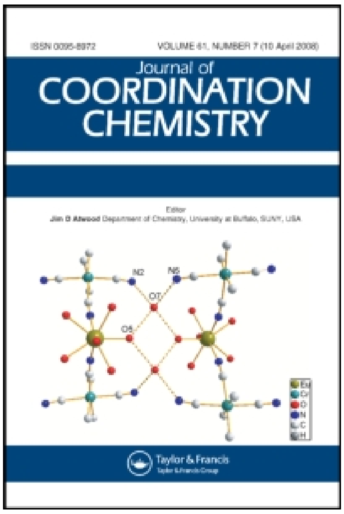

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

SYNTHESIS AND STRUCTURE OF 1,2-BIS(DIPHENYLPHOSPHINO)ETHANE COMPLEXES OF COPPER(I) ACETATE. CATALYSTS FOR THE DECARBOXYLATION OF CARBOXYLIC ACIDS

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To cite this Article Darensbourg, Donald J. , Longridge, Elisabeth M. , Khandelwal, Bandana and Reibenspies, Joseph H.(1994) 'SYNTHESIS AND STRUCTURE OF 1,2-BIS(DIPHENYLPHOSPHINO)ETHANE COMPLEXES OF COPPER(I) ACETATE. CATALYSTS FOR THE DECARBOXYLATION OF CARBOXYLIC ACIDS', Journal of Coordination Chemistry, 32: 1, 27 — 37

To link to this Article: DOI: 10.1080/00958979408024235

URL: http://dx.doi.org/10.1080/00958979408024235

J. Coord. Chem., 1994, Vol 32, pp. 27–37
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SYNTHESIS AND STRUCTURE OF 1,2-BIS (DIPHENYLPHOSPHINO)ETHANE COMPLEXES OF COPPER(I) ACETATE. CATALYSTS FOR THE DECARBOXYLATION OF CARBOXYLIC ACIDS[†]

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(Received October 20, 1993; in final form December 15, 1993)

Several dimeric complexes of copper(I) acetate with bidentate phosphine ligands have been synthesized. The solid-state structure of one of these derivatives, dppe$(CuO_2CCH_3)_2$, where dppe = 1,2-bis(diphenylphosphino)ethane, has been determined. The complex is shown to exist in the solid-state as a polymeric chain of dimeric copper(I) units containing a dppe and two acetate ligands, with the dimers being linked together *via* weaker Cu-O interactions. The Cu-Cu bond length in the dimeric units is considerably longer, at 2.712(2) Å, than that observed in copper(I) acetate of 2.556(2) Å. The use of these derivatives as catalyst precursors for the catalytic decarboxylation of cyanoacetic acid to acetonitrile and carbon dioxide is discussed. Crystal data for dppe$(CuO_2CCH_3)_2$: space group $P2_1/n$, $a = 14.976(6)$ Å, $b = 11.676(3)$ Å, $c = 16.999(6)$ Å, $\beta = 107.59(3)°$, $Z = 4$, $R = 7.33\%$

KEYWORDS: decarboxylation, copper acetate catalysis, carboxylic acids

INTRODUCTION

Due to the proven ability of certain copper(I) carboxylates to readily decarboxylate in the presence of amine and phosphine ligands[1], current research in our laboratory has focused on the synthesis and characterization of copper(I) acetate and cyanoacetate complexes containing phosphine or amine ligands. Previously, we demonstrated that a copper(I) acetate complex containing 1,10-phenanthroline is an efficient catalyst for the decarboxylation of cyanoacetic acid.[2] More recent studies revealed the reversible decarboxylation/carboxylation exhibited by phosphine derivatives of Cu(I) cyanoacetate.[3] Specifically, it was shown that the complex $[(Ph_3P)_2CuO_2CCH_2CN]_2$ reversibly extrudes CO_2 (eq.1). Exchange reaction (1) was demonstrated to be first-order in the copper(I) dimer and to proceed with a rate constant quite similar to that noted for the catalytic decarboxylation of cyanoacetic acid in the presence of the copper(I) dimer. Because this latter process is zero-order in acid concentration, the behavior is consistent with a reaction pathway for the decarboxylation reaction in which the rate determining step is CO_2 extrusion. To

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[†] Dedicated to Professor Theodore L. Brown on the occasion of his 65th birthday.
* Author for correspondence.

further investigate complexes of this nature, derivatives of copper(I) acetate with bidentate phosphines were investigated. We report herein the synthesis and X-ray structural characterization of a 1,2-bis(diphenylphosphino)ethane complex of copper(I) acetate, dppe(CuO_2CCH_3)$_2$, and its reactivity as a decarboxylation catalyst. In addition the synthesis and characterization of other bidentate phosphine copper(I) acetate complexes is presented.

$$[(Ph_3P)_2CuO_2CCH_2CN]_2 + {}^{13}CO_2 \rightleftharpoons [(Ph_3P)_2CuO_2{}^{13}CCH_2CN]_2 + {}^{12}CO_2 \quad (1)$$

EXPERIMENTAL

All manipulations were carried out either in an argon drybox or on a double-manifold Schlenk vacuum line, using freshly distilled solvents. Copper(I) acetate was prepared by the reduction of $Cu(O_2CCH_3)_2$ by copper turnings with acetic acid/acetic anhydride in acetonitrile according to published procedures.[4] 1,2-bis(diphenylphosphino)ethane (dppe), 1,2-bis(diphenylphosphino)propane (dppp), and 1,2-bis(dimethylphosphino)ethane (dmpe) were purchased from Aldrich Chemical Co. Infrared spectra were recorded on a Mattson 6021 spectrometer with DTGS and MCT detectors.

Synthesis of dppe(CuO_2CCH_3)$_2$

To a suspension of copper(I) acetate (0.55 g, 4.47 mmol) in benzene (20 ml) was added a benzene solution (20 ml) of 1,2-bis(diphenylphosphino)ethane (1.57 g, 3.94 mmol). The resulting off-white suspension was stirred for 24h after which a white powder was isolated by removing the clear yellow supernatant and washing the solid with benzene and diethyl ether. The white powder was dried in *vacuo* (yield 75%). *Anal* Calcd for $Cu_2P_2O_4H_{30}C_{30}$%: C 55.99; H, 4.70. Found: C, 54.95; H, 5.44. IR(CH_2Cl_2) ν(CO_2) 1582 (s), 1415 (ms), 1363 (w). Colorless crystals suitable for X-ray structure analysis were grown by slow diffusion of hexane into a dichloromethane solution of the complex at room temperature over several days.

Synthesis of a two-to-one dppe derivative of Cu(I) acetate

A similar reaction was performed with 2 equivalents of dppe (1.3 g, 3.2 mmol) and one equivalent of copper(I) acetate (0.20 g, 1.6 mmol) in benzene. A pale yellow solution immediately formed which turned cloudy after five min of stirring. A fine white precipitate formed after 24 h. The white powder was isolated by removing the supernatant *via* cannula and washing the precipitate with 3 x 30 ml of diethyl ether. Yield 79%. IR(CH_2Cl_2) 1596 (s), 1434 (s), 1372 (s), 1325 (m).

Synthesis of dmpe and dppp derivatives of Cu(I)acetate

Similar procedures were followed to prepare the dmpe and dppp complexes as reported above for dppe(CuO_2CCH_3)$_2$. The reactions were carried out in a one-to-one ratio. For the dmpe derivative: IR(CH_2Cl_2)1581 (s), 1381(ms). *Anal.* Calc. for $CuP_2O_2C_8H_{19}$%: C, 35.23; H, 7.02. Found: C, 35.79; H, 7.88. For the dppp derivative: IR(C_6H_6) 1587 (s), 1377 (ms).

Kinetics of cyanoacetic acid decarboxylation in the presence of $dppe(CuO_2CCH_3)_2$

The rate of the catalytic decomposition of $NCCH_2CO_2H$ was monitored by infrared spectroscopy. Solution temperatures were controlled by a thermostated water bath (± 0.1°C). A solution of $NCCH_2CO_2H$ in DME was equilibrated to the desired temperature and transferred to a flask containing a DME solution of the specified catalyst or catalyst precursor. Small aliquots of the solution (~0.2 ml) were withdrawn periodically by syringe and examined by IR. The rate of catalysis was monitored by following the disappearance of the carboxylate band of the acid at 1749 cm^{-1}. A base-line correction was made on each spectrum by subtracting the absorbance in a region free of any peaks. This value was arbitrarily chosen as 2200 cm^{-1}. Rate constants were determined from the slope of a plot of (A_t/A_0) *versus* time, where A_t is the absorbance at 1749 cm^{-1} at a time, t, and A_0 is the absorbance at time = 0. Zero-order rate constants were then obtained by multiplying the slope obtained by the initial concentration of acid used.

X-ray crystallographic study of $dppe(CuO_2CCH_3)_2$

Crystal data and details of data collection are given in Table 1. A colorless sphere (0.4 mm diameter) was mounted on a glass fiber with epoxy cement, at room temperature and cooled to 193 K in a N_2 cold stream (Nicolet LT-2). Preliminary examination and data collection were performed on a Nicolet R3m/V X-ray diffractometer (oriented graphite monochromator; Mo Kα λ = 0.71073 Å radiation). Cell parameters were calculated from the least-squares fitting of the setting angles for five reflections. Omega scans for several intense reflections indicated acceptable crystal quality. Data were collected for $4.0° \leq 2\theta \leq 50.0°$ [ω (*Wyckoff*) *scans*, $-17 \leq h \leq 16$, $0 \leq k \leq 13$, $0 \leq 1 \leq 20$] at 193 K. Scan width on ω for the data collection was 0.60° with a variable scan rate of 1.50 to 14.65°min^{-1}. Three control reflections, collected every 97 reflections showed no significant trends. Background measurements were obtained by stationary crystal and stationary counter techniques at the beginning and end of each scan for 0.50 of the total scan time.

Lorentz and polarization corrections were applied to 4958 reflections. An empirical absorption correction was applied. A total of 4076 unique reflections,

Table 1 Crystallographic data for $C_{30}H_{30}O_4P_2Cu_2$

Empirical Formula	$C_{30}H_{30}O_4P_2Cu_2$
fw	643.6
Space Group	Monoclinic, $P2_1/n$
a,Å	14.976(6)
b,Å	11.676(3)
c,Å	16.999(6)
b,deg	107.59(3)
V,Å^3	2833.5(17)
Z	4
*D*calcd, g/cm^3	1.509
m(Mo Ka).mm^{-1}	1.649
wavelength, Å	0.71073
R_F,%^{a}	8.21
R_wF, %^{a}	7.33%

$^aR_F = \Sigma \mid F_o\text{-}F_c \mid / \Sigma F_o$ and $wR_F = \{[\Sigma w(F_o\text{-}F_c)^2]/[\Sigma w(F_o)^2]\}^{1/2}$

with $|I| \geq 1.0\,\sigma I$, were used in further calculations. The structure was solved by Direct Methods [SHELXSs, SHELXTL-PLUS program package, Sheldrick (1988)]. Full-matrix least-squares anisotropic refinement for all non-hydrogen atoms (SHELXLS, SHELXTL-PLUS program package, Sheldrick (1988), number of least-squares parameters = 344; quantity minimized $\Sigma w(F_o\text{-}F_c)^2$; $w^{-1} = \sigma^2 F + gF^2$, $g = 0.00001$] yielded $R = 0.082$, $wR = 0.073$ and $S = 4.65$ at convergence [largest $\Delta/\sigma = 0.0210$; mean $\Delta/\sigma = 0.0035$; largest positive peak in the final Fourier difference map = 1.43e$^-$Å^3; largest negative peak in the final Fourier difference map = $-$0.84e$^-$Å^3]. Hydrogen atoms were placed in idealized positions with isotropic thermal parameters fixed at 0.08Å^3. Neutral atom scattering factors and anomalous scattering correction terms were taken from *International Tables for X-ray Crystallography.*

RESULTS

Synthesis and Characterization of Bidentate Phopshine Complexes of Copper(I) Acetate

Copper(I) complexes of dppp, dppe and dmpe were prepared from the reaction of copper(I) acetate and the respective bidentate phosphine in dichloromethane at room temperature. The complexes are white powders displaying ν(CO_2) frequencies in CH_2Cl_2 typical of copper(I) carboxylates. Table 2 provides the observed ν(CO_2) stretching frequencies for the bidentate phosphine complexes of copper(I) acetate. Two distinct copper(I) complexes were synthesized with the dppe ligand. In the one-to-one reaction, a copper(I) polymeric chain with bridging phosphines was obtained with the formula dppe$(CuO_2CCH_3)_2$ as determined by X-ray crystallography. The second complex was prepared from a two-to-one reaction (dppe to copper(I) acetate) and resulted in a different IR band pattern than that observed for the former dppe complex, indicating a new species had been produced. Elemental analysis of the complex supported formation of a copper(I) dimer with both a bridging and bidentate dppe moiety as suggested in a previous report (species1)[5], however the exact nature of this complex was not crystallographically determined. Attempts at obtaining X-ray quality crystals of the complexes of dppp and dmpe were not successful.

The difference between the symmetric and asymmetric carboxylate stretches (Δν) in dppe$(CuO_2CCH_3)_2$ of 167 cm^{-1} is quite close to the Δν value observed in NaO_2CCH_3(164 cm^{-1})[6] supporting the presence of a bridging acetate. Indeed, bridging acetates are observed in the crystal structure of the complex. Infrared characterization of the remaining complexes containing bidentate ligands provided

Table 2 Observed ν(CO_2) frequencies for copper(I) acetate complexes containing bidentate phosphine ligands (P_2) in CH_2Cl_2

P_2	ν(CO_2)cm^{-1}	Δ(cm^{-1})
dppe[a]	1582,1415	167
dppe	1596,1372	224
dmpe	1581,1381	200
dppp	1587,1377	210

[a] dppe$(CuO_2CCH_3)_2$

Δv values of 200 cm^{-1} or greater, thus indicating unidentate coordination of the carboxylate.

Structural Characterization of dppe(CuO_2CCH_3)$_2$

In order to define precisely the molecular structure of dppe(CuO_2CCH_3)$_2$, an X-ray diffraction investigation at −80°C was carried out. Colorless crystals of dppe (CuO_2CCH_3)$_2$ were grown by slow diffusion of hexane into a dichloromethane solution of the complex at room temperature over several days. The final atomic coordinates for all non-hydrogen atoms are provided in Table 3. Pertinent bond lengths and bond angles are reported in Table 4 and 5, respectively. Figure 1 depicts

Table 3 Atomic coordinates ($\times 10^4$)[a] and equivalent isotropic displacement parameters (Å^2 $\times 10^3$)[b] for $C_{30}H_{30}O_4P_2Cu_2$.

	x	y	z	U(eq)[a,b]
PCu1	4647(1)	- 542(1)	785(1)	23(1)
Cu2	3228(1)	541(1)	1162(1)	29(1)
P1	3915(2)	- 2153(2)	788(1)	22(1)
P2	2348(2)	- 487(2)	1680(1)	23(1)
O1	4260(5)	1519(5)	1854(4)	41(3)
O2	5421(4)	406(4)	1735(3)	34(2)
O3	2867(5)	1064(5)	- 13(3)	34(2)
O4	4223(4)	660(4)	- 198(3)	25(2)
C1	5113(7)	1221(7)	2044(5)	30(4)
C2	5822(8)	1932(8)	2697(6)	60(5)
C3	3400(6)	1028(6)	- 441(5)	20(3)
C4	3034(7)	1419(8)	- 1325(5)	37(4)
C5	5051(7)	- 3931(7)	1697(5)	37(4)
C6	5780(8)	- 4718(7)	1837(6)	42(4)
C7	6229(8)	- 4905(7)	1269(6)	44(4)
C8	5989(8)	- 4259(7)	554(6)	43(4)
C9	5268(7)	- 3462(7)	406(5)	31(3)
C10	4797(6)	- 3283(6)	985(5)	24(3)
C11	3020(7)	- 1993(7)	- 911(5)	31(4)
C12	2350(7)	- 2282(7)	- 1645(5)	38(4)
C13	1708(7)	- 3127(7)	- 1674(5)	40(4)
C14	1744(7)	- 3747(7)	- 975(5)	34(4)
C15	2443(7)	- 3485(6)	- 233(5)	31(4)
C16	3051(6)	- 2599(6)	- 183(5)	24(3)
C17	3285(6)	- 2515(6)	1540(5)	26(3)
C18	2299(6)	- 2002(6)	1376(5)	27(3)
C19	2165(8)	- 1238(6)	3209(5)	37(4)
C20	2493(10)	- 1443(7)	4046(6)	53(5)
C21	3385(10)	- 1094(10)	4479(6)	66(6)
C22	3925(10)	- 500(11)	4104(6)	82(6)
C23	3571(9)	- 268(8)	3262(6)	55(5)
C24	2694(6)	- 636(6)	2802(5)	23(3)
C25	380(7)	- 820(7)	1169(5)	36(4)
C26	- 538(7)	- 450(9)	892(5)	40(4)
C27	- 735(8)	725(9)	849(5)	46(4)
C28	12(8)	1482(9)	1075(6)	46(4)
C29	923(7)	1115(7)	1327(5)	32(3)
C30	1125(7)	- 101(7)	1383(5)	25(3)

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

Table 4 Bond lengths (Å)[a] for $C_{30}H_{30}O_4P_2Cu_2$

Cu1 - Cu2	2.712(2)	Cu1 - P1	2.178(2)
Cu1 - O2	2.012(5)	Cu1 - O4	2.126(5)
Cu1 - O4A	2.214(7)	Cu2 - P2	2.157(3)
Cu2 - O1	1.995(6)	Cu2 - O3	2.001(5)
P1 - C10	1.824(8)	P1 - C16	1.839(7)
P1 - C17	1.85(1)	P2-C18	1.838(8)
P2 - C24	1.828(8)	P2 - C30	1.80(1)
O1 - C1	1.27(1)	O2 - C1	1.24(1)
O3 - C3	1.23(1)	O4 - C3	1.25(1)
O4 - Cu1A	2.214(7)	C1 - C2	1.53(1)
C3-C4	1.50(1)		

[a] Estimated standard deviations are given in parentheses.

Table 5 Bond angles (°)[a] for $C_{30}H_{30}O_4P_2Cu_2$

Cu2 - Cu1 - P1	88.3(1)	Cu2 - Cu1 - O2	81.7(2)
P1 - Cu1 - O2	129.9(2)	Cu2 - Cu1 - O4	79.0(2)
P1 - Cu1 - O4	122.8(2)	O2 - Cu1 - O4	103.3(2)
Cu2 - Cu1 - O4A	153.7(1)	P1 - Cu1 - O4A	113.7(1)
O2 - Cu1 - O4A	93.6(2)	O4 - Cu1 - O4A	77.0(2)
Cu1 - Cu2 - P2	117.1(1)	Cu1 - Cu2 - O1	83.3(2)
P2 - Cu2 - O1	122.6(2)	Cu1 - Cu2 - O3	84.3(2)
P2 - Cu2 - O3	124.3(2)	O1 - Cu2 - O3	109.9(3)
Cu1 - P1 - C10	106.8(3)	Cu1 - P1 - C16	117.4(3)
C10 - P1 - C16	103.6(3)	Cu1 - P1 - C17	124.1(2)
C10 - P1 - C17	101.5(4)	C16 - P1 - C17	100.8(4)
Cu2 - P2 - C18	113.5(3)	Cu2 - P2 - C24	117.6(3)
C18 - P2 - C24	100.2(3)	Cu2 - P2 - C30	116.1(3)
C18 - P2 - C30	102.2(4)	C24 - P2 - C30	105.0(4)
Cu2 - O1 - C1	122.4(5)	Cu1 - O2 - C1	124.4(6)
Cu2 - O3 - C3	123.5(5)	Cu1 - O4 - C3	121.1(6)
Cu1 - O4 - Cu1A	103.0(2)	C3 - O4 - Cu1A	133.1(5)
O1 - C1 - O2	125.2(7)	O1 - C1 - C2	117.5(8)
O2 - C1 - C2	117.3(9)	O3 - C3 - O4	124.4(7)
O3 - C3 - C4	118.2(7)	O4 - C3 - C4	117.3(8)

[a] Estimated standard deviations are given in parentheses.

the structure of the dppe(CuO_2CCH_3)$_2$ complex, along with the atomic labelling scheme. The complex is an infinite chain of copper(I) dimers. In each dimer the two copper centers of the dimer are bound to one another through a longer Cu-O bond forming a subunit of the polymeric chain (Figure 2).

Decarboxylation of Cyanoacetic Acid

The dppe(CuO_2CCH_3)$_2$ complex was found to serve as a catalyst precursor for the decarboxylation of cyanoacetic acid (eq. 2). This is to be anticipated since we have previously shown that copper(I) acetate, upon the *in situ* addition of a variety of amine and phosphine ligands to the reaction mixture, readily catalyzes the decarboxylation of selected carboxylic acids under mild reaction conditions.[2] Acetonitrile and carbon dioxide were the only reaction products as determined by FTIR and GC-MS spectroscopies.[7] These reactions were established to be first-order in copper complex and zero-order in acid concentrations.[2] The zero-order depen-

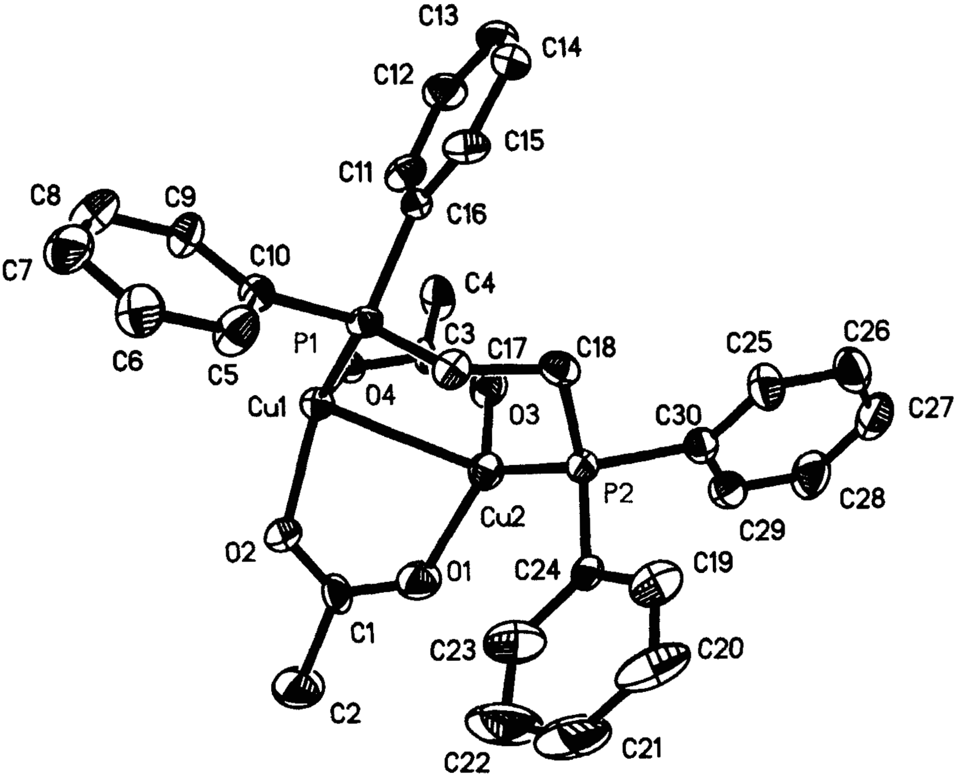


Figure 1 Molecular structure of dppe$(CuO_2CCH_3)_2$ with thermal ellipsoids drawn at the 50% probability level

dence in [acid] is depicted for the decarboxylation reaction investigated herein in Figure 3. In the presence of dppe$(CuO_2CCH_3)_2$ as catalyst the rate constant for decarboxylation of cyanoacetic acid was determined to be 1.07×10^{-2} sec^{-1} @ 65°C in ethylene glycol dimethylether (DME).

$$NCCH_2COOH \xrightarrow{[cat]} CH_3CN + CO_2 \tag{2}$$

DISCUSSION

The air-sensitive product resulting from the one-to-one reaction of copper(I) acetate and dppe in dichloromethane has been isolated in crystalline form and structurally characterized. The dmpe and dppp derivatives likewise have been isolated, however the exact nature of these complexes remains in question. It is likely based on infrared evidence, that these complexes possess a unidentate acetate and are dimers bridged by the phosphine ligand.

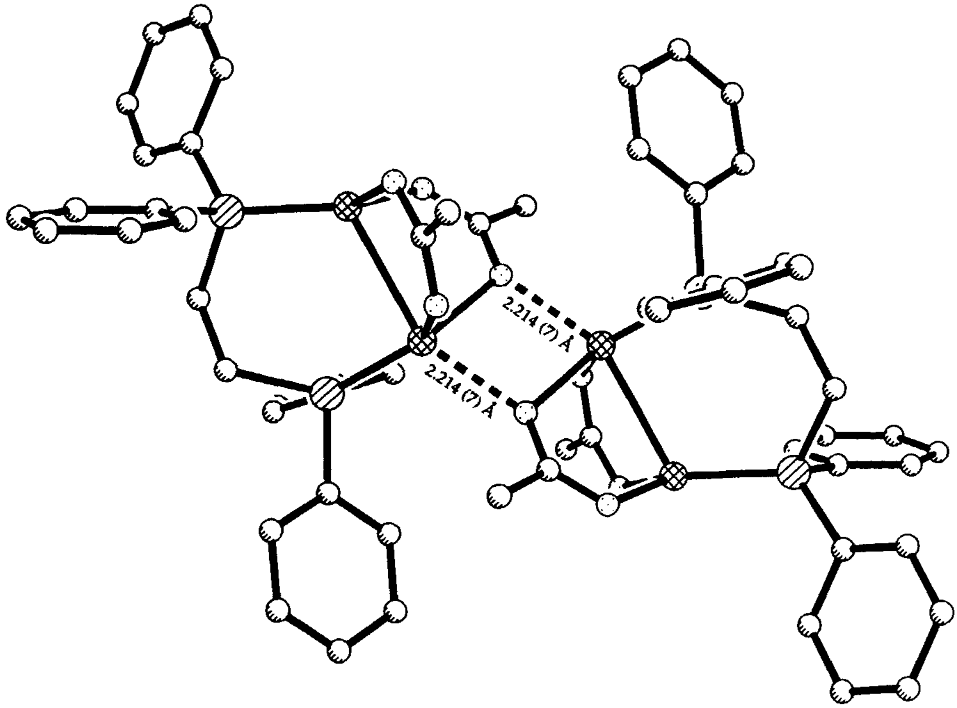


Figure 2 Ball - and - stick representation of dppe((CuO$_2$CCH$_3$)$_2$ indicating the intermolecular interaction between dimer units.

The complex, dppe(CuO$_2$CCH$_3$)$_2$ is a polymeric chain in which two neighboring copper atoms are bridged by a dppe and two acetate ligands. The structure is essentially a distortion of the planar copper(I) acetate structure previously reported.[8,9] This Cu-O bond (2.214 (7) Å) is longer than the Cu-O bonds (avg. 2.034 (6) Å) within the dimer. The dppe ligand bridges the copper(I) atoms resulting in a decrease in the O-Cu-O angle from 180° to 103.3 (2)°. The Cu-Cu distance (2.712 (2) Å) is longer than that found in copper(I) acetate (Cu-Cu 2.556 (2) Å), thus indicating less of a Cu-Cu interaction in the dppe complex. The geometry about the copper centers is a distorted trigonal bypyramid with the two oxygen atoms and phosphorus forming the trigonal plane, where the bond angles are 129.9(2)° P1-Cu1-O2, 122.8 (2)° P1-Cu1-O4, and 103.3 (2)° O2-Cu1-O4. The remaining coordination sphere about CuI is occupied by a carboxylate oxygen atom (O4A) of the neighboring dimer along with the second copper atom of the dimer (Cu2). The Cu1-Cu2-O4A angle, at 153.7(1)°, deviates significantly from linearity.

During prolonged periods of attempted recrystallization from dichloromethane, bidentate phosphine complexes of copper(I) acetate were found to undergo reaction with the solvent to afford copper(I) chloride derivatives with concomitant displacement of the acetate ligands. Two different chloride structures resulted from these presumably radical processes and were characterized crystallographically; one with

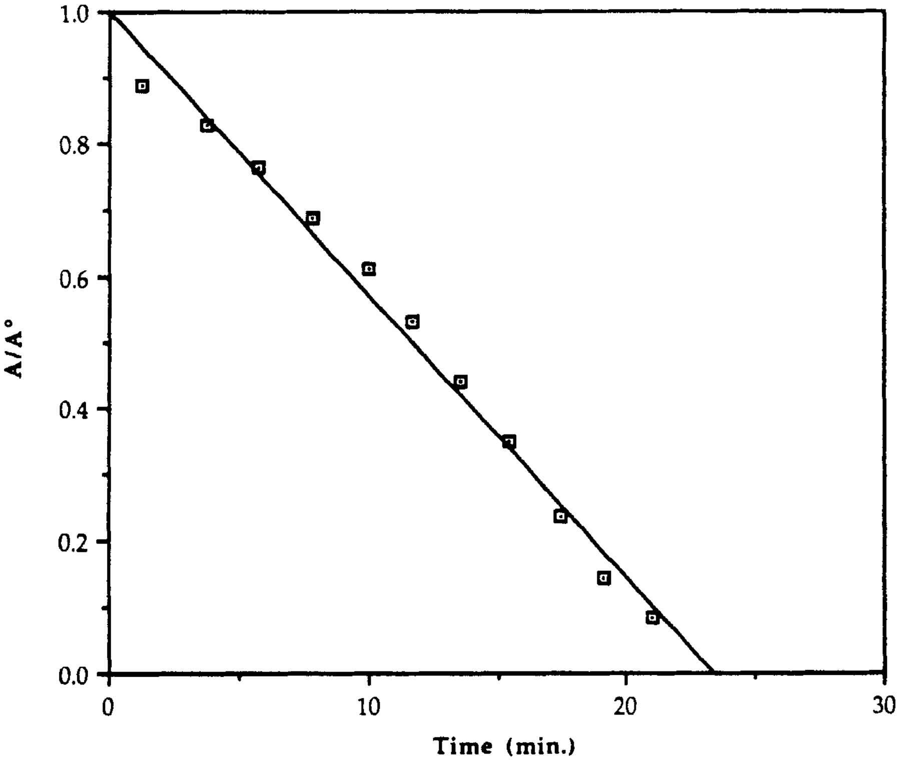
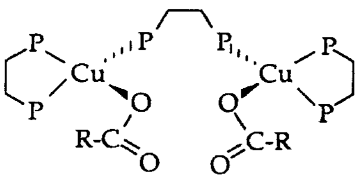


Figure 3 Decarboxylation of cyanoacetic acid (0.09 M) in DME in the presence of 0.006 M dppe $(CuO_2CCH_3)_2$ at 65°C illustrating the zero-order dependence on [acid].

dmpe (2) and one with dppe (3) as the phosphine ligand. Species 3 is a dimer that has been reported previously.[10] The structure of the dmpe copper(I) chloride complex has been reported by our group elsewhere.[11] The dmpe complex (2) is a polymeric chain, and although it is quite similar to a recently reported copper(I) complex with dmpe ligands,[12] its structure demonstrates a novel arrangement of the dmpe ligand linking the copper(I)dimers.

The copper(I) acetate complexes with bidentate phosphine ligands reported herein demonstrate reactivity as catalyst precursors for the decarboxylation of $NCCH_2CO_2H$. Although these complexes are less reactive than the nitrogen-donor analogs,[2] it is proposed that the decarboxylation mechanism is the same for both systems where the nature of the ligands influence the copper(I)'s ability to promote the carboxylation reaction. As expected, electron-donating ligands are more effective.[13] The rate constant determined for the dppe derivative (1.07×10^{-2} sec^{-1} @ 65°C) is quite similar to that noted (9.40×10^{-3} sec^{-1} @ 65°C) when employing the well-characterized $[(Ph_3P)_2CuO_2CCH_2CN]_2$ dimer as catalyst.[3,14] Indeed, the addition of one equivalent of dppe to a dichloromethane solution of $Cu(I)O_2CCH_2CN$ results in the production of a white powder with $\nu(CO_2)$ frequencies at 1628 and 1383 cm^{-1}. These vibrations are analogous to those



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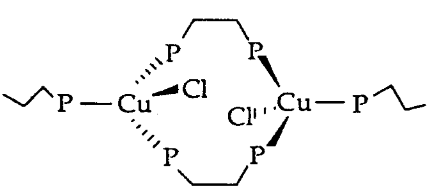

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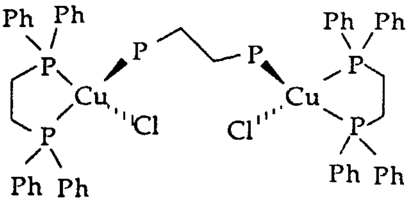

3

observed at 1609 and 1372 cm^{-1} in the PPh_3 derivative, and hence suggest a similar unidentate carboxylate dimeric structure to that observed both in solution and in the solid-state for the PPh_3 complex.[3]

In *summary* the stronger carboxylic acid, $NCCH_2COOH$, displaces the acetate ligand in the bis(phosphine)copper(I) acetate derivatives to afford $L_2CuO_2CCH_2CN$ derivatives. The nature of the ligands (L) influence the copper(I)'s ability to promote the decarboxylation reaction, with electron-donating ligands being more effective.[2]

Acknowledgements

Financial support of this research by the National Science Foundation (Grant 91-19737) and the Robert A. Welch Foundation is greatly appreciated.

Supplementary Material

Tables providing complete listings of bond lengths, bond angles, and anisotropic thermal parameters for complexes 1 and 2 (3 pages) are available upon request from the author.

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14. The rate constant for this latter process was interpolated from data contained in Table 1 of reference 3.