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Coordination Complexes of Bis(triphenylphosphine) Copper(I) Carbonate and Bicarbonate

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

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

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Introduction

Transition metal carbonates and bicarbonates have attracted considerable interest.[1] In part this attention stems from studies pertaining to carbonic anhydrase and to transition metal catalyzed organic reactions with carbon dioxide.[2] Several such investigations have focused on phosphine complexes of copper(I) carbonates and bicarbonates; for example, phosphine derivatives of Cu(I) bicarbonate have been shown to undergo reversible carbon dioxide extrusion.[3] Extensive spectroscopic studies of (triphenylphosphine)copper(I) carbonates and bicarbonates have been undertaken by Yamamoto and co-workers.[4] In spite of the speculation which exists regarding the solution structures of these complexes, definitive solid-state structures of these species have not been obtained from X-ray diffraction studies. However, a plethora of Cu(II) carbonates have been isolated and characterized by X-ray crystallography, revealing several coordination modes of carbonate to the Cu(II) metal center.[5] Therefore, it is likely that several Cu(I) carbonates may be obtained with different structural motifs. Indeed, it has been shown that the solution structures of Cu(I) bicarbonates are quite sensitive to the experimental conditions employed in their synthesis.[4]

Attempts in our laboratory to crystallize the decarboxylation products of bis(triphenylphosphine)copper(I) cyanoacetate[6] and bis(triphenylphosphine)copper(I) phenylmalonate benzyl ester[7] have resulted in the isolation of crystalline solids of bis(triphenylphosphine)copper(I)carbonates and bicarbonates. The appearance of Cu(I) carbonates has previously been noted in other investigations involving CO_2 insertions into Cu(I) alkyls and alkoxides, and these have been attributed to the presence of adventitious H_2O impurities.[4] Relevant to this subject we wish to report the single crystal X-ray diffraction studies of $[(Ph_3P)_2Cu]_2CO_3$, **1**, and $[(Ph_3P)_2CuOCO_2H]_2$, **2**.

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. Bis(triphenylphosphine) cuprous cyanoacetate and bis(triphenylphosphine)cuprous hydrogen phenylmalonate benzyl ester were prepared according to the published procedures.[6,7] Infrared spectra were recorded on a Mattson 6021 spectrometer with DTGS and MCT detectors.

Table 1. Crystallographic Data for Complexes **1** and **2**

	1	**2**
empirical formula	$C_{73.8}H_{61.6}O_3P_4Cl_{1.6}Cu_2$	$C_{74}H_{62}O_6P_4Cu_2$
fw	1303.4	1298.2
space group	$P\bar{1}$	$P2_12_12$
V, Å^3	3228(5)	3134.8(7)
Z	2	2
D_{calcd}, g/cm^3	1.341	1.375
a, Å	11.584(12)	14.721(2)
b, Å	14.535(10)	23.113(2)
c, Å	19.78(2)	9.2130(10)
α, deg	77.04(6)	
β, deg	88.90(8)	
γ, deg	83.97(7)	
T, K	193	293
μ, mm^{-1}	0.869(Mo Kα)	2.220 (Cu Kα)
wavelength, Å	0.710 73	1.541 78
R_F, % [a]	7.7	5.0
R_{wF}, % [a]	8.4	5.0

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

$[(Ph_3P)_2Cu]_2CO_3$, 1. Bis(triphenylphosphine)cuprous cyanoacetate (0.200 g) was placed in a 25 mL Schlenk tube and dissolved in 10 mL of tetrahydrofuran. The solution was heated at 40 °C for 2 h under a stream of argon. Tetrahydrofuran was added as needed to maintain a constant volume. After cooling to room temperature, the solution was layered with 3 mL of dichloromethane followed by 1 mL of hexane and stored at −10 °C for three weeks during which time a few transparent needles were isolated.

$[(Ph_3P)_2CuOCO_2H]_2$, 2. Bis(triphenylphosphine)cuprous phenylmalonate benzyl ester was dissolved in 10 mL of tetrahydrofuran under argon in a 25 mL Schlenk tube. The solution was heated at 55.4 °C for 5 min during which total decarboxylation had occurred as indicated by infrared spectroscopy. The solution was allowed to cool to room temperature. Transparent crystals grew overnight.

X-ray Crystallographic Study of 1 and 2. Crystal data and details of data collection are given in Table 1. A colorless needle (0.14 mm × 0.18 mm × 0.38 mm), **1**, was mounted on a glass fiber with epoxy cement at room temperature and cooled to 193 K in a N_2 cold stream. A colorless plate (0.05 mm × 0.22 mm × 0.25 mm), **2**, was mounted in capillary tube at room temperature. Preliminary examinations and data collections were performed on Siemens R3m/V and on Rigaku AFC5R X-ray diffractometers (oriented graphite monochromator) for complexes **1** and **2**, respectively. Cell parameters were calculated from the least squares fitting of the setting angles for 19 reflections ($2\theta_{av} = 9.8$) for **1** and 25 reflections ($2\theta_{av} > 15°$) for **2**. ω scans for several intense reflections indicated acceptable crystal quality. Data for **1** was collected for $4.0° \leq 2\theta \leq 40.0°$ ($-11 \leq h \leq 11$, $-13 \leq k \leq 13$, $0 \leq l \leq 18$) at 193 K. Data for **2** was collected for $5.0° \leq 2\theta \leq 120.0°$ ($0 \leq h \leq 16$, $0 \leq k \leq 25$, $0 \leq l \leq 10$) at 293 K. Three control reflections collected every 97 reflections for **1** and every 150 reflections for **2** 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 2292 reflections for **1** and 2688 for **2**. An empirical absorption correction was applied to **1** and a semiempirical absorption correction was applied to **2** ($T_{max} = 0.999$, $T_{min} = 0.927$). A total of 1312 unique reflections with $|I| > 4.0\sigma(I)$, for **1** and 1678 unique reflections with $|I| > 2.0\sigma(I)$ for **2** were used in further calculations. In **2** the Rodgers absolute configuration parameter η was refined to 1.4(2) indicating the correct absolute configuration was chosen.[8a] The structures were solved by direct methods (SHELXS, SHELXTL[8b]). Hydrogen atoms were placed in idealized positions with

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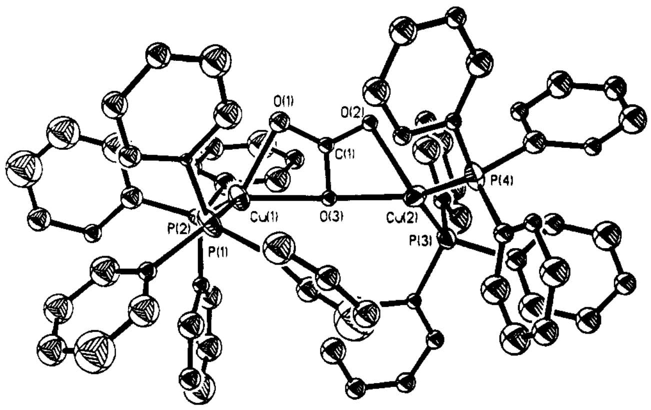
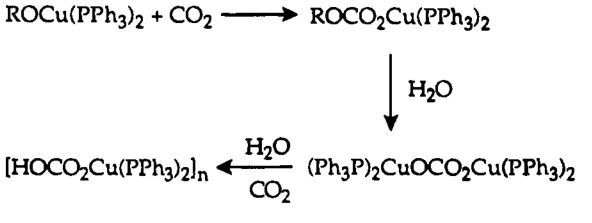


Figure 1. Thermal ellipsoid drawing of complex **1** in 50% probability with the atomic numbering scheme.

Scheme 1



$$\begin{tikzcd}
\mathrm{ROCu(PPh_3)_2 + CO_2} \arrow[r] & \mathrm{ROCO_2Cu(PPh_3)_2} \arrow[d, "H_2O"] \\
\mathrm{[HOCO_2Cu(PPh_3)_2]_n} & \mathrm{(Ph_3P)_2CuOCO_2Cu(PPh_3)_2} \arrow[l, "H_2O"', "CO_2"]
\end{tikzcd}$$

isotropic thermal parameters fixed at 0.08 Å^2. Neutral-atom scattering factors were taken from the ref 8c.

The phenyl rings for **1** in the final stages of refinement were constrained to a idealized hexagon. This constrained model was allowed to refine to convergence.

A molecule of CH_2Cl_2 for **1** was included in the structure refinement. This CH_2Cl_2 molecule in **1** refined to a partial occupancy of 0.79.

In complex **2** atoms, O(2), O(3), C(1), and C(2) were found to be on special positions. The model was used to refine the structure to convergence.

Results and Discussion

Bis(triphenylphosphine)copper(I) carbonate and bicarbonate derivatives were isolated inadvertently during the crystallization of the decarboxylation products of bis(triphenylphosphine)-copper(I) cyanoacetate and bis(triphenylphosphine)copper(I) phenylmalonate benzyl ester. These decarboxylation processes involve the production of carbanion intermediates. In the presence of a proton donor these carbanions afford base which subsequently reacts with CO_2 to provide binuclear copper(I) carbonates and bicarbonates. Copper(I) carbonates and bicarbonates which appear to be identical to these reported herein have previously been synthesized during insertion reactions of CO_2 into Cu(I) alkyls and alkoxides in the presence of adventitious moisture (See Scheme 1).[4] However, definitive assignment of their structures has not until now been presented. The molecular structures of **1** and **2** were determined by single crystal X-ray diffraction studies. Diagrams of the obtained structures, along with the atomic numbering schemes are shown in Figures 1 and 2 . The final fractional atomic coordinates are provided in Tables 2 and 3. Selected bond distances and angles are listed in Tables 4 and 5.

The dimeric structure of complex **1** contains two inequivalent copper(I) ions which possess distorted tetrahedral geometries, where each metal center is coordinated to two PPh_3 ligands and two oxygen atoms of an apportioned carbonate anion. This asymmetric ligand arrangement is depicted in the skeletal drawing as shown in Figure 3. The Cu(1)−O(1) and Cu(1)−O(3) bond distances are 2.12(1) and 2.20(1) Å whereas the Cu(2)−O(2) and Cu(2)−O(3) bond distances are 2.18(1) and 2.11(1) Å, respectively. These bond lengths are reminiscent of previously structurally characterized bis(triphenylphosphine)copper(I) carboxylates which also contain asymmetric carboxylate coordination.[9] As noted in Figure 3, the two copper(I) ions are bonded to the bridging oxygen of the carbonate ligand in an asymmetrical fashion, with Cu−O distances differing by 0.09[1] Å. The P(2)−Cu(1)−P(1) and P(3)−Cu(2)−P(4) bond angles are 127.0(6) and 119.1(6)°, respectively. The Cu−P bond distances, which average 2.24[1] Å, are typical of bis(triphenylphosphine)copper(I) complexes.[9,10] In related studies two types of asymmetric coordination of a carbonate ligand to two copper(II) centers have been reported by Churchill and coworkers.[5] These are displayed in line drawings **A** and **B**.

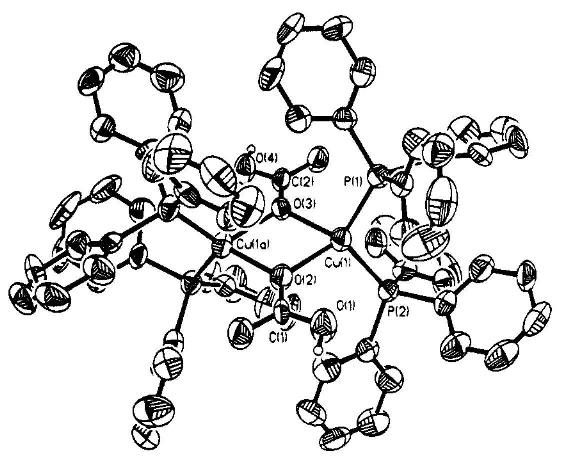
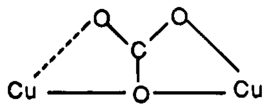
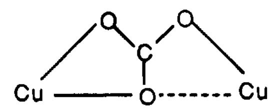


Figure 2. Thermal ellipsoid drawing of complex **2** in 50% probability with the atomic numbering scheme.

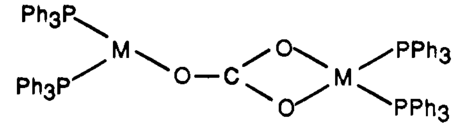


A



B

The bis(triphenylphosphine)cuprous carbonate dimer previously synthesized was characterized by infrared and NMR spectroscopies, and it is proposed to be similar in structure to the solid-state structures of $Pd_2Me_2(CO_3)(Ph_3P)_3$[11,12] and $Rh_2(CO_3)(Ph_3P)_5$.[13] These species have the asymmetric structure shown in the line drawing **C**, which is to be contrasted with



C

the molecular structure of complex **1** (Figure 1). Hence, the inherent difficulty in assigning definitive geometries for metal carbonate complexes based on spectroscopic data alone is evident.

As depicted in Figure 2, the bis(triphenylphosphine)cuprous bicarbonate complex, **2**, exhibits a distorted tetrahedral geometry at each metal center. Two symmetrically coordinated bicarbonates bridge the two copper ions to form a four-membered, rigorously planar $[Cu-O]_2$ ring. The coordination sphere of

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Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **1**

	x	*y*	*z*	*U*(eq)^{a,b}
Cu(1)	329(5)	1489(4)	7522(3)	32(3)
Cu(2)	1934(6)	3517(4)	8383(3)	34(3)
Cl(1)	−5203(22)	2400(20)	4880(18)	200(22)
Cl(2)	−5831(24)	667(21)	5708(16)	197(21)
P(1)	1524(12)	145(9)	7738(7)	35(7)
P(2)	−791(12)	2049(10)	6600(7)	33(7)
P(3)	1989(12)	4956(9)	7681(6)	29(7)
P(4)	3123(13)	3085(10)	9326(7)	34(7)
O(1)	−451(24)	1884(19)	8406(13)	26(9)
O(2)	255(22)	3077(18)	8770(12)	15(8)
O(3)	1111(25)	2582(19)	7919(14)	15(7)
C(1)	295(37)	2487(30)	8401(20)	17(13)
C(2)	833(21)	−539(18)	6585(16)	53(17)
C(3)	1042(1)	−1083(1)	6088(1)	49(16)
C(4)	2116(1)	−1610(1)	6070(1)	48(16)
C(5)	2979(1)	−1594(1)	6548(1)	89(21)
C(6)	2769(1)	−1050(1)	7044(1)	51(17)
C(7)	1696(1)	−522(1)	7062(1)	19(13)
C(8)	3388(26)	1215(19)	7650(12)	35(15)
C(9)	4502(1)	1397(1)	7799(1)	100(22)
C(10)	5187(1)	739(1)	8292(1)	36(15)
C(11)	4757(1)	−103(1)	8635(1)	30(14)
C(12)	3642(1)	−285(1)	8485(1)	51(16)
C(13)	2958(1)	374(1)	7993(1)	18(13)
C(14)	916(21)	−1665(20)	8458(11)	26(14)
C(15)	649(1)	−2312(1)	9061(1)	33(14)
C(16)	497(1)	−2020(1)	9685(1)	30(14)
C(17)	613(1)	−1081(1)	9706(1)	50(16)
C(18)	880(1)	−434(1)	9103(1)	41(16)
C(19)	1031(1)	−726(1)	8479(1)	8(12)
C(20)	−1516(20)	3803(23)	6899(13)	48(16)
C(21)	−2293(1)	4608(1)	6886(1)	29(14)
C(22)	−3408(1)	4662(1)	6616(1)	67(20)
C(23)	−3745(1)	3912(1)	6359(1)	44(16)
C(24)	−2968(1)	3107(1)	6372(1)	27(14)
C(25)	−1853(1)	3052(1)	6642(1)	34(15)
C(26)	−1684(22)	885(19)	5846(13)	22(14)
C(27)	−2310(1)	146(1)	5767(1)	36(16)
C(28)	−2912(1)	−343(1)	6328(1)	91(22)
C(29)	−2889(1)	−93(1)	6968(1)	72(19)
C(30)	−2263(1)	645(1)	7047(1)	61(18)
C(31)	−1661(1)	1135(1)	6486(1)	33(15)
C(32)	916(25)	1928(16)	5609(13)	46(16)
C(33)	1493(1)	2193(1)	4981(1)	31(14)
C(34)	1074(1)	3007(1)	4496(1)	72(20)
C(35)	78(1)	3557(1)	4639(1)	52(17)
C(36)	−500(1)	3293(1)	5267(1)	42(16)
C(37)	−81(1)	2478(1)	5752(1)	19(13)
C(38)	2785(18)	6260(20)	8345(14)	32(14)
C(39)	3603(1)	6764(1)	8572(1)	56(18)
C(40)	4755(1)	6663(1)	8357(1)	32(14)
C(41)	5088(1)	6059(1)	7915(1)	40(15)
C(42)	4270(1)	5555(1)	7688(1)	53(17)
C(43)	3119(1)	5655(1)	7903(1)	30(14)
C(44)	−269(31)	5390(16)	8087(13)	57(17)
C(45)	−1305(1)	5968(1)	8105(1)	34(15)
C(46)	−1450(1)	6878(1)	7678(1)	55(17)
C(47)	−560(1)	7209(1)	7234(1)	37(15)
C(48)	475(1)	6630(1)	7216(1)	70(19)
C(49)	621(1)	5721(1)	7643(1)	22(13)
C(50)	2880(21)	5628(15)	6306(14)	22(13)
C(51)	3067(1)	5559(1)	5619(1)	27(14)
C(52)	2803(1)	4753(1)	5406(1)	29(15)
C(53)	2352(1)	4016(1)	5879(1)	43(16)
C(54)	2165(1)	4085(1)	6566(1)	33(14)
C(55)	2429(1)	4891(1)	6779(1)	15(13)
C(56)	5106(27)	3165(16)	8547(13)	47(17)
C(57)	6288(1)	2955(1)	8438(1)	50(16)
C(58)	7004(1)	2471(1)	8991(1)	34(15)
C(59)	6537(1)	2197(1)	9652(1)	43(16)
C(60)	5355(1)	2407(1)	9760(1)	16(13)
C(61)	4639(1)	2891(1)	9208(1)	21(13)
C(62)	2438(21)	2098(16)	10686(14)	38(15)
C(63)	2126(1)	1284(1)	11143(1)	22(14)
C(64)	2189(1)	426(1)	10933(1)	37(15)
C(65)	2563(1)	382(1)	10266(1)	37(15)
C(66)	2875(1)	1196(1)	9809(1)	18(13)
C(67)	2812(1)	2054(1)	10019(1)	15(13)
C(68)	1741(23)	4521(19)	9730(12)	19(13)
C(69)	1455(1)	5281(1)	10046(1)	42(16)
C(70)	2301(1)	5596(1)	10407(1)	31(14)
C(71)	3433(1)	5151(1)	10451(1)	46(16)
C(72)	3719(1)	4391(1)	10135(1)	18(13)
C(73)	2873(1)	4076(1)	9774(1)	32(14)
C(74)	−5231(74)	1539(62)	5675(42)	143(41)

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

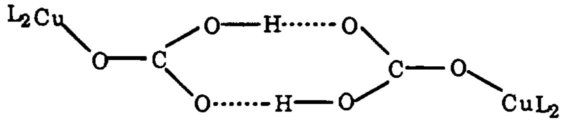
Table 3. Selected Bond Lengths (Å)[a] and Bond Angles (deg) for **1**

Cu(1)−P(1)	2.23(1)	Cu(1)−P(2)	2.21(1)
Cu(1)−O(1)	2.12(1)	Cu(1)−O(3)	2.20(1)
Cu(2)−P(4)	2.27(1)	Cu(2)−P(3)	2.24(1)
Cu(2)−O(3)	2.11(1)	Cu(2)−O(2)	2.18(1)
O(1)−C(1)	1.29(1)	O(2)−C(1)	1.24(1)
P(1)−Cu(1)−P(2)	127.0(6)	P(1)−Cu(1)−O(1)	115.3(8)
P(2)−Cu(1)−O(1)	110.5(8)	P(1)−Cu(1)−O(3)	109.3(8)
P(2)−Cu(1)−O(3)	114.4(8)	O(1)−Cu(1)−O(3)	63(1)
P(1)−Cu(1)−C(1)	117(1)	P(2)−Cu(1)−C(1)	117(1)
P(3)−Cu(2)−P(4)	119.1(6)	P(3)−Cu(2)−O(2)	118.6(7)
P(4)−Cu(2)−O(2)	104.4(7)	P(3)−Cu(2)−O(3)	112.7(8)
P(4)−Cu(2)−O(3)	125.8(8)	O(2)−Cu(2)−O(3)	60(1)
P(3)−Cu(2)−C(1)	124.2(9)	P(4)−Cu(2)−C(1)	114.6(9)
Cu(1)−P(1)−C(7)	118(1)	Cu(1)−P(1)−C(13)	110(1)
Cu(1)−P(2)−C(25)	116(1)	Cu(1)−P(2)−C(31)	108.7(9)
Cu(1)−P(2)−C(37)	118(1)	Cu(2)−P(4)−C(67)	119(1)
Cu(2)−P(3)−C(49)	114(1)	Cu(2)−O(2)−C(1)	91(1)
Cu(2)−P(3)−C(43)	115(1)	Cu(1)−O(3)−C(1)	87(1)
Cu(2)−P(3)−C(55)	112.5(9)	Cu(1)−C(1)−Cu(2)	118(1)
Cu(2)−P(4)−C(61)	119(1)	Cu(1)−C(1)−O(2)	172(1)
Cu(2)−P(4)−C(73)	104.8(9)	Cu(1)−C(1)−O(3)	62(1)
Cu(1)−O(1)−C(1)	91(1)	O(2)−C(1)−O(3)	115(1)
Cu(1)−O(3)−Cu(2)	174(1)	O(1)−C(1)−O(2)	126(1)
Cu(2)−O(3)−C(1)	92(1)	O(1)−C(1)−O(3)	119(1)
Cu(2)−C(1)−O(1)	174(1)		

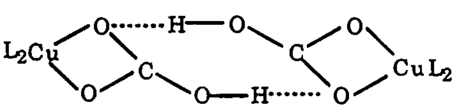
[a] Estimated standard deviations are given in parentheses.

each copper(I) is completed by two triphenylphosphine ligands. The dimeric units are intermolecularly hydrogen-bonded at an O···O distance of 2.50 Å to provide polymeric chains as seen in Figure 4. The copper(I) center is equidistant from the bridging oxygen atoms of the two carbonate ligands, i.e., Cu(1)−O(2) and Cu(1)−O(3) bond distances are 2.154(3) and 2.150(3) Å, respectively. Typical Cu−P bond distances of 2.272(3) and 2.283(3) Å are observed for Cu(1)−P(1) and Cu(1)−P(2), whereas, the P(1)−Cu(1)−P(2) bond angle is 116.9(1)°.

For the previously reported bicarbonate complex, prepared from the reaction of $PhOCu(PPh_3)_2$ with CO_2 in moist solvents, which possesses the same stoichiometry as complex **2** described herein, several solution structures were proposed (e.g., **D** and **E**).[4] Although, there were slight differences in the complexes depending on preparation conditions, all species exhibited ν-(O−H···O) vibrations in the solid-state which disappeared upon



D



E

Table 4. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **2**

	x	y	z	U(eq)[a,b]
Cu(1)	1014(1)	319(1)	136(2)	47(1)
P(1)	1095(2)	1282(1)	−340(3)	44(1)
P(2)	2356(2)	−155(1)	495(3)	43(1)
O(1)	653(6)	239(4)	3672(8)	69(3)
O(2)	0	0	1619(12)	49(4)
O(3)	0	0	−1340(11)	39(4)
O(4)	−627(5)	−256(3)	−3406(8)	61(3)
C(1)	0	0	2993(20)	37(6)
C(2)	0	0	−2661(19)	41(7)
C(3)	1333(8)	1560(6)	2549(17)	69(6)
C(4)	1380(11)	1915(8)	3728(17)	109(8)
C(5)	1234(10)	2489(7)	3575(20)	95(8)
C(6)	1061(9)	2717(6)	2240(18)	72(6)
C(7)	1010(8)	2359(4)	1072(14)	61(5)
C(8)	1138(8)	1775(5)	1207(13)	49(4)
C(9)	2764(8)	1880(5)	−902(13)	54(4)
C(10)	3524(9)	1968(6)	−1743(20)	82(7)
C(11)	3668(10)	1688(7)	−3016(20)	99(8)
C(12)	3040(11)	1290(7)	−3458(18)	99(7)
C(13)	2275(9)	1177(5)	−2624(17)	69(5)
C(14)	2139(7)	1486(5)	−1372(14)	51(5)
C(15)	326(8)	1972(5)	−2559(16)	71(5)
C(16)	−385(9)	2253(6)	−3232(17)	86(6)
C(17)	−1261(8)	2173(6)	−2752(16)	68(6)
C(18)	−1407(8)	1830(7)	−1598(18)	86(7)
C(19)	−687(8)	1539(6)	−976(14)	67(5)
C(20)	195(7)	1607(4)	−1424(12)	42(4)
C(21)	3647(7)	729(5)	763(14)	61(5)
C(22)	4258(8)	1075(5)	1492(17)	72(6)
C(23)	4454(9)	968(6)	2881(18)	74(6)
C(24)	4059(10)	520(6)	3563(15)	75(6)
C(25)	3414(8)	180(6)	2875(14)	70(5)
C(26)	3212(7)	272(5)	1452(12)	40(4)
C(27)	3116(9)	−1187(6)	1640(15)	75(6)
C(28)	3096(10)	−1669(6)	2484(18)	88(7)
C(29)	2350(11)	−1810(6)	3240(16)	79(6)
C(30)	1612(10)	−1485(6)	3158(16)	79(6)
C(31)	1605(8)	−989(5)	2322(15)	66(5)
C(32)	2362(8)	−827(4)	1547(13)	48(4)
C(33)	2425(8)	−477(5)	−2386(16)	66(5)
C(34)	2824(11)	−673(6)	−3652(17)	86(7)
C(35)	3736(10)	−736(6)	−3732(16)	76(6)
C(36)	4275(9)	−623(5)	−2573(17)	71(5)
C(37)	3887(8)	−428(5)	−1297(13)	57(4)
C(38)	2944(7)	−362(4)	−1182(11)	42(4)

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

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

Cu(1)−O(2)	2.154(3)	Cu(1)−O(3)	2.150(3)
Cu(1)−P(1)	2.271(3)	Cu(1)−P(2)	2.283(3)
P(1)−C(8)	1.83(1)	P(1)−C(14)	1.87(1)
P(1)−C(20)	1.82(1)	P(2)−C(26)	1.83(1)
P(2)−C(32)	1.83(1)	P(2)−C(38)	1.83(1)
O(1)−C(1)	1.27(1)	O(2)−C(1)	1.27(1)
O(3)−C(2)	1.22(1)	O(4)−C(2)	1.29(1)
C(1)−O(1A)	1.27(1)	C(2)−O(4A)	1.29(1)
C(3)−C(4)	1.36(1)	C(3)−C(8)	1.36(1)
C(4)−C(5)	1.35(1)	C(5)−C(6)	1.36(1)
P(1)−Cu(1)−P(2)	116.9(1)	Cu(1)−P(1)−C(8)	117.5(4)
Cu(1)−P(1)−C(14)	112.9(4)	C(8)−P(1)−C(14)	102.3(5)
Cu(1)−P(1)−C(20)	118.2(4)	C(8)−P(1)−C(20)	101.3(5)
C(14)−P(1)−C(20)	102.4(5)	Cu(1)−P(2)−C(26)	114.0(3)
Cu(1)−P(2)−C(32)	119.2(4)	C(26)−P(2)−C(32)	101.5(5)
Cu(1)−P(2)−C(38)	114.3(3)	C(26)−P(2)−C(38)	102.8(5)
C(32)−P(2)−C(38)	102.8(5)	O(1)−C(1)−O(2)	119.4(8)
O(1)−C(1)−O(1A)	121(1)	O(2)−C(1)−O(1A)	119.4(8)
O(3)−C(2)−O(4)	122.0(7)	O(3)−C(2)−O(4A)	122.0(7)
O(4)−C(2)−O(4A)	116(1)	C(4)−C(3)−C(8)	121(1)
C(3)−C(4)−C(5)	120(1)	C(4)−C(5)−C(6)	120(1)

[a] Estimated standard deviations are given in parentheses.

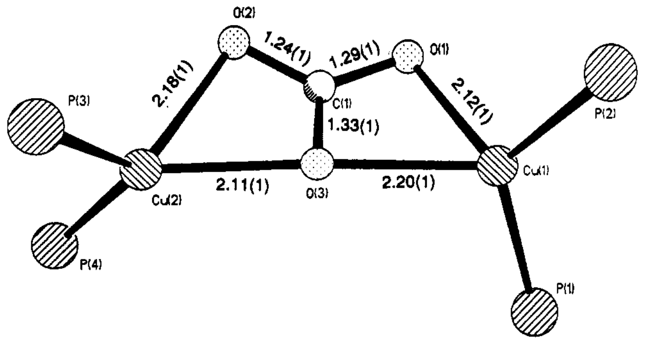


Figure 3. Ball-and-stick drawing of complex **1** indicating intramolecular bond distances.

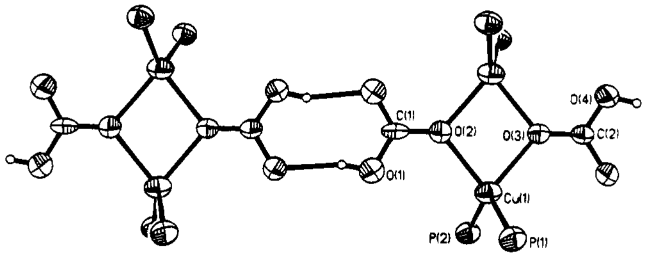


Figure 4. Partial thermal ellipsoid drawing of complex **2** in 50% probability illustrating the intermolecular hydrogen bonding between bicarbonate groups.

dissolution with concomitant appearance of new bands ascribed to ν(O−H) motions. It is possible that the solid-state structures of these Cu(I) bicarbonates are similar to that observed for complex **2**.

Conclusions

The X-ray structures of the copper(I) carbonate and bicarbonate complexes reported upon herein provide valuable insight into the coordination modes of these ligands bound to Cu(I). Similar dinuclear bridging tridentate carbonato coordination to Cu(II), i.e., μ-η^2-η^2-CO_3 binding, is also common, which differ slightly in the nature of the asymmetry in the carbonato−Cu(II) interactions.[5,14] However, these Cu(II) derivatives contain three ancillary ligands bound to each copper center, and hence are five-coordinate. On the other hand the structure of $[(LCu^{II})_2CO_3]^{+2}$, where L is the tetradentate ligand tris(2-pyridylmethyl)amine, contains a bridged carbonato group (μ-η^1-η^1-CO_3) in a dinuclear unit with each Cu(II) ion in a distorted square-pyramidal geometry.[15] These present studies serve to underscore the propensity of the Cu(I) center to be three or four coordinate.

Since Cu(I) is isoelectronic with Zn(II) it is of interest to contrast the structures of the carbonate and bicarbonate derivatives of these two metals. For example, $[\eta^3$-HB(3-Bu^t-5-Mepz)$_3$Zn]$_2$CO$_3$, has a bridging μ-η^1-η^1-CO_3 unit, where each zinc is a distorted tetrahedral with Zn−O distances of 1.850(7) Å and a Zn−distal oxygen interaction of 3.20Å.[16] However, in the case of the sterically less demanding tris(pyrazolyl)hydroborate ligand, $[\eta^3$-HB(3,5-Pr$^i{}_2$pz)$_3$Zn]$_2$CO$_3$, the carbonato ligand is asymmetrically bound in a μ-η^1-η^2-CO_3 fashion where one zinc is five-coordinate and the other is four-coordinate. Conversely, whereas the (η^3-HB(3-Bu^t-5-Mepz)$_3$Zn(OCO$_2$H) derivative which results from CO_2 insertion into the corresponding Zn−OH complex is proposed to be a monomer containing a unidentate

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carbonato group based on infrared spectroscopy,[17] the copper(I) bicarbonate is dimeric and bridged by a single oxygen atom of the bicarbonate group. This latter structural type is uncommon in bicarbonate or carboxylate complexes,[18] although it is proposed on metal surfaces.[19] In the present instance the bridging of a single oxygen atom of the bicarbonate to the two copper(I) centers is complemented by strong intermolecular hydrogen-bonding. This mode of interaction as compared to the more common μ-O,O′ binding should allow for a shorter Cu···Cu separation. However, because of the steric bulk of the triphenylphosphine ligands, the Cu···Cu separation is actually longer at 3.30 Å (see space-filling model in Figure 5). For example, the Cu···Cu distances in $Cu_2(O_2CCH_3)_2$ and $Cu_2(O_2CCH_3)_2$(dppe) are 2.556(2)[20] and 2.712(2) Å,[21] respectively.

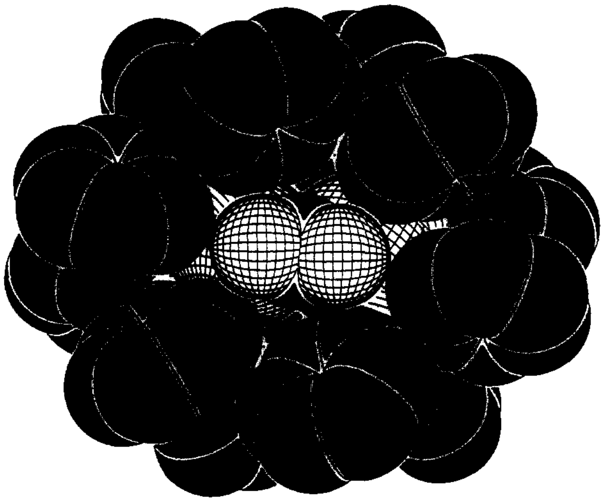

Figure 5. Space-filling model of complex **2**. The two central atoms (crosshatched) are O(1)'s bound to a single C(1) (black, behind).

Acknowledgment. The financial support of this research by the National Science Foundation (Grant CHE91-19737) is greatly appreciated.

Supporting Information Available: Tables of anisotropic thermal parameters, bond lengths, and bond angles and fully labeled ORTEP diagrams for complexes **1** and **2** (11 pages). Ordering information is given on any current masthead pages.

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Additions and Corrections

1995, Volume 34

Jiann T. Lin,* Shih-Sheng Sun, Jiann Jung Wu, Liangshiu Lee, Kuan-Jiuh Lin, and Yi Fong Huang: Dinuclear Metal Carbonyls Bridged by Pyridyl Ligands Incorporating an Alkyne Entity.

Page 2329. In Table 5, footnote *e* should be corrected to **24** = $(CO)_4(PPh_3)W(\eta^1$-**DPB**$)$. In Figure 2, the ordinate scale should be an order of magnitude greater; that is, ν_{MLCT} (cm^{-1}) values should be corrected to 25 000, ..., 17 000.

Page 2330. In the first line of the figure caption for Figure 3, "Electroni Pergamon Pressc spectra..." should be corrected to "Electronic spectra...".

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