig. 1 depicts the structure of complex **1** in which Cu(I) exhibits a distorted tetrahedral geometry.

In a manner analogous to that employed for complex **1**, crystals of copper(I) hippurate (**2**), vinyl acetate (**3**), and fluoreneate (**4**) were obtained from slow diffusion of diethyl ether into a dichloromethane solution of the corresponding carboxylate complex at ambient tem-

Table 2
Carboxyl stretching frequencies in the IR spectra of copper(I) carboxylate complexes^a

Complex	$\nu_{\text{asym}} \text{ (cm}^{-1}\text{)}$	$\nu_{\text{sym}} \text{ (cm}^{-1}\text{)}$	Δ^b	Δ_{ionic}^c
$(\text{Ph}_3\text{P})_2\text{Cu}(\text{acetate})$ (1)	1558	1415	143	164
$(\text{Ph}_3\text{P})_2\text{Cu}(\text{hippurate})$ (2)	1581(1580)	1410(1406)	171(174)	205
$(\text{Ph}_3\text{P})_2\text{Cu}(\text{vinyl acetate})$ (3)	1599(1564)	1395(1395)	164(169)	172
$(\text{Ph}_3\text{P})_2\text{Cu}(\text{fluoreneate})$ (4)	1568(1575)	1378(1373)	191(202)	210

^a Solution spectra were measured in dichloromethane. Values in parentheses were obtained in the solid state as KBr pellets.

^b $\Delta = \nu_{\text{asym}} - \nu_{\text{sym}}$.

^c Values were determined from the sodium salts in KBr pellets.

Table 3

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for complex **1**

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}^{\text{a,b}}$
Cu(1)	7351(1)	562(1)	9007(1)	24(1)
P(1)	8144(1)	2122(1)	9676(1)	21(1)
P(2)	6875(1)	-107(1)	7710(1)	20(1)
O(1)	7437(2)	-1101(2)	9750(2)	33(1)
O(2)	6481(2)	289(2)	9524(1)	30(1)
C(1)	6823(2)	-708(3)	9831(2)	30(2)
C(2)	6477(3)	-1448(4)	10313(3)	64(3)
C(3)	7069(2)	3968(4)	9616(2)	34(2)
C(4)	6644(3)	5052(4)	9344(2)	45(2)
C(5)	6786(3)	5784(4)	8798(3)	51(2)
C(6)	7355(3)	5440(4)	8520(3)	47(2)
C(7)	7794(2)	4355(3)	8797(2)	35(2)
C(8)	7660(2)	3615(3)	9358(2)	24(1)
C(9)	9674(2)	3196(3)	9946(2)	34(2)
C(10)	10451(2)	3147(4)	9958(2)	43(2)
C(11)	10685(2)	2137(4)	9655(2)	43(2)
C(12)	10148(2)	1187(4)	9317(2)	40(2)
C(13)	9364(2)	1234(3)	9293(2)	30(2)
C(14)	9129(2)	2229(3)	9618(2)	24(1)
C(15)	8709(2)	3159(3)	11279(2)	28(2)
C(16)	8996(2)	3073(4)	12132(2)	33(2)
C(17)	9063(2)	1949(4)	12502(2)	35(2)
C(18)	8835(2)	901(4)	12029(2)	33(2)
C(19)	8535(2)	977(3)	11171(2)	27(1)
C(20)	8482(2)	2109(3)	10798(2)	21(1)
C(21)	6919(2)	2127(3)	7020(2)	29(2)
C(22)	6673(2)	3013(3)	6405(2)	37(2)
C(23)	5970(2)	2843(4)	5680(2)	39(2)
C(24)	5514(2)	1790(4)	5572(2)	40(2)
C(25)	5760(2)	902(3)	6176(2)	31(2)
C(26)	6465(2)	1054(3)	6903(2)	21(1)
C(27)	7620(2)	-805(3)	6676(2)	30(2)
C(28)	8198(2)	-1416(4)	6502(3)	38(2)
C(29)	8793(2)	-2105(4)	7107(3)	42(2)
C(30)	8815(3)	-2177(4)	7884(3)	49(2)
C(31)	8239(2)	-1567(4)	8054(2)	37(2)
C(32)	7629(2)	-877(3)	7451(2)	23(1)
C(33)	5940(2)	-2180(3)	6889(2)	31(2)
C(34)	5252(2)	-2926(3)	6645(2)	36(2)
C(35)	4661(2)	-2696(3)	6919(2)	35(2)
C(36)	4765(2)	-1744(3)	7458(2)	38(2)
C(37)	5450(2)	-1006(3)	7709(2)	30(2)
C(38)	6037(2)	-1203(3)	7415(2)	21(1)

^a Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor.

^b E.s.d.s are given in parentheses.

perature. The final atomic positional and equivalent isotropic displacement parameters for complex **2** are listed in Table 5, with selected interatomic distances and angles provided in Table 6. Fig. 2 illustrates the perspective drawing of complex **2** with the atomic numbering scheme. Copper(I) is bound via the carboxylate functionality of the hippurate anion and the two PPh_3 ligands in **2** in a distorted tetrahedral arrangement. The Cu–O bond distances and Cu–O–C bond angles differ significantly, with Cu1–O1 and Cu1–O2 being 2.136(5) and 2.370(6) Å, respectively,

Table 4

Comparative bond lengths (Å) and bond angles ($^\circ$) in **1**

	This study ^a	Ref. [14] ^b	Ref. [5a] ^c
Cu(1)–P(1)	2.224(1)	2.223(1)	2.233(2)
Cu(1)–P(2)	2.231(1)	2.227(1)	2.240(3)
Cu(1)–O(1)	2.228(3)	2.205(2)	2.257(7)
Cu(1)–O(2)	2.166(3)	2.171(2)	2.162(5)
O(1)–C(1)	1.258(5)	1.248(4)	1.247(9)
O(2)–C(1)	1.260(4)	1.261(4)	1.261(11)
C(1)–C(2)	1.506(7)	1.505(6)	1.519(14)
P(1)–Cu(1)–P(2)	133.3(1)	133.19(4)	133.4(1)
O(1)–Cu(1)–O(2)	60.3(1)	60.28(8)	59.4(2)
Cu(1)–O(1)–C(1)	87.3(2)	88.1(2)	87.4(5)
Cu(1)–O(2)–C(1)	90.0(3)	89.3(2)	91.3(4)

^a Determination carried out at 193 K.

^b Determination carried out at 153 K.

^c Determination carried out at ambient temperature.

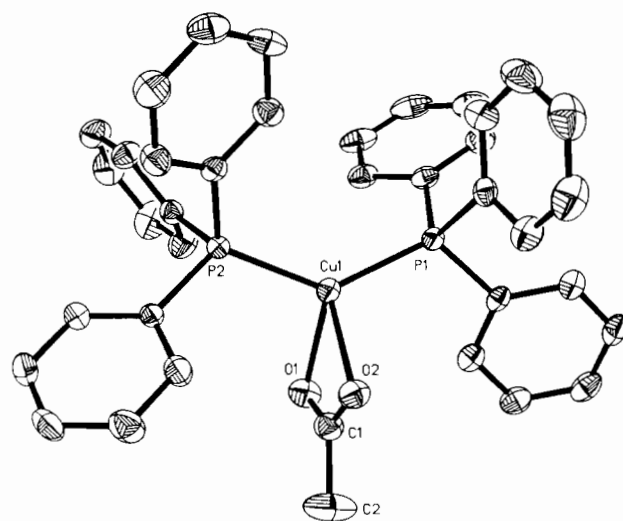


Fig. 1. An ORTEP drawing of **1** showing the atom numbering scheme. Thermal ellipsoids are drawn at the 50% probability level.

whereas, the Cu–O–C angles were found to be 93.5(3) and 83.6(3) $^\circ$. The P–Cu–P bond angle is slightly less obtuse than in complex **1** at 130.9(1) $^\circ$. In general P–Cu–P angles are largest for planar chelating anions, and decrease as the non-planarity and steric crowding of the anion increases [15]. The Cu–P bond distances are comparable to those in **1** at 2.267(5) and 2.236(5) Å, and are quite typical for what is normally found in copper(I) phosphine derivatives [5a,15,16].

The final atomic positional and equivalent isotropic displacement parameters for complex **3** are given in Table 7. A perspective drawing of complex **3** with the atomic numbering scheme is shown in Fig. 3, and selected bond lengths and angles are given in Table 8. The coordination about the copper(I) center in **3** is similar to that noted in complexes **1** and **2** except for slight differences. That is, the Cu–O bond distances and

Table 5

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for complex 2

	x	y	z	$U_{\text{eq}}^{\text{a,b}}$
Cu(1)	5059(1)	2123(1)	7774(1)	29(1)
P(1)	6249(2)	2512(1)	9355(1)	27(1)
P(2)	5734(1)	2629(1)	6648(1)	24(1)
O(1)	2815(3)	1462(3)	7458(3)	35(2)
O(2)	3955(4)	269(3)	6886(3)	34(2)
O(3)	322(4)	-1835(3)	7464(3)	54(3)
N(1)	1792(5)	-1334(3)	6648(3)	38(3)
C(1)	2869(6)	517(5)	7086(4)	25(3)
C(2)	1554(6)	-323(4)	6941(4)	36(3)
C(3)	1213(6)	-2024(5)	6959(4)	31(3)
C(4)	1659(6)	-2991(5)	6696(4)	34(3)
C(5)	2787(7)	-3171(5)	6277(5)	59(4)
C(6)	3205(9)	-4060(6)	6114(6)	77(5)
C(7)	2483(10)	-4802(6)	6340(7)	89(6)
C(8)	1411(9)	-4598(6)	6827(7)	90(6)
C(9)	1019(7)	-3713(5)	6986(6)	67(5)
C(10)	7816(5)	2049(4)	9372(4)	25(3)
C(11)	8436(6)	1827(4)	8559(4)	40(3)
C(12)	9641(7)	1501(5)	8551(5)	49(4)
C(13)	10208(6)	1354(5)	9370(5)	44(4)
C(14)	9595(6)	1560(4)	10181(4)	36(3)
C(15)	8423(6)	1917(4)	10197(4)	31(3)
C(16)	6016(6)	4498(5)	10643(4)	35(3)
C(17)	6945(5)	3926(4)	10266(4)	27(3)
C(18)	6495(7)	5591(5)	11255(4)	43(4)
C(19)	7913(7)	6143(5)	11502(4)	42(3)
C(20)	8857(6)	5579(5)	11148(4)	40(3)
C(21)	8386(6)	4484(5)	10539(4)	36(3)
C(22)	5190(5)	1909(4)	9977(4)	28(3)
C(23)	5203(6)	2409(5)	11017(4)	40(3)
C(24)	4338(6)	1877(5)	11402(5)	45(4)
C(25)	3469(6)	846(5)	10770(5)	42(4)
C(26)	3472(6)	343(5)	9746(5)	40(3)
C(27)	4329(5)	871(4)	9357(4)	31(3)
C(28)	6390(5)	4046(4)	7098(4)	23(3)
C(29)	6347(6)	4499(5)	6460(5)	40(3)
C(30)	6936(6)	5582(5)	6824(5)	55(4)
C(31)	7564(6)	6225(5)	7860(6)	54(4)
C(32)	7634(6)	5791(5)	8519(5)	46(4)
C(33)	7038(6)	4708(4)	8151(4)	36(3)
C(34)	7210(5)	2140(4)	6257(4)	24(3)
C(35)	8495(5)	2805(4)	6309(4)	32(3)
C(36)	9610(6)	2404(5)	6084(4)	40(3)
C(37)	9475(6)	1349(5)	5795(4)	37(3)
C(38)	8206(6)	678(5)	5716(4)	35(3)
C(39)	7077(6)	1084(4)	5961(4)	30(3)
C(40)	4468(5)	2157(4)	5417(4)	25(3)
C(41)	4670(5)	1514(4)	4477(4)	25(3)
C(42)	3696(6)	1216(4)	3561(4)	31(3)
C(43)	2510(6)	1564(4)	3599(5)	37(3)
C(44)	2270(6)	2191(4)	4533(4)	36(3)
C(45)	3225(5)	2469(4)	5446(4)	30(3)

^a Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

^b E.s.d.s are given in parentheses.

Cu–O–C bond angles are more equivalent at 2.194(3) Å (Cu1–O2) and 2.229(3) Å (Cu1–O1) and 88.5(2)° (Cu1–O1–C1) and 90.7(2)° (Cu1–O2–C1), respectively.

Table 6

Selected bond lengths (Å) and bond angles (°) for complex 2^a

Cu(1)–P(1)	2.267(5)	Cu(1)–P(2)	2.236(5)
Cu(1)–O(1)	2.136(5)	Cu(1)–O(2)	2.370(6)
P(1)–C(10)	1.830(7)	P(1)–C(17)	1.831(6)
P(1)–C(22)	1.824(8)	P(2)–C(28)	1.820(7)
P(2)–C(34)	1.826(7)	P(2)–C(40)	1.839(7)
O(1)–C(1)	1.271(8)	O(2)–C(1)	1.245(8)
P(1)–Cu(1)–P(2)	130.9(1)	P(1)–Cu(1)–O(1)	113.6(2)
P(2)–Cu(1)–O(1)	113.9(2)	P(1)–Cu(1)–O(2)	106.6(2)
P(2)–Cu(1)–O(2)	107.9(2)	Cu(1)–P(1)–C(10)	114.2(2)
Cu(1)–P(1)–C(17)	114.9(3)	C(10)–P(1)–C(17)	103.6(3)
Cu(1)–P(1)–C(22)	113.5(2)	C(10)–P(1)–C(22)	103.6(3)
C(17)–P(1)–C(22)	105.8(3)	Cu(1)–P(2)–C(28)	116.6(2)
Cu(1)–P(2)–C(34)	109.4(3)	C(28)–P(2)–C(34)	104.4(3)
Cu(1)–P(2)–C(40)	119.2(2)	C(28)–P(2)–C(40)	102.6(3)
C(34)–P(2)–C(40)	102.7(3)	Cu(1)–O(1)–C(1)	93.5(3)
Cu(1)–O(2)–C(1)	83.6(3)	C(2)–N(1)–C(3)	124.4(5)
O(1)–C(1)–O(2)	123.3(5)	O(1)–C(1)–C(2)	117.0(5)
O(2)–C(1)–C(2)	119.6(6)		

^a E.s.d.s are given in parentheses.

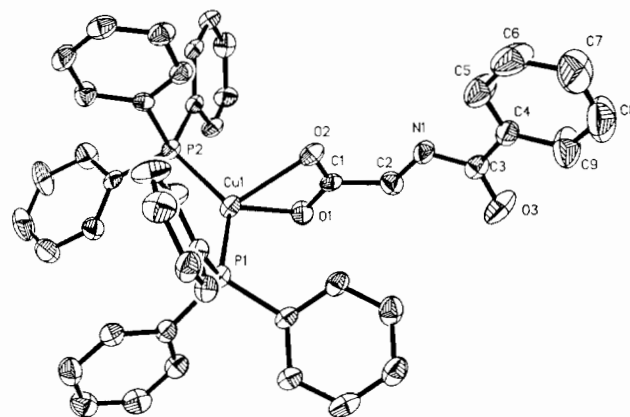


Fig. 2. An ORTEP drawing of 2 showing the atom numbering scheme. Thermal ellipsoids are drawn at the 50% probability level.

The Cu–P bond distances and P–Cu–P bond angle were determined to be 2.241(1) and 2.254(1) Å, and 127.3(1)°.

Positional and thermal parameters of the atoms in the structure of complex 4 are given in Table 9, and selected bond distances and angles are listed in Table 10. Fig. 4 shows the coordination environment of the copper atom and the numbering scheme used in the tables. The copper atom has a distorted tetrahedral coordination with Cu1–O1 and Cu1–O2 distances of 2.29(1) and 2.156(6) Å, and an average Cu–P bond distance of 2.237[3] Å. The P–Cu–P angle is 128.6(1)°, whereas the Cu1–O2–C1 and Cu1–O1–C1 bond angles are 91.5(6) and 85.8(9)°, respectively.

4. Discussion

The solid-state structures of the four copper(I) carboxylates reported upon herein were shown to possess

Table 7

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for complex **3**

	x	y	z	$U_{\text{eq}}^{\text{a,b}}$
Cu(1)	2288(1)	2778(1)	1680(1)	44(1)
P(1)	2535(1)	1218(1)	1893(1)	40(1)
P(2)	3276(1)	3692(1)	967(1)	38(1)
O(1)	1931(3)	4211(3)	3311(3)	76(2)
O(2)	606(2)	3072(2)	1358(3)	70(2)
C(1)	947(3)	3904(3)	2509(4)	56(2)
C(2)	138(4)	4612(4)	2984(5)	92(3)
C(3)	593(6)	5870(6)	3716(9)	162(6)
C(4)	489(9)	6747(8)	3763(11)	220(10)
C(5)	3532(3)	-458(3)	428(4)	53(2)
C(6)	3551(4)	-1368(3)	-725(4)	68(3)
C(7)	2615(4)	-1902(3)	-1885(4)	70(2)
C(8)	1666(4)	-1530(3)	-1898(4)	66(2)
C(9)	1645(3)	-611(3)	-756(3)	56(2)
C(10)	2575(3)	-66(3)	431(3)	42(2)
C(11)	4851(3)	2412(3)	3438(3)	51(2)
C(12)	5891(3)	2749(3)	4420(4)	61(2)
C(13)	5968(3)	2260(4)	5175(4)	66(2)
C(14)	5017(4)	1433(4)	4948(4)	75(3)
C(15)	3979(3)	1089(3)	3956(4)	62(2)
C(16)	3882(3)	1589(3)	3195(3)	42(2)
C(17)	825(3)	-680(3)	1537(3)	49(2)
C(18)	63(3)	-1104(4)	1941(4)	65(2)
C(19)	-66(3)	-344(4)	3068(4)	72(3)
C(20)	547(3)	879(4)	3798(4)	71(3)
C(21)	1285(3)	1320(3)	3391(3)	59(2)
C(22)	1464(3)	546(3)	2280(3)	42(2)
C(23)	3330(3)	1559(3)	-1072(3)	52(2)
C(24)	3296(3)	782(3)	-2307(4)	63(2)
C(25)	3115(3)	1115(4)	-3214(4)	68(2)
C(26)	2986(3)	2235(4)	-2862(4)	69(2)
C(27)	3028(3)	3035(3)	-1617(3)	55(2)
C(28)	3204(3)	2706(3)	-698(3)	41(2)
C(29)	1844(3)	5044(4)	703(4)	70(3)
C(30)	1591(4)	6030(5)	698(6)	95(4)
C(31)	2417(4)	7005(4)	1014(5)	77(3)
C(32)	3531(3)	7018(3)	1345(4)	59(2)
C(33)	3802(3)	6022(3)	1342(3)	50(2)
C(34)	2965(3)	5030(3)	1009(3)	42(2)
C(35)	5650(3)	4116(3)	1478(3)	46(2)
C(36)	6797(3)	4588(3)	2322(4)	56(2)
C(37)	7097(3)	5245(3)	3650(4)	59(2)
C(38)	6271(3)	5462(3)	4159(3)	60(2)
C(39)	5132(3)	5002(3)	3337(3)	51(2)
C(40)	4805(3)	4309(3)	1979(3)	37(2)

^a Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

^b E.s.d.s are given in parentheses.

distorted tetrahedral geometries, with varying degrees of asymmetric bidentate binding of the carboxylate group. Furthermore, the complexes were demonstrated to have similar structures both in solution and in the solid-state as indicated by IR spectroscopy. That is, in all instances the bidentate ligation of the carboxylates produced a characteristic IR spectrum with Δ , both in CH_2Cl_2 and KBr, smaller than the corresponding values in the free ion (see Table 2). Table 11 summarizes the

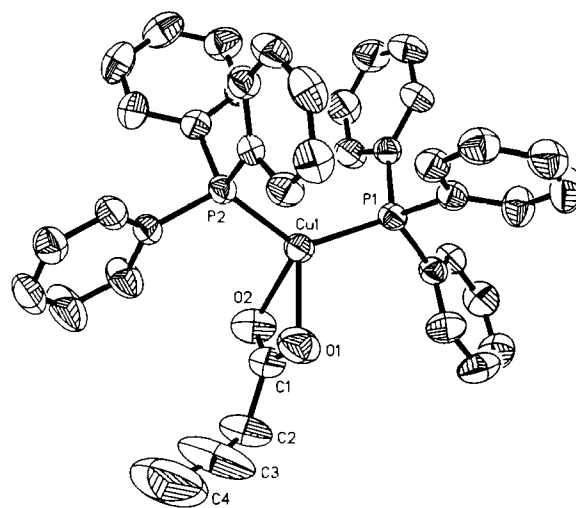


Fig. 3. An ORTEP drawing of **3** showing the atom numbering scheme. Thermal ellipsoids are drawn at the 50% probability level.

Table 8

Selected bond lengths (\AA) and bond angles ($^\circ$) for complex **3**^a

Cu(1)–P(1)	2.241(1)	Cu(1)–P(2)	2.254(1)
Cu(1)–O(1)	2.229(3)	Cu(1)–O(2)	2.194(3)
Cu(1)–C(1)	2.522(5)	P(1)–C(10)	1.818(3)
P(1)–C(16)	1.827(3)	P(1)–C(22)	1.827(4)
P(2)–C(28)	1.820(3)	P(2)–C(34)	1.829(4)
P(2)–C(40)	1.819(3)	O(1)–C(1)	1.239(5)
O(2)–C(1)	1.218(4)	C(1)–C(2)	1.530(7)
C(2)–C(3)	1.377(8)	C(3)–C(4)	1.15(1)
P(1)–Cu(1)–P(2)	127.3(1)	P(1)–Cu(1)–O(1)	113.7(1)
P(2)–Cu(1)–O(1)	108.5(1)	P(1)–Cu(1)–O(2)	119.7(1)
P(2)–Cu(1)–O(2)	108.7(1)	P(1)–Cu(1)–C(1)	121.3(1)
P(2)–Cu(1)–C(1)	111.0(1)	Cu(1)–P(1)–C(10)	113.4(2)
Cu(1)–P(1)–C(16)	114.8(1)	C(10)–P(1)–C(16)	103.2(2)
Cu(1)–P(1)–C(22)	116.5(1)	C(10)–P(1)–C(22)	104.9(2)
C(16)–P(1)–C(22)	102.5(2)	Cu(1)–P(2)–C(28)	115.8(1)
Cu(1)–P(2)–C(34)	118.1(1)	C(28)–P(2)–C(34)	104.2(2)
Cu(1)–P(2)–C(40)	111.3(1)	C(28)–P(2)–C(40)	103.7(1)
C(34)–P(2)–C(40)	101.9(1)	Cu(1)–O(1)–C(1)	88.5(2)
Cu(1)–O(2)–C(1)	90.7(2)	Cu(1)–C(1)–O(1)	62.1(2)
Cu(1)–C(1)–O(2)	60.4(2)	O(1)–C(1)–O(2)	122.5(4)
Cu(1)–C(1)–C(2)	177.8(4)	O(1)–C(1)–C(2)	118.6(3)
O(2)–C(1)–C(2)	118.9(4)	C(1)–C(2)–C(3)	115.8(5)
C(2)–C(3)–C(4)	144.1(9)		

^a E.s.d.s are given in parentheses.

structural results for the four bis-triphenylphosphine copper(I) carboxylates described in this report, where the asymmetry of the carboxylate ligand is best illustrated by the parameters Δd , $\Delta\alpha$ and plane (md). These structural parameters are defined in the schematic view of the copper carboxylate depicted in Fig. 5.

As portrayed in Fig. 5 and quantified in Table 11 the three carboxylate atoms and the copper center define a least-squares plane with a mean deviation generally less than 0.006 \AA . The only exception is complex **2**, where the greatest amount of asymmetry was noted, with the mean deviation in the least-squares

Table 9

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for complex 4

	x	y	z	$U_{\text{eq}}^{\text{a,b}}$
Cu(1)	155(1)	4333(1)	2785(1)	59(1)
P(1)	-1784(2)	5070(2)	2838(2)	56(1)
P(2)	1763(2)	5046(2)	2112(2)	56(1)
O(1)	427(6)	2868(6)	2617(7)	83(5)
O(2)	549(6)	2909(5)	4015(6)	66(4)
O(3)	7206(27)	10301(28)	-119(23)	712(28)
C(1)	592(9)	2448(8)	3499(12)	68(7)
C(2)	824(9)	1292(7)	3998(9)	68(6)
C(3)	2062(11)	882(8)	3657(10)	69(7)
C(4)	2518(13)	984(9)	2732(11)	99(9)
C(5)	3676(18)	533(11)	2550(15)	158(14)
C(6)	4357(17)	-42(12)	3314(18)	165(17)
C(7)	3939(14)	-139(10)	4240(14)	119(11)
C(8)	2778(11)	313(8)	-4406(12)	77(8)
C(9)	2055(14)	307(9)	5297(12)	84(8)
C(10)	2343(18)	-179(11)	6249(17)	134(13)
C(11)	1459(26)	-72(13)	6956(16)	166(18)
C(12)	349(23)	479(12)	6754(16)	162(16)
C(13)	60(15)	947(9)	5780(14)	111(10)
C(14)	914(12)	857(8)	5066(11)	78(8)
C(15)	-2629(10)	6939(9)	2940(9)	88(8)
C(16)	-2699(13)	7550(10)	3420(15)	118(11)
C(17)	-2262(13)	7202(14)	4293(13)	100(12)
C(18)	-1760(11)	6225(13)	4729(10)	87(8)
C(19)	-1700(10)	5620(9)	4264(12)	77(8)
C(20)	-2104(8)	5975(8)	3352(9)	53(6)
C(21)	-3502(10)	5817(9)	1451(9)	79(7)
C(22)	-3898(11)	6380(10)	522(11)	102(9)
C(23)	-3167(12)	6905(9)	-211(10)	89(8)
C(24)	-2080(12)	6903(9)	-54(10)	98(8)
C(25)	-1665(9)	6349(8)	858(10)	82(7)
C(26)	-2392(8)	5808(7)	1637(8)	59(6)
C(27)	-3917(8)	4539(8)	3996(8)	71(6)
C(28)	-4670(9)	3872(9)	4539(8)	81(7)
C(29)	-4324(10)	2905(9)	4671(9)	86(8)
C(30)	-3249(10)	2603(8)	4235(9)	81(7)
C(31)	-2494(9)	3254(8)	3691(8)	74(7)
C(32)	-2826(8)	4241(7)	3558(7)	52(5)
C(33)	1361(10)	5582(9)	204(12)	81(9)
C(34)	1213(10)	6249(12)	-781(11)	83(8)
C(35)	1357(11)	7178(11)	-1096(10)	86(8)
C(36)	1689(13)	7495(10)	-505(13)	113(10)
C(37)	1834(11)	6852(9)	464(10)	86(8)
C(38)	1663(8)	5919(8)	823(8)	56(6)
C(39)	1028(9)	6365(8)	3012(9)	81(8)
C(40)	1156(12)	6953(9)	3424(10)	95(9)
C(41)	2254(13)	6957(10)	3584(10)	99(9)
C(42)	3212(11)	6417(11)	3280(11)	120(11)
C(43)	3122(10)	5817(9)	2842(9)	91(8)
C(44)	2011(9)	5811(7)	2691(7)	55(5)
C(45)	4156(8)	4469(8)	1408(7)	63(6)
C(46)	5230(9)	3799(9)	1459(9)	78(7)
C(47)	5350(9)	2868(9)	2177(9)	79(7)
C(48)	4411(9)	2601(8)	2877(9)	80(6)
C(49)	3349(8)	3252(7)	2839(8)	64(6)
C(50)	3193(8)	4207(7)	2110(8)	56(6)
C(51)	9286(20)	8921(20)	841(20)	673(38)
C(52)	8282(25)	9549(22)	167(21)	575(31)
C(53)	6205(24)	11052(20)	-611(19)	513(26)
C(54)	5387(21)	11494(19)	-1453(17)	587(32)

^a Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

^b E.s.d.s are given in parentheses.

Table 10

Selected bond lengths (\AA) and bond angles ($^\circ$) for complex 4^a

Cu(1)–P(1)	2.238(3)	Cu(1)–P(2)	2.236(3)
Cu(1)–O(1)	2.29(1)	Cu(1)–O(2)	2.156(6)
Cu(1)–C(1)	2.52(1)	P(1)–C(20)	1.80(2)
P(1)–C(26)	1.84(1)	P(1)–C(32)	1.82(1)
P(2)–C(38)	1.83(1)	P(2)–C(44)	1.85(1)
P(2)–C(50)	1.812(9)	O(1)–C(1)	1.24(2)
O(2)–C(1)	1.25(2)	O(3)–C(52)	1.44(4)
O(3)–C(53)	1.45(4)	C(1)–C(2)	1.55(1)
P(1)–Cu(1)–P(2)	128.6(1)	P(1)–Cu(1)–O(1)	112.4(2)
P(2)–Cu(1)–O(1)	110.6(2)	P(1)–Cu(1)–O(2)	112.7(2)
P(2)–Cu(1)–O(2)	112.9(2)	P(1)–Cu(1)–C(1)	116.1(2)
P(2)–Cu(1)–C(1)	115.2(2)	Cu(1)–P(1)–C(20)	114.1(4)
Cu(1)–P(1)–C(26)	115.0(3)	C(20)–P(1)–C(26)	102.1(5)
Cu(1)–P(1)–C(32)	115.7(3)	C(20)–P(1)–C(32)	103.4(5)
C(26)–P(1)–C(32)	105.0(5)	Cu(1)–P(2)–C(38)	113.5(4)
Cu(1)–P(2)–C(44)	113.9(3)	C(38)–P(2)–C(44)	103.5(5)
Cu(1)–P(2)–C(50)	116.3(3)	C(38)–P(2)–C(50)	103.7(4)
C(44)–P(2)–C(50)	104.6(5)	Cu(1)–O(1)–C(1)	85.8(9)
Cu(1)–O(2)–C(1)	91.5(6)	C(52)–O(3)–C(53)	168(3)
Cu(1)–C(1)–O(1)	64.9(6)	O(1)–C(1)–O(2)	124(1)
Cu(1)–C(1)–C(2)	177(1)	O(1)–C(1)–C(2)	118(1)
O(2)–C(1)–C(2)	118(1)		

^a E.s.d.s are given in parentheses.

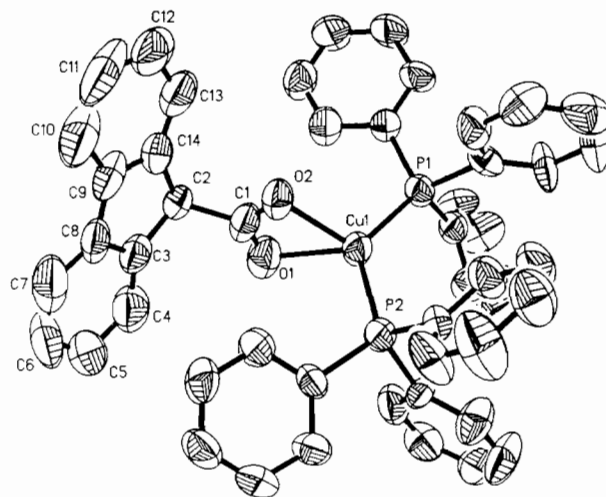


Fig. 4. An ORTEP drawing of 4 showing the atom numbering scheme. Thermal ellipsoids are drawn at the 50% probability level.

plane being 0.0396 \AA . It has previously been noted based on IR spectral measurements that carboxylic acids with low $\text{p}K_{\text{a}}$ values generally gave monodentate structures, while acids with high $\text{p}K_{\text{a}}$ values provided monodentate or bidentate structures [2b]. Therefore, it might be anticipated that the more basic carboxylates would favor more symmetric bidentate coordination. Indeed in a series of closely related copper(I) carboxylates, namely acetate and its fluoro-substituted derivatives, the asymmetry in carboxylate coordination was observed to decrease systematically with increasing base strength [6]. The carboxylates investigated herein

Table 11
Summary of structural results for copper(I) carboxylates^a

	Complex			
	1	2	3	4
d_1 (Å)	2.166(3)	2.136(5)	2.194(3)	2.156(6)
d_2 (Å)	2.228(3)	2.370(6)	2.229(3)	2.29(1)
Δd (Å)	0.062(3)	0.234(6)	0.035(3)	0.134(8)
α_1 (°)	90.0(3)	93.5(3)	90.7(2)	90.0(3)
α_2 (°)	87.3(2)	83.6(3)	88.5(2)	87.3(2)
$\Delta\alpha$ (°)	2.7(3)	9.9(3)	2.2(2)	2.7(3)
Plane (md ^b) (Å)	0.00321	0.0396	0.0062	0.0001
$\Delta\Delta^c$ (cm ⁻¹)	-21	-31	-3	-8

^a All complexes are bidentate carboxylate derivatives of the general formula $(\text{Ph}_3\text{P})_2\text{CuO}_2\text{CR}$.

^b Mean deviation from the least-squares plane defined by the Cu atom and the $-\text{CO}_2$ atoms of the carboxylate ligand.

^c This value represents the difference between Δ in the complex and Δ in the ionic salt.

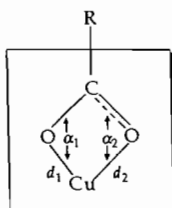


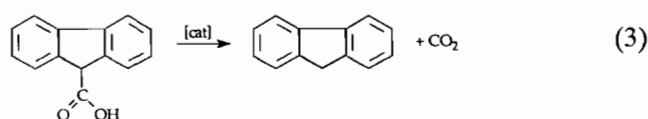
Fig. 5. Schematic view of the carboxylate ligand asymmetrically bonded to copper(I). The least-squares plane is indicated by the box.

do not vary greatly in their basicities, having $\text{p}K_a$ ranging from 3.8 to 4.8. Hence, we did not observe a correlation between the extent of asymmetric carboxylate binding and the nature of the carboxylate. However, for the related complexes, $(\text{Cy}_3\text{P})_2\text{Cu}(\text{cyanoacetate})$ and $(\text{Cy}_3\text{P})_2\text{Cu}(\text{butyrate})$, the carboxylate from the strong acid (cyanoacetic) is monodentate and that from the weaker acid (butyric) is bidentate¹. Nevertheless, there are many exceptions to this, e.g. in the structures of the weakly basic carboxylate, $2\text{-NO}_2\text{C}_6\text{H}_4\text{CO}_2^-$ and $4\text{-NO}_2\text{C}_6\text{H}_4\text{CO}_2^-$, bistrisphenylphosphine derivatives of copper(I), the carboxylates are bidentate [17]. Similarly, bistrisphenylphosphine copper(I) formate contains a bidentate formate ligand [18]. It is worth noting that for symmetrically bonded bidentate acetate ligands, Δ is small (less than 100 cm^{-1}), i.e. significantly less than the ionic value of 164 cm^{-1} [19–22]. Therefore, it might be expected that asymmetrically bonded acetate would provide Δ values which are larger, as observed herein, approaching those of monodentate coordination. Some examples of other asymmetrically bonded acetate ligands

¹ The solid-state structures of $(\text{Cy}_3\text{P})_2\text{Cu}(\text{cyanoacetate})$ and $(\text{Cy}_3\text{P})_2\text{Cu}(\text{butyrate})$ have been determined in our laboratory. The former complex is of trigonal planar geometry with a monodentate bound cyanoacetate ($\text{Cu}-\text{O}$, $2.119(7)\text{ Å}$), whereas the latter complex is a distorted tetrahedron with a bidentate, asymmetrically bonded butyrate ligand ($\text{Cu}-\text{O}$, $2.182(4)$ and $2.276(5)\text{ Å}$).

which are structurally well-characterized are given in Ref. [23].

Relevant to the subject of the intermediacy of copper(I) carboxylate derivatives in copper(I) catalyzed decarboxylation processes, although all the bisphosphine carboxylate complexes reported upon are structurally quite similar, only the fluorenone derivative undergoes decarboxylation (Eq. (3)) [10a]. Nevertheless, complex **4** represents the first structurally characterized bidentate carboxylates which undergoes decarboxylation. Hence, it is indeed correct to ascribe the major contributing factor to the ease with which copper(I) carboxylates extrude carbon dioxide to the presence of electron-withdrawing and/or resonance-stabilized substituents on the carboxylate, i.e. the ability to afford stabilized carbanions [9].



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5. Supplementary material

Tables providing complete listings of bond lengths, bond angles and anisotropic thermal parameters for complexes **1–4** are available from the authors on request.

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