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Reactions of Copper(I) Halides with Tertiary Phosphines. The Unique Structure of [Cu(tribenzylphosphine)$_2$][CuBr$_2$]

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Introduction

A wide variety of overall and local metal structures has been observed in Cu(I) coordination compounds, the prevailing one in each case being subject to the ligand donor ability and steric demands. In the case of copper(I) halide coordination compounds with tertiary phosphines, structures ranging from mononuclear two-coordinate to larger aggregations of the formula [CuLX]$_n$ have been realized, while cubanes of the formula [CuLX]$_4$ are also quite common.[1] Aiming at the expansion of the series of monodendate tertiary phosphine−copper(I) compounds already studied,[2] we investigated the reaction of copper halides with tribenzylphosphine.

Experimental Section

Synthesis. To a solution of 1 mmol (144 mg) of CuBr in 20 mL of acetonitrile was added 1 mmol (304 mg) of solid tribenzylphosphine (PBz$_3$). The resulting solution was left to reflux under atmospheric conditions for 3 h and was then cooled to room temperature. Upon standing at room temperature colorless crystals were deposited and their stoichiometry was proved to be [CuBr(PBz$_3$)]$_n$ Anal. Calcd for $C_{42}H_{42}Br_2Cu_2P_2$: C, 56.25; H, 4.69. Found: C, 56.83; H, 4.63.

Measurements. The spectroscopic infrared, solution electronic, and NMR data were obtained on a Perkin-Elmer 1600 FTIR, a Shimadzu 160A, and a Bruker AM 300 spectrometer, respectively, at ambient temperature. The solvents used were of the highest possible purity.

X-Ray Structure Determination. A crystal with approximate dimensions 0.25 × 0.30 × 0.50 mm was mounted in air. Diffraction measurements were made on a P2$_1$ Nicolet diffractometer upgraded by Crystal Logic using Zr-filtered Mo radiation. Unit cell dimensions were determined and refined by using the angular settings of 25 automatically centered reflections in the range $11° < 2\theta < 23°$, and they appear in Table 1. Intensity data were recorded using a $\theta-2\theta$ scan to $2\theta(\max) = 50°$ with scan speed 4.5 deg/min and scan range 2.5 plus $\alpha_1\alpha_2$ separation. Three standard reflections monitored every 97 reflections showed less than 3% variation and no decay. Lorentz, polarization, and Ψ-scan absorption correction were applied using Crystal Logic software. Symmetry equivalent data were averaged with $R = 0.0299$ to give 1133 independent reflections from a total of 3503 collected. The structure was solved by direct methods using SHELXS-86 and refined by full-matrix least-squares techniques on F^2 with SHELX-93 using 1126 reflections and refining 102 parameters.[3] All hydrogen atoms were located by difference maps and their positions refined isotropically. All non-hydrogen atoms were refined anisotropically. The final values for R1, wR2, and GOF, for observed data are given in Table 1 for all data. Positional and equivalent thermal parameters are given in Table 2 and selected bond distances and angles in Table 3.

Table 1. Summary of Crystal, Intensity Collection, and Refinement Data

empirical formula	$C_{42}H_{42}Br_2Cu_2P_2$
fw	895.60
temp (K)	298
wavelength (Å)	Mo Kα 0.71070
space group	$R\bar{3}$
a (Å)	13.829 (1)
b (Å)	13.829 (1)
c (Å)	17.429 (2)
V (Å^3)	2886.8 (5)
Z	3
D_{calcd}/D_{measd} (Mg·m^{-3})	1.546/1.52
abs coeff (μ), mm^{-1}	3.293
max abs corrn mode	1.24
W^a	$a = 0.0284$ $b = 7.0416$
goodness-of-fit on F^2	1.276
R indices [738 reflcns with $I > 2\sigma(I)$]^b	R1 = 0.0265, wR2 = 0.0657

[a] $W = 1/[\sigma^2F_o^2 + (aP)^2 + bP]$, $P = (\mathrm{Max}(F_o^2,0) + 2F_c^2)/3$. [b] R1 based on F's, wR2 based on F^2.

Table 2. Positional and Equivalent Thermal Parameters (Å^2 × 10^4) of the Non-H Atoms with Esd's in Parentheses

	x	y	z	U(eq),^{a}
Cu(1)	0	0	0	42(1)
P	0	0	1260(1)	35(1)
Cu(2)	0	0	5000	54(1)
Br	0	0	3733(1)	79(1)
C(1)	−739(4)	−1407(4)	1670(3)	47(1)
C(2)	−375(3)	−2154(3)	1310(2)	40(1)
C(3)	−853(4)	−2721(3)	640(2)	51(1)
C(4)	−494(5)	−3386(4)	301(3)	64(1)
C(5)	350(5)	−3485(4)	614(3)	72(1)
C(6)	828(5)	−2943(5)	1273(4)	74(1)
C(7)	475(4)	−2282(4)	1618(3)	59(1)

[a] $U(\mathrm{eq}) = {}^1/_3(U_{11} + U_{22} + U_{33})$.

Table 3. Relevant Bond Distances (Å) and Angles (deg) of the Title Compound^a

a. Cation			
Cu(1)−P^1	2.1955(14)	P−Cu−P^1	180.0
Cu(1)−P	2.1955(14)	C(1)^2−P−C(1)	105.8(2)
P−C(1)^2	1.831(4)	C(1)^2−P−C(1)^3	105.8(2)
P−C(1)	1.831(4)	C(1)−P−C(1)^3	105.8(2)
P−C(1)^3	1.831(4)	C(1)^2−P−Cu(1)	113.0(2)
		C(1)^3−P−Cu(1)	113.0(2)
		C(1)−P−Cu(1)	113.0(2)
b. Anion			
Cu(2)−Br	2.2076(8)	Br−Cu(2)−Br^4	180.0
Cu(2)−Br^4	2.2077(8)		

[a] Symmetry transformations used to generate equivalent atoms: (1) $-x, -y, -z$; (2) $-x + y, -x, z$; (3) $-y, x - y, z$; (4) $-x, -y, -z + 1$.

Results and Discussion

Room temperature NMR spectra recorded in deuterated chloroform reflect coordination to the d^{10} metal center. In the

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(3) (a) Sheldrick, G. M. SHELXS-86: Structure Solving Program. University of Göttingen, Germany, 1986. (b) Sheldrick, G. M. SHELX-93: Structure Refinement Program. University of Göttingen, Germany, 1993.

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^{1}H spectrum the phenyl protons resonate in the region δ 7.25−7.33 ppm (5H, multiplet) and the methylene ones at 3.06 ppm (2H, doublet, $^2J_{P-H} = 14.1$ Hz) while the corresponding resonances in the free ligand are observed at 7.10−7.35 and at 2.72 ppm respectively. The methylene carbon atom resonates at δ 34.4 ppm ($^1J_{P-C} = 61.6$ Hz) relative to 33.5 ppm in tribenzylphosphine. The phenyl carbon atom resonances appear at 131.6, 129.6, 128.6, and 126.7 ppm (corresponding values in the ligand are 137.6, 129.2, 129.2, 129.1, 128.3, and 125.7). ^{31}P NMR spectra reveal a broad singlet ($\nu_{1/2}$ *ca.* 50 Hz) at 6.7 ppm downfield from the free phosphine. The infrared spectrum of the compound, recorded in mid- and far-infrared regions, revealed sharp maxima at *ca.* 218 and 172 cm^{-1} attributed to Br−Cu−Br group vibrations,[4] since they are outside the region where Cu−terminal Br bonds have been observed. Electronic spectra recorded in methanol, acetonitrile, and cyclohexane (10^{-4} M based on the [CuBr(PBz$_3$)]$_2$ stoichiometry) appear to be mainly of intraligand character, presenting maxima in the region 220−230 nm. The compound does not reveal any emission (fluorescence or phosphorescence) in ethanol solutions even at liquid nitrogen temperature, therefore implying a marked difference in structure from analogous complexes with the isoelectronic tritolylphosphines[2] which have emission maxima in the region 330−450 nm[5] under similar conditions. Furthermore, recording of its mass spectrum (FAB) reveals [Cu{PBz$_3$}$_2$ − 2H] (*m*/*e* = 671, relative intensity 4%) as the highest mass ion, while the most prominent of the high mass ions is [Cu(PBz$_3$)$_2$ − 2H − 2Ph] (*m*/*e* = 517, relative intensity 53%). Also [Bz$_3$P−PBz$_3$ − 2H] and its further fragmentation products are observed, a fact accounted for by weak Cu−P bonding and proximity of two tribenzylphosphine units in the initial compound.

A study of the compound's crystal structure was undertaken to further characterize it. Crystals were obtained by slow evaporation at room temperature of an acetonitrile solution. The complex proved to be ionic, thus presenting the first example of a linear cationic copper(I) unit with a CuP$_2$ chromophore.[6] The copper atoms are situated on 3-fold inverse axes and their neighboring P and Br ones on 3-fold axes within the unit cell. The two ions are at a noninteractive distance from one another. The reaction therefore may be summarized as follows:

$$2\mathrm{CuBr} + 2\mathrm{PBz_3} \rightarrow [\mathrm{Cu(PBz_3)_2}][\mathrm{CuBr_2}]$$

The reaction conditions do not support CuBr$_2^-$ formation, which has been observed in aqueous media in the presence of the corresponding potassium or sodium halide.[7] In this respect, the structure of the product is unique, whether it emerges directly from the above reaction or as a dissociation product of the initially formed dimer {Cu(μ-Br)PBz$_3$}$_2$. This behavior of tribenzylphosphine, probably originating from the concerted effect of its bulk and bascicity, is the main scope of a further study already underway, involving a series of low valent coinage metal coordination compounds with this and related phosphine ligands.[8]

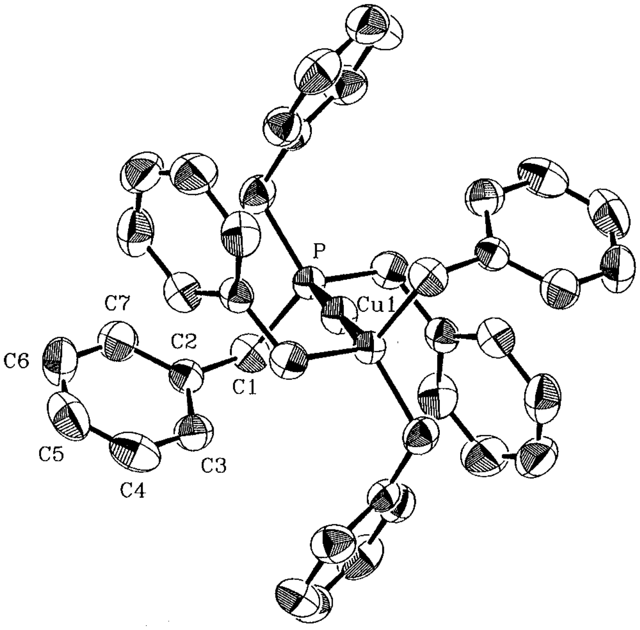

Figure 1. ORTEP drawing of the cationic unit of the title compound with 50% probability ellipsoids.

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Supporting Information Available: Tables of crystal data, hydrogen atom positional and isotropic thermal parameters, anisotropic thermal parameters for non-hydrogen atoms, and complete bond distances and angles (2 pages). Ordering information is given on any current masthead page.

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(4) Bowmaker, G. A.; Skelton, B. W.; White, A. H.; Healy, P. C. *J. Chem. Soc., Dalton Trans.* **1988**, 2825 and references cited therein.

(5) Emission spectra recorded in 10^{-4} mol·L^{-1} concentrations on a Perkin-Elmer MPF 44 B spectrofluorimeter using its standard equipment. Stoyanov, S.;Stoyanova, T.; Akrivos, P. D.; Karagiannidis, P; Nikolov, P. Work in progress.

(6) CuC$_2$, CuN$_2$ and CuS$_2$ chromophores have been observed with CuBr$_2^-$ counteranions as stated in: Hathaway B. J. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard R. D., McCleverty, J. A., Eds.; Pergamon Press: Oxford, England, 1987; Vol. 5, Chapter 53.3.2.1 and references therein.

(7) (a) Asplund, M.; Jagner, S. *Acta Chem. Scand., A* **1985**, *39*, 47. (b) Asplund, M.; Jagner, S. *Acta Chem. Scand., A* **1984**, *38*, 135. Under similar conditions 2,6-bis[1-phenyl-1-(pyridin-2-yl)ethyl]pyridine formed the ionic compounds [Cu(L)(MeCN)][CuCl$_2$] and [Cu(L)(MeCN)][Cu$_2$X$_4$] where X = Br or I: Canty, A. J.; Engelhardt, L. M.; Healy, P. C.; Kildea, J. D.; Minchin, N. J.; White, A. H. *Aust. J. Chem.* **1987**, *40*, 1881. Tris(2,4,6-trimethoxyphenyl)phosphine in MeCN produced [Ag(phosphine)$_2$][Ag$_5$I$_7$]: Baker, L.-J.; Bowmaker G. A.; Effendy, Skelton, B. W.; White, A. H. *Aust. J. Chem.* **1992**, *45*, 1909.

(8) Preliminary ^{31}P NMR studies of a series of silver(I)−phosphine complexes also hint at a unique behavior of tribenzylphosphine with respect to the nature and structure of the species present in solution. Akrivos, P. D.; McFarlane, W; Karagiannidis, P. Work in progress.