Inorg. Chem. **1995**, *34*, 2389−2398 **2389**

A More Intimate Examination of the Role of Copper(I) in the Decarboxylation of Derivatives of Malonic Acid. Comparisons with Zinc(II) Analogs

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

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

Received November 8, 1994⊗

The mechanism by which Cu(I) and Zn(II) influence the decarboxylation of malonic acid derivatives has been investigated comprehensively by means of structural and kinetic studies. The air-sensitive bis(phosphine)copper(I) complexes of phenylmalonic acid and its benzyl hemiester have been synthesized from 1 equiv of the acid and cuprous butyrate in the presence of phosphine ligands. As revealed by structural studies the copper(I) center is three-coordinate containing two phosphine ligands and a monodentately bound carboxylate group. On the other hand, soluble zinc(II) phenylmalonic acid and ester derivatives were prepared from $(HB(3\text{-}Phpz)_3)ZnO_2CCH_3$, $HB(3\text{-}Phpz)_3$ = tris(3-phenylpyrazolyl)hydroborate, and the corresponding malonic acid or hemiester. The Zn(II) complexes were all shown by X-ray crystallography to be four-coordinate with monodentately bound carboxylates. Kinetic evidence is presented herein which demonstrates that decarboxylation of malonic acid or hemiester derivatives in the presence of bis(phosphine)copper(I) or η^3-$HB(3\text{-}Phpz)_3Zn^{II}$ carboxylate salts occurs via a predissociation step involving metal−carboxylate bond rupture. Consistent with this mechanistic proposal, the rates of decarboxylation are greatly enhanced upon sequestering the metal cations with chelating nitrogen bases or upon replacing the Cu(I) or Zn(II) cations with a noninteracting counterion. Furthermore, because of the stronger Zn−O carboxylate bonds as compared with their Cu(I)−O analogs, the zinc carboxylates are more stable toward decarboxylation or $^{13}CO_2$ exchange processes. Indeed, the rates of these processes parallel the Zn−O bond lengths with the pyrazolylhydroborato complex, which has a shorter Zn−O bond distance than its triazacyclododecane analog, undergoing decarboxylation at a much slower rate. Crystal data for $(Ph_3P)_3CuO_2CC(C_2H_5)(C_6H_5)CO_2H$ (**1**): triclinic space group $P\bar{1}$, a = 11.631(5) Å, b = 12.206(4) Å, c = 20.000(6) Å, α = 85.91(3)°, β = 89.61(3)°, γ = 71.24(3)°, Z = 2, R = 4.20%. Crystal data for η^3-$HB(3\text{-}Phpz)_3ZnO_2CCH_2COOH$ (**2**): triclinic space group $P\bar{1}$, a = 11.935(3) Å, b = 12.227(4) Å, c = 12.643(5) Å, α = 77.56(3)°, β = 72.18(3)°, γ = 73.21(2)°, Z = 2, R = 7.00%. Crystal data for η^3-$HB(3\text{-}Phpz)_3ZnO_2CCH_2Ph$: triclinic space group $P\bar{1}$, a = 9.884((2) Å, b = 12.189(3) Å, c = 15.482(2) Å, α = 105.80(1)°, β = 92.46(1)°, γ = 90.94(2)°, Z = 2, R = 8.21%.

Introduction

Several carboxylic acids are known to decarboxylate in the presence of Cu(I) salts.[1] For example, malonic acid derivatives decarboxylate under mild conditions in the presence of Cu(I) salts.[2] The hypothesized mechanism involves a Cu(I) carboxylate derivative which loses CO_2 to form a Cu(I) alkyl intermediate, with subsequent protonation affording the substituted acetic acid (Scheme 1).[2,3] Because of our interest in CO_2 activation, we have investigated the Cu(I) systems which promote decarboxylation and CO_2 insertion reversibility.[3,4]

We have synthesized a variety of phosphine Cu(I) malonic acid derivatives and subjected them to decarboxylation kinetic studies.[3] In these initial kinetic studies, we determined that $(Ph_3P)_2Cu^I(O_2CCH(C_6H_5)CO_2H)$ decarboxylated via a first-order process to obtain the corresponding $(Ph_3P)_2Cu^I(O_2CCH(C_6H_5))$. Furthermore, we have found these phosphine Cu(I) carboxylates to be active catalysts for the decarboxylation of phenylmalonic acid. Kinetic studies indicated that phenylmalonic acid decarboxylated in the presence of a catalyst via a pathway first-order in [catalyst] and zero-order in [acid]. These results were consistent with earlier mechanisms which had been proposed by Toussaint et al.[2] Further evidence for Cu(I)'s role in the decarboxylation of malonic acid stemmed from the observation that the copper(I) phenylmalonate hemiester also decarboxylated under mild conditions, while the sodium phenylmalonate hemiester is stable toward decarboxylation.[5] However, we recently found evidence which minimizes Cu(I)'s role in the decarboxylation process.

Herein, we report the synthesis and structural characterization of several Cu(I) and Zn(II) complexes, namely, $(Ph_3P)_3Cu(O_2CC(C_2H_5)(C_6H_5)CO_2H)$, [tris-(3-phenylpyrazolyl)hydroborato]zinc(II) hydrogen malonate, and [(1,5,9-triazacyclododecane)Zn(acetate)][BPh_4]. These complexes are of importance in establishing a more definitive assessment of the mechanistic aspects of the decarboxylation of selected metal carboxylates and their subsequent role in catalyzing the decarboxylation of

---

⊗ Abstract published in *Advance ACS Abstracts,* April 1, 1995.

[1] (a) Shepard, A. F.; Winslow, N. R.; Johnson, J. R. *J. Am. Chem. Soc.* **1930**, *52*, 2083. (b) Leake, P. H. *Chem. Rev.* **1956**, *56*, 27 and references cited therein. (c) Fieser, L. F.; Fieser, M. *Organic Chemistry*, 3rd ed.; D. C. Heath and Co.: Boston, MA, 1956; p 549. (d) Cairncross, A.; Roland, J. R.; Henderson, R. M.; Sheppard, W. A. *J. Am. Chem. Soc.* **1970**, *92*, 3187. (e) Toussaint, O.; Capdevielle, P.; Maumy, M. *Tetrahedron Lett.* **1987**, *28*, 539. (f) Cohen, T.; Schambach, R. A. *J. Am. Chem. Soc.* **1970**, *92*, 3189. (g) Cohen, T.; Berninger, R. W.; Wood, J. T. *J. Org. Chem.* **1978**, *43*, 837. (h) Darensbourg, D. J.; Longridge, E. M.; Atnip, E. V.; Reibenspies, J. H. *Inorg. Chem.* **1992**, *31*, 3951.

[2] (a) Toussaint, O.; Capdevielle, P.; Maumy, M. *Synthesis* **1986**, 1029. (b) Toussaint, O.; Capdevielle, P.; Maumy, M. *Tetrahedron* **1984**, *40*, 3229.

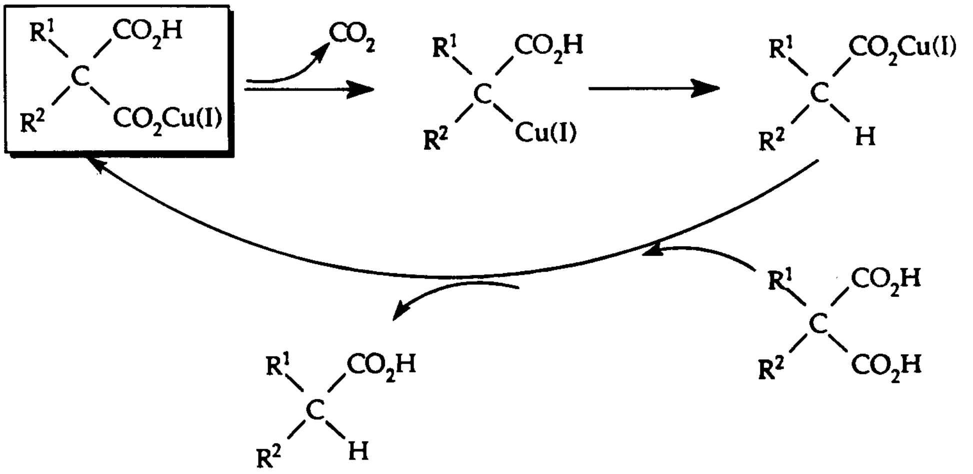
[3] Darensbourg, D. J.; Holtcamp, M. W.; Khandelwal, B.; Reibenspies, J. H. *Inorg. Chem.* **1993**, *33*, 531.

[4] (a) Darensbourg, D. J.; Longridge, E. M.; Holtcamp, M. W.; Klausmeyer, K. K.; Reibenspies, J. H. *J. Am. Chem. Soc.* **1993**, *115*, 8839. (b) Darensbourg, D. J.; Longridge, E. M.; Atnip, E. V.; Reibenspies, J. H. *Inorg. Chem.* **1991**, *30*, 357.

[5] Challis, B. C.; Kerr, S. H.; McDermott, I. R. *J. Chem. Soc., Perkin Trans. 2*, **1974**, *15*, 1829.

0020-1669/95/1334-2389\$09.00/0

Scheme 1



the corresponding organic acids. In particular, we will describe evidence which implicates a mechanism where dissociation of the carboxylate ligands in Cu(I) and Zn(II) carboxylates actually enhances the rate of decarboxylation of malonic acid derivatives. Furthermore, bases containing noninteracting cations, such as $[(C_2H_5)_4N][O_2CCH_2CO_2H]$ and $[Na(Kryptofix\text{-}221)][O_2CCH_2CO_2H]$ more effectively catalyze the decarboxylation of phenylmalonic acid when compared to the Cu(I) and Zn(II) catalysts.

Experimental Section

Methods and Materials. All manipulations were carried out under an inert atmosphere unless otherwise stated. The solvents were freshly distilled prior to use. Triphenylphosphine, tribenzylphosphine, tri-*o*-tolylphosphine, butyric anhydride, butyric acid, phenylmalonic acid, phenylacetic acid, cupric butyrate, and zinc acetate were purchased from Aldrich Chemical Co. and used as received. Ethylphenylmalonic acid and phenylmalonic acid monobenzyl ester were purchased from Lancaster Chemicals. 1,5,9-Triazacyclododecane ($[12]aneN_3$) was purchased from Fluka and was used as received. Kryptofix-221 was purchased from MC/B. Cuprous butyrate was prepared from the reduction of cupric butyrate by copper turnings in acetonitrile according to the published procedure.[6] Potassium hydrotris(3-phenylpyrazol-1-yl)borate was prepared according to the published procedure.[7] Infrared spectra were recorded on a Mattson 6021 spectrometer with DTGS and MCT detectors. ^1H NMR spectra were recorded on a Varian XL-200E superconducting high-resolution spectrometer. Elemental analyses were carried out by Galbraith Laboratories Inc.

Synthesis of $[(Ph_3P)_2CuO_2CC(C_6H_5)(C_2H_5)CO_2H]$. Cuprous butyrate (1.0 g), ethylphenylmalonic acid (0.47 g), and triphenylphosphine (0.87 g) were loaded into a 50 mL Schlenk flask. Diethyl ether (20 mL) was cannulated into the above mixture, and the resultant mixture was allowed to stir at room temperature for 3 h. The white precipitate formed was filtered off, washed with diethyl ether (30 mL), and dried under vacuum. The complex was recrystallized from dichloromethane, yielding 1.2 g (91%) of product. Anal. Calcd for $C_{47}H_{41}CuO_4P_2$: C, 70.44: H, 4.86. Found: C, 70.83; H, 4.69. IR (THF; $\nu(CO_2)$, cm^{-1}): 1734 (s), 1559 (s), 1395 (s). IR (KBr; $\nu(CO_2)$, cm^{-1}): 1722 (s), 1587 (w), 1379 (m).

Synthesis of $[(Ph_3P)_2CuO_2CCH(C_6H_5)(C_2H_5)]$. In a 25 mL Schlenk flask was placed $[(Ph_3P)_2CuO_2CC(C_6H_5)(C_2H_5)CO_2H]$ (0.4 g). Tetrahydrofuran (10 mL) was added to the flask via cannula, and the solution was heated to 55.4 °C. Total decarboxylation occurred within 1 h. The decarboxylation was monitored with infrared spectroscopy by following the disappearance of the free acid peak at 1732 cm^{-1}. After complete decarboxylation, the solution was cooled to room temperature and allowed to stand overnight, after which 0.32 g (85% yield) of complex was obtained. Anal. Calcd for $C_{46}H_{41}CuO_2P_2$: C, 73.54; H, 5.5. Found: C, 73.10; H, 5.46. IR (CH_2Cl_2; $\nu(CO_2)$, cm^{-1}): 1558 (s), 1395 (s).

Synthesis of $[(tri\text{-}o\text{-}tolylphosphine)Cu]_2(O_2CCH(C_6H_5)CO_2)$. Cuprous butyrate (0.3 g), phenylmalonic acid (0.5 g), and tri-*o*-tolylphosphine (1.21 g) were loaded into a 50 mL Schlenk flask. Diethyl ether (30 mL) was cannulated into the above mixture, and the solution was left to stir overnight. The white precipitate obtained was filtered off, washed with diethyl ether (30 mL), and dried under vacuum to yield a 0.8 g amount of fine white powder. Anal. Calcd for $C_{51}H_{48}Cu_2O_4P_2$: C, 67.02; H, 5.29. Found: C, 66.55; H, 5.87. IR (CH_2Cl_2; $\nu(CO_2)$, cm^{-1}): 1606 (s), 1416 (m). IR (KBr; $\nu(CO_2)$, cm^{-1}): 1603 (s), 1410 (m).

Synthesis of $[(Bz_3P)_2CuO_2CCH(C_6H_5)CO_2H]$. This complex was prepared in a manner analogous to that for the (triphenylphosphine)-cuprous malonate described earlier using cuprous butyrate (0.3 g), phenylmalonic acid (0.47 g), and tribenzylphosphine (1.21 g). A 1.44 g amount (84%) of product was obtained. Anal. Calcd for $C_{51}H_{49}CuO_4P_2$: C, 71.94; H, 5.8. Found: C, 71.40; H, 6.1. IR (THF; $\nu(CO_2)$, cm^{-1}): 1745 (s) 1601 (s), 1473 (m), 1454 (m). IR (KBr; $\nu(CO_2)$, cm^{-1}): 1738 (s), 1643 (s), 1601(s), 1452 (s), 1404 (s).

Synthesis of $(HB(3\text{-}Phpz)_3)ZnO_2CCH_3{\cdot}H_2O{\cdot}THF$. Potassium hydrotris(3-phenylpyrazol-1-yl)borate was prepared according to the published procedure. Zinc acetate (1.8 g) and $KHB(3\text{-}Phpz)_3$ (3.0 g) were placed in a 100 mL flask. Tetrahydrofuran (30 mL) was added, and the mixture was allowed to stir at room temperature for 2 h. Addition of water (40 mL) led to the precipitation of the product which was filtered off, washed with water (3 × 10 mL), hexane (3 × 10 mL), and dried under vacuum for two hours. A 3.28 g amount (91%) of compound was obtained. Anal. Calcd for $BC_{29}H_{25}N_6O_2Zn{\cdot}H_2O{\cdot}THF$: C, 60.43; H, 5.38. Found: C, 60.44; H, 4.99. IR (THF; $\nu(CO_2)$, cm^{-1}): 1606 (s), 1369 (m); $\nu(B{-}H)$ 2496 (w). IR (KBr; $\nu(CO_2)$, cm^{-1}): 1605 (s), 1395 (sh); $\nu(B{-}H)$ 2484 (w). ^1H NMR ($CDCl_3$): δ 1.60 [3H, s, {$Zn{-}O_2CCH_3$}], δ 1.86 [4H, br, {THF}], δ 3.76 [4H, br, {THF}], δ 6.45 [3H, d, {η^3-HB(3-Ph*Pz*)$_3$Zn}], δ 7.38 and 7.68 [15H, m, {η^3-HB(3-*Ph*Pz)$_3$Zn}], δ 7.80 [3H, d, {η^3-HB(3-Ph*Pz*)$_3$Zn}].

Synthesis of $[(HB(3\text{-}Phpz)_3)ZnO_2CCH_2COOH]{\cdot}H_2O$. Into a 50 mL flask were loaded $[(HB(3\text{-}Phpz)_3)ZnO_2CCH_3]$ (1.0 g) and malonic acid (0.23 g). Tetrahydrofuran (10 mL) was cannulated into the above mixture, and the resulting mixture was allowed to stir at room temperature for 2 h. Addition of hexane (20 mL) led to precipitation. The precipitate was filtered off, washed with water (2 × 10 mL) and then hexane (2 × 10 mL), and dried under vacuum for 2 h. A 0.92 g amount (85%) of white powder was obtained. Anal. Calcd for $BC_{30}H_{25}N_6O_4Zn{\cdot}H_2O{\cdot}THF$: C, 58.35; H, 5.04. Found: C, 57.91; H, 5.28. IR (THF; $\nu(CO_2)$, cm^{-1}): 1744 (s), 1605 (s), 1406 (s); $\nu(B{-}H)$ 2501 (w). IR (KBr; $\nu(CO_2)$, cm^{-1}): 1748 (s), 1603 (s), 1411 (s); $\nu(B{-}H)$ 2483 (s). ^1H NMR ($CDCl_3$): δ 1.86 [4H, br, {THF}], δ 3.8 [2H, br, {$Zn{-}O_2CCH_2CO_2H$}], δ 3.75 [4H, br, {THF}], δ 6.44 [3H, d, {η^3-HB(3-Ph*Pz*)$_3$Zn}], δ 7.2–7.6 [15H, m, {η^3-HB(3-*Ph*Pz)$_3$Zn}], δ 7.86 [3H, s, {η^3-HB(3-Ph*Pz*)$_3$Zn}].

---

(6) Edwards, D. A.; Richards, R. *J. Chem. Soc., Dalton Trans.* **1973**, 2463.

(7) Trofimenko, S.; Calabrese, J. C.; Thompson, J. S. *Inorg. Chem.* **1987**, *26*, 1507.

Synthesis of [(HB(3-Phpz)$_3$)ZnO$_2$CCHC$_6$H$_5$COOH]. Into a 50 mL flask were loaded [(HB(3-Phpz)$_3$)ZnO$_2$CCH$_3$] (1.0 g) and phenylmalonic acid (0.4 g). Tetrahydrofuran (10 mL) was cannulated into the above mixture, and the resulting mixture was allowed to stir at room temperature for 2 h. Addition of hexane (20 mL) led to precipitation. The precipitate was filtered off, washed with hexane (2 × 10 mL), and dried under vacuum overnight. A 1.134 g amount (94%) of white powder was obtained. Anal. Calcd for $BC_{36}H_{29}N_6O_4Zn$: C, 63.04; H, 4.26. Found: C, 63.28; H, 5.04. IR (THF; $\nu(CO_2)$, cm^{-1}): 1752 (s), 1601 (s); ν(B−H) 2485 (w). IR (KBr; $\nu(CO_2)$, cm^{-1}): 1746 (s), 1597 (s); ν(B−H) 2484 (w). ^{1}H NMR (CDCl$_3$): δ 4.01 [1H, s, {Zn−O$_2$CH(Ph)CO$_2$H}], δ 6.45 [3H, d, {η^3-HB(3-Ph*Pz*)$_3$Zn}], δ 7.16−7.51 [20H, m, {η^3-HB(3-*Ph*Pz)$_3$Zn}], δ 7.82 [3H,d, {η^3-HB(3-Ph*Pz*)$_3$Zn}]. Trace amounts of THF were observed at δ 1.86 and 3.76.

Synthesis of [(HB(3-Phpz)$_3$)ZnO$_2$CCH$_2$C$_6$H$_5$]. Method 1. [HB(3-Phpz)$_3$ZnO$_2$CCH$_3$] (0.5 g) and phenylacetic acid (0.143 g) were loaded into a 50 mL flask. Tetrahydrofuran (10 mL) was cannulated into the above mixture, and the resulting mixture was allowed to stir at room temperature for 2 h. Addition of hexane (20 mL) led to precipitation. The precipitate was filtered off, washed with water (3 × 10 mL) and then hexane (2 × 10 mL), and dried under vacuum for 2 h. A 0.42 g amount (74%) of white powder was obtained. Anal. Calcd for $BC_{35}H_{29}N_6O_2Zn{\cdot}H_2O{\cdot}THF$: C, 64.09; H, 5.38. Found C, 64.10; H, 5.21. IR (THF; $\nu(CO_2)$, cm^{-1}): 1610 (w), 1370 (sh); ν(B−H) 2496 (w). IR (KBr; $\nu(CO_2)$, cm^{-1}): 1611 (s), 1370 (sh); ν(B−H) 2484 (s). ^{1}H NMR (CDCl$_3$): δ 1.86 [4H, br, {*THF*}], δ 3.15 [2H, s, {Zn−O$_2$C*CH$_2$*(Ph)}], δ 3.76 [4H, br, {*THF*}], δ 6.43 [3H, s, {η^3-(3-Ph*Pz*)$_3$Zn}], δ 7.06−7.30 [20H, m, {η^3-(3-*Ph*Pz)$_3$Zn−O$_2$CCH$_2$(*Ph*)}], δ 7.78 [3H, s, {η^3-(3-Ph*Pz*)$_3$Zn}].

Method 2. [(HB(3-Phpz)$_3$)ZnO$_2$CCH$_2$C$_6$H$_5$] was also obtained by the decarboxylation of [(HB(3-Phpz)$_3$)ZnO$_2$CCHC$_6$H$_5$COOH] (0.4 g) at 55.4 °C in THF (10 mL). The decarboxylation was monitored by IR spectroscopy, following the complete disappearance of the ν(COOH) stretch at 1746 cm^{-1}. A 0.323 g (87%) amount of the product was isolated after the removal of the solvent under vacuum. IR (KBr; $\nu(CO_2)$, cm^{-1}): 1611 (s), 1370 (sh); ν(B−H) 2484 (s).

Synthesis of [Ph$_4$B][([12]aneN$_3$)ZnO$_2$CCH$_3$]. 1, 5, 9-Triazacyclododecane (0.1 g) and zinc acetate (0.11 g) were loaded into a 50 mL flask. Ethanol (50 mL) was added to the above mixture; sodium tetraphenylborate (0.2 g) in tetrahydrofuran (10 mL) was then added dropwise from a dropping funnel over a period of 30 min. After the solution was left to stir overnight, it was filtered through Celite and the volume of the solvent was reduced under vacuum. Diethyl ether (50 mL) was added to the solution for complete precipitation. The product was filtered off, washed with diethyl ether (2 × 10 mL), and dried under vacuum. A 0.29 g amount (80%) of compound was obtained. Anal. Calcd for $BC_{35}H_{44}N_3O_2Zn{\cdot}H_2O$: C, 66.53; H, 7.33. Found: C, 65.53; H, 7.21. IR (THF; $\nu(CO_2)$, cm^{-1}): 1582 (s), 1393 (s). IR (KBr; $\nu(CO_2)$, cm^{-1}): 1583 (s), 1402 (s).

Synthesis of (neocuproine)$_2$CuO$_2$CCH$_2$CH$_2$CH$_3$. Cuprous butyrate (1.0 g) and neocuproine (2.76 g) were loaded into a 50 mL flask. Benzene (30 mL) was transferred into the flask, and the reaction mixture was left to stir at room temperature for 6 days. The red precipitate obtained was filtered off, washed with diethyl ether (2 × 20 mL), and dried under vacuum. A 3.75 g amount (99.7%) of product was collected. IR (KBr; $\nu(CO_2)$, cm^{-1}): 1586 (sh) 1564 (s), 1410 (w). Note: An infrared KBr spectrum of neocuproine revealed peaks at 1670, 1614, 1591, 1508, 1495, and 1423 cm^{-1}, making assignments of the carboxylate stretches extremely difficult.

Decarboxylation of the (Phosphine)copper(I) Malonate Derivatives. These reactions were carried out according to the published procedure.[4]

Catalytic Decarboxylation of Phenylmalonic Acid Using Tetraethylammonium Phenylmalonate. Phenylmalonic acid (0.210 g) and tetraethylammonium phenylmalonate (0.018 g) were weighed into two separate 25 mL flasks. Tetrahydrofuran (5 mL) was added to each flask. Both flasks were warmed to 55.4 °C with subsequent transfer of the acid solution via cannula into the catalyst-containing flask. Infrared spectra were obtained every 5−10 min. A plot of A/A_0 vs time was linear, indicating zero-order dependence in acid.

Kinetic data for other catalysts such as (neocuproine)copper(I) butyrate and bis(neocuproine)copper(I) butyrate were obtained in an analogous manner.

Table 1. Crystallographic Data for Complexes **1−3**

	1	**2**	**3**
empirical formula	$C_{65}H_{57}O_4P_3Cu$	$C_{34}H_{33}BN_6O_6Zn$	$C_{39}H_{37}BN_6O_3Zn$
fw,	1058.6	697.8	713.93
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
V, Å^3	2681(2)	1665.2(10)	1792.3(6)
Z	2	2	2
D_{calcd}, g/cm^3	1.311	1.392	1.323
a, Å	11.631(5)	11.935(3)	9.884(2)
b, Å	12.206(4)	12.227(4)	12.189(3)
c, Å	20.000(6)	12.643(5)	15.482(2)
α, deg	85.91(3)	77.56(3)	105.80(1)
β, deg	89.61(3)	72.18(3)	92.46(1)
γ, deg	71.24(3)	73.21(2)	90.94(2)
T, K	293	193	293(2)
μ(Mo Kα), mm^{-1}	1.793 (Cu Kα)	0.805	0.731
wavelength, Å	1.541 78	0.710 73	0.710 73
R_F, %[a]	4.2	7.0	8.21
R_{wF}, %[a]	5.2	7.9	18.97[b]

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

Decarboxylation of Phenylmalonate Benzyl Ester Using Zinc(II) Acetate and 1,10-Phenanthroline. Phenylmalonic acid benzyl ester (0.3232 g) and zinc acetate (0.011 g) were weighed into a 50 mL flask. In a separate flask was placed 1,10-phenanthroline (0.011 g). Tetrahydrofuran (5 mL) was added to each of the above flasks, and the solutions were equilibrated to 55.4 °C. The solutions were then mixed via cannula, and the decarboxylation was monitored by IR spectroscopy. Complete decarboxylation took 20 min.

Catalytic Decarboxylation of Phenylmalonate Benzyl Ester Using ([12]aneN$_3$)zinc(II) Acetate Tetraphenylborate. Phenylmalonate benzyl ester (0.0253 g) and (1,5,9-triazacyclododecane)zinc(II) acetate tetraphenylborate (0.0360 g) were loaded into two separate flasks. Tetrahydrofuran (5 mL) was added to each of the above flasks, and the solutions were equilibrated to 55.4 °C. The solutions were then mixed via cannula, and the decarboxylation was monitored by IR spectroscopy.

Kinetic rates for other catalysts such as [Et$_4$N][O$_2$CCH$_2$CO$_2$H] and bis(neocuproine)copper(I) butyrate were obtained in an analogous manner.

Decarboxylation of Zinc(II) Phenylmalonate Benzyl Ester in the Presence of 1,10-Phenanthroline. Zinc(II) acetylacetonate (0.5 g) and phenylmalonate monobenzyl ester (1.02 g) were loaded into a 50 mL flask. Tetrahydrofuran (10 mL) was cannulated into the above flask, and the reaction mixture was left to stir for 1 h. Addition of hexane (40 mL) at −78 °C to the above solution led to the precipitation of an oily product characterized as zinc(II) phenylmalonate benzyl ester. IR (THF; $\nu(CO_2)$, cm^{-1}): 1746 (s), 1645 (s), 1394(s)

Zinc(II) phenylmalonate benzyl ester.(0.5 g) and 1,10-phenanthroline (0.152 g) were placed in a 50 mL Schlenk flask. Tetrahydrofuran (10 mL) was added to the above mixture, and an immediate color change was observed from colorless to red which was followed by a concomitant formation of an air-sensitive yellow precipitate that was insoluble in all solvents. An IR spectrum indicates rapid decarboxylation. Anal. Found: C, 61.8; H, 4.29; N, 5.20. IR (KBr; $\nu(CO)_2$, cm^{-1}): 1737 (s), 1585 (w), 1516 (s), 1497 (m), 1427 (s), 1393 (sh), 1344 (sh).

^{13}CO$_2$ Exchange with Zinc(II) Phenylmalonate Benzyl Ester. Zinc(II) phenylmalonate benzyl ester (0.2 g) was loaded into a 25 mL Schlenk flask. Tetrahydrofuran (5 mL) was added into the above flask, and ^{13}CO$_2$ atmosphere was placed over the solution. The solution was maintained at 55.4 °C. The ^{13}CO$_2$ exchange rate data were collected by following the disappearance of the $\nu(CO_2)$ asymmetric stretch at 1645 cm^{-1} and simultaneous appearance of the $\nu(^{13}CO_2)$ infrared band at 1603 cm^{-1}.

X-ray Crystallographic Study of 1−3. Crystal data and details of the data collection are given in Table 1. A colorless needle of **1** was mounted in a capillary tube at room temperature, and a colorless crystal of **2** was mounted on a glass fiber with epoxy cement at room temperature and cooled to 193 K in a N$_2$ cold stream. Preliminary examination and data collection were performed on a Rigaku AFC5R X-ray diffractometer, for structures **1** and **3**, and on a Siemens R3m/V

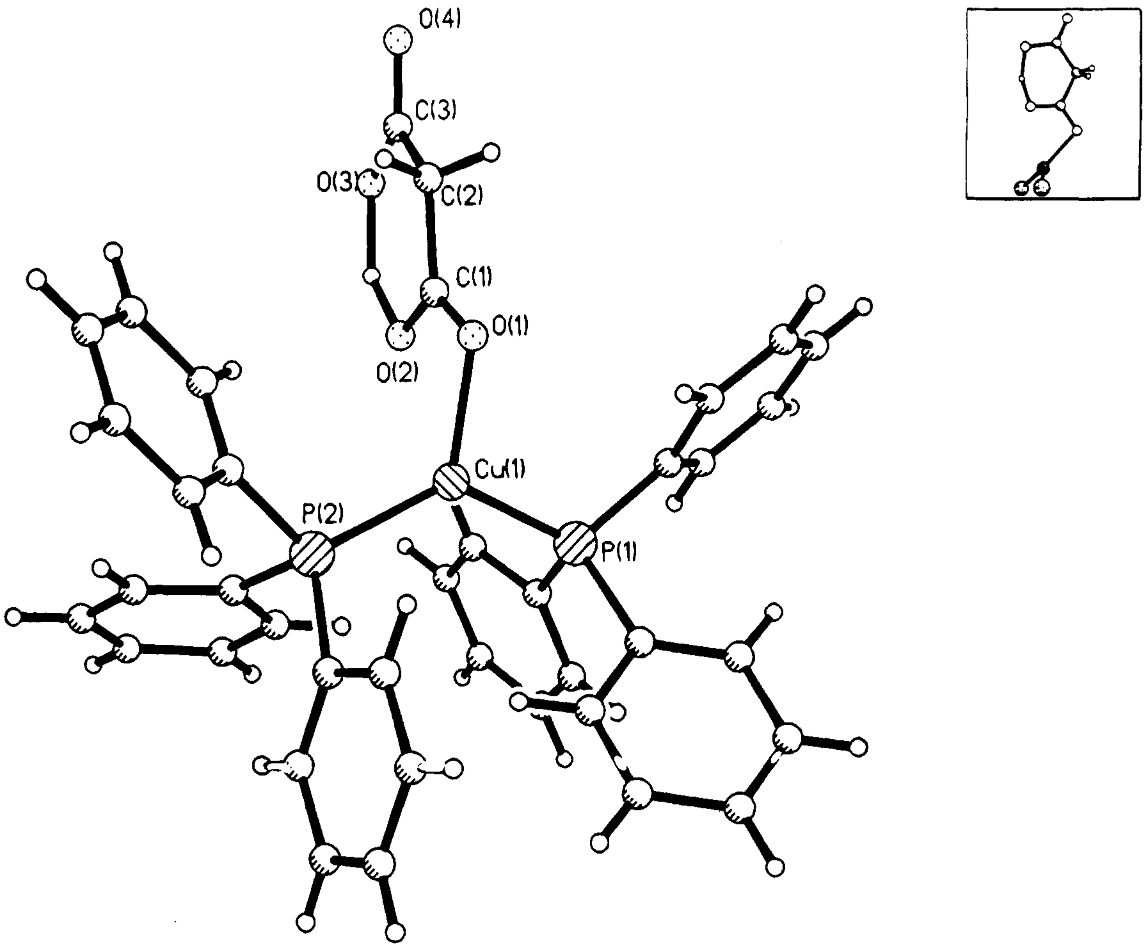


Figure 1. Ball-and-stick drawing of complex **4**, with insert depicting intramolecular hydrogen bonding (O···O = 2.500 Å).

X-ray diffractometer, for structure **2** (oriented graphite monochromator; Cu Kα λ = 1.541 78 Å radiation for **1** and Mo Kα λ = 0.710 73 Å radiation for **2** and **3**). Cell parameters were calculated from the least-squares fitting of the setting angles for 25 reflections (24 reflections for **2**). ω scans for several intense reflections indicated acceptable crystal quality. Data for **1** were collected for $5.0° \leq 2\theta \leq 120°$ [θ–2θ scans; $-13 \leq h \leq 12$, $-12 \leq k \leq 0$, $-22 \leq l \leq 22$] at 293 K. Scan width for the data collection for **1** was $(1.27 + 0.30 \tan \theta)°$, with a fixed scan rate of 16.00° min^{-1}. The weak reflections were rescanned (maximum of two rescans) and the counts for each scan accumulated. Data for **2** were collected for $4.0° \leq 2\theta \leq 50.0°$ at 193 K. Data for **3** were collected for $4.0° \leq 2\theta \leq 50.0°$ at room temperature. Three control reflections, collected every 150 reflections for **1**, 97 reflections for **2**, and 150 reflections for **3**, showed no significant trends. Background measurements by stationary-crystal and stationary-counter techniques were taken at the beginning and end of each scan for half of the total scan time. Lorentz and polarization corrections were applied to 7517 reflections for **1**, 6158 reflections for **2**, and 6681 reflections for **3**. A semiempirical absorption correction was applied (ellipsoid approximation; $\mu r = 0.00$; $T_{\max} = 0.9999$, $T_{\min} = 0.8705$ for **1**, $\mu r = 0.10$; $T_{\max} = 0.9428$, $T_{\min} = 0.8098$ for **2**; $T_{\max} = 0.9999$, $T_{\min} = 0.8937$ for **3**). A total of 5679 unique reflections for **1**, 2347 for **2**, and 6359 for **3** with $|I| \geq 2.0\sigma(I)$ for **1** and $|I| \geq 3.0\sigma(I)$ for **2** were used in further calculations. Structures **1** and **2** were solved by Direct Methods, and structure **3** was solved by XS [SHELXS, SHELXTL-PLUS program package, Sheldrick (1990) for **1** and **2**; SHELXL-93, Sheldrick (1993) for **3**]. Full-matrix least-squares anistropic refinement for all non-hydrogen atoms yielded $R(F) = 0.042$, $R_w(F) = 0.052$, and $S(F) = 1.72$ for **1**, $R(F) = 0.070$, $R_w(F) = 0.079$, and $S(F) = 1.45$ for **2**, and $R(F)[I > 2\sigma(I)] = 0.082$, $R_w(F^2)[I > 2\sigma(I)] = 0.1897$, and $S(F) = 1$ for **3** at convergence. Hydrogen atoms were placed in idealized positions with isotropic thermal parameters fixed at 0.08 Å^2. Neutral atom scattering factors and anomalous scattering correction terms were taken from the *International Tables for X-ray Crystallography*.

Results

We have previously reported the synthesis of several bis(phosphine)copper(I) malonate derivatives from the reaction of malonic acid and cuprous butyrate in the presence of 2 equiv of phosphine ligand.[3] Equation 1 describes the preparation of

$$\text{copper(I) butyrate} + HOOCCH_2COOH + 2Ph_3P \rightarrow \underset{\mathbf{4}}{(Ph_3P)_2CuO_2CCH_2COOH} + \text{butyric acid} \quad (1)$$

the triphenylphosphine malonate complex, $(Ph_3P)_2CuO_2CCH_2COOH$, **4**, which has been characterized both in solution and in the solid state. A ball-and-stick drawing of this molecule is shown in Figure 1, where the copper(I) center is three-coordinate composed of two phosphine ligands and a monodentate carboxylate ligand. The appended carboxylic acid forms a strong intramolecular hydrogen bond with the distal oxygen atom of the carboxylate group monodentately bound to copper.

In the course of the present investigation we were able to crystallize a tris(triphenylphosphine)copper(I) derivative of ethylphenylmalonic acid, which we include herein for comparison purposes. Crystals of $(Ph_3P)_3Cu(O_2CC(C_2H_5)(C_6H_5)CO_2H)$, **1**, were obtained by slow diffusion of diethyl ether into a solution of $(Ph_3P)_2Cu(O_2CC(C_2H_5)(C_6H_5)CO_2H)$ and 1 equiv of triphenylphosphine. Selected interatomic distances and angles are given in Table 2. The structure of complex **1** is depicted in Figure 2. In most cases, recrystallization of tris(phosphine)copper(I) carboxylates results in the isolation of the bis(phosphine) species. Therefore, it was unexpected to isolate complex **1** in the solid state. Although others have previously synthesized a number of tris(phosphine)copper(I) carboxylates,

Table 2. Selected Bond Lengths (Å)[a] and Bond Angles (deg)[a] for **1**

Cu(1)−P(1)	2.320(1)	Cu(1)−P(2)	2.364(2)
Cu(1)−P(3)	2.321(2)	Cu(1)−O(1)	2.115(3)
O(2)−C(1)	1.246(6)	O(1)−C(1)	1.246(4)
O(4)−C(3)	1.210(7)	O(3)−C(3)	1.299(8)
C(2)−C(3)	1.547(6)	C(1)−C(2)	1.549(6)
C(2)−C(11)	1.523(6)	C(2)−C(4)	1.520(7)
C(6)−C(7)	1.379(9)	C(4)−C(5)	1.499(9)
		C(6)−C(11)	1.393(7)
P(1)−Cu(1)−P(2)	116.1(1)	P(1)−Cu(1)−P(3)	110.3(1)
P(2)−Cu(1)−P(3)	117.5(1)	P(1)−Cu(1)−O(1)	102.1(1)
P(2)−Cu(1)−O(1)	95.5(1)	P(3)−Cu(1)−O(1)	13.3(1)
Cu(1)−P(1)−C(17)	118.9(1)	Cu(1)−P(1)−C(23)	113.1(1)
Cu(1)−P(2)−C(35)	118.2(1)	Cu(1)−P(1)−C(29)	114.3(1)
Cu(1)−P(3)−C(52)	114.9(1)	Cu(1)−P(2)−C(41)	118.1(1)
Cu(1)−O(1)−C(1)	128.7(3)	Cu(1)−P(2)−C(47)	112.4(1)
O(1)−C(1)−C(2)	116.7(4)	Cu(1)−P(3)−C(58)	115.8(1)
C(1)−C(2)−C(3)	115.9(4)	Cu(1)−P(3)−C(64)	116.8(1)
C(3)−C(2)−C(4)	106.4(3)	O(1)−C(1)−O(2)	124.3(4)
C(3)−C(2)−C(11)	104.7(4)	O(2)−C(1)−C(2)	119.0(3)
O(3)−C(3)−O(4)	122.8(4)	C(1)−C(2)−C(4)	108.2(3)
O(4)−C(3)−C(2)	120.3(5)	C(1)−C(2)−C(11)	107.8(3)
		C(4)−C(2)−C(11)	114.0(4)
		O(3)−C(3)−C(2)	116.9(5)
		C(2)−C(4)−C(5)	113.7(5)

[a] Estimated standard deviations are given in parentheses.

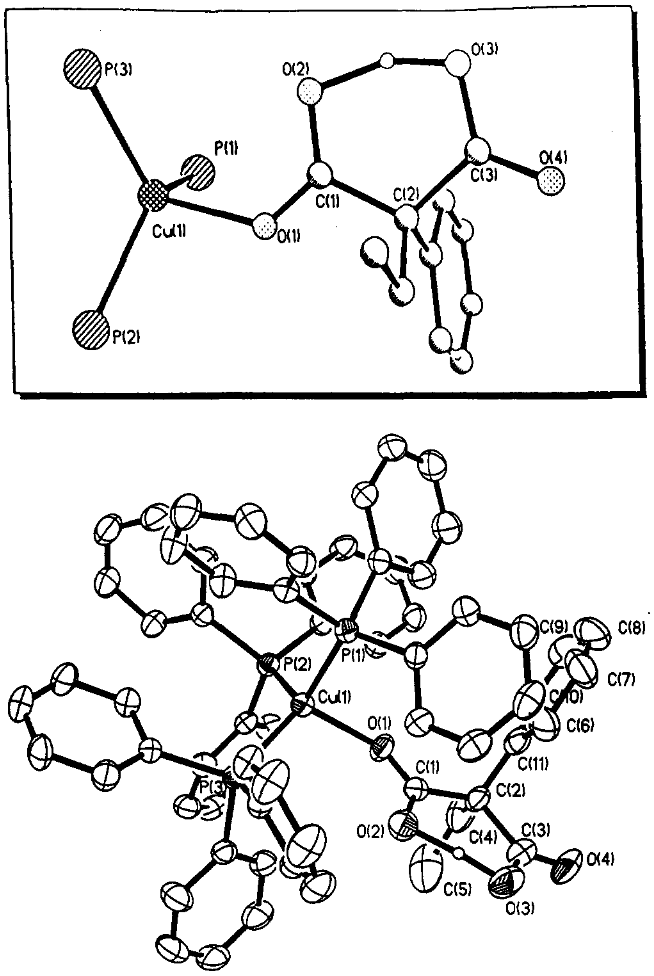


Figure 2. ORTEP drawing of complex **1** showing the atom-numbering scheme. Thermal elipsoids are drawn at the 50% probability level. Insert depicts coordination sphere around the copper(I) center, along with the intramolecular hydrogen-bonding motif.

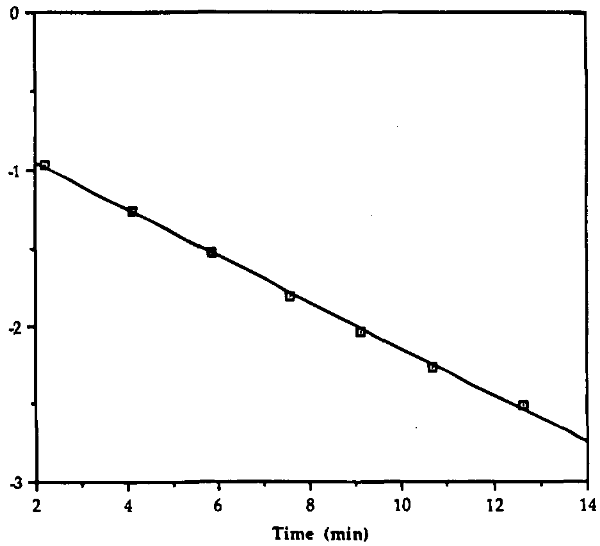


Figure 3. First-order dependence of CO_2 extrusion from $((C_6H_5CH_2)_3P)_2CuO_2CH(Ph)COOH$ in THF at 55.4 °C.

these complexes were found to dissociate one phosphine upon recrystallization.[8] To our knowledge, there are only two other X-ray structural characterizations of tris(phosphine)copper(I) carboxylates. Bianchini and co-workers isolated the dimeric cation containing a bridging formate between two $(Ph_3P)_3Cu$ units.[9] These same researchers have also obtained the structure of a monomeric tris(phosphine)copper(I) formate possessing a tripod phosphine ligand.[10] Complex **1** is distorted from an ideal geometry in which the phosphines are sterically hindered and open up closer to the hydrogen ethylphenylmalonate carboxylate. The hydrogen ethylphenylmalonate's acidic proton was hydrogen bonded *via* intramolecular hydrogen bonding as noted in Figure 2. Further evidence for intramolecular hydrogen bonding is the absence of intermolecular hydrogen bonding apparent from the long O(3)−O(4a) separation of 3.500 Å. We formerly observed similar intramolecular hydrogen bonding for bis(triphenylphosphine)copper(I) hydrogen malonate.[3]

We have previously reported preliminary kinetic data for the decarboxylation of a few (phosphine)copper(I) malonate complexes to afford the corresponding (phosphine)cuprous acetate derivatives (eq 2). The CO_2 extrusion was shown to occur *via*

$$(R_3P)_2CuO_2CC(R'R'')CO_2H \xrightarrow[THF]{\Delta} (R_3P)_2CuO_2CCH(R'R'') + CO_2 \qquad (2)$$

a process which was first-order in metal complex. Herein, we wish to describe a more comprehensive analysis of the mechanistic aspects of this decarboxylation process. A prototypical example of the rate data obtained from the monitoring of reaction 2 by infrared spectroscopy in the carboxylate region is depicted in Figure 3 for the $((C_6H_5CH_2)_3P)_2CuO_2CCH(C_6H_5)COOH$ derivative. The first-order rate constant for the decarboxylation process was calculated from the slope of the linear plot obtained for ln [complex] *vs* time.[11]

Table 3 lists the first-order rate constants for the decarboxylation of various phosphine derivatives of copper(I) malonate. A dramatic decrease in the rate constant (by a factor of 100) was observed upon changing the malonate derivative from

---

(8) Hammond, B.; Jardine, F. H.; Vohra, A. G. *J. Inorg. Nucl. Chem.* **1971**, 1017.

(9) Bianchini, C.; Ghilardi, C. A.; Meli, A.; Midollini, S.; Orlandini, A. Unpublished observations cited in ref 10b.

(10) (a) Bianchini, C.; Ghilardi, C. A.; Meli, A.; Midollini, S.; Orlandini, A. *J. Organomet. Chem.* **1983**, *248*, C13. (b) Bianchini, C.; Ghilardi, C. A.; Meli, A.; Midollini, S.; Orlandini, A. *Inorg. Chem.* **1985**, *24*, 924.

(11) The decrease in absorbance of the asymmetric carboxylate stretching frequency of the −COOH group, which is proportional to the [complex], was employed in observing the time dependence of these decarboxylation processes.

Table 3. Rate Constants for the Decarboxylation of Malonate Complexes[a]

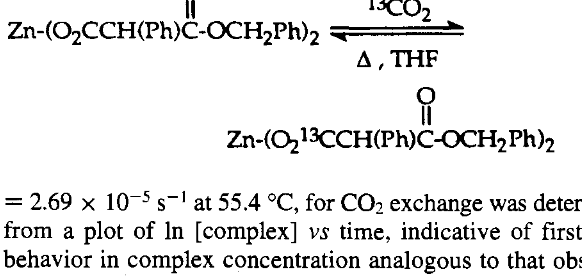
complex	$10^3k_{\rm obs}$ (s^{-1})[b]	pK_a of [H] [phosphine][c]	cone angle (deg)[c]
$(Ph_3P)_2Cu^I$(phenylmalonate)	3.75 (3.42)[d]	2.73	145
$(Bz_3P)_2Cu^I$(phenylmalonate)	2.49	6.0	165
$(Cy_3P)_2Cu^I$(phenylmalonate)	3.33	9.70	170
$(Ph_3P)_2Cu^I$(ethylphenylmalonate)	0.0378	2.73	145
$(Cy_3P)_2Cu^I$(ethylphenylmalonate)	0.0645	9.70	170

[a] Reactions were carried out in THF solutions at 55.4 °C. [b] The concentration of the complex was 0.0522 M. [c] pK_a and cone angles taken from: Rahman, M.; et al. *Organometallics* **1989**, *8*, 1 and references cited therein. [d] This experiment was repeated to provide the value in parentheses.

phenylmalonate to ethylphenylmalonate. For example, in the case of the bis(triphenylphosphine)copper(I) derivatives, the rate constants determined for the decarboxylation of the phenylmalonate and ethylphenylmalonate complexes were found to be 3.59×10^{-3} s^{-1} and 3.78×10^{-5} s^{-1} at 55.4 °C, respectively. That is, as expected an increase in basicity of the malonate anion leads to an increase in stability of the malonate toward decarboxylation. However, no trend in the rate of decarboxylation of the phenylmalonate derivatives was observed upon varying the nature of the phosphine ligand bound to the copper(I) center. Indeed, the rate constants did not change significantly as a function of the phosphine ligand. There was only a slight increase (by a factor of 1.7) in the rate of decarboxylation of the sterically more demanding ethylphenylmalonate ligand in proceeding from Ph_3P to the more basic and bulkier Cy_3P ligand.

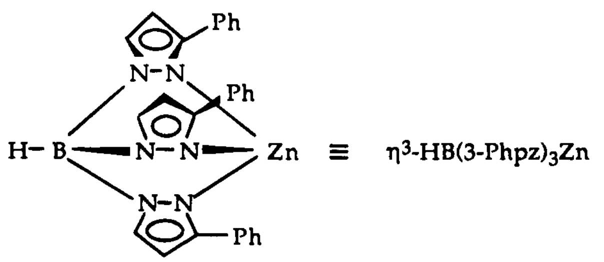
The decarboxylation of $(Ph_3P)_2CuO_2CCH(C_6H_5)CO_2H$ was examined over the concentration range 0.0253−0.0745M. This narrow concentration range of the copper(I) complex was defined by the accuracy of our infrared measurements. Nevertheless, over this confined concentration regime $k_{\rm obsd}$ for decarboxylation did not vary significantly $(2.82-3.59) \times 10^{-3}$ s^{-1} at 55.4 °C), nor were there notable changes in the nature of the infrared spectra in the carboxylate region. The above experiments were carried out in an effort to discern whether there was enhanced metal−carboxylate dissociation as [complex] was decreased. However, on the basis of these restricted concentration studies, no conclusion, other than the reaction is first-order in the concentration of the copper(I) complex, can be reached. More definitive data addressing this issue will be provided (*vide infra*).

In order to obtain additional information concerning the mechanistic aspects of the decarboxylation reaction (eq 2), we have varied the metal center from Cu(I) to the harder Zn(II) center. Zinc(II) acetate was unsuitable for the decarboxylation of phenylmalonic acid due to the formation of insoluble, most likely polymeric, zinc(II) phenylmalonate. However, zinc(II) phenylmalonate hemiester, which is soluble, was found to undergo exchange with $^{13}CO_2$ (eq 3). The rate constant, $k_{\rm obsd}$ = 2.69×10^{-5} s^{-1} at 55.4 °C, for CO_2 exchange was determined from a plot of ln [complex] *vs* time, indicative of first-order behavior in complex concentration analogous to that observed in the copper(I) system. However, the rate of CO_2 exchange was much slower than in the Cu(I) complexes.

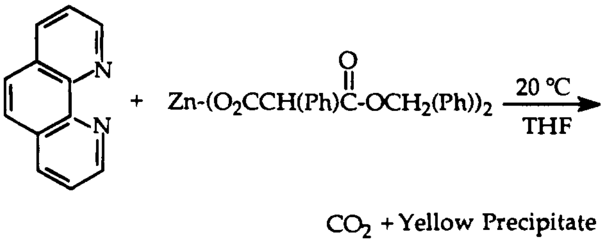


$$Zn\text{-}(O_2CCH(Ph)\overset{O}{\overset{\|}{C}}\text{-}OCH_2Ph)_2 \xrightleftharpoons[\Delta,\ THF]{^{13}CO_2} Zn\text{-}(O_2{}^{13}CCH(Ph)\overset{O}{\overset{\|}{C}}\text{-}OCH_2Ph)_2 \quad (3)$$

Chart 1



The addition of 1 equiv of 1,10-phenanthroline to a THF solution of $Zn(O_2CCH(Ph)C(O)OCH_2Ph)_2$ at ambient temperature resulted in the formation of a bright red solution, with concomitant decarboxylation of the zinc(II) phenylmalonate hemiester and formation of an insoluble yellow precipitate (eq 4). The bright red color is indicative of the production of a transient (1,10-phenanthroline)zinc(II) alkyl complex.[12] Indeed, we observed that zinc(II) acetate in the presence of 1,10-phenanthroline serves as an effective catalyst for the decarboxylation of phenylmalonic acid benzyl ester to afford the corresponding phenylacetate ester. A rate constant of 1.7×10^{-2} s^{-1} at 55.4 °C was obtained from the zero-order plot of acid disappearance as a function of time.



(4)

As a means of obtaining a more soluble Zn(II) catalytic system for study, we synthesized the tris(3-phenylpyrazolyl)-hydroborate derivative of zinc(II) malonate. A schematic representation of the tris(pyrazolyl)hydroborato ligand employed in this investigation is shown in Chart 1. (η^3-HB(3-Phpz)$_3$)-zinc(II) hydrogen malonate, complex **2**, was synthesized from the corresponding zinc(II) acetate derivative and malonic acid. Crystals of **2**, suitable for X-ray structural analysis, were obtained from a concentrated THF solution of the complex layered with hexane and stored at −20 °C for several days. Selected interatomic distances and angles are given in Table 4. An ORTEP view of the molecule, along with the atomic numbering scheme, is displayed in Figure 4.

Complex **2** contains a monodentate bound carboxylate ligand as is evidenced by a Zn−O(1) bond distance of 1.883(9) Å and a Zn−O(2) separation of 2.900 Å. Formation of a monodentate malonate complex was apparent in THF solution as well on the basis of infrared spectroscopy, where the difference ($\Delta\nu(CO_2)$) between $\nu_{\rm asym}(CO_2)$ and $\nu_{\rm sym}(CO_2)$ was 191 cm^{-1} ($\Delta\nu(CO_2)$ = 198 cm^{-1} in KBr), which is diagnostic of η^1-coordination.[13] Complex **2** is slightly distorted from ideal tetrahedral geometry as noted by the N−Zn−O(1) angles, 116.7(4), 125.6(4), and 123.6(3)°. The N−Zn−N angles are somewhat closer to ideal tetrahedral angles, averaging 94.4[4]°. The molecular structure of this complex is similar to that of {η^3-HB(3-Bu^{t}pz)$_3$}zinc acetate, which was characterized in Parkin's laboratory.[14] A related nitrato complex containing the η^3-bound

---

(12) (a) Rau, H.; Thiele, K. H. *Z. Anorg. Allg. Chem.* **1967**, *335*, 253. (b) Noltes, J. G.; Boersma, J. *J. Organomet. Chem.* **1967**, *9*, 1. (c) Noltes, J. G.; Van Den Hurk, J. W. G. *J. Organomet. Chem.* **1965**, *3*, 222.

(13) Deacon, G. B.; Phillips, R. J. *Coord. Chem. Rev.* **1980**, *33*, 227.

(14) Han. R.; Gorell, I. B.; Looney, A. G.; Parkin, G. *J. Chem. Soc., Chem. Commun.* **1991**, 717.

Table 4. Selected Bond Lengths (Å)[a] and Bond Angles (deg)[a] for **2**

Zn(1)−O(1)	1.883(9)	Zn(1)−N(2)	2.062(9)
Zn(1)−N(4)	2.028(8)	Zn(1)−N(6)	2.02(1)
O(1)−C(28)	1.31(1)	O(2)−C(28)	1.23(1)
O(3)−C(30)	1.18(1)	O(4)−C(30)	1.33(1)
C(26)−C(27)	1.38(1)	C(28)−C(29)	1.48(1)
C(29)−C(30)	1.53(1)	C(31)−C(32)	1.29(1)
C(31)−C(32A)	2.03(1)	C(32)−O(5A)	1.42(1)
O(1)−Zn(1)−N(2)	116.7(4)	O(1)−Zn(1)−N(4)	125.6(4)
N(2)−Zn(1)−N(4)	94.3(3)	O(1)−Zn(1)−N(6)	123.6(3)
N(2)−Zn(1)−N(6)	93.3(4)	N(4)−Zn(1)−N(6)	95.5(4)
Zn(1)−O(1)−C(28)	117.5(8)	Zn(1)−N(2)−C(3)	142.7(9)
Zn(1)−N(2)−N(1)	108.6(6)	N(4)−N(3)−B(1)	119.2(9)
N(1)−N(2)−C(3)	108.6(9)	B(1)−N(3)−C(4)	130.(1)
N(4)−N(3)−C(4)	110.(1)	Zn(1)−N(4)−C(6)	141.0(9)
Zn(1)−N(4)−N(3)	111.9(7)	N(6)−N(5)−B(1)	120.(1)
N(3)−N(4)−C(6)	106.0(9)	B(1)−N(5)−C(7)	128.(1)
N(6)−N(5)−C(7)	112.1(8)	Zn(1)−N(6)−C(9)	142.8(9)
Zn(1)−N(6)−N(5)	112.4(6)	N(1)−B(1)−N(3)	109.(1)
N(5)−N(6)−C(9)	105.(1)	N(3)−B(1)−N(5)	107.8(9)
N(1)−B(1)−N(5)	110.2(8)	O(1)−C(28)−O(2)	122(1)
C(22)−C(27)−C(26)	119.(1)	O(2)−C(28)−C(29)	124(1)
O(1)−C(28)−C(29)	114(1)	O(3)−C(30)−O(4)	122(1)
C(28)−C(29)−C(30)	118(1)	O(4)−C(30)−C(29)	114(1)
O(3)−C(30)−C(29)	124(1)		

[a] Estimated standard deviations are given in parentheses.

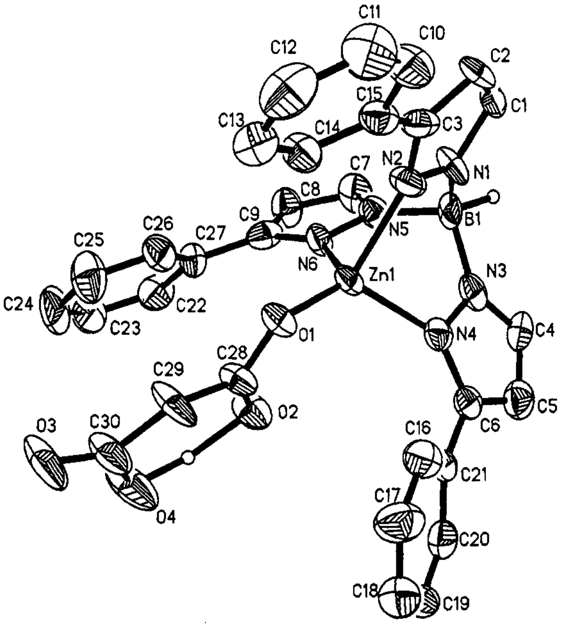


Figure 4. ORTEP drawing of complex **2** showing the atom-numbering scheme. Thermal ellipsoids are drawn at the 50% probability level.

HB(3-Phpz)$_3$ ligand was structurally characterized by the Vahrenkamp group and found to contain a nitrato ligand whose coordination was intermediate between monodentate and bidentate (Zn−O bond distances are 1.95 and 2.47 Å).[15] Hence, it is interesting that the two carboxylate complexes are monodentate regardless of the steric requirements of the pyrazolyl hydroborate ligand.

More important to our studies, however, is the observation that the Zn−O bond is short compared to those found in other Zn carboxylate structures.[14,16] The hydrogen malonate ligand was found to display intramolecular hydrogen bonding (O(2)−H−O(4) = 2.530 Å), analogous to the prevously reported copper(I) malonate complex.[3] Possible intermolecular hydrogen bonding was also observed in the crystal lattice as noted in the distance found between O(3a) and C(2b) of 3.291 Å.

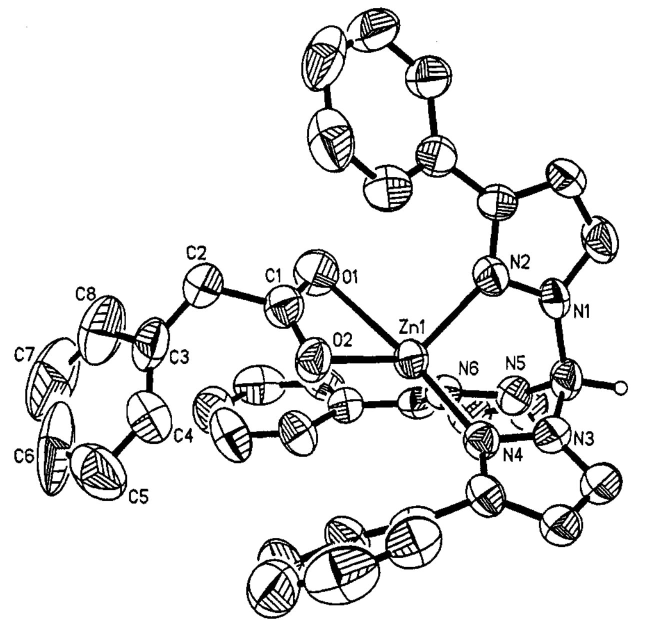


Figure 5. ORTEP drawing of complex **3** showing the atom-numbering scheme. Thermal ellipsoids are drawn at the 50% probability level.

The phenylmalonate derivative of complex **2** decarboxylates in THF solution according to eq 5 to afford the corresponding

$$(\eta^3\text{-HB(3-Phpz)}_3)\text{ZnO}_2\text{CCH(Ph)COOH} \rightarrow \underset{\mathbf{3}}{(\eta^3\text{-HB(3-Phpz)}_3)\text{ZnO}_2\text{CCH}_2\text{Ph}} + \text{CO}_2 \quad (5)$$

zinc(II) phenylacetate, complex **3**. Crystals of **3** were obtained by storing a concentrated tetrahydrofuran solution of the complex layered with hexane at −11 °C for several days. An X-ray crystal structure determination revealed a coordination motif nearly identical to that of the nitrato complex prepared by Vahrenkamp's group and discussed earlier. Figure 5 depicts an ORTEP diagram of the molecular structure of **3**, along with atomic numbering scheme. Selected interatomic distances and angles are given in Table 5. Complex **3** was asymmetrically chelated by the carboxylate ligand as seen by the two Zn−O bond distances of 1.941(5) and 2.439(6) Å. Both solution and solid-state infrared data support a monodentately bound or a very asymmetrically chelated carboxylate as noted by the large differences between $\nu_{\text{asym}}(\text{CO}_2)$ and $\nu_{\text{sym}}(\text{CO}_2)$ ($\Delta\nu$ = 241 and 229 cm^{-1}).

The decarboxylation reaction for (η^3-HB(3-Phpz)$_3$)zinc(II) hydrogen phenylmalonate described in eq 5 was observed to proceed *via* a first-order process with $k_{\text{obsd}} = 6.40 \times 10^{-4}$ s^{-1} at 55.4 °C. This rate constant is significantly smaller than that found for any of the bis(phosphine) derivatives of copper(I) hydrogen phenylmalonate, where k_{obsd} values span a range of (2.49−3.59) × 10^{-3} s^{-1} at 55.4 °C. This reduced rate of carbon dioxide extrusion in the case of Zn(II) emphasized the need to obtain other zinc(II) complexes with different structural parameters. In this regard, we turned our attention to the neutral tridentate ligand 1,5,9-triazacyclododecane ([12]aneN$_3$) as a suitable alternative to the pyrazolylborate grouping. For

---

(15) Alsfasser, R.; Powell, A. K.; Vahrenkamp, H. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 898.

(16) (a) Liles, D. C.; McPartlin, M.; Tasker, P. A. *J. Am. Chem. Soc.* **1977**, *99*, 7704. (b) Kirchner, C.; Krebs, B. *Inorg. Chem.* **1987**, *26*, 3569. (c) Ahlgren, M.; Turpeinen, U.; Hamalainen, R. *Acta Chem. Scand. A* **1982**, *36*, 841. (d) Chaudhuri, P.; Stockeim, C.; Wieghardt, K.; Deck, W.; Gregorzik, R.; Vahrenkamp, H.; Nuber, B.; Weiss, J. *Inorg. Chem.* **1992**, *31*, 1451. (e) Darensbourg, D. J.; Holtcamp, M. W.; Longridge, E. M.; Khandelwal, B.; Klausmeyer, K. K.; Reibenspies, J. H. *J. Am. Chem. Soc.* **1995**, *117*, 318.

Table 5. Selected Bond Lengths (Å)[a] and Bond Angles (deg)[a] for **3**

Zn(1)−O(2)	1.941(5)	Zn(1)−N(6)	2.030(7)
Zn(1)−N(2)	2.074(7)	Zn(1)−N(4)	2.079(7)
Zn(1)−O(1)	2.439(6)	Zn(1)−C(1)	2.499(9)
O(1)−C(1)	1.223(10)	O(2)−C(1)	1.254(10)
C(1)−C(2)	1.525(12)	C(2)−C(3)	1.469(14)
O(2)−Zn(1)−N(6)	132.5(3)	O(2)−Zn(1)−N(2)	125.0(3)
N(6)−Zn(1)−N(2)	96.1(3)	O(2)−Zn(1)−N(4)	110.1(3)
N(6)−Zn(1)−N(4)	90.4(3)	N(2)−Zn(1)−N(4)	90.1(3)
O(2)−Zn(1)−O(1)	58.2(2)	N(6)−Zn(1)−O(1)	100.1(3)
N(2)−Zn(1)−O(1)	94.7(3)	N(4)−Zn(1)−O(1)	167.8(2)
O(2)−Zn(1)−C(1)	29.5(3)	N(6)−Zn(1)−C(1)	119.1(3)
N(2)−Zn(1)−C(1)	111.6(3)	N(4)−Zn(1)−C(1)	139.5(3)
O(1)−Zn(1)−C(1)	28.7(2)	C(1)−O(1)−Zn(1)	78.4(6)
C(1)−O(2)−Zn(1)	100.7(5)	C(17)−N(6)−Zn(1)	139.4(6)
N(5)−N(6)−Zn(1)	112.6(5)	O(1)−C(1)−O(2)	122.7(9)
O(1)−C(1)−C(2)	119.4(9)	O(2)−C(1)−C(2)	118.0(9)
O(1)−C(1)−Zn(1)	72.9(5)	O(2)−C(1)−Zn(1)	49.7(4)
C(2)−C(1)−Zn(1)	167.6(8)	C(3)−C(2)−C(1)	113.0(8)

[a] Estimated standard deviations are given in parentheses.

example, it has been shown that the activity of a (η^3-[12]aneN_3)-Zn^{II} complex more closely resembled that of carbonic anhydrase for the decarboxylation of carbonic acid.[17,18] Furthermore, a review of the literature revealed that in general Zn(II) carboxylates containing neutral ligands have longer, and presumably weaker, Zn−O bonds.[14,16,19,20]

Using the neutral tridentate ligand, ([12]aneN_3), we have synthesized (η^3-[12]aneN_3)zinc(II) acetate tetraphenylborate, complex **5**, and have obtained crystals suitable for X-ray diffraction studies by the slow diffusion of ether into a dichloromethane solution of the complex at −11 °C. The solid-state structure of **5**, which has been deposited elsewhere,[21] revealed a complex which contained an acetate ligand that is intermediate between monodentate and bidentate. The acetate ligand is bonded asymmetrically to the zinc(II) center, with Zn−O(2) and Zn−O(1) bond distances of 1.990(5) and 2.413(6) Å, respectively. The solid-state and solution infrared spectra support this structure, where the $\nu_{asym}(CO_2)$ and $\nu_{sym}(CO_2)$ vibrations are observed at 1583 and 1402 cm^{-1} ($\Delta\nu = 181$ cm^{-1}). This $\Delta\nu$ value is significantly smaller than what is expected for a monodentately bound acetate ligand.[22] Indeed, the $\Delta\nu$ in Parkin's {η^3-HB(3-$Bu^tpz)_3$}Zn (OAc) complex is 300 cm^{-1}, where the sterically demanding tris(3-*tert*-butylpyrazolyl)-hydroborato ligand leads to a monodentately bound acetate ligand with disparate Zn−O distances of 1.859(6) and 2.90 Å.[14] The average Zn−N distance in complex **5** is 2.038 Å, whereas the corresponding distances in complexes **3** and {η^3-HB(3-$bu^tpz)_3$}Zn(OAc)[14] average 2.061 and 2.081 Å, respectively. Hence, the negatively charged pyrazolylhydroborato ligand has slightly longer Zn−N bond lengths than those seen in the neutral triazacyclododecane complex, which results in shorter Zn−O bond distances for the bound carboxylate ligand. Therefore, it would be expected that the carboxylate group in Zn(II) complexes containing the neutral 1,5,9-triazacyclododecane ligand would be more labile than those in the corresponding pyrazolylhydroborato complexes.

Table 6. Rates Constants as a Function of Catalyst for the Catalytic Decarboxylation of Phenylmalonic Acid Benzyl Ester[a]

catalyst	[cat.] (M)	[acid] (M)	10^2k_{obs} (s^{-1})
$[Et_4N][O_2CCH_2CO_2H]$			*b*
$[(TCDD)Zn(O_2CCH_3)][Ph_4B]$[c]	0.00585	0.062	1.0
1,10-phen/$Zn(O_2CCH_3)_2$	0.00600	0.12	1.7
$(Neocup)_2Cu^I$(butyrate)			*b*

[a] Reactions were carried out in THF solutions at 55.4 °C. [b] Rate constant was not determined due to extremely fast decarboxylation rate. [c] TCDD = 1,5,9-triazacyclododecane.

Table 7. Rate Constants as a Function of Catalyst for the Catalytic Decarboxylation of Phenylmalonic Acid[a]

catalyst	10^3[cat.] (M)	[acid] (M)	10^2k_{obs} (s^{-1})
$(PPh_3)_2Cu(O_2CCH(Ph)CO_2H)$[b]			0.4
$[Et_4N][O_2CCH_2CO_2H]$	1.64	0.370	4.06
$[Et_4N][O_2CCH_2CO_2H]$	1.79	0.125	5.96
$[Et_4N][O_2CCH_2CO_2H]$	2.68	0.125	6.56
$(Neocup)Cu^I$(butyrate)	1.80	0.125	2.8
$(Neocup)_2Cu^I$(butyrate)	1.76	0.125	8.8

[a] Reactions were carried out in THF solutions at 55.4 °C. [b] Information obtained from ref 3.

Indeed, ([12]aneN_3)zinc(II) acetate tetraphenylborate, **5**, was found to be an efficient catalyst for the decarboxylation of phenylmalonic acid benzyl ester. From the zero-order plot of the disappearance of the acid, a k_{obsd} of 1.0×10^{-2} s^{-1} at 55.4 °C was determined. This rate is several orders of magnitude faster than that found for the decarboxylation of $Zn(O_2CCH(Ph)C(O)OCH_2Ph)_2$ in the absence of 1,10-phenanthroline (eq 3). Table 6 contains comparable catalytic activities for the decarboxylation of phenylmalonic acid benzyl ester utilizing various catalysts. However, further kinetic studies employing complex **5** were inhibited due to the formation of insoluble precipitates which resulted upon the addition of phenylmalonic acid. In addition, **5** has been shown to be an efficient catalyst for the decarboxylation of cyanoacetic acid.[16e]

Because experiments suggest that carboxylate dissociation from the metal center enhances the decarboxylation process, we have investigated the use of salts of the half-neutralized malonic acid with noninteracting cations as possible catalysts for the decarboxylation of phenylmalonic acid. It should be noted that earlier studies showed the decarboxylation of the monosodium salt of phenylmalonic acid in DMSO at 55.4 °C occurred with a rate constant of $(4.8-7.0) \times 10^{-3}$ s^{-1} at 55.4 °C.[5] This is quite similar to results using well-characterized bis(phosphine) derivatives of copper(I); see Table 3. Surprisingly, these half-neutralized salts of malonic acid with noninteracting counterions, namely, $[(C_2H_5)_4N][O_2CCH_2COOH]$ and [Na−Kryptofix-221]$[O_2CCH_2COOH]$, catalytically decarboxylate phenylmalonic acid much faster than the Cu(I) and Zn(II) catalysts reported herein (Table 7). Analogous to those of the Cu(I) and Zn(II) systems, this process was found to be first-order in [catalyst] and zero-order in [acid].[23]

However, in the presence of a sequestering reagent, neocuproine, copper(I) butyrate is a very effective catalyst for the decarboxylation of phenylmalonic acid. For example, an enhanced rate of decarboxylation was observed when 2 equiv of neocuproine per Cu(I) was used compared to the addition of 1 equiv of neocuproine per Cu(I). 2 equiv of neocuproine

---

(17) Kimura, E.; Shiota, T.; Koike, T.; Shiro, M.; Kodama, M. *J. Am. Chem. Soc.* **1990**, *112*, 5805.

(18) Zhang, X.; van Eldik, R.; Koike, T.; Kimura, E. *Inorg. Chem.* **1993**, *32*, 5749.

(19) Looney, A.; Han, R.; McNeill, K.; Parkin, G. *J. Am. Chem. Soc.* **1993**, *115*, 4690.

(20) Han, R.; Looney, A.; McNeill, K.; Parkin, G.; Rheingold, A. L.; Haggerty, B. S. *J. Inorg. Biochem.* **1993**, *49*, 105.

(21) Reibenspies, J. H.; Holtcamp, M. W.; Khandelwal, B.; Darensbourg, D. J. *Z. Kristallogr.* **1995**, *210*, 148.

(22) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed.; Wiley: New York, 1986; pp 231−233.

(23) It should as well be noted that the monosodium salt of phenylmalonic acid was not investigated as a catalyst for the decarboxylation of phenylmalonic acid in ref 5. It was however reported that, at 55.4 °C in DMSO, phenylmalonic acid, in the absence of a catalyst, undergoes decarboxylation to phenylacetic acid and carbon dioxide with a first-order rate constant of 2.6×10^{-4} s^{-1}.

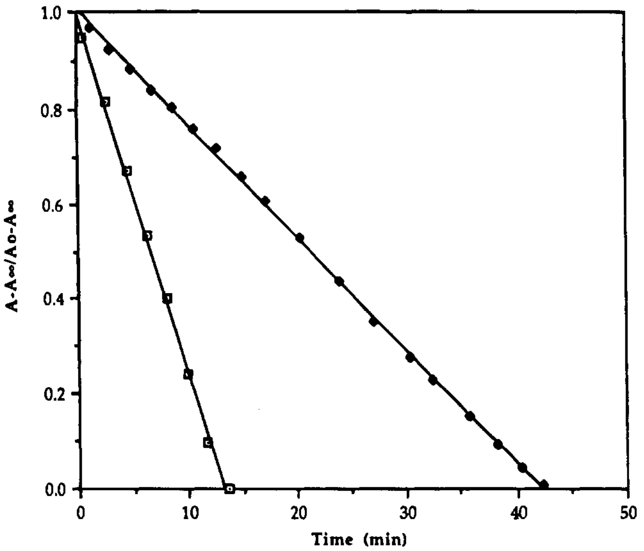
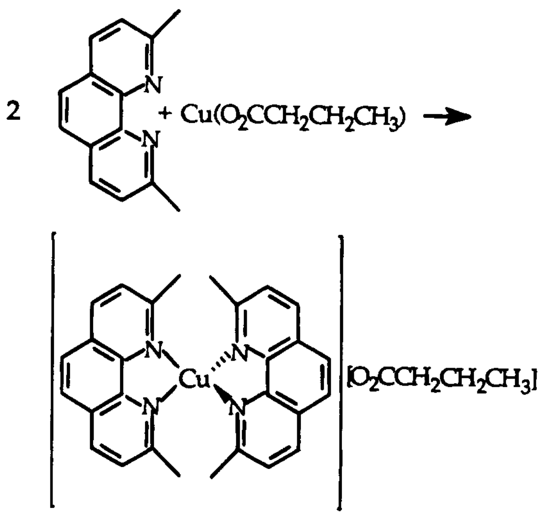


Figure 6. Zero-order dependence on [acid] for the catalytic decarboxylation of phenylmalonic acid in the presence of copper(I) butyrate in THF at 55.4 °C with (■) 1 equiv of neocuproine and (□) 2 equiv of neocuproine.

should totally complex the Cu(I) center, hence promoting complete dissociation of the carboxylate (eq 6). Indeed, the



(6)

rate constant at 55.4 °C determined upon the addition of 2 equiv of neocuproine ($k_{obs} = 8.8 \times 10^{-2}$ s^{-1}) was comparable to the rate constant obtained for salts of half-neutralized malonic acids and noninteracting cations ($k_{obs} = 6.5 \times 10^{-2}$ s^{-1}). Figure 6 portrays the different slopes of [acid] *vs* time obtained upon varying the amount of neocuproine added to copper(I) butyrate from 1 to 2 equiv for the same initial concentration of acid.

Discussion

Evidence presented herein intimates that decarboxylation of malonic acid derivatives in the presence of bis(phosphine)-copper(I) carboxylate complexes occurs *via* a predissociation step involving the copper(I) complex (Scheme 2). This is strongly supported by the observations that the rates of decarboxylation are greatly enhanced upon sequestering the Cu(I) cation with chelating nitrogen bases or upon replacing the Cu(I) cation with a noninteracting counterion. Hence, in polar solvents where these decarboxylation processes take place, it is proposed that a preequilibrium step affords a small quantity of the ion pair ($(R_3P)_2Cu^+/O_2CCH(Ph)CO_2H^-$), with the resulting free half-neutralized acid readily losing CO_2. This latter step is driven by the formation of carbanions stabilized by electron-withdrawing and/or resonance-stabilized substituents. Rate data indicate that the extent of dissociation of the carboxylate ligand from the copper(I) cation need only be about 5% in order to account for the kinetic behavior (see supplementary material). Consistent with this conclusion reached from kinetic measurements, no uncomplexed carboxylate ligand is observed in the $\nu(CO_2)$ region of the infrared spectra of these copper(I) salts in THF solution. At this point, it is important to recall that in our previous studies $(Cy_3P)_2CuO_2CCH(Ph)COOH$ was found not to undergo CO_2 extrusion in the less-polar methylene chloride solvent.[3]

Hence, the important deficiency in Scheme 1 which should be amplified on the basis of these studies is that the skeletal reaction depicted in eq 7 does not occur in a concerted manner.

$$CuO_2CR \rightleftharpoons CuR + CO_2 \qquad (7)$$

That is, CO_2 extrusion from the copper carboxylate with concomitant Cu−C bond formation does not take place as in the reverse process which has been **definitively** assessed for the group 6 zerovalent metal derivatives (Scheme 3).[24] In the latter instance, it has been demonstrated that carbon dioxide insertion occurs with a high degree of retention of configuration at the α-carbon atom, as indicated by the conversion of *threo*-$W(CO)_5CHDCHDPh^-$ with CO_2 to *threo*-$W(CO)_5O_2CCHDCHDPh^-$.[25] Nevertheless, it should be noted that in Scheme 2 when one starts with the copper(I) hemiester derivative, when there are no protons available for facile quenching of the carbanion formed upon decarboxylation, a metal−alkyl intermediate may result from recombination of the carbanion with the metal center. For example, during the decarboxylation of $Zn(O_2CCH(Ph)C(O)OCH_2Ph)_2$ in the presence 1,10-phenanthroline, a transient zinc−alkyl intermediate was observed. In addition, it is possible in some instances that the free or ion-paired carboxylate resulting from metal dissociation can interact with the electrophilic metal center to enhance the stability of the incipient carbanion, hence increasing the rate of decarboxylation, as was observed for the cyanoacetate group in the presence of copper(I) (*vide infra*).[4a,c]

The catalytic activity observed for various Zn(II) carboxylate complexes is in agreement with the mechanistic aspects of the decarboxylation process described in Scheme 2. That is, zinc(II) carboxylates are much poorer catalysts than their copper(I) analogs, consistent with Zn(II) being a harder acid than Cu(I), thus forming stronger M−O bonds. A comparison of the M−O bond lengths with the activity of the catalysts supports this hypothesis. Furthermore, by using the appropriate ligands, the M−O bond can be weakened, as seen with the ligands tris(3-phenylpyrazol-1-yl)hydroborate and 1,5,9-triazacyclododecane in the Zn(II) complexes. We have shown that complexes which have weaker metal carboxylate interactions result in enhanced catalytic activity for the decarboxylation of carboxylic acids.

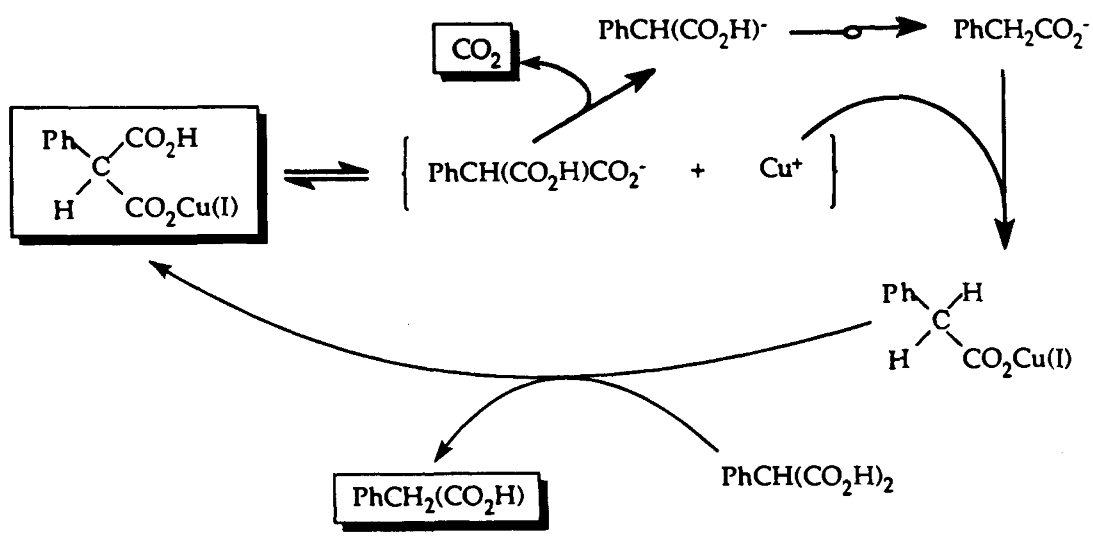
While noninteracting salts were superior catalysts in our studies, it is clear that Cu(I) and Zn(II) promote instability in malonic acid derivatives. For example, we have seen that binding 1,10-phenanthroline to zinc(II) phenylmalonic acid benzyl ester results in a red solution and CO_2 loss at room temperature. The red solution is indicative of the formation of a Zn(II) alkyl complex. That is, several studies have shown 2,2′-bipyridine and 1,10-phenanthroline form colored solutions with Zn(II) alkyl complexes. A red solution is not observed under catalytic decarboxylation reactions, and it is probable that the rapid protonation from the carboxylic acid intercepts Zn

---

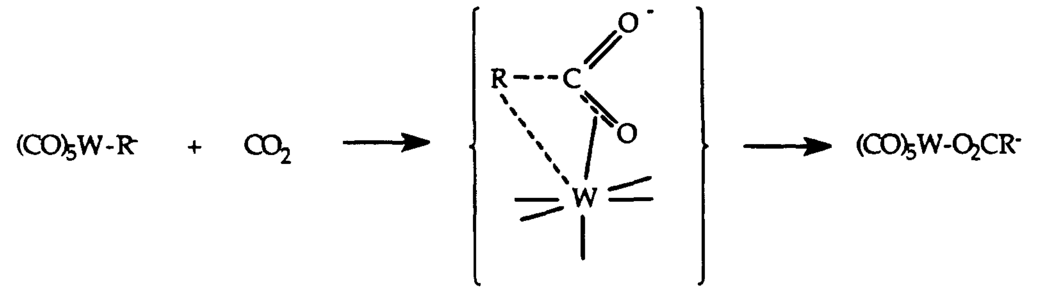
(24) Darensbourg, D. J.; Hanckel, R. K.; Bauch, C. G.; Pala, M.; Simmons, D.; White, J. N. *J. Am. Chem. Soc.* **1985**, *107*, 7463.

(25) Darensbourg, D. J.; Grötsch, G. *J. Am. Chem. Soc.* **1985**, *107*, 7473.

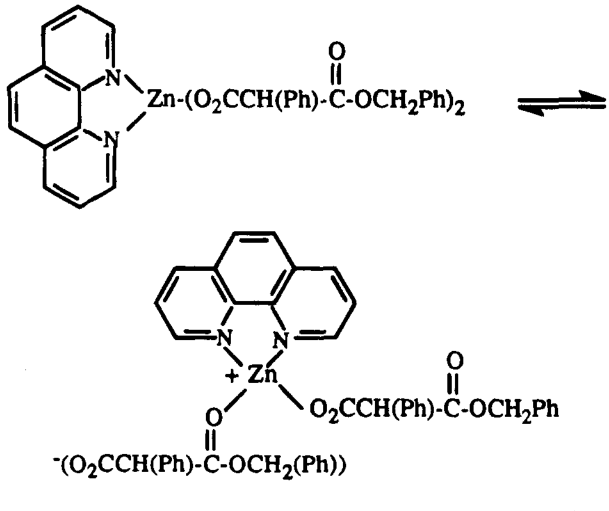
Scheme 2



Scheme 3



alkyl formation. Therefore, we propose that the carboxylate dissociates and an interaction *via* the ketonic oxygen of the ester group favors an electron density shift which results in CO_2 loss (eq 8). The complex may rearrange to form a Zn(II) alkyl complex resulting in the red solution. Consistent with the formation of a zinc–alkyl intermediate in these reactions, the $Zn(O_2CCH(Ph)C(O)OCH_2Ph)_2$ derivative undergoes the $^{13}CO_2$ exchange reaction as indicated in eq 3. Appropriate conditions for metal-assisted malonic acid decarboxylation may occur in systems where the carboxylate binding to the metal center is negligible and where coordination of the ketonic oxygen may promote electrophilic enhanced decarboxylation. The asymmetrical decarboxylation of substituted phenylmalonic acids and phenylmalonic hemiesters by Cu(I) salts may be proceeding *via* such electrophilic enhancement.[1e]



(8)

Further support for this mechanism stems from the work of Steinberger and Westheimer involving the catalytic decarboxylation of dimethyloxalacetic acid.[26] The dimethyloxalacetic anion, $^{-}O_2CC(CH_3)_2(C{=}O)CO_2H$, has a structural motif similar to that of the malonate anion, $^{-}O_2CC(R'R'')(C{=}O)OH$, in which the carbanion obtained after CO_2 loss forms stable resonance structures. These researchers found that Cu(II) catalytically decarboxylated this acid *via* electrophilic catalysis. The proposed mechanism was supported by the observed rate enhancement upon addition of complexing agents to the catalytic systems. Furthermore, other metals such as Zn(II) were active catalysts, although Cu(II) was the best.

Acknowledgment. Financial support of this research by the National Science Foundation (Grant 91-19737) and the Robert A. Welch Foundation is greatly appreciated. In addition, we wish to thank Professor G. Parkin for samples of butyl derivatives of tris(pyrazolyl)hydroborate which were employed in our initial studies of these zinc(II) systems.

Supplementary Material Available: Tables providing complete listings of atomic coordinates, bond lengths, bond angles, anisotropic thermal parameters, and H atom coordinates and isotropic displacement parameters for complexes **1**–**3** and the derivation of the rate expression for Cu(I) carboxylate dissociation into ion pairs (26 pages). Ordering information is given on any current masthead page.

IC941286+

---

[26] Steinberger, R.; Westheimer, F. H. *J. Am. Chem. Soc.* **1951**, *73*, 429.