Inorganica Chimica Acta, 206 (1993) 163–168

Study of the geometric preferences of copper(I) halide coordination compounds with triarylphosphines. Crystal structure of $[Cu_2I_2\{P(m\text{-tolyl})_3\}_3]$

P. D. Akrivos, S. K. Hadjikakou, P. Karagiannidis*

Aristotle University of Thessaloniki, Department of Chemistry, Laboratory of General and Inorganic Chemistry, P. O. Box 135, GR–540 06 Thessaloniki (Greece)

D. Mentzafos and A. Terzis

N.C.N.R. Democritos, Department of Materials Research, GR-135 10 Agia Paraskevi (Greece)

(Received July 6, 1992; revised November 27, 1992)

Abstract

The copper(I) halide adducts with tri-*m*-tolylphosphine are prepared and studied by spectroscopic methods. The crystal structure of $[Cu_2I_2\{P(m\text{-tolyl})_3\}_3]$ is reported. The title compound crystallizes in the $P1$ space group with $a = 17.729(1)$, $b = 13.682(2)$, $c = 24.635(3)$ (Å), $\alpha = 117.769(4)$, $\beta = 104.966(4)$, $\gamma = 107.536(3)$° and $Z = 2$. The versatility of the above adducts as revealed by the present and analogous compounds is investigated computationally using EHT calculations. These support the relative stability of the observed geometric arrangement in relation to ones where both copper atoms possess identical local environments, either trigonal planar or pseudotetrahedral provided that the phosphine bulk is not the determining factor in the complex formation.

Introduction

The protean structural behaviour of copper is not limited to the extensively studied Cu^{2+} ion with its d^9 configuration but involves the d^{10} Cu^{1+} as well. In an effort to unravel the factors influencing it in the latter case, several ligand combinations have been used [1], inducing different steric demands and electronic effects in the metal's coordination sphere. We regard monodendate ligands more useful, since they introduce minimal intraligand steric interactions which complicate the coordination environment. Tertiary phosphines especially appear very interesting because they cover a wide range both in steric and electronic effects. Numerous studies on copper(I) halide–tertiary phosphine reactions and their products have been published [2] and a variety of structures obtained, ranging from binuclear three-coordinate Cu(I) species of the formula $[CuX(PR_3)]_2$ [3] to cubane-like ones $[CuX(PR_3)]_4$ [4], containing both three- and four-coordinated copper atoms but the pre-determination of the preferred structure in each case has not yet been achieved.

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 [5] or tri-*o*-tolylphosphine [6] gave rise to mononuclear three-coordinate compounds whereas tri-*m*- and tri-*p*-tolylphosphine produced dimer compounds with tetrahedrally coordinated copper atoms [7], we undertook the present investigation on the structure of tritolylphosphine adducts of copper(I) halides. 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 compound, prepared in acetonitrile is discussed in view of EHT computational results, while a more thorough study, involving all three tritolylphosphines is currently under way.

Experimental

Materials and instruments

The tolylphosphine (Aldrich) and copper(I) halides (Merck) were used as received and 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

---

*Author to whom correspondence should be addressed.

0020-1693/93/$6.00

and ^{1}H NMR spectra were recorded in deuterated chloroform solutions with internal TMS standard on a Bruker 60 W spectrometer.

Preparative

In a typical procedure, 1 mmol of copper halide was suspended in 20 ml of acetonitrile or toluene and a solution of 1 mmol of phosphine in 10 ml of the same solvent was added slowly over a period of 10 min. The reaction was led to completion by moderate heating for about 30 min. The unreacted solid substances were removed by filtration and the volume of the solution was reduced to one third of its original one before being placed in the refrigerator. Over a period of several days, a crop of white crystals appropriate for X-ray analysis were obtained in this way.

Computational

The calculations were carried out using models based on the crystallographic data of the studied compound. Besides the observed structure (a), a model with both copper atoms in a trigonal planar environment (b), and another with tetrahedral coordination (c) were studied (see Fig. 2). For each local copper environment, the mean value of the observed Cu–I and Cu–P bond lengths was used. The mean value of the P–C bond lengths and the C–P–C angles was used for the PMe_3 which were substituted for the tri-*m*-tolylphosphine ligands. The commonly used Extended Hückel parameters (H_{ii} and ζ_i) were adopted for the rest of the elements, while for copper those applied in analogous compounds and studies were used [8].

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 of $11<2\theta<23°$ 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 [9]. The structure was solved by direct methods and refined by full-matrix least-squares, in which $\Sigma w\Delta^2$ was minimized using SHELX76 [10]. 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. Positional and thermal parameters of the non-H atoms are given in Table 2.

TABLE 1. Summary of crystal and intensity collection data

Formula	$C_{63}Cu_2H_{63}I_2P_3$
Molecular weight	1294.01
a (Å)	17.729(1)
b (Å)	13.682(2)
c (Å)	24.635(3)
α (°)	117.769(4)
β (°C)	104.966(4)
γ (°)	107.536(3)
V (Å^3)	4870.72
Z	2
D_{calc} (M gm^{-3})	1.461
D_{meas}	1.45
Space group	$P1$
Crystal dimensions (mm)	$0.35\times0.18\times0.40$
Radiation used	Mo Kα ($\lambda=0.71069$)
μ (cm^{-1})	18.97
Scan speed (°/min)	4.5
Scan range (°)	2.9 plus (α_1–α_1)
2θ Limit (°)	52.0
Data collected	12099
Data unique	11509
Data used	9198
$F_o>$	6.0σ (F_o)
R_{int}	0.0194
hkl range	$-14\rightarrow0$ $-16\rightarrow16$ $-29\rightarrow29$
Weighting scheme	$\frac{1}{w}=\sigma^2(F_o)+0.0002F_0^2$
$F(000)$	1300
Refined parameters	811
$\lvert\Delta\sigma\rvert_{max}$	0.190
$(\Delta\rho)_{max}$ (e Å^{-3})	0.655
$(\Delta\rho)_{min}$ (e Å^{-3})	0.302
S[a]	0.99
R_{obs}[b]	0.0246
$R_{all\ data}$[b]	0.0377
R_{obs}[c]	0.0356
$R_{all\ data}$[c]	0.0396

[a] $\left[\frac{\Sigma w(\Delta F)^2}{(N-P)}\right]^{1/2}$, N = no. observed reflections, P = no. parameters.

[b] $R=\left[\frac{\Sigma|\Delta F|}{\Sigma|F_o|}\right]$. [c] $R_w=\left[\frac{\Sigma(\Delta F)^2}{\Sigma|F_o|^2}\right]^{1/2}$.

Results and discussion

Spectroscopic studies

Compounds prepared in toluene and acetonitrile possessed essentially identical UV–Vis spectra, recorded in chloroform, except for minor differences in the log ϵ values.

The characteristic bands ascribed to the coordinated tritolylphosphine were detected in the IR spectra of the compound. The Cu–X bonds could not be observed, since they fall outside the range of the spectrometer, therefore no assignment can be done for the local environment of each or both copper atoms.

The ^{1}H NMR spectra are only indicative of the presence of several aromatic protons which give rise to a complicated pattern at 7.4–6.9 (δ, downfield from

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

Atom	x	y	z	U_{eq}[a]
I(1)	3826.9(2)	5365.3(1)	6577.3(1)	443
I(2)	2700.7(2)	7406.0(2)	8133.6(1)	451
CU(1)	4437.6(3)	7792.5(3)	7593.8(1)	377
CU(2)	2446.4(3)	5307.5(3)	7216.9(2)	450
P(1)	6462.5(6)	8659.8(6)	8515.8(3)	347
P(2)	3777.2(6)	8494.1(5)	6958.3(3)	321
P(3)	929.1(6)	3582.8(6)	7033.6(3)	376
C(1)	6379(2)	7796(2)	8909(1)	391
C(2)	6018(3)	6530(3)	8491(2)	483
C(3)	5933(3)	5831(3)	8758(2)	597
C(4)	6185(3)	6385(3)	9433(2)	654
C(5)	6526(3)	7634(3)	9863(2)	593
C(6)	6634(3)	8350(3)	9597(1)	497
C(7)	6790(5)	8260(4)	10616(2)	956
C(11)	7151(3)	10299(2)	9259(1)	378
C(12)	6266(3)	10638(3)	9484(2)	486
C(13)	6761(3)	11856(3)	10072(2)	582
C(14)	8124(3)	12739(3)	10418(2)	521
C(15)	9016(3)	12450(3)	10200(1)	469
C(16)	8521(3)	11215(3)	9622(1)	437
C(17)	10501(4)	13427(3)	10573(2)	667
C(21)	7870(2)	8661(2)	8326(1)	381
C(22)	8899(3)	8554(3)	8685(2)	613
C(23)	9942(3)	8571(3)	8518(2)	760
C(24)	9992(3)	8719(3)	8007(2)	669
C(25)	8990(3)	8852(3)	7646(2)	570
C(26)	7921(3)	8799(3)	7807(1)	472
C(27)	9077(4)	9082(4)	7112(2)	1019
C(31)	4784(2)	8771(2)	6530(1)	367
C(32)	5341(3)	9899(3)	6601(1)	457
C(33)	6067(3)	10026(3)	6248(2)	552
C(34)	6205(3)	9016(3)	5815(2)	528
C(35)	5652(3)	7880(3)	5731(1)	520
C(36)	4948(3)	7777(3)	6098(1)	484
C(37)	5798(4)	6771(4)	5263(2)	862
C(41)	2031(2)	7490(2)	6244(1)	344
C(42)	1667(3)	7315(2)	5610(1)	448
C(43)	310(3)	6602(3)	5113(1)	479
C(44)	−685(3)	6056(3)	5242(2)	453
C(45)	−349(3)	6203(2)	5867(1)	461
C(46)	1015(3)	6917(3)	6363(1)	426
C(47)	−1429(3)	5582(3)	6008(2)	704
C(51)	3871(2)	10033(2)	7474(1)	385
C(52)	2820(3)	10266(3)	7279(1)	467
C(53)	2985(3)	11472(3)	7680(2)	654
C(54)	4192(3)	12442(3)	8268(2)	568
C(55)	5273(3)	12248(2)	8477(1)	460
C(56)	5081(3)	11023(2)	8079(1)	421
C(57)	6614(4)	13328(3)	9119(2)	615
C(61)	1115(3)	3686(2)	7821(1)	391
C(62)	2396(3)	4479(3)	8397(2)	486
C(63)	2602(3)	4525(3)	8988(2)	592
C(64)	1543(4)	3793(3)	9011(2)	677
C(65)	243(4)	3006(3)	8448(2)	618
C(66)	50(3)	2959(3)	7855(2)	497
C(67)	−957(5)	2187(4)	8463(2)	1119
C(71)	−799(2)	3286(2)	6635(1)	414
C(72)	−1675(3)	2377(3)	5926(1)	477
C(73)	−2946(3)	2235(3)	5648(2)	512
C(74)	−3356(3)	2983(3)	6054(2)	607
C(75)	−2497(3)	3911(3)	6753(2)	651
C(76)	−1216(3)	4058(3)	7039(2)	523
C(77)	−2915(5)	4777(5)	7210(2)	1122
C(81)	853(3)	2064(2)	6485(1)	409
C(82)	−157(3)	904(3)	6258(2)	510
C(83)	−114(3)	−186(3)	5869(2)	559
C(84)	931(3)	−137(3)	5704(2)	550
C(85)	1962(3)	995(3)	5932(1)	538
C(86)	1906(3)	2105(3)	6323(1)	468
C(87)	3150(4)	1081(4)	5787(2)	898

[a] $U_{eq} = (U_{11} + U_{22} + U_{33})/3$.

TMS). The existence of three discrete single, rather sharp signals, ascribed to methyl protons, at 2.40, 1.98 and 1.51, respectively, is noteworthy. The shape of the lines observed remained unchanged after successive scans, while their ratio was observed to be roughly 2:1:1, presenting minor shifts with time; these were attributed to the well-known fact that in solution phosphine ligands tend to establish an equilibrium between their coordinated and free forms [11]. The differences observed were not present in the spectra of mononuclear copper(I) complexes with more than one coordinated phosphine ligand, even when the crystal structure of the compound revealed relatively different local environments for phosphorous [12], therefore they could only be ascribed to a polynuclear compound, with distinct copper environments, something that could be verified by an X-ray structure determination.

Structural investigation

The crystal structure determination revealed, in support of the elemental analysis and the spectroscopic results, a $Cu_2I_2\{P(m\text{-tolyl})_3\}_3$ molecular structure, two discrete units of which are occupying a unit cell. The crystal structure of the dimer unit is depicted in Fig. 1; selected bond lengths and angles are reported in Table 3.

The closest structurally determined analogue is $Cu_2I_2(PPh_3)_3$ [13] which will be used for our subsequent comparison and discussion (hereafter refered to as complex **1**); nevertheless, comparison will be done with other $Cu_2X_2(PR_3)_3$ compounds reported [14] regardless of the halogen and phosphine ligands participating in them.

The two copper atoms adopt trigonal planar and pseudotetrahedral coordination environments, respectively, depending on the number of phosphine ligands attached to each of them. A general comparison with **1**, reveals a more 'symmetric' compound in the present case.

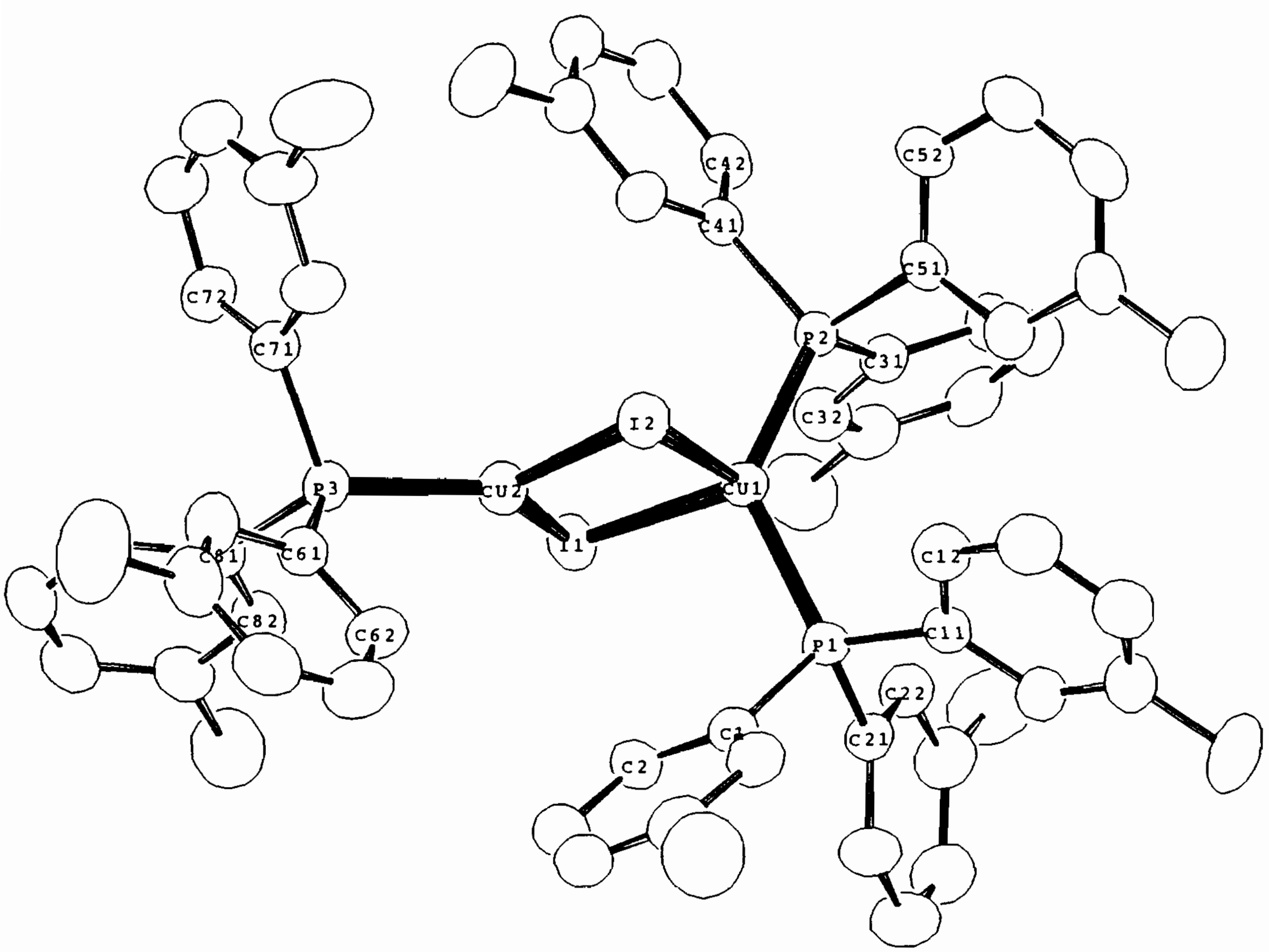

Fig. 1. PLUTO drawing of the dimer unit of [$Cu_2I_2\{P(m\text{-tol})_3\}_3$].

The Cu–I distances of 2.543(1) and 2.555(1) Å for the trigonal copper atom lie towards the higher limit of those observed for trigonal Cu(I) compounds (ref. 13 and refs. therein), while the values of 2.757(1) and 2.776(1) Å observed for the tetrahedral one are definitely larger than those reported for example in [$CuI(PPh_3)]_4$ [14] (2.620(2)–2.728(2) Å). The bond lengths observed form two sets of closely lying values and are on average slightly longer than the ones reported for **1**, which vary within wider limits. As a consequence, the copper–copper separation is 3.005(1) Å and does not raise the question of metal–metal interaction as has been the case in several analogous compounds, where this distance is certainly lower in magnitude. The Cu–Cu vector almost bisects the I–Cu–I angle (Cu2–Cu1–I1 = 52.0(1)° while Cu2–Cu1–I2 = 52.4(1)°).

The Cu–P bond of the three-coordinate copper (2.236(1) Å) is normal, while for the tetrahedral copper the two almost equivalent (2.279(1) and 2.283(1) Å) bonds are longer than those observed in [$CuI(PPh_3)]_4$, (2.228(5)–2.242(4) Å). On average, the Cu–P bond lengths are 0.015 Å longer than their counterparts in **1** and 0.030 Å than in $Cu_2Cl_2(PPh_3)_3$ [14a].

The angles around the two copper atoms are closer to the ideal ones (i.e. 118(1)° for the trigonal one and 104.4(1)° for the tetrahedral one) than in any of the related compounds, on the other hand, owing to interligand repulsions, the P–Cu–P angle in the tetrahedral copper is clearly greater (130.8(1)°) than that in **1** (125.2°). These interligand repulsions provoke a slight elongation of the P–C bonds (on average 1.835 versus 1.830 Å) and a closing of the C–P–C angles (on average 102.9 versus 103.6°) in the neighbouring phosphine ligands coordinated to the tetrahedral copper relative to the single one coordinated to the trigonal copper.

Finally, a general remark ought to be made in connection with the overall structure. The present compound is more 'planar' than most of the compounds with a Cu_2I_2 core, which usually appear folded around the I–I axis [13–15]. The dihedral angle between the (Cu1, I1, I2) and (Cu2, I1, I2) planes is 8.56°; relative

TABLE 3. Relevant structural data of the studied compound

Bond distances (Å)			
Cu1–I1	2.776(1)	P1–C1	1.840(4)
Cu1–I2	2.757(1)	P1–C11	1.830(2)
Cu2–I1	2.543(1)	P1–C21	1.829(3)
Cu2–I2	2.555(1)	P2–C31	1.843(3)
Cu1–P1	2.283(1)	P2–C41	1.836(2)
Cu1–P2	2.279(1)	P2–C51	1.831(3)
Cu2–P3	2.236(1)	P3–C61	1.828(4)
		P3–C71	1.828(3)
		P3–C81	1.833(3)
Bond angles (°)			
I1–Cu1–I2	104.4(1)	C1–P1–C11	103.1(1)
I1–Cu2–I2	118.0(1)	C1–P1–C21	102.2(2)
Cu1–I1–Cu2	68.6(1)	C11–P1–C21	104.4(1)
Cu1–I2–Cu2	68.8(1)	C31–P2–C41	102.8(1)
P1–Cu1–I1	106.9(1)	C31–P2–C51	102.3(1)
P1–Cu1–I2	100.4(1)	C41–P2–C51	102.9(1)
P2–Cu1–I1	102.5(1)	C61–P3–C71	103.7(1)
P2–Cu1–I2	109.4(1)	C61–P3–C81	102.2(2)
P1–Cu1–P2	130.8(1)	C71–P3–C81	105.0(1)
P3–Cu2–I1	126.9(1)		
P3–Cu2–I2	115.0(1)		

to values between 11.7 and 21.7° reported for the above-mentioned compounds.

Computational results

It is by now a well-known fact that steric effects determine to a great extent the coordination environment in copper(I) dimer compounds, formation of $Cu_2X_2(PR_3)_4$ being precluded on the grounds of strong interligand repulsions between the bulky PR_3 molecules. It seemed though interesting to investigate the relative stability of all possible compounds, since it is also well-established that phosphine compounds of Cu(I) participate in complex equilibria in solution.

The computations performed on the model compounds depicted in Fig. 2 reveal that in every case, the metal–metal interaction is very small, antibonding in nature [7, 16]. Although the Cu...Cu distance varies very slightly in these models, the 'trigonal' (Fig. 2(b)) reveals the lowest and the 'tetrahedral' (Fig. 2(c)) the highest (-0.0043 e) metal–metal interaction. The non-linear dependence of this interaction with the metal–metal separation is obvious from the value obtained for the 'real' model (Fig. 2(a)) which is lower than the mean of the above two cases, although structurally it represents the 'half-between' structure. An analogous observation also holds for the orbital stabilization energy, which favors the 'real' model by *c.* 6% relative to the mean value of 2(b) and 2(c). This stabilization is not cancelled by the slight destabilization of 2(a) (*c.* 3% relative to the mean of 2(b) and 2(c) regarding core repulsions.

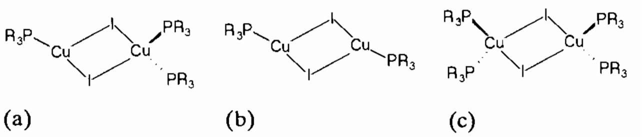

Fig. 2. Model compounds studied in the computations: (a) the 'real' compound, (b) and (c) are idealized dimers, produced by reflection of the appropriate site of (a) with respect to the center of the Cu...Cu distance.

Of course, the study of these models aims at the understanding of their relative stability in solution and in the solid state, therefore it is of interest to investigate their donor–acceptor abilities, which might give rise to formation of cubane or step-type polymers, especially in the case of 2(b) and under specific conditions for 2(a). Considering the FMO eigenvalues, 2(c) is predicted to be both a better donor and poorer acceptor than 2(b) while 2(a) represents a median of the two. The LUMO of 2(c) is a σ-type orbital delocalized among the four atoms of the core, therefore not directly available for chemical interactions. On the contrary, the LUMO of 2(b) is mainly a copper p_z–$d_z{}^2$ hybrid, indicating substantial reactivity toward incoming ligands. Furthermore, the HOMO is a σ-bonding MO corresponding to the Cu–I bond, its partition among metal and halogen no doubt determined by the electron donating ability of the phosphine ligand. The concerted effect of halogen and phosphine is most probably the crucial factor for determining the step or cubane form of the polymerization process 2(b) is capable of following. Furthermore, the polarity of the solvent and its affinity towards Cu(I) may give rise to solvation (acetone and acetonitrile being two well known examples in this case), while the bulk of the phosphine must certainly play a role in invoking even this solvation effect.

It is worth noting that in 2(a) the trigonal copper appears to be less accessible to such reactions, owing to its higher energy and the partial delocalization of the LUMO towards the iodine atoms. Furthermore, owing to the near-orthogonality of the bonding MOs at each iodine, each copper center in 2(a) retains the characteristics observed in its counterparts in 2(b) and 2(c), including charge delocalization, Cu–I and Cu–P overlap population etc.

References

1 (a)F. H. Jardine, *Adv. Inorg. Chem. Radiochem., 17* (1975) 115; (b) K. B. Karlin and J. Zubieta (eds.), *Copper Coordination Chemistry Biochemical and Inorganic Perspectives,* Adenine, New York, 1983.

2 (a) I. G. Dance, *Polyhedron, 5* (1986) 1037. (b) S. J. Lippard and J. J. Mayerle, *Inorg. Chem., 11* (1972) 753.

3 M. R. Churchill and F. J. Rotella, *Inorg. Chem., 18* (1979) 166.

4 J. C. Dyason, P. C. Healy, L. N. Engelhardt, V. A. Patrick, C. L. Raston and A. H. White, *J. Chem. Soc., Dalton Trans.* (1985) 831.

5 P. D. Akrivos, G. Kapsomenos, P. Karagiannidis, S. Skoulika and A. Aubry, *Inorg. Chim. Acta, 202* (1992) 73.

6 (a) S. K. Hadjikakou, P. Aslanidis, P. Karagiannidis, D. Mentzafos and A. Terzis, *Inorg. Chim. Acta, 186* (1991) 199; (b) S. K. Hadjikakou, P. Aslanidis, P. Karagiannidis, A. Aubry and A. Skoulika, *Inorg. Chim. Acta, 193* (1992) 129.

7 S. K. Hadjikakou, P. Aslanidis, P. Karagiannidis, A. Hountas and A. Terzis, *Inorg. Chim. Acta, 184* (1991) 161, and refs. therein.

8 M. K. Mertz and R. Hofmann, *Inorg. Chem., 27* (1988) 2120.

9 *International Tables for X-ray Crystallography* Vol. IV, Birmingham, Kynoch, UK, 1974.

10 G. M. Sheldrick, *SHELX76,* program for crystal structure determination, University of Cambridge, UK, 1976.

11 G. Costa, E. Reisnhofer and L. Stefani, *J. Inorg. Nucl. Chem., 27* (1965) 2581.

12 P. Karagiannidis, P. D. Akrivos and J. Herema, unpublished results.

13 P. G. Eller, G. J. Kubas and R. R. Ryan, *Inorg. Chem., 16* (1977) 2454.

14 (a) D. F. Lewis, S. J. Lippard and P. S. Welcker, *J. Am. Chem. Soc., 92* (1970) 3805; (b) V. G. Albano, P. L. Bellon, G. Ciani and M. Manossero, *J. Chem. Soc., Dalton Trans.,* (1972) 171; (c) J. C. Dyason, L. M. Engelhardt and P. C. Healy, *Aust. J. Chem., 38* (1985) 1243.

15 M. R. Churchill, B. G. DeBoer and D. J. Donovan, *Inorg. Chem., 14* (1975) 617.

16 P. K. Mehrota and R. Hoffmann, *Inorg. Chem., 17* (1978) 2187.