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Synthesis and Characterization of $[Cu_3Ph_2(PMDTA)_2]^+$: A Cationic Organocopper(I) Species[1]

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Currently known organocopper(I) compounds, which enjoy widespread use as reagents in organic synthesis,[2] can be divided into two broad categories.[3] The simplest are neutral compounds of the general formula $(CuR)_n$ (R = alkyl or aryl groups; $n = 4$, most commonly). Ionic organocopper(I) compounds (organocuprates) form the second major class of organocopper(I) species. These are generally obtained by the addition of more than 1 equiv of an organolithium reagent to a copper salt. The best known examples correspond to the simple empirical formula $LiCuR_2$ (i.e., Gilman reagents). A key feature of such compounds is the fact that the organocopper moiety invariably bears a negative charge. In effect, solid lithium organocuprates can be visualized as salt-like aggregates composed of lithium cations and organocuprate anions. Previously, there appears to have been no example of an alkyl or aryl organocopper compound in which a discrete organocopper(I) entity bears a positive charge. The synthesis and characterization of the first example of such a species is described below.

The compound $[Cu_3Ph_2(PMDTA)_2][Cu_5Ph_6]$, **1** (PMDTA = *N,N,N′,N″,N″*-pentamethyldiethylenetriamine), was synthesized[4] by the treatment of phenylcopper[5] with excess PMDTA in dimethyl sulfide (DMS) solution. The crystal structure of **1** features discrete cations and anions[6] arranged so that each asymmetric unit has two crystallographically independent half cation molecules (which have slightly different structures) and one anion. The structure of the anion $[Cu_5Ph_6]^-$ has a flattened trigonal bipyramidal array of five coppers and has metric features that are very similar to those previously described by Bau.[7] The crystallographically independent cations, one of which is illustrated in Figure 1, display interesting and unique structural features. In each cation two phenyl groups bridge three copper atoms, Cu(2)···Cu(1)···Cu(2a) and Cu(4)···Cu(3)···Cu(4a), which are arranged in a (crystallographically imposed) linear fashion with Cu(1)···Cu(2) and Cu(3)···Cu(4) separations of 2.444(1) and 2.392(1) Å, respectively. The C(1)–Cu(1), C(1)–Cu(2), C(16)–Cu(3), and C(16)–Cu(4) bond lengths are 2.006(7), 1.989(5), 1.980(7), and 2.064(5) Å, respectively. The phenyl rings are oriented essentially perpendicular (86.5° and 83.8°) to the Cu···Cu···Cu axis, and the Cu–C–Cu angles are 75.4(2)° and 72.5(2)°. The coordination at the terminal coppers is different in each cation, however. For Cu(4) the Cu–N distances to the three nitrogens of PMDTA are in the narrow range 2.152(5)–2.187(5) Å such that the terminal copper geometry is, in effect, distorted trigonal bipyramidal. In contrast, the Cu(2)–N distances have the values 2.087(5) Å for N(2), 2.206(5) Å for N(3), and a significantly longer 2.467(5)-Å interaction for N(1). Apparently, there is little energy difference between the terminal coppers interacting equally with all three nitrogens as with Cu(4) and Cu(4a) or the variable strength interactions found for Cu(2) and Cu(2a). The relatively long Cu–C distances in the cation may be accounted for in terms of the fact that they involve bridging phenyl groups and terminal coppers with a high coordination number.

The phenyl ^1H and ^{13}C NMR signals of **1** in DMS/toluene-d_8 (4:1 ratio) at 25 °C match an authentic sample of CuPh dissolved in DMS[8] as well as displaying peaks due to free PMDTA. It appears that the copper solution species in this case is the tetramer $(CuPh)_4{\cdot}(DMS)_2$, **2**.[9] If this solution is cooled to −30 °C, however, two new sets of phenyl resonances (along with one new set of peaks attributable to bound PMDTA) are observed. Moreover, these two sets of phenyl peaks are in the intensity ratio of 1:3 and can be assigned to the cation and anion, respectively: δ (cation) = 150.3 (ipso C), 144.9 (*o*-C), 126.7 (*m*-C), 124.7 (*p*-C); δ (anion) = 145.7 (ipso C), 143.0 (*o*-C), 126.3 (*m*-C), and 124.9 (*p*-C) ppm. From the coalescence temperature of 5 °C, an energy barrier to the dynamic process of 15 ± 1 kcal mol^{-1} was calculated from an approximate formula.[10] It is not known with certainty what the rate-determining step in this process is, but the overall equilibrium may be written as shown below.

$$\underset{\mathbf{1}}{[Cu_3Ph_2(PMDTA)_2][Cu_5Ph_6]} \xrightleftharpoons[2PMDTA]{4DMS} \underset{\mathbf{2}}{2[Cu_4Ph_4(DMS)_2]}$$

The synthesis of **1** originated from attempts to isolate a monomeric solvated L_nCuPh (L = donor ligand) molecule in order to establish a ^{13}C NMR chemical shift of the ipso carbon in unassociated CuPh.[8] This approach was based upon the observation that PMDTA breaks down $(PhLi)_4$ to PhLi·PMDTA.[11] In the presence of excess PMDTA in DMS solvent, however, separation of a monomeric CuPh species was not attained even though all the solvating DMS molecules were displaced from the coordination sphere of copper.

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(1) New Copper Chemistry. 22. Part 21: See ref 8.

(2) (a) Bertz, S. H.; Fairchild, E. H. *Encyclopedia of Reagents for Organic Synthesis*; John Wiley & Sons: New York, in press. (b) Lipshutz, B. H.; Sengupta, S. *Org. React.* (*N.Y.*) **1992,** *41*, 135. (c) Posner, G. H. *An Introduction to Synthesis Using Organocopper Reagents*; Wiley: New York, 1980.

(3) For a recent review of the structures of organocuprates, see: Power, P. P. *Prog. Inorg. Chem.* **1991,** *39*, 75.

(4) All manipulations were carried out under anaerobic and anhydrous conditions. $(CuPh)_4{\cdot}(DMS)_2$ (1.02 g, 1.5 mmol) was dissolved in DMS (20 mL) and cooled to *ca.* −40 °C. PMDTA (6.2 mL, 29.5 mmol) was then added via syringe with rapid stirring, after which the reaction mixture was slowly (*ca.* 6 h) allowed to come to room temperature. The orange-red solution was concentrated to 8–10 mL under reduced pressure and stored in a −20 °C freezer for 2 days. This afforded the product **1** as yellow crystals: yield, 0.7 g, 63%; mp 132–134 °C. ^1H NMR (DMS/C_7D_8, −30 °C) 8.23 (br, s, 4H, *o*-H, cation), 7.76 (br s, 6H, *m*- and *p*-H, cation), 7.20 (br s, 18H, *m*- and *p*-H, anion), 7.04 (s, 12H, *o*-H, anion), 2.30 (br s, 16H, PMDTA), 2.25 (br, s, 30H, PMDTA); $^{13}C\{^1H\}$ NMR (DMS/C_7D_8, −30 °C) 150.3 (br s, ipso C, cation), 145.7 (br, s, ipso C, anion), 144.9 (s, *o*-C, cation), 143.0 (s, *o*-C, anion), 126.7 (s, *m*-C, cation), 126.3 (s, *m*-C, anion), 124.9 (s, *p*-C, anion), 126.7 (s, *m*-C, cation). DMS solutions of **1** are very air-sensitive and rapidly become red (and ultimately blue or green) in the presence of air. Red crystals have been obtained from these solutions. Preliminary X-ray data show that the copper species has a large cage structure composed of at least 24 coppers bound to phenyls, PMDTA ligands, and oxygens.

(5) (a) Reich, M. R. *C. R. Hebd. Seances Acad. Sci.* **1923,** *177*, 322. (b) Costa, G.; Camus, A.; Gatti, L.; Marsich, N. *J. Organomet. Chem.* **1966,** *5*, 568. (c) Bertz, S. H.; Dabbagh, G. *Tetrahedron* **1989,** *45*, 425.

(6) Crystal data at 130 K with Mo Kα (λ = 0.710 73 Å) radiation: a = 11.773(4) Å, b = 11.800(4) Å, c = 25.689(9) Å, α = 88.91(3)°, β = 84.15(3)°, γ = 63.64(2)°, V = 3180(2) Å^3, triclinic, space group $P\bar{1}$, Z = 2, R = 0.048 for 9541 ($I > 3\sigma(I)$) data. For crystal handling method, see the following: Hope, H. In *Experimental Organometallic Chemistry: A Practicum in Synthesis and Characterization*; Wayda, A. L., Darensbourg, M. Y., Eds.; ACS Symposium Series 357; American Chemical Society: Washington, DC, 1987; Chapter 10, p 257.

(7) Edwards, P. G.; Gellert, R. W.; Marks, M. N.; Bau, R. *J. Am. Chem. Soc.* **1982,** *104*, 2072.

(8) Bertz, S. H.; Dabbagh, G.; He, S.; Power, P. P. *J. Am. Chem. Soc.* **1993,** *115*, 11640.

(9) Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1990,** *112*, 8008.

(10) Kost, D.; Carlson, E. H.; Raban, M. J. *J. Chem. Soc., Chem. Commun.* **1971,** 656.

(11) Schümann, U.; Kopf, J.; Weiss, E. *Angew. Chem., Int. Ed. Engl.* **1985,** *24*, 215.

0002-7863/94/1516-6963$04.50/0

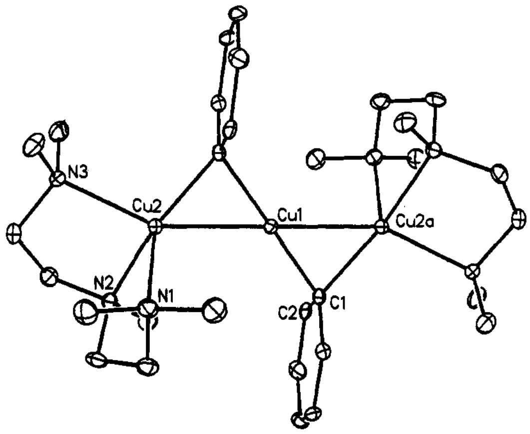

Figure 1. Thermal ellipsoidal plot of one of the crystallographically independent cations of **1**. Interatomic distances (Å) and angles (deg) are as follows: Cu(1)···Cu(2) = 2.444(1), Cu(1)–C(1) = 2.006(7), Cu(2a)–C(1) = 1.989(5), Cu(2)···N(1) = 2.467(5), Cu(2)–N(2) = 2.087(3), Cu(2)–N(3) = 2.206(5), Cu(1)–C(1)–Cu(2a) = 75.4(2), Cu(1)–Cu(2)–N(3) = 151.2(1), C(1a)–Cu(2)–N(1) = 113.5(1), Cu(1a)–Cu(2)–N(2) = 158.4(1), N(1)–Cu(2)–N(2) = 81.6(1). Note that each crystallographically independent cation possesses an inversion center at the central copper.

The failure to prevent aggregation of copper centers in the cation may be attributed, at least in part, to the fact that PMDTA is a type-a donor and is ineffective in achieving separation of Cu^+, a type-b cation.[12] (Li^+ is type-a.) In this system, at least, PMDTA appears to be incapable of fully solvating a separate copper center, and the partial solvation observed in **1** is the result. This situation stands in contrast to the complete separation of Cu^+ cations observed when 1,2-bis(diphenylphosphino)ethane (dppe) is added to CuAr (Ar = Ph or 2,4,6-$Me_3C_6H_2$ (Mes)) to give $[Cu(dppe)_2][CuAr_2]$[8,13a] or when 1,2-bis(dimethylphosphino)ethane (dmpe) is added to CuMe to give $[Cu(dmpe)_2][CuMe_2]$.[13b] Clearly, phosphine ligands (type b)[11] are more effective than amines in coordinating the Cu^+ ion.

Several kinds of clusters containing three copper atoms are known at present.[14] In trimeric Cu(I) thiolates,[15] amides,[16] and carboranes,[17] which are neutral, there is a triangular arrangement of Cu(I) atoms. This is also true for the $Cu_3Cl_4^-$ anion,[18a] in which a halide bridges two Cu(I) atoms on each of the three sides of a Cu_3 triangle and one halide caps all three Cu(I) atoms. A similar arrangement of Cu(I) atoms and halides is present in $Cu_3(AsPh_3)_3I_4^-$.[18b] Trigonal bipyramidal complexes with three equatorial Cu(I) atoms and two apical Li[19a] or Ir[19b] atoms have been characterized. The Cu–S compounds $[Cu_3S_{12}]^{3-}$ and $[Cu_3S_{18}]^{3-}$ have alternating Cu and S atoms in a six-membered ring which holds the Cu atoms in an equilateral triangle.[20] Cu_3 triangles are also enforced in "cubane-like" structures such as $(ReOS_3)Cu_3Cl_4^{2-}$ and $(ReS_4)Cu_3I_4^{2-}$.[21] A number of other, nonequilateral Cu(I) triangles are present in organometallic complexes.[22] In contrast, few linear Cu_3 complexes are known. (This discussion does not include one-dimensional, "nonmolecular" structures.[14])

The $[Cu_3Ph_2(PMDTA)_2]^+$ species is the first linear array of three Cu(I) atoms in which the linearity is not enforced by multidentate ligands. In **1** there are two tridentate ligands, but they merely complex one terminal Cu(I) atom each. In contrast, each tridentate N_5-ligand in $[Cu\{(EtOC_6H_4N)_2N_3\}]_3$ coordinates every copper atom,[23] and the same is true for each dpmp ligand in $[Cu_3\{(Ph_2PCH_2)_2PPh\}_2(MeCN)_2(\mu\text{-}Cl)_2][ClO_4]$.[24] (Currently, it appears that all linear Cu(II) complexes are held together by tridentate ligands.[25,26]) These structures have average Cu–Cu distances of 2.35 and 3.28 Å, respectively. One obvious difference is the fact that the PMDTA ligand has two spacer atoms between coordinating atoms rather than one. While the latter complex is cationic, $[Cu_3Ph_2(PMDTA)_2]^+$ is the first cationic organocopper compound with aryl (or alkyl) groups, which may have synthetic potential.

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Note Added in Proof: After this manuscript was prepared, another complex with three Cu(I) atoms in a linear arrangement (4.5 Å average separation) appeared.[27]

Supplementary Material Available: Data collection and refinement parameters, tables of atom coordinates, bond distances and angles, hydrogen coordinates and anisotropic thermal parameters (14 pages); listing of observed and calculated structure factors (53 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(12) Ahrland, S.; Chatt, J.; Davies, N. R. *Q. Rev. Chem. Soc.* **1958**, *12*, 265. Pearson, R. G. *J. Am. Chem. Soc.* **1963**, *85*, 3533; *J. Chem. Educ.* **1968**, *45*, 581, 643.

(13) (a) Leoni, P.; Pasquali, M.; Ghilardi, C. A. *J. Chem. Soc., Chem. Commun.* **1983**, 240. (b) Dempsey, D. F.; Girolami, G. *Organometallics* **1988**, *7*, 1208.

(14) Dance, I. G. *Polyhedron* **1986**, *5*, 1037.

(15) (a) Knotter, D. M.; van Koten, G.; van Maanen, H. L.; Grave, D. M.; Spek, A. L. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 341. (b) Knotter, D. M.; Grove, D. M.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *J. Am. Chem. Soc.* **1992**, *114*, 3400.

(16) Chen, H.; Olmstead, M. M.; Shoner, S. C.; Power, P. P. *J. Chem. Soc., Dalton Trans.* **1992**, 451.

(17) Kang, H. C.; Do, Y.; Knobler, C. B.; Hawthorne, M. F. *Inorg. Chem.* **1988**, *27*, 1716.

(18) (a) Uechi, T.; Yamaguchi, H.; Ueda, I.; Yasukouchi, K. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 3483. (b) Bowmaker, G. A.; Camus, A.; Hart, R. D.; Kidea, J. D.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1990**, 3753.

(19) (a) Hope, H.; Oram, D.; Power, P. *J. Am. Chem. Soc.* **1984**, *106*, 1149. (b) Rhodes, L. F.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1985**, *107*, 1759.

(20) (a) Müller, A.; Baumann, F.-W.; Bögge, H.; Römer, M.; Krickemeyer, E.; Schmitz, K. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 632. (b) Müller, A.; Schimanski, U. *Inorg. Chim. Acta* **1983**, *77*, L187.

(21) (a) Müller, A.; Hildebrand, A.; Krickemeyer, E.; Sölter, D.; Bögge, H.; Armatage, A. *Z. Anorg. Allg. Chem.* **1992**, *614*, 115. (b) Müller, A.; Krickemeyer, E.; Bögge, H. *Z. Anorg. Allg. Chem.* **1987**, *554*, 61. (c) It is interesting to compare the $Cu_3X_4^-$ moieties in refs 21a and 21b with those in 18a and 18b, respectively.

(22) (a) Camus, A.; Marsich, N.; Nardin, G.; Randaccio, L. *J. Organomet. Chem.* **1973**, *60*, C39. (b) Aalten, H. L.; van Koten, G.; Goubitz, K.; Stam, C. H. *J. Am. Chem. Soc.* **1989**, *8*, 2293. (c) Diez, J.; Gamasa, M. P.; Gimeno, J.; Lastra, E.; Aguirre, A.; Garcia-Granda, S. *Organometallics* **1993**, *12*, 2213. (d) Yam, V. W.-W.; Lee, W.-K.; Lai, T.-F. *Organometallics* **1993**, *12*, 2383. (e) Dance, I. G.; Fitzpatrick, L. J.; Scudder, M. L. *J. Chem. Soc., Chem. Commun.* **1983**, 546. (f) Ho, D. M.; Bau, R. *Inorg. Chem.* **1983**, *22*, 4079.

(23) Schmid, R.; Strähle, J. *Z. Naturforsch.* **1989**, *44b*, 105.

(24) Li, D.; Yip, H.-K.; Chi, C.-H.; Zhou, Z.-Y.; Mak, T. C. W.; Liu, S.-T. *J. Chem. Soc., Dalton Trans.* **1992**, 2445.

(25) Chiari, B.; Piovesana, O.; Tarantelli, T.; Zanazzi, P. F. *Inorg. Chem.* **1985**, *24*, 4615.

(26) Angaroni, M.; Ardizzoia, G. A.; La Monica, G.; Bocalli, E. M.; Mascrocchi, N.; Moret, M. *J. Chem. Soc., Dalton Trans.* **1992**, 2715.

(27) Potts, K. T.; Horwitz, C. P.; Fessak, A.; Keshavarz, M.; Nash, K. E.; Toscano, P. J. *J. Am. Chem. Soc.* **1993**, *115*, 10444.