Reversible Decarboxylation of Phosphine Derivatives of Cu(I) Cyanoacetate. Mechanistic Aspects Germane to Catalytic Decarboxylation of Carboxylic Acids

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Copper(I) complexes which act as carbon dioxide carriers and transcarboxylating agents have been reported.[1] For example, Cu(I) cyanoacetate has been found to transfer CO_2 to propylene oxide to produce propylene carbonate.[1a] Consistent with this observation, Cu(I) cyanoacetate has been shown to quantitatively undergo irreversible decarboxylation to provide the stable (cyanomethyl)copper(I) derivative.[2] In the presence of tri-*n*-butylphosphine the decarboxylation reaction is reversible.[3,4] However, the copper(I)–tri-*n*-butylphosphine complex was reported to be too unstable with respect to decarboxylation at ambient temperature to be characterized, in particular with respect to the mode of bonding of the cyanoacetate ligand to the copper(I) center. Owing to the importance of copper(I) derivatives as nonoxidative decarboxylation catalysts as well as the interest in the reverse process for the utilization of CO_2 in chemical synthesis, the identification of reaction intermediates and kinetic parameters for this process is highly significant. In this connection, we have undertaken the synthesis and structural characterization of species derived from the reaction of copper(I) carboxylates with phosphines.[5-8] Herein is reported the preparation, reactivity, and X-ray structural characterization of the resultant complex from the reaction of Cu(I) *n*-butyrate,[9] $NCCH_2CO_2H$, and PPh_3.[10-12]

The dimeric complex $[(Ph_3P)_2CuO_2CCH_2CN]_2$ (**1**) was obtained from the reaction of Cu(I) *n*-butyrate with 1 equiv of $NCCH_2CO_2H$ and 2 equiv of PPh_3 in diethyl ether at room temperature. An initially clear solution of the reactants turned cloudy after being stirred for 15 min, and a fine white powder was isolated after the solution was stirred for 12 h (yield 80%). Recrystallization of the product from a dichloromethane solution layered with diethyl ether maintained at -20 °C resulted in X-ray quality crystals.[13]

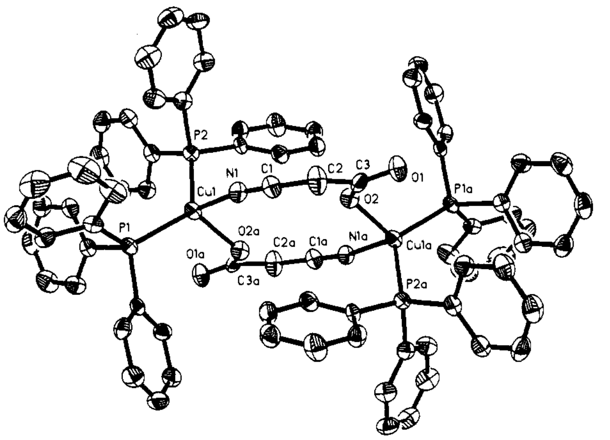

Figure 1. Molecular structure and atom labeling scheme for $[(Ph_3P)_2CuO_2CCH_2CN]_2$ (**1**). Selected intramolecular distances (Å): Cu(1)–O(2), 2.078(3); Cu-N, 2.061(3); Cu-P, 2.240(2) and 2.283(2). Selected bond angles (deg): P-Cu-P, 122.1(1); N-Cu-O, 91.3(1); Cu-N-C, 162.0(4).

The infrared spectrum of **1** in CH_2Cl_2 revealed the presence of both the carboxylate and the cyano groups. The carboxylate stretching frequencies were observed at 1611 and 1370 cm^{-1} and confirmed by isotopic substitution: ($\nu(^{12}CO_2)$ in DME 1609 and 1372 cm^{-1}; $\nu(^{13}CO_2)$ 1560 and 1347 cm^{-1}). The large difference ($\Delta = 241$ cm^{-1}) between the asymmetric and symmetric stretches supports a monodentate coordination mode of the carboxylate.[14] The $C{\equiv}N$ stretch, noted at 2255 cm^{-1}, is similar to that observed for a previously reported N-bound cyanoacetate complex of Cu(I).[5] Importantly, this mode of cyanoacetate binding persists in the solid state, as confirmed by observations of the $\nu(CO_2)$ stretches at 1609 and 1373 cm^{-1} and the $\nu(CN)$ at 2255 cm^{-1} in KBr. The structure of **1** was verified by an X-ray analysis, as shown in Figure 1.[15]

Complex **1** readily undergoes a reversible decarboxylation/carboxylation reaction in the temperature range 30–50 °C, as evidenced by its exchange with $^{13}CO_2$ in DME (eq 1). Infrared

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

spectroscopy monitored the disappearance of the asymmetric $\nu(^{12}CO_2)$ stretch at 1609 cm^{-1}. Concomitantly, the appearance of the corresponding $\nu(^{13}CO_2)$ vibration at 1560 cm^{-1} and the ^{13}C NMR signal at 167.4 ppm for the carboxylate indicated carbon dioxide exchange. Attendant with this exchange process was an increase in the free $^{12}CO_2$ in solution (2338 cm^{-1}) relative to dissolved $^{13}CO_2$ (2272 cm^{-1}).[16] Reaction 1 was found to be first order in [**1**], as indicated by a linear plot of ln[**1**] *vs* time.[17] The first-order rate constants for CO_2 exchange were determined as a function of temperature, and these data are listed in Table I,

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(1) (a) Tsuda, T.; Chujo, Y.; Saegusa, T. *J. Chem. Soc. Chem. Commun.* **1976**, 415. (b) Tsuda, T.; Sanada, S.; Ueda, K.; Saegusa, T. *Inorg. Chem.* **1976**, *15*, 3239. (c) Tsuda, T.; Washita, H.; Watanabe, K.; Miwa, M.; Saegusa, T. *J. Chem. Soc., Chem. Commun.* **1978**, 815. (d) Tsuda, T.; Chujo, Y.; Saegusa, T. *J. Am. Chem. Soc.* **1980**, *102*, 431.

(2) Tsuda, T.; Nakatsuka, T.; Hirayama, T.; Saegusa, T. *J. Chem. Soc., Chem. Commun.* **1974**, 557.

(3) Tsuda, T.; Chujo, Y.; Saegusa, T. *J. Am. Chem. Soc.* **1978**, *100*, 630.

(4) Consistent with this observation, it has been demonstrated that phosphine ligands greatly enhance the rate of CO_2 insertion into metal–carbon bonds. (a) Darensbourg, D. J.; Kudaroski, R. *J. Am. Chem. Soc.* **1984**, *106*, 3672. (b) Darensbourg, D. J.; Hanckel, R. K.; Bauch, C. G.; Pala, M.; Simmons, D.; White, J. N. *J. Am. Chem. Soc.* **1985**, *107*, 7463.

(5) Darensbourg, D. J.; Longridge, E. M.; Atnip, E. V.; Reibenspies, J. H. *Inorg. Chem.* **1991**, *30*, 357.

(6) The synthesis of a triphenylphosphine dervative of copper(I) acetate by the reaction of copper(I) acetate and PPh_3 has previously been reported.[7] The complex has been synthesized by an alternative route,[8] characterized by X-ray crystallography,[9] and shown to possess a bidentate carboxylate.

(7) Miyashita, A.; Yamamoto, A. *J. Organomet. Chem.* **1976**, *113*, 187.

(8) Edwards, D. A.; Richards, R. *J. Chem. Soc., Dalton Trans.* **1975**, 637.

(9) Drew, M. G. B.; Othman, A. H.; Edwards, D. A.; Richards, R. *Acta Crystallogr., Sect. B* **1975**, *31*, 2695.

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

(11) Presumably this same product should be produced *via* the reaction of $(Ph_3P)_3CuCH_3$ with 1 equiv of cyanoacetic acid accompanied by phosphine dissociation. However, because of the extreme thermal instability of $(Ph_3P)_3CuCH_3$, it is very difficult to accurately control the stoichiometry of this reaction.[12]

(12) (a) Coan, P. S.; Folting K.; Huffman, J. C.; Caulton, K. G. *Organometallics* **1989**, *8*, 2724. (b) An earlier report of the synthesis of this complex has appeared: Miyashita, A.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 1102.

(13) Anal. Calcd for $C_{39}H_{32}P_2O_2NCu$: C, 69.69; H, 4.80. Found: C, 69.96; H, 5.07.

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

(15) The details of the structure analysis may be found in the supplementary materials.

(16) Nielsen, A. H.; Lagemann, R. T. *J. Chem. Phys.* **1954**, *22*, 36.

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Table I. Temperature-Dependent Rate Data for the Exchange of CO_2 in $[(PPh_3)_2CuO_2CCH_2CN]_2$[a]

T (K)	$k(\times 10^3\ s^{-1})$[b]	T (K)	$k(\times 10^3\ s^{-1})$[b]
302.9	0.234	318.0	1.12
308.0	0.456	323.0	2.33
313.0	0.690		

[a] Activation parameters determined. $\Delta H^{*} = 21.5 \pm 1.1$ kcal, $\Delta S^{*} = -6.2 \pm 3.7$ eu. [b] These are all measured at a [**1**] of 0.0223 M.

along with the derived activation parameters. These activation parameters are quite comparable to those previously reported for CO_2 exchange involving the square-planar nickel(II) complex, $HNi(O_2CH)(PCy_3)_2$.[18] As manifested by changes in the infrared spectrum, complex **1** reacts with excess PPh_3 to afford presumably the monomeric complex, $(Ph_3P)_3CuO_2CCH_2CN$.[19,20] This latter complex undergoes CO_2 exchange at a slightly enhanced rate as compared with complex **1**.

Importantly, complex **1** is an efficient catalyst for the decarboxylation of cyanoacetic acid to acetonitrile and carbon dioxide.[21] At modest concentrations of carboxylic acid where complex **1** remains intact, the decarboxylation process is first order in [**1**] and zeroth order in [acid].[22] Furthermore, the rate constants for decarboxylation and CO_2 exchange (eq 1) are very similar, e.g., k_1 at 40 °C for decarboxylation is 9.03×10^{-4} *vs* 6.90×10^{-4} sec^{-1} for CO_2 exchange. This behavior is consistent with a reaction pathway for the decarboxylation reaction in which the rate determining step is CO_2 extrusion, with CH_3CN formation occurring in a subsequent rapid protonation step.

The rate of decarboxylation is quite sensitive to the nature of the phosphine ligands bound to Cu(I) in the catalyst or catalyst precursor, with enhanced catalytic activity being noted for more basic phosphine ligands. Indeed, better donating ligands bound to Cu(I), such as amines, are so effective at catalyzing the decarboxylation reaction that it is arduous to assess the mechanistic aspects of the process.[23] Current investigations, which involve the systematic variation of steric and electronic influences about the copper(I) center, are in progress in an effort to better define the environment about the active site.

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Supplementary Material Available: Figures illustrating a kinetic plot of $^{13}CO_2$ exchange with $[(Ph_3P)_2CuO_2CCH2CN]_2$ and kinetic plots for the catalytic decarboxylation of cyanoacetic acid; tables summarizing crystal structure determination data, atomic coordinates and equivalent isotopic displacement coefficients, bond lengths and angles, and anisotropic thermal parameters for complex **1** (9 pages). Ordering information is given on any current masthead page.

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(17) In order to accurately monitor the $\nu(CO_2)$ bands of complex **1** by infrared spectroscopy, it is necessary to have a relatively concentrated solution of the complex (approximately 0.020 M). The solubility of $^{13}CO_2$ in DME at ambient temperature is about 0.330 M.[4] Hence, even employing a sizable gas head space, there is a small contribution to the kinetics from the back-reaction with $^{12}CO_2$. This contribution was estimated to be less than 10%. Nevertheless, we plan to completely account for this by studying a fully ^{13}C-labeled complex (**1**) undergoing exchange with $^{12}CO_2$ at high pressure. The rate constant at a particular temperature was found to decrease with decreasing [**1**], suggesting that the exchange is occurring in the dimeric unit. Because of the narrow concentration range allowed by solubility and infrared detection limits, more definitive kinetic measurements are required. Plans are underway to perform similar studies on the more soluble tricyclohexylphosphine derivative.

(18) Darensbourg, D. J.; Wiegreffe, P.; Riordan, C. G *J. Am Chem. Soc.* **1990**, *112*, 5759.

(19) The infrared bands assigned to the asymmetric $\nu(CO_2)$ vibration shifts to higher frequency at 1641 cm^{-1}, as is expected for formation of a $(Ph_3P)_3CuO_2CR$ derivative.[20] Upon $^{13}CO_2$ exchange, the asymmetric $\nu(CO_2)$ band in this derivative appears at 1596 cm^{-1}.

(20) Hammond, B.; Jardine, F. H.; Vohra, A. G. *J. Inorg. Nucl. Chem.* **1971**, *33*, 1017.

(21) Quantitative assessment of acetonitrile as the only organic product was established by GC–MS.

(22) We have previously described a complex in the solid state which contains a Cu(I) center bound, in addition to two PPh_3 ligands, to two N-bonded acetates connected to a second molecule by intermolecular hydrogen bonding.[5] Upon dissolution of this complex in THF, it is now possible to conclude that quantitative formation of complex **1** and 2 equiv of cyanoacetic acid results. Furthermore, the addition of *large excesses* of cyanoacetic acid to a THF solution of **1** disrupts the dimer with formation of a monomeric copper(I) unit containing an added N-bonded cyanoacetic acid ligand. This is akin to the reaction of **1** with excess PPh_3 to afford $(Ph_3P)_3CuO_2CCH_2CN$. This resultant Cu(I) species is a less reactive catalyst for decarboxylation and hence constitutes an inhibition of the process in large excesses of substrate.

(23) Darensbourg, D. J.; Longridge, E. M.; Atnip, E. V.; Reibenspies, J. H. *Inorg. Chem.* **1992**, *31*, 3951.