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Preparation and Solid-State Structure of a Novel Carboxylate Derivative of Copper(I), $(Ph_3P)_2Cu(O_2CCH_2CN)_2H$

The suitability of copper(I) complexes as carbon dioxide carriers has been reported.[1] Although copper(I) cyanoacetate has been found to quantitatively undergo irreversible decarboxylation to provide (cyanomethyl)copper(I),[2] in the presence of tri-*n*-butylphosphine the decarboxylation reaction is reversible (eq 1).[3] Indeed, the instability of the copper(I) tri-*n*-butylphosphine complex toward decarboxylation has prevented its characterization with respect to the number of phosphine ligands as well as the mode of bonding of the cyanoacetate ligand to the copper(I) center.

$$NCCH_2CO_2Cu(P\text{-}n\text{-}Bu_3)_x \rightleftarrows NCCH_2Cu(P\text{-}n\text{-}Bu_3)_x + CO_2 \quad (1)$$

A focus of our efforts in carbon dioxide chemistry is to define the mechanistic aspects of carboxylation/decarboxylation processes catalyzed by transition-metal complexes. For these investigations fully characterized complexes are a prerequisite to conducting the studies. Therefore, we have undertaken the synthesis and structural characterization of species derived from the reaction of the $MeCu(PPh_3)_3$ derivative[4] with carboxylic acids, where a copper(I) carboxylate complex containing phosphine ligands would be anticipated.[5-8] We report herein the preparation and X-ray structural characterization of the resultant complex from the reaction of $MeCu(PPh_3)_3$ and cyanoacetic acid, $(Ph_3P)_2Cu(O_2CH_2CN)_2H$, in which the cyanoacetate ligand exhibits a novel bonding mode.

Approximately 2 equiv (25 mg) of cynoacetic acid was cannulated into a flask containing a solution of $CH_3Cu(PPh_3)_3$ (130 mg) in THF maintained at −78 °C. When the flask was allowed to slowly warm to ambient temperature, the yellow solution became colorless. The solution was carefully layered with an equal volume of hexane and maintained at −20 °C for several days, resulting in the formation of clear, X-ray-quality crystals (**1**). The yield of isolated product was greater than 80% based on $CH_3Cu(PPh_3)_3$. Both the solid-state and solution infrared spectra of **1** revealed the presence of the cyanoacetate moiety.[9]

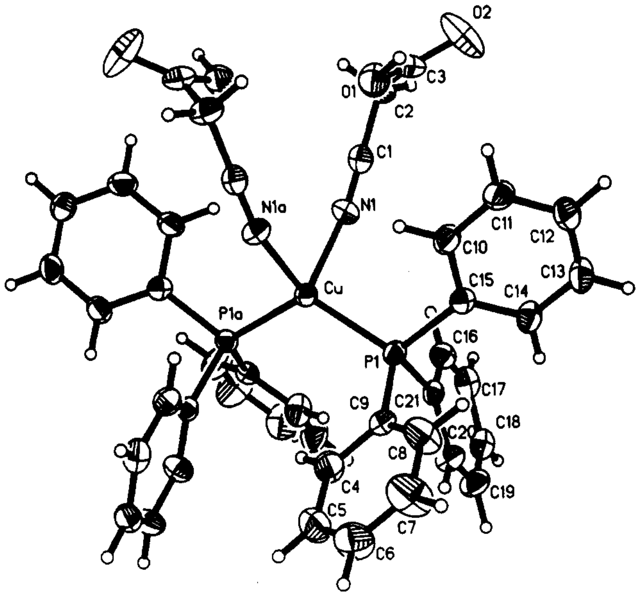

Figure 1. ORTEP diagram of $(Ph_3P)_2Cu(O_2CCH_2CN)_2H$ (**1**), showing 50% probability thermal ellipsoids.

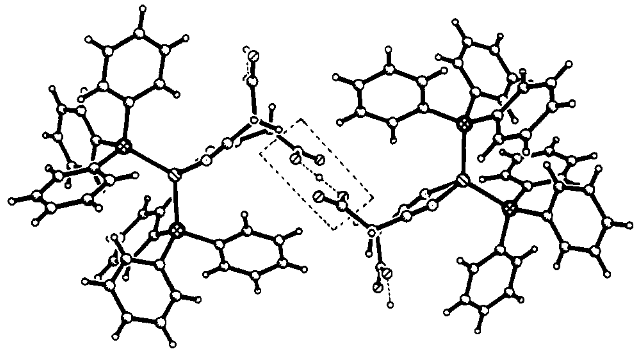

Figure 2. Diagram illustrating one of the intermolecular hydrogen bonds between molecules of **1**.

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

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(4) (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.

(5) An analogous reaction of $RCuL_n$ complexes with R′COOH to provide $(R'CO_2)CuL_n$ derivatives, where the R′ group does not contain a functional group capable of interacting with the Cu(I) center, has been briefly reported.[6] Although no details were provided, it was stated that products derived from the reactions of alkylcopper complexes with carboxylic acids were identical with those obtained from CO_2 insertion into the corresponding $R'CuL_n$ derivatives. The latter carboxylates were shown by infrared spectroscopy to be bound to Cu(I) by way of both oxygen atoms. Similar (acetato)copper(I) phosphine complexes have been prepared by an alternative route[7] and characterized by X-ray crystallography.[8]

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(8) Drew, M. G. B.; Othman, A. H.; Edwards, D. A.; Richards, R. *Acta Crystallogr., Sect. B* **1975**, *B31*, 2695.

(9) The ν(CN) stretching vibrations were observed at 2283 and 2260 cm^{-1} in KBr and at 2254 cm^{-1} in THF solution. Similarly, in the carboxylate region of the infrared spectrum a band is seen at 1735 cm^{-1} in KBr, with corresponding vibrations in THF solution at 1746 and 1609 cm^{-1}.

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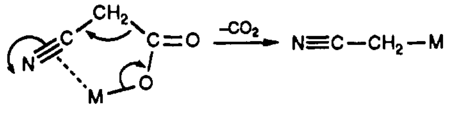
Confirmation of the structure of the product (**1**) was accomplished by single-crystal X-ray analysis.[10] **1** crystallizes from a hexane/THF mixture in space group *C*2/*c* with four molecules per unit cell. **1** sits about the crystallographic 2-fold axis with Cu on the special position ($^1/_2$, 0.7021, $^1/_4$). The complex involves a highly distorted tetrahedral environment of two phosphorus and two nitrogen atoms about a Cu(I) center (Figure 1). The most striking feature of the structure is that it contains two cyanoacetate units, both bonded to Cu(I) via the cyano moiety as opposed to the carboxylate functionality, with strong intermolecular hydrogen bonding between molecular units (Figure 2). The Cu-N(1)-C(1) angle is nonlinear, being 153.3 (3)°. Because of the large steric requirements of the triphenylphosphine ligands, the P-Cu-P angle is obtuse at 123.1 (1)°; correspondingly, the N-Cu-N angle is acute at 86.2 (2)°. The P-Cu-P angle in triphenylphosphine derivatives of Cu(I) generally differ greatly from the tetrahedral value of 109.5°, ranging 120-133°.[8,11] The Cu-P and Cu-N bond distances, 2.264 (2) and 2.083 (4) Å, respectively, are similar to those reported for related derivatives.[8,11,12]

The carboxylate groups are all equivalent, where the C(3)-O(1)H distance is 1.272 (6) Å, with the C(3)-O(2) bond length being 1.216 (9) Å. The O···H···O distance at 2.487 Å is considerably less than the sum of the van der Waals radii of the two oxygen atoms.[13] This is consistent with related carboxylate species, which contain strong symmetric hydrogen bonds; e.g., in $KH(CF_3CO_2)_2$ the hydrogen's position was found centered between the two oxygen atoms by both neutron and X-ray diffraction data, with an O···H···O distance of 2.435 Å.[14] These very strong centered hydrogen bonds generally have associated bond energies greater than 50 kJ/mol.

The solution structure of **1** is compatible with what would be anticipated upon dissolution on the basis of its solid-state structure; i.e., it possesses both an acid (-COOH) and a carboxylate ($-CO_2^-$) functionality. For example, free cyanoacetic acid exhibits a C=O stretching vibration at 1746 cm^{-1} in THF solution, whereas complex **1** in THF displays C=O vibrations at 1746 and 1609 cm^{-1}. This latter frequency corresponds to the asymmetrical stretching band of the carboxylate ion. On the other hand, the solid-state infrared spectrum of **1** exhibits only a -COOH vibrational mode shifted slightly to lower frequency at 1735 cm^{-1} due to the observed intermolecular hydrogen bonding. Concomitantly, the -C≡N stretch in THF solution in the free acid at 2261 cm^{-1} is shifted to lower frequency at 2254 cm^{-1} in the solution spectrum of **1**. This latter observation is consistent with both cyanoacetate ligands being bound through the nitrogen donor and is most likely indicative of a small degree of π back-bonding from the Cu(I) into the π^* orbitals of the nitrile group.[15]

Present studies are underway to assess the possible role of species containing cyanoacetate ligands bound as in complex **1** in the decarboxylation reaction of cyanoacetic acid with copper(I) phosphine derivatives. Additionally, we are pursuing investigations aimed at determining the conditions for affording copper(I) phosphine complexes containing the cyanoacetate ligand bound via the carboxylate functionality. Indeed, the role of both types of interaction at the metal center (**2**) has been suggested to be of general importance in decarboxylation processes.[16]



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Supplementary Material Available: Listings of atomic coordinates and isotropic thermal parameters, anisotropic thermal parameters, H atom coordinates and isotropic displacement parameters, and all bond distances and bond angles (4 pages); a listing of observed and calculated structure factors (14 pages). Ordering information is given on any current masthead page.

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(10) Crystal data for **1** ($C_{42}H_{35}N_2O_4P_2Cu$): M_r = 757.2; space group *C*2/*c* (No. 15); a = 17.377 (11), b = 23.962 (14), c = 11.363 (3) Å; β = 117.44 (4)°; V = 4199 (4) Å^3; Z = 4; d_{calc} = 1.198 g cm^{-3}; Nicolet R3m instrument; 193 K; Mo Kα (λ = 0.71073 Å); scan method ω (Wyckoff); data collection range $4 < 2\theta < 50°$; number of unique data 3726; number of total data used 2953 ($I > 2\sigma(I)$); solution by heavy-atom methods (Patterson and Fourier) with full-matrix least-squares refinement to convergence (number of refined parameters 231); R = 0.054; R_w = 0.067, S = 2.86.

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(13) A similar hydrogen-bonding interaction is seen between the dicyanoacetate anions in the solid-state structure of $[H_2Ir(PMe_3)_4][O_2CCH(CN)_2]$, where the dicyanoacetate anion is not bonded to the iridium center: Behr, A.; Herdtweck, E.; Herrmann, W. A.; Keim, W.; Kipshagen, W. *J. Chem. Soc., Chem. Commun.* **1986**, 1262.

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(15) Purcell, K. F.; Dargo, R. S. *J. Am. Chem. Soc.* **1966**, *88*, 919.

(16) Deacon, G. B.; Faulks, S. J.; Pain, G. N. *Adv. Organomet. Chem.* **1986**, *25*, 237.

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Comments on the Substitutional Lability of the Dimetal Carboxylates of Molybdenum and Rhodium. Effects of M-M MO Configuration

The substitutional lability of mononuclear transition-metal ions is greatly influenced by electronic configuration. For example, the rate of H_2O exchange in the aquo ions $M(H_2O)_6^{n+}$ spans a range of 10^{16} at room temperature and the effects of electronic configuration far outweigh the combined effects of the charge and size of the ion; cf. $k_{exch}(H_2O) = 10^9$ s^{-1} for $Cr(H_2O)_6^{2+}$ and 10^{-6} s^{-1} for $Cr(H_2O)_6^{3+}$.[1] Substitutionally inert octahedral ions are associated with the t_{2g}^6 (e.g. Co^{III}, Rh^{III}) and t_{2g}^3 (Cr^{III}) configurations, while *super labile* ions are found for the configurations $t_{2g}^3e_g^1$ (Cr^{2+}) and $t_{2g}^6e_g^3$ (Cu^{2+}) that contain an odd number of electrons in the destabilized e_g orbitals (M-L σ^*) and are subject to pronounced Jahn-Teller distortions. These ground-state effects underscore the kinetic applications of crystal field theory. We wish here to note that the substitutional lability of closely related dinuclear complexes is likewise influenced by electronic structure and, in particular, the M-M MO configuration.

The ligand redistribution reaction shown in eq 1 has been followed by NMR spectroscopy. For M = Mo there is rapid

$$M_2(O_2CR)_4 + M_2(O_2CR')_4 \underset{\text{benzene-}d_6}{\overset{T\ °C}{\rightleftharpoons}} M_2(O_2CR)_n(O_2CR')_{4-n} \qquad (1)$$

scrambling (T = 22 °C) with the formation of all possible $Mo_2(O_2CR)_n(O_2CR')_{4-n}$ (R = *t*-Bu, R' = CH$_2$-*t*-Bu or *p*-*t*-BuC$_6$H$_4$). No similar exchange (T = 60 °C) occurs for rhodium (R = *t*-Bu, R' = CH$_2$-*t*-Bu).

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