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Study of the geometric preferences of copper(I) halide coordination compounds with triarylphosphines. Crystal structures of $[CuCl\{P(o\text{-tolyl})_3\}]_2$ and $[CuBr\{P(o\text{-tolyl})_3\}]_2$

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Abstract

The crystal structures of $[CuCl(totp)]_2$ and $[CuBr(totp)]_2$, totp = tri-*o*-tolylphosphine, are reported. They present planar Cu_2X_2 cores with trigonal-planar Cu(I) atoms, the Cu–P axes bisecting in both cases the X–Cu–X angles. Crystallographic data: for $[CuCl(totp)]_2$ $a=9.1758(7)$, $b=10.4805(8)$, $c=20.481(1)$ Å, $\beta=99.279(2)°$, with $Z=2$ and space group $P2_1/n$; for $[CuBr(totp)]_2$ $a=9.215(1)$, $b=10.203(1)$, $c=11.275(1)$ Å, $\alpha=78.422(5)$, $\beta=100.691(5)$, $\gamma=80.789(4)°$, with $Z=1$ and space group $P\bar{1}$. The slight geometric changes observed between the two compounds, especially the more acute X–Cu–X angle in the case of $[CuCl(totp)]_2$ are investigated with Extended Hückel calculations on model compounds.

Introduction

Monovalent copper with its filled d orbitals does not provide much ground for the synergic bonding with the ligands usual in most of the transition elements. The coordination to copper(I) is, therefore, mainly determined by the Lewis basicity of the ligands and the local copper environment is subject to their steric effects which may lead to a variety of structures ranging from mononuclear three-coordinate species CuLL′L″ to cubanes $[CuLL']_4$ containing both three- and four-coordinated copper atoms and to polymer step-like formations of the formula $[CuLL']_n$. In all the above-mentioned cases, both bridging and terminal ligands may be present in the structure and in many instances products of quite different stoichiometry and structure were obtained by slightly varying the preparation procedure. The pre-determination, therefore, of the prevailing structure in each case is a goal yet to be achieved although, in specific cases with a limited variety of ligands, simple considerations apply satisfactorily [1].

Aiming at the expansion of the series of tertiary phosphine–copper(I) compounds studied and inspired by the fact that mixed ligand Cu(I) coordination compounds with heterocyclic thiones and tricyclohexyl [2] or tri-*o*-tolylphosphine [3] gave rise to mononuclear three-coordinate compounds whereas tri-*m*- and tri-*p*-tolylphosphine produced dimer compounds with tetrahedrally coordinated copper atoms [4], we have initiated the investigation of the tritolylphosphine adducts of copper(I) halides. In fact, we have been using these species for quite some time as non-isolated precursors for the preparation of the aforementioned mixed ligand complexes. The crystal structure of the title compounds, prepared in acetonitrile is discussed in view of E.H.T. computational results.

Experimental

Materials and instruments

Tolylphosphine (Aldrich) was used as received while copper(I) halides (Merk) were treated in methanol with an equimolar amount of the corresponding stannic halides in order to remove traces of copper(II) salts present. The solvents were dried by conventional methods prior to their use. A Perkin-Elmer 1430 spectrophotometer was used to record IR spectra (KBr pellets), the UV–Vis spectra were obtained on a Shimadzu 160 A spectrophotometer and ^1H NMR spectra were re-

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corded in deuterated chloroform solutions with internal TMS standard on a Bruker AW 80 spectrometer.

Preparative

In a typical procedure, 1 mmol of the appropriate copper halide was dissolved in 20 ml of acetonitrile and a solution of 1 mmol of the phosphine in 10 ml of the same solvent was added slowly over a period of 5 min. The solution was then gently refluxed for a period of 1 h. In the case of the chloro compounds this proved insufficient as the presence of unreacted copper(I) chloride indicated (verified by elemental analysis and the IR spectrum of the residue), therefore the reflux was continued for 5 more hours. In every case clear solutions were obtained and traces of solid substances, when present, were removed at this stage by filtration. The volume of the solution was reduced to one third of the initial one before being placed in the refrigerator. The white-coloured solids separating were microcrystalline and were redissolved in an acetonitrile–methanol 1:1 mixture. Slow evaporation at room temperature of this solution produced crystals appropriate for crystal structure analysis. It was verified that a slight excess of tri-*o*-tolyl phosphine (1.2:1 relative to the copper halide) did not give rise to different products as was verified by identical m.p. or decomposition of the two reaction products but led the reaction to completion at somewhat reduced periods of time.

Crystal structure determination

Complete crystal data and parameters for data collection are reported in Table 1. The space group was determined by preliminary Weissenberg and Precession photographs. Unit cell dimensions were derived from a least-squares refinement of the setting angles of 30 automatically centered reflections in the range $11<2\theta<23°$ on a Syntex P2$_1$ diffractometer upgraded by CRYSTAL LOGIC with Nb-filtered Mo Kα radiation. Three standard reflections measured every 97 reflections showed <3.0% intensity fluctuation. Lp and absorption corrections were applied. Scattering factors were taken from the International Tables for X-ray Crystallography [5]. The structure was solved by direct methods and refined by full-matrix least-squares, in which $\Sigma w\Delta^2$ was minimized using SHELX76 [6]. The hydrogen atoms of the methyl groups were calculated as riding on carbon atoms at 0.96 Å, the rest were located from a difference Fourier map. The non-H atoms were refined anisotropically and the H-atoms isotropically. Fractional positional parameters are reported in Tables 2 and 3 and representation of the molecular structures are shown in Figs. 1 and 2.

TABLE 1. Summary of crystal and intensity collection data

	$C_{42}H_{42}Cl_2Cu_2P_2$	$C_{42}H_{42}Br_2Cu_2P_2$
Formula weight	806.73	895.65
a (Å)	9.1758(7)	9.215(1)
b (Å)	10.4805(8)	10.203(1)
c (Å)	20.481(1)	11.275(1)
α (°)		78.422(5)
β (°)	99.279(2)	100.691(5)
γ (°)		80.789(4)
V (Å^3)	1943.85	998.79
Z	2	1
D_{calc} (Mg m^{-3})	1.378	1.489
D_{meas} (Mg m^{-3})	1.37	1.49
Space group	$P2_1/n$	$P\bar{1}$
Crystal dimensions (mm)	0.24×0.27×0.42	0.38×0.21×0.29
Radiation	Mo Kα (0.71069 Å)	
μ (cm^{-1})	13.39	31.42
Scan speed (°/min)	4.5	4.5
Scan range (°)	2.5	2.7 plus $\alpha_1\alpha_2$
20 limit (deg)	55	52
Data collected	5242	4187
Data unique	4445	3925
Data used	3342	2814
$F_o>$	$6\sigma F_o$	$4\sigma F_o$
R_{int}	0.0304	0.0195
Range of h	−10 10	−11 11
Range of k	0 13	0 12
Range of l	0 25	0 13
Weighting scheme	$1/w=\sigma^2(F_o)+0.0002F_o^2$	unit weights
$F(000)$	832	452
No. refined parameters	301	304
$\lvert\Delta/\sigma\rvert_{max}$	0.032	0.041
$(\Delta\rho)_{max}$ (e Å^{-3})	0.4057	0.811
$(\Delta\rho)_{min}$ (e Å^{-3})	−0.3527	0.412
S[a]	0.87	0.00
R (obs)[b]	0.0298	0.0392
R (all data)[b]	0.0473	0.0643
R_w (obs)[c]	0.0312	0.0418
R_w (all data)[c]	0.0459	0.0617

[a] $S=[\Sigma w(\Delta F)^2/(N-P)]^{1/2}$, $N=$ no. of observed reflections, $P=$ no. of parameters. [b] $R=\Sigma|\Delta F|/\Sigma|F_o|$. [c] $R_w=[\Sigma w(\Delta F)^2/\Sigma w|F_o|^2]^{1/2}$.

Computational details

Model compounds, where trimethylphosphine was substituted for tris-*o*-tolylphosphine were studied applying the Extended Hückel formalism [7]. The parameters (H_{ii} and ζ_i) used were the traditional ones; those proposed by Mertz and Hoffmann [8] were applied for Cu(I), since they proved adequate enough in previous analogous studies [9]. The models were constructed on the basis of the observed structural data. The inequality of the two Cu–X bonds was not retained due to its small magnitude, therefore for all the internal coordinates (i.e. Cu–X, Cu–P, C–P bond lengths and C–P–C angles) mean values were used. Strictly tetrahedral environment was imposed on the phosphine carbon atoms, with C–H bond lengths equal to 1.07 Å and H–C–H angles equal to 109.47°.

TABLE 2. Positional ($\times 10^4$) and equivalent thermal ($\times 10^4$) parameters of the non-H atoms with e.s.d.s in parentheses

Atom	x	y	z	U_{eq}[a]
Cu	707.2(4)	742.5(3)	4473.8(2)	454
P	1577.9(7)	1845.6(6)	3710.3(3)	364
Cl	766.9(8)	1062.0(7)	5585.0(3)	551
C(1)	1578(3)	3579(2)	3841(1)	376
C(2)	368(3)	4183(2)	4053(1)	402
C(3)	461(4)	5488(3)	4172(2)	519
C(4)	1676(4)	6184(3)	4085(2)	601
C(5)	2842(4)	5606(3)	3868(2)	611
C(6)	2799(3)	4307(3)	3748(1)	502
C(7)	−1011(3)	3481(3)	4135(2)	538
C(8)	452(3)	1605(2)	2898(1)	413
C(9)	−205(4)	2637(3)	2538(2)	542
C(10)	−1188(4)	2467(4)	1962(2)	741
C(11)	−1530(4)	1248(5)	1737(2)	821
C(12)	−869(4)	225(4)	2076(2)	704
C(13)	131(3)	359(3)	2655(1)	515
C(14)	884(5)	−801(3)	2979(2)	684
C(15)	3475(3)	1508(2)	3595(1)	415
C(16)	4622(3)	1479(3)	4139(1)	501
C(17)	6041(3)	1211(3)	4016(2)	619
C(18)	6334(4)	996(3)	3385(2)	686
C(19)	5221(4)	1042(3)	2861(2)	601
C(20)	3797(3)	1293(3)	2963(1)	468
C(21)	4391(5)	1755(5)	4832(2)	705

[a] $U_{eq} = 1/3(U_{ij} + U_{22} + U_{33})$.

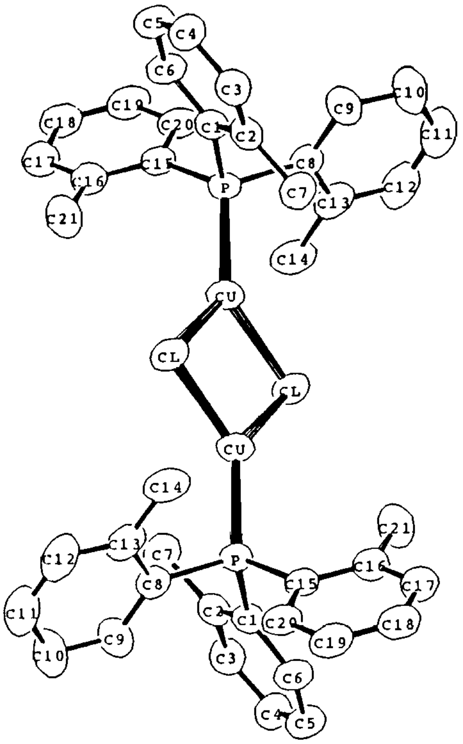

Fig. 1. Molecular structure of the $[CuCl(totp)]_2$ compound.

TABLE 3. Positional and equivalent thermal parameters ($\times 10^4$) of the non-H atoms

Atom	x	y	z	U
Br	4436.0(7)	906.3(6)	1169.3(5)	585
Cu	3793.4(7)	1058.1(6)	−1052.3(6)	464
P	2181(1)	2637(1)	−2551(1)	375
C(1)	2714(5)	2729(5)	−4052(4)	388
C(2)	3057(6)	3933(5)	−4670(5)	465
C(3)	3564(7)	4006(7)	−5756(5)	599
C(4)	3756(7)	2875(7)	−6224(6)	677
C(5)	3415(7)	1684(7)	−5644(6)	587
C(6)	2892(6)	1577(5)	−4546(4)	449
C(7)	2498(9)	261(6)	−3986(6)	592
C(8)	213(5)	2437(5)	−2875(4)	412
C(9)	−586(6)	2638(5)	−4089(5)	467
C(10)	−2027(6)	2419(6)	−4353(6)	567
C(11)	−2680(7)	1956(6)	−3407(7)	675
C(12)	−1931(7)	1786(7)	−2195(7)	678
C(13)	−494(6)	2022(6)	−1891(5)	540
C(14)	240(10)	1890(20)	−557(7)	908
C(15)	2063(6)	4372(5)	−2315(4)	446
C(16)	665(7)	5250(6)	−2542(5)	572
C(17)	575(9)	6565(7)	−2354(7)	753
C(18)	1870(10)	6998(7)	−1932(6)	836
C(19)	3240(10)	6145(7)	−1709(6)	719
C(20)	3385(6)	4826(5)	−1874(4)	522
C(21)	4928(7)	3940(8)	−1611(7)	637

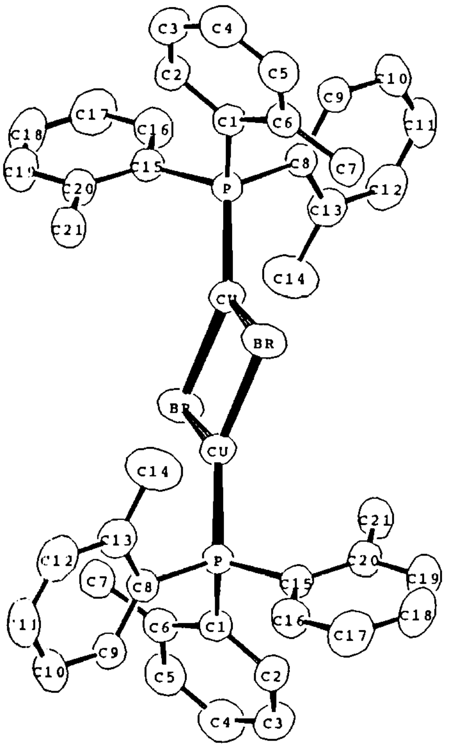

Fig. 2. Molecular structure of the $[CuBr(totp)]_2$ compound.

Results and discussion

The spectral characteristics of the studied compounds are typical of all the analogous ones reported so far in the literature. Small shifts of the UV–Vis absorption maxima are observed both in chloroform and acetonitrile solutions relative to the spectra of the free ligand, except an apparent broadening on the low energy side of the maximum, attributed to the presence of charge transfer excitations. The IR spectra reveal the characteristic complicated pattern of the phosphine in the region 800–600 cm^{-1} and the ^{1}H NMR spectra are indicative of the coordination of the phosphine to the copper halides since the ratio of the aromatic protons, appearing as a complicated multiple in the region 6.6–7.6 δ (ppm, downfield from TMS) and the methyl ones which show a sharp signal at *c.* 2.6–2.8 δ, is almost 4:3 and the former are shifted slightly in accordance with the shielding effect of the halogen atom.

Considering the molecular structure of the title compounds, the relevant internal coordinates are reported in Table 4. With respect to the copper–halogen bond distances observed Cu–Cl is slightly shorter than 2.302(2) Å reported for the analogous tricyclohexylphosphine compound [10], quite close to the corresponding distance for the three-coordinate copper atom in di-μ-chloro-tris-triphenylphosphine dicopper(I) which is 2.28 Å [11] and almost identical to the Cu–Cl bond distance in the monomeric three-coordinate CuCl(totp)-(pyrimidine-2-thione) (2.293(2) Å) [3a]. The Cu–Br distance observed is also comparable to analogous bonds in bromo-bridged copper compounds, e.g. $[NMe_4]_3Cu_2Br_5$ and $[NMe_4]_2Cu_2Br_4$ [12], lying almost half-way between the two values which are 2.392(3) and 2.448(1) Å, respectively. The inequality of the Cu–X bonds is more pronounced in the case of the chloro compound (difference 25 pm relative to 15 pm in the bromo compound).

TABLE 4. Relevant bond lengths (Å) and angles (°) of the studied compounds

Parameter	$[CuCl(totp)]_2$	$[CuBr(totp)]_2$
Cu–X	2.292(1)	2.432(1)
Cu–Xi	2.317(1)	2.416(1)
Cu–P	2.196(1)	2.206(1)
P–C1	1.837(2)	1.837(4)
P–C8	1.828(3)	1.835(5)
P–C15	1.829(2)	1.832(5)
Cu...Cu	3.107(1)	3.116(1)
P–Cu–X	132.60(3)	129.91(4)
P–Cu–Xi	132.00(3)	129.81(4)
X–Cu–Xi	95.23(3)	100.11(3)
Cu–X–Cu	84.77(3)	79.89(3)
Cu–P–C1	114.1(1)	111.7(1)
Cu–P–C8	111.0(1)	117.2(2)
Cu–P–C15	117.0(1)	113.9(2)
C1–P–C8	104.8(1)	103.9(2)
C1–P–C15	103.4(1)	104.7(2)
C8–P–C15	105.4(1)	104.3(2)

The Cu–P bond lengths are 2.196(1) Å for the chloro and 2.206(1) Å for the bromo complex, extremely close to each other taking into consideration that there is a certain influence of the bridging ligand on the metal–terminal ligand bond, although no canon for the derivation of such relationships have yet been set except in limited series of compounds. For example, one should notice the difference between the analogous tricyclohexylphosphine complexes, where the Cu–P distance varies from 2.18 for the chloro complex [10] to 2.23 Å for the iodo one [13] or the case of monomer compounds [3] where the same parameter varies smoothly from 2.241(2) Å in CuCl(totp)(pyrimidine-2-thione) to 2.269(2) Å for CuI(totp)(pyridine-2-thione).

Within the phosphine ligands, both the P–C distances ranging between 1.83 and 1.84 Å and the C–P–C angles varying from 103.4 to 105.4° are quite normal.

Inspection of the coordination environment around the copper atoms reveals, as usual, strong deviations from the ideal 120° bond angles, the one within the Cu_2X_2 core, i.e. X–Cu–X being 95.23(3)° for the chloro and 100.11(3)° for the bromo compound. The Cu–P axes, in both cases, almost bisect the X–Cu–X angles and the corresponding average angles are P–Cu–Cl = 132.3° and P–Cu–Br = 129.85°. The sum of angles around copper is exactly 360°, implying strict planarity and the Cu_2X_2 core in each case is strictly planar, as the sum of the angles within it is exactly 180°.

Finally, a remark about the Cu...Cu separation in both compounds is that it is well above the distance of 2.54 Å proposed to be the sum of two copper(I) covalent radii [14].

In a recent study of tri-*m*-tolylphosphine adducts with copper halides [9] an Extended Hückel study provided a suitable means for the interpretation, to some extent, of the preferability of each possible overall conformation of the compounds as well as local copper environments. In the present case, such a study is not relevant, since the steric bulk of the ligands prescribes the local copper environment as three-coordinate and, provided that dimer formation is confirmed, the overall structure of the compound as well. Nevertheless, the difference of *c.* 5° in the bonding angles of the Cu_2X_2 cores led to the present study, in which, the molecular and electronic structure of these compounds are examined with respect to the above bond angles.

Initially, the angles observed in the Cu_2Br_2 core were introduced to the Cu_2Cl_2 on keeping the rest of the structural parameters standard. Naturally, since the Br–Cu–Br angle is more obtuse than the Cl–Cu–Cl one (see Table 2) the two copper atoms approach slightly (Cu...Cu 2.962 Å in this model relative to 3.106 Å in the true dimer). During this approach, the sum of the core repulsions decreases slightly (by 0.07 eV) due mainly to the diminishing of the Cl...Cl interactions, but the decrease in orbital stabilization (by 0.13 eV) is more pronounced resulting in an overall destabilizing effect. Furthermore, the new conformation appears to be more ionic, especially within the core, where the copper atoms lose 0.015 to the chlorines, the net atomic charge on phosphorous being practically unaffected. The Cu–Cl overlap population decreases as well, by *c.* 4%, while a slight decrease is also evident in the Cu–P bond. It should be noticed that on going from the 'real' to the 'imaginary' model, i.e. during the approach of the copper atoms, their antibonding interaction [15] drops slightly in magnitude (from -0.013 to -0.011 e) without, though, giving indication of metal–metal bond formation.

A slightly better overlap population between the metal centers (-0.009 e) is observed in the bromo compound in accord with simple reasoning, i.e. better donor ability of the halide bridging atoms and with recent observations in analogous models [13]. In a subsequent step it was assumed that the Cu_2Br_2 core could adopt the more acute Cl–Cu–Cl angle, thus enhancing the separation of the two copper atoms from 3.116 Å in the true compound to 3.270 Å. Upon this separation, the sum of core repulsions is practically unaffected since the changes in Cu...Cu and Br...Br repulsions contradict each other, while the orbital stabilization is diminished (by 0.12 eV). The preference for the 'real' structure thus obtained is greater than the one for the chloro model. The conformation created in this way is more covalent than the 'real' one, the phosphorous atom being again the least affected. Finally, the copper–copper interaction gains slightly in antibonding character. It seems therefore, that, the nature of the bridging halide plays a role in determining the magnitude of the X–Cu–X angle, and therefore the Cu...Cu separation in $(PR_3)Cu(\mu\text{-}X)_2Cu(PR_3)$ complexes.

In view of the contradicting results about the dependence of several properties of halogen-bridged copper(I)–phosphine adducts on the nature of both the terminal and bridging ligands and within our interest to examine the factors influencing their structural and chemical behaviour a series of bulky phosphine ligands, possessing widely varying donor abilities (i.e. diphenyl-*o*-tolyl phosphine, dicyclohexylphenyl phosphine and tribenzylphosphine) are currently being studied in an analogous manner [16].

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