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Mononuclear and dinuclear copper(I) complexes with a particularly bulky phosphine ligand. Unusual synthesis and crystal structure characterizations

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Summary

The addition of NPm (diphenylaminodiphenylphosphinomethane) to CuI or the addition of KI to $(NPm)_2CuNO_3$ leads to the same P-bonded Cu^I complex, $(NPm)_2CuI$, presenting a trigonal geometry around the Cu atom. The reaction of this new complex (or of its chloro analogue) with a Cu^{II} salt yields dinuclear species of general formula $[(NPm)Cu(\mu\text{-}X)_2Cu(NPm)]$ (X = Cl or I). X-ray analysis of these complexes show that they are isostructural and retain the trigonal geometry around the metal atom. The Cu···Cu distances are 2.775(1) Å for X = Cl and 2.642(1) Å for X = I. The Cu—(μ-X)—Cu angle is more acute for the iodide [61.48(3)°] than for the chloride [74.17(8)°] complex. These values are discussed in terms of Cu···Cu interactions induced by the electron donor ability of X and the bulk of the phosphine L.

Introduction

Tertiary phosphine–copper(I) halide complexes of general formula $L_m(CuX)_n$ have been the subject of numerous crystallographic investigations, and a wide variety of coordination geometries and stereochemistries have been described. The chemistry of monodentate tertiary phosphine complexes was surveyed some years ago by Lippard and Mayerle$^{(1)}$. The phosphine:copper ratio may vary through the range 4:1 in ionic $[L_4Cu]^+X^-$ complexes, 3:1 in L_3CuX complexes, 2:1 in $[L_2Cu(\mu\text{-}X)_2CuL_2]$ and L_2CuX complexes, and 1:1 in $[LCuX]_4$ complexes. Generally, where the ligand bulk is small, m may be as high as 3, but with increased steric bulk m is reduced to 2 or 1. Concerning the tetrameric 1:1 complexes, it has been established that the 'cubane' structure is destabilized relative to the chair one when large halogen atoms are accompanied by bulky ligands on the metal atom$^{(2-14)}$. However, this analysis is not complete, since with sufficiently bulky ligands the chair form is unstable and apparently tends to break into smaller units, as observed for the 1:1 complex of tricyclohexylphosphine which exists as a halide-bridged dimer$^{(10)}$. Moreover, this complex is one of the scarce examples of trigonal-planar geometry for a copper(I) complex. A monomeric two-coordinate 1:1 complex of copper(I) has been obtained with trimesitylphosphine due to the large steric effects of this ligand$^{(15)}$. However, although tri-*tert*-butylphosphine is one of the bulkiest phosphines known, expected to lead to low molecular weight molecules, the single crystal X-ray diffraction study showed that bromo(tri-*tert*-butylphosphine)-copper(I) is a cubane-type tetramer$^{(16)}$.

We have precedently presented, with diphenylphosphinodiphenylaminomethane (NPm) as ligand, monomeric and neutral 2:1 complexes of general formula L_2CuX (X = Cl or NO_3)$^{(17)}$, the copper atom being in a trigonal coordination. We have now completed the study of copper(I) complexes with this ligand and report here 1:1 complexes of general formula $[LCu(\mu\text{-}X)_2CuL]$ (X = Cl or I).

Experimental

Syntheses

All the compounds were prepared using a vacuum line under an Ar atmosphere. Solvents were deoxygenated by bubbling N_2 and degassed immediately before use. Commercially available, reagent grade chemicals were used. The ligand $Ph_2PCH_2NPh_2$ (NPm) was prepared as previously described$^{(18)}$ and recrystallized from CH_2Cl_2–EtOH.

Preparation of $(NPm)_2CuI$ (1)

Method a. To a suspension of Cu^I iodide (0.200 g) in PhMe (30 cm^3) were added two equivalents of NPm (0.772 g) in PhMe (20 cm^3). After 1 h of stirring, the residual CuI was removed by filtration and the solution was concentrated to 10 cm^3. On addition of three vols of n-hexane a white solid precipitated and was recrystallized from CH_2Cl_2 and Et_2O. (Found: C, 64.4; H, 4.8; N, 2.9; Cu, 6.8; $C_{50}H_{44}ICuN_2P_2$ calcd.: C, 64.9; H, 4.8; N, 3.0; Cu, 6.9%.) The same product was obtained regardless of the ligand:metal ratio used.

Method b. A solution of KI (0.038 g) in MeCN (20 cm^3) was added dropwise to a $CHCl_3$ solution of $Cu(NPm)_2NO_3$$^{(17)}$ (0.200 g in 20 cm^3). After 1 h of stirring, KNO_3 was removed by filtration and the solution was concentrated to 10 cm^3. White microcystals were obtained by addition of 30 cm^3 of n-hexane.

Elemental analysis and n.m.r. data are identical for the two products obtained from methods a and b.

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Preparation of $[(NPm)CuX]_2$*:* $X = Cl$ *(2),* $X = I$ *(3)*

To a solution of $(NPm)_2CuX$ ($X = Cl$(17), 0.400 g; $X = I$, 0.444 g) in $CHCl_3$ (20 cm^3) was added dropwise an EtOH solution (20 cm^3) of two equivalents of $CuCl_2 \cdot 2H_2O$ (0.163 g) or $Cu(NO_3)_2 \cdot 3H_2O$ (0.116 g). The mixture was stirred for 2 h. After filtration on Celite, the resulting solution was concentrated to 10 cm^3 and then 30 cm^3 of *n*-hexane was added slowly. The mixture was left for three days at 5 °C to give colourless microcrystals that were separated by filtration. (X = Cl, Found: C, 66.2; H, 4.7; N, 2.6; Cu, 11.5; Cl, 6.7; $CuC_{25}H_{22}ClNP$ calcd.: C, 64.4; H, 4.7; N, 3.0; Cu, 13.6; Cl, 7.6%; X = I, Found: C, 53.1; H, 3.9; N, 2.5; Cu, 11.7; $CuC_{25}H_{22}INP$ calcd.: C, 53.8; H, 3.9; N, 2.5; Cu, 11.4%.)

Physical measurements

I.r. spectra were recorded on a Perkin-Elmer 983G spectrophotometer in the solid state (polyethylene or CsBr mulls). ^{31}P- and ^{13}C-n.m.r. spectra were recorded on WHM 200 Bruker Fourier transform spectrometers in $CDCl_3$ solution. Chemical shifts were referenced to external H_3PO_4:D_2O (85:15 vol) and recorded from 323 to 213 K. Analyses were carried out by the Interuniversity Microanalytical Services. Mass spectroscopy analysis were done on a Nermag 10–10 spectrometer using NH_3 DCI technique.

X-ray crystal structure determination

Crystal data, intensity measurements and structure refinements are summarized in Table 1. Unit cell parameters and diffracted intensities were measured at room temperature on an automatic diffractometer [Enraf-Nonius CAD4 diffractometer for *(1)*, STOE STADI 4 diffractometer for *(2)* and *(3)*] using graphite monochromated MoK_α radiation. Data were corrected for Lorentz and polarization effects, and for absorption(19). The structure was solved by direct methods [*SHELXS* program(20) for *(1)*, *MULTAN87*(21) for *(2)* and *(3)*] and refined by *CRYSTALS*(22) for *(1)*, and *XTAL* program(23) for *(2)* and *(3)*. Atomic scattering factors and anomalous dispersion terms are taken from Ref. 24. The coordinates of the H atoms have been calculated for *(1)*, and observed and refined for *(2)* and *(3)*. Compounds *(2)* and *(3)* are isostructural. The ORTEP plot of the molecules *(1)* and *(3)* are shown in Figures 1 and 2, respectively. For *(1)–(3)*, selected interatomic distances and angles are listed in Table 2. Complete crystal data and final fractional atomic coordinates with their estimated standard

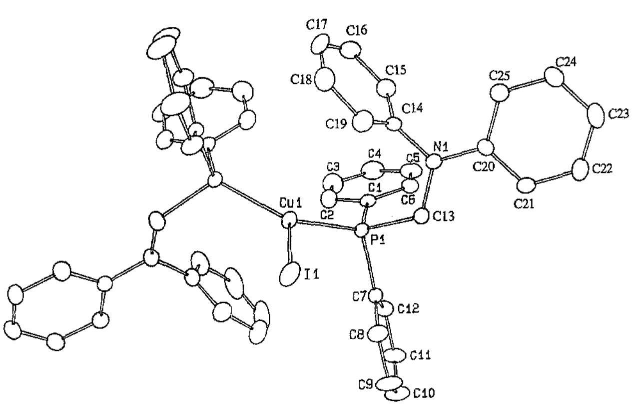


Figure 1. Structure of $[(NPm)_2CuI]$.

Table 1. Summary of crystal data, intensity measurements and structure refinement for *(1)*–*(3)*[a]

	(1)	*(2)*	*(3)*
Formula	$CuC_{50}H_{44}IN_2P_2$	$Cu_2C_{50}H_{44}Cl_2N_2P_2$	$Cu_2C_{50}H_{44}I_2N_2P_2$
Molecular weight	925.3	932.8	1115.8
Crystal size (mm)	0.10 × 0.10 × 0.10	0.10 × 0.13 × 0.58	0.14 × 0.25 × 0.25
Crystal system	Monoclinic	Monoclinic	monoclinic
Space group	C2/c	$P2_1/c$	$P2_1/c$
a (Å)	12.417(5)	9.975(1)	9.936(1)
b (Å)	16.609(6)	19.917(3)	20.476(4)
c (Å)	21.321(8)	11.153(2)	11.368(1)
β (°)	99.80(1)	93.413(9)	97. 480(8)
V (Å^3)	4333	2211.9(6)	2293.1(5)
Z	4	2	2
F_{000}	1880	960	1104
D_c (g cm^{-3})	1.42	1.40	1.62
λ (Å)	0.70930, 0.71359	0.71069	0.71069
μ (MoK_α) (mm^{-1})	1.317	1.192	2.379
$2\theta_{max}$ (°)	60	50	50
A^* (min, max)	1, 2.61	1.121, 1.179	1.364, 1.647
No. of measured reflections	6590	4117	4277
No. of observed reflections $[\lvert F_0 \rvert > 4\sigma(F_0)]$	3199	2359	2778
No. of parameters	255	328	328
Min and max. $\Delta\rho$ (eA^{-3})	$-0.32 + 0.46$	$-0.64 + 0.61$	$-0.99 + 0.80$
S	–	1.87	2.13
R, wR	0.0382; 0.0418	0.054, 0.025	0.048, 0.026

[a] Temp., 298 K; full-matrix refinement (on F); $\omega = 1/\sigma^2(F_0)$.

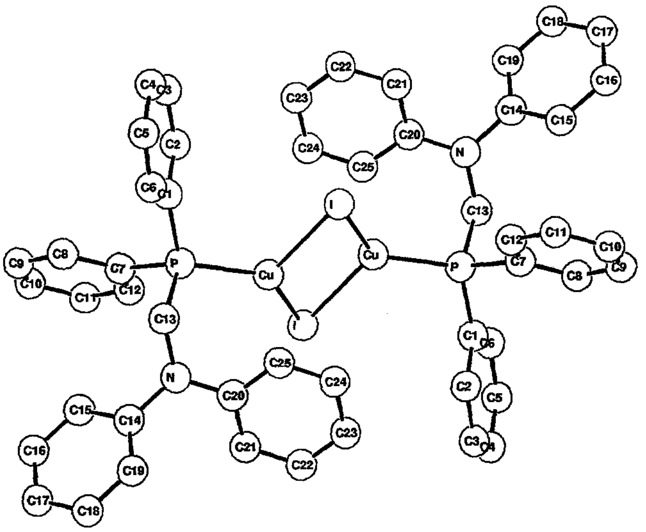


Figure 2. Structure of [(NPm)Cu(μ-I)$_2$Cu(NPm)] *(3)* with atom numbering. Ellipsoids are represented with 40% probability. Compound *(2)* is isostructural.

deviations have been deposited when the Editor as Supplementary material.

Results and discussion

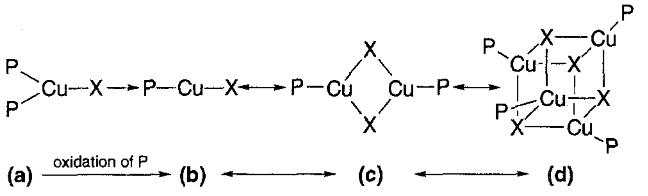
Chemistry and n.m.r. data

(NPm)$_2$CuI *(1)* can be prepared as previously described for (NPm)$_2$CuCl, by addition of two equivalents of the phosphine ligand on CuI; the same compound is obtained by substituting (NPm)$_2$CuNO$_3$ in the poor coordinating nitrato group by iodide.

Synthesis of the dinuclear copper(I) complexes [(NPm)CuX]$_2$ [X = Cl *(2)*; X = I *(3)*] from (NPm)$_2$CuX implies a more complex mechanism. From reaction of a copper(II) salt to the tricoordinated species (NPm)$_2$-CuX, complexes of general formula [(NPm)CuX]$_2$ are obtained. This implies that the copper(II) salt does not coordinate to nitrogen but may act as an oxidative agent and is able to induce the rupture of a metal–phosphine bond. This oxidation process is confirmed by the identification in the reacting pot of the ultimate form of the oxidized ligand (characteristic signal of the phosphine oxide at +27.3 p.p.m. in the ^{31}P-n.m.r. spectra). This process leads to a very unstable dicoordinated species, '(NPm)CuX', that dimerizes by formation of two halogen

Table 2. Selected interatomic distances (Å) and bond angles (°) with e.s.d.s in parentheses

	(1)	*(2)*	*(3)*
Metal environment *for (1) and (3) X = I, for (2) X = Cl*			
Bond length			
Cu—P	2.244(3)	2.172(1)	2.210(2)
Cu—X	2.559(3)	2.332(3)	2.5549(9)
Cu—X′		2.270(2)	2.612(1)
Cu—Cu′		2.775(1)	2.642(1)
Bond angles			
X—Cu—P	110.3(1)	118.96(6)	109.71(5)
P—Cu—X′		133.61(8)	130.02(6)
Cu—X—Cu′		74.17(8)	61.48(3)
X—Cu—X′		105.83(8)	118.52(3)
P—Cu—P′	139.5(2)		
Ligand			
Bond lengths			
P—C(1)	1.81(1)	1.806(5)	1.816(6)
P—C(7)	1.84(1)	1.826(5)	1.820(6)
P—C(13)	1.85(1)	1.850(5)	1.848(8)
N—C(13)	1.45(1)	1.449(6)	1.438(9)
N—C(14)	1.43(1)	1.427(6)	1.440(8)
N—C(20)	1.41(1)	1.400(6)	1.394(8)
Bond angles			
Cu—P—C(1)	120.4(4)	116.3(2)	115.3(2)
Cu—P—C(7)	113.9(4)	115.8(2)	117.9(2)
Cu—P—C(13)	115.6(4)	111.5(2)	110.7(2)
C(1)—P—C(7)	101.8(5)	104.7(2)	103.6(3)
C(1)—P—C(13)	105.5(6)	102.9(2)	104.0(3)
C(7)—P—C(13)	96.0(5)	104.0(2)	103.9(3)
C(13)—N—C(14)	121.0(10)	117.7(4)	118.6(5)
C(13)—N—C(20)	118.3(10)	119.4(4)	119.3(5)
C(14)—N—C(20)	118.1(9)	121.2(4)	120.7(5)



Scheme 1. Different conformations for $[LCuX]_n$ complexes. (a) Very bulky ligand such as trimesitylphosphine$^{(15)}$; (b) bulky ligands such as tricyclohexylphosphine$^{(27)}$ and this work; (c) less bulky ligands.

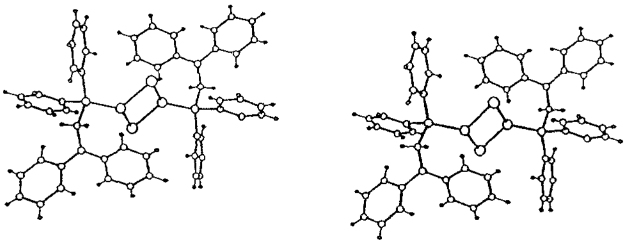


Figure 3. A stereoscopic view of $[(NPm)Cu(\mu\text{-}I)_2Cu(NPm)]$.

bridges to give a dimeric species with tricoordinated copper atoms. This confirms the expectation that tetrameric M_4X_4 clusters will fragment into M_2X_2 species, or even into MX units if the associated ligand is sufficiently bulky$^{(15)}$ (Scheme 1).

Concerning $(NPm)_2CuI$, the ^{13}C-n.m.r. data may be strictly compared to those observed for $(NPm)_2CuCl$ or $(NPm)_2Cu(NO_3)^{(17)}$, *i.e.* the shift of the carbons bonded to nitrogen is practically unchanged upon complexation while the shift of the carbons bonded to phosphorus is significantly shifted (130 p.p.m. in the complex *versus* 137.3 p.p.m. in the free ligand). At 293 K the ^{31}P-n.m.r. spectra of *(1)* exhibits only one broad signal at −16 p.p.m., while −19 p.p.m. is the value observed for the chloride homologue and −26 p.p.m. for the free ligand. Concerning $[(NPm)CuX]_2$, on the ^{31}P-n.m.r. spectra at 293 K a sharp signal is observed at −15.3 p.p.m. for X = Cl; for X = I an unexpected broad peak was observed at −23 p.p.m. (room temperature) which converted into a single sharp signal at −28.4 p.p.m. at 203 K.

Structure of (1)

Selected interatomic distances and bond angles are given in Table 2. The structure consists of discrete molecules of $[(NPm)_2CuI]$, a three-coordinate monomer in the solid state and the unit presents a C_{2v} symmetry. As in its chlorine analogues$^{(17)}$, the phosphine–amine ligand is only coordinated by phosphorus. The Cu—P bond length of 2.244(3) Å is identical to that observed for the chloride analogues. However, *(1)* differs from the $[(NPm)_2CuCl]$ complex already described, since the latter is not strictly C_{2v}, the two Cu—P bond distances being slightly different and the Cl—Cu—P angles being 109.24(8) and 117.84(8), respectively. However, $[(NPm)_2CuCl]$ is, as *(1)*, planar at copper (sum of angles equals to 359.72°). The I—Cu—P angle [110.3(1)°] is smaller than the P—Cu—P angle [139.5(2)°] due the greater bulk of the phosphine ligand. We have noted in the Experimental section that the same product is obtained regardless of the ligand:metal ratio used; the bulk of this phosphine ligand prevents tetracoordination of copper. NPm seems to be the bulkiest phosphine ligand already described since the P—Cu—P angle reported here is larger than the corresponding values of 126.9° observed for $PPh_3^{(25)}$, 126.4° for $PPh_2(o\text{-tolyl})^{(26)}$ and 134.06° for $P(Cy)_3^{(27)}$ in their P_2CuI compounds. It may be emphasized that the same remark is available for the complexes $[(NPm)_2CuCl]$ and $[(NPm)_2Cu(NO_3)]$ with P—Cu—P angles of 132.64 and 137.2°, respectively, while in $[(PPh_3)_2CuCl]$ this value is 125.48°.

Structures of (2) and (3)

It was shown for 1:1 complexes that the bulk of the phosphine prevented tetramer formation and that very bulky ligands form the uncharged dimeric complexes $[LCu(\mu\text{-}X)_2CuL]$. In fact, with NPm as ligand, tetrameric complexes are not obtained but we succeeded in obtaining dimeric complexes.

Chloro compound *(2)* is isomorphous with iodo complex *(3)*. The structure consists of discrete molecules of centrosymetric dimers $[LCu(\mu\text{-}X)_2CuL]$ (X = Cl or I). Geometries within the phosphine ligand are standard; however, it may be emphasized that the geometry at phosphorus is nearly tetrahedral while the geometry at nitrogen is nearly planar [the sum of the angles at nitrogen being 358.3° for *(2)* and 358.6° for *(3)*]. This confirms the sp^2 character of nitrogen associated with its poor donor ability. The two independent Cu—(μ-X) distances are nearly identical [they differ by only 0.062 Å for *(2)* and 0.057 Å for *(3)*]. These distances are also very close to the terminal Cu—X distances observed in $[(NPm)_2CuCl]$ and *(1)* [2.257(2) Å *versus* mean value of 2.30 Å for *(2)* and 2.559(3) Å *versus* a mean value of 2.583 Å for *(3)*]. Although the Cu—X bond distances are only slightly different in going from mononuclear to $(\mu\text{-}X)_2$ dinuclear species, ν(Cu—Cl) is observed at 215 cm^{-1} for the dimer and is indicative of bridging chlorine atoms$^{(28-30)}$, by contrast, terminal Cu—Cl occurs at higher frequencies, *i.e.* at 269 cm^{-1} for $[(NPm)_2CuCl]$. Concerning the Cu—P bond distances, they are shortened on going from the complex L_2CuX to the complexes $[LCu(\mu\text{-}X)_2CuL]$. The core $[Cu(\mu\text{-}X)_2Cu]$ is planar and copper is also coplanar with its three attached ligands; the sum of the angles around copper being 358.4 and 358.25° for *(2)* and *(3)*, respectively. A major difference between the structures of *(2)* and *(3)* is that the iodide complex presents a shorter Cu—Cu separation. The Cu—Cu distances are 2.775(1) and 2.642(1) Å for *(2)* and *(3)*, respectively. Correlatively, the Cu—(μ-X)—Cu angle is more acute for the iodide [62.48(3)°] than for the chloride [74.17(8)°] complex. It is noteworthy that these complexes are the second example of dinuclear phosphine complexes; by comparison, in $[P(Cy)_3Cu(\mu\text{-}X)_2CuP(Cy)_3]$ the Cu···Cu distance and the Cu—(μ-X)—Cu bond angles are 3.07 Å and 83.4° (X = Cl), and 2.89 Å and 68.5° (X = I), the Cu—Cu distance being longer and the Cu—(μ-X)—Cu angle less acute. Short Cu—Cu bond distances (2.586 Å) have also been observed in the dinuclear complex *bis*-(μ-iodo)*bis*(2,6-dimethylpyridine)dicopper(I)$^{(31)}$.

Influence of X → M donation on Cu^{I}···Cu^{I} interactions in molecules having a $[Cu(\mu\text{-}X)_2Cu]$ core has been extensively developed by Caultron and coworkers[27], and studied by extended Hückel calculations. There is a clear indication of increased Cu···Cu interaction in the case of a better μ-X electron donor centre (I *versus* Cl). The shortening of the Cu—μ-X bond distances (*vide supra*) compared to terminal Cu—X, which implies some multiple bonding of the Cu—μ-X bond, testifies to this electron donor ability. The significant changes in the metal–metal interactions involve direct electronic transfer into the π_z system from the orbitals of the bridged X atoms to the s and p orbitals of copper. Consequently, π_z orbitals play an important role in Cu···Cu interactions, its energy level should be as low as possible and NPm should not be a good π-donor ligand. However, it is difficult to predict if NPm is really a worse phosphine ligand than $P(Cy)_3$ since it has largely been assumed that the molecular structure is also controlled by the size of the ligand, and that quite small modifications on the ligand could substantially affect the structure and even the chemical reactivity of the compounds.

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