Crystal and Molecular Structure of Monoclinic Di-μ-chloro-tris(triphenylphosphine)dicopper(I), $Cu_2Cl_2(PPh_3)_3$

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The structure of di-μ-chloro-tris(triphenylphosphine)dicopper(I), $Cu_2Cl_2(PPh_3)_3$ has been determined from three-dimensional *X*-ray data collected by counter methods. The crystals are monoclinic, space-group $P2_1/c$ and have Z = 4 in a unit cell of dimensions a = 19·27(2), b = 9·81(1), c = 27·02(3) Å, β = 112° 5′(8′). The structure was refined to R 0·055 for 2046 independent reflections. The crystal contains discrete molecules in which two copper atoms are held together by two chlorine bridges. Two of the three phosphine ligands are bonded to one of the copper atoms and the third to the other, so that one metal atom is four- and the other three-co-ordinate. The mean values for the bonds to four- and three-co-ordinate copper are Cu–P 2·240 and 2·183, and Cu–Cl 2·436 and 2·272 Å. These values and certain angular distortions found in the molecule are discussed.

We are currently studying the crystal structures of mono- and poly-nuclear complexes of copper and gold in the oxidation states +1 and 0. Simple compounds, like $Au(CN)(PPh_3)$,[1,2] $Cu_2Cl_2(PPh_3)_3$,[3,4] and $Cu_2Cl_2(Ph_2P{\cdot}[CH_2]_2{\cdot}PPh_2)_3$ (ref. 5), are the starting materials for obtaining novel metal-atom clusters by reduction, as has been shown for the family of compounds having the general formula $Au_{11}X_3L_7$ [6-8] [X = I, SCN, or CN; L = PPh_3, $P(p\text{-}FC_6H_4)_3$, $P(p\text{-}ClC_6H_4)_3$, or $P(p\text{-}MeC_6H_4)_3$]. We now describe the structure of $Cu_2Cl_2(PPh_3)_3$ (I). This work was already under way when a communication appeared describing the same complex in a triclinic modification containing a benzene molecule of crystallization, $Cu_2Cl_2(PPh_3)_3,C_6H_6$ (II).[9] A comparative discussion of the two structures gives useful information regarding the packing effects on the molecular geometry.

EXPERIMENTAL

Crystal Data.—$Cu_2Cl_2(PPh_3)_3$, M = 983·9, Monoclinic, a = 19·27(2), b = 9·81(1), c = 27·02(3) Å, β = 112° 5′(8′), U = 4736·4 Å^3, D_m = 1·37(2) (by flotation), Z = 4, D_c = 1·38, $F(000)$ = 2024. Space-group $P2_1/c$ (No. 14) from systematic absences. Cell parameters were determined by precession photographs and refined on a PAILRED diffractometer by use of Mo-K_{α_1} radiation, λ = 0·70930 Å; μ(Mo-K_α) = 11·07 cm^{-1}.

Intensity Measurements.—The compound crystallizes from chloroform upon addition of ethanol. The crystal used for data collection was long prismatic, with dimensions 0·12 × 0·30 × 0·65 mm, elongated along the b axis. By use of a PAILRED linear equi-inclination diffractometer with Mo-K_α monochromatized radiation (silicon monochromatizing crystal), nine levels of the reciprocal lattice, h0—8l, were collected within the sphere 2θ ⩽ 42°. Outside this region only a small number of reflections were significantly above background. Integrated diffraction intensities for 4117 reflections were measured with the ω-scan method at a scan rate of 0·5° min^{-1}, and the backgrounds were counted for 1 min at the extreme points of the scan range. During the whole period of data collection the intensities of four well spaced zero-level reflections were measured at regular intervals, and no significant change in the scattering power of the crystal was observed. The absorption correction was computed by the method of ref. 10 by use of a sampling of 8 × 8 × 8 points. The transmission factors were found to range from 0·80—0·92. The integrated intensities were reduced to F_o values by correction for Lorentz and polarization factors. The latter were evaluated by taking into account the partial polarization of the incident beam.[11] No correction for extinctions was made since no significant effects were observed. A final set of 2046 independent reflections was obtained after removing all those with $\sigma(I)/I > 0{\cdot}25$.

Determination of the Structure.—The atomic co-ordinates of the $Cu_2Cl_2P_3$ group were found from a Fourier map computed with the strongest reflections phased by direct methods as previously described.[12] After a preliminary least-squares refinement of the heavy-atom parameters, a difference-Fourier synthesis revealed all the carbon atom positions. A block-diagonal refinement, in which the heavy atoms were assigned anisotropic temperature factors and the phenyl rings were constrained to rigid-body motion (D_{6h} symmetry, C–C taken as 1·392 Å, one mean temperature factor), led to R 0·07. A difference synthesis at this stage showed the peaks due to the hydrogen atoms of the phenyl groups, and these were thereafter included in the rigid group model, at a distance of 1·08 Å from the corresponding carbon atoms. Four cycles of full-matrix least-squares refinement gave a complete convergence of the parameter shifts. The final R value was 0·055, and of the weighted factor, R', 0·076 $\{R' = [\Sigma w(F_o - k|F_c|)^2/\Sigma wF_o^2]^{\frac{1}{2}}\}$. Weights were assigned according to the formula $w = 1/(A + BF_o + CF_o^2)$, where, in the final stages of refinement, A was 7·0, B 0·5, and C 10^{-4}, in order to obtain a reasonably constant distribution of the weighted mean quadratic error as a function of sin θ/λ and F_o. The refinement was carried out on F_o values, the minimized function being $\Sigma w(F_o - k|F_c|)^2$. The atomic scattering factors used in the least-squares and structure factor computations were taken from ref. 13 for neutral copper, chlorine, phosphorus,

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and carbon, and from ref. 14 for hydrogen atoms. The real part of the anomalous scattering of copper, chlorine, and phosphorus was taken into account.[15] The final difference Fourier synthesis, in which the residual values of the electron density were in the range $\pm 0{\cdot}4$ eÅ^{-3}, had no significant features. The results of the refinement are reported in the Tables. Tables 1 and 2 report the final parameters of the atoms with their estimated standard deviations. The final list of computed and observed structure factor moduli is listed in Supplementary Publication No. SUP 20246 (3 pp., 1 microfiche).*

Computations.—All computations were carried out on an IBM 7040 computer. For absorption correction a local programme was used, in which the directions of primary and diffracted beams are evaluated as recently described.[16] Counter data reduction, phase determination, and statistical analysis for weighting schemes were also based upon Fortran programmes written in our laboratory. In addition, local versions of entries Nos. 7528, 7531, 7532, and 7535 in the 1966 ' International World List of Crystallographic Programs ' were used for Fourier analysis, structure-factor and least-squares calculations; Johnson's ORTEP was used for thermal ellipsoid plotting, and a programme by Domenicano and Vaciago for computation of the molecular parameters.

TABLE 1

Positional and thermal [a] parameters ($\times 10^4$), with estimated standard deviations in parentheses, for the $Cu_2Cl_2P_3$ moiety

Atom	x/a	y/b	z/c	b_{11}	b_{12}	b_{13}	b_{22}	b_{23}	b_{33}
Cu(1)	3246(1)	2275(2)	5082(0)	31(0)	−23(2)	14(0)	113(2)	−19(1)	14(0)
Cu(2)	2242(0)	632(1)	4210(0)	27(0)	−20(2)	18(0)	88(2)	−7(1)	11(0)
Cl(1)	3327(2)	−36(4)	4978(1)	32(1)	11(4)	11(1)	101(5)	−7(3)	14(0)
Cl(2)	2455(2)	3102(3)	4297(1)	39(1)	−24(4)	16(1)	75(4)	−4(2)	16(0)
P(1)	3995(2)	3227(3)	5820(1)	25(1)	−12(4)	13(1)	85(4)	−5(3)	12(0)
P(2)	2350(2)	180(3)	3431(1)	32(1)	−7(4)	20(1)	65(4)	1(3)	13(0)
P(3)	1301(1)	296(3)	4495(1)	23(1)	−8(3)	13(1)	62(4)	1(2)	12(0)

[a] The anisotropic temperature factors are given by $\exp[-(h^2b_{11} + k^2b_{22} + l^2b_{33} + hkb_{12} + hlb_{13} + klb_{23})]$.

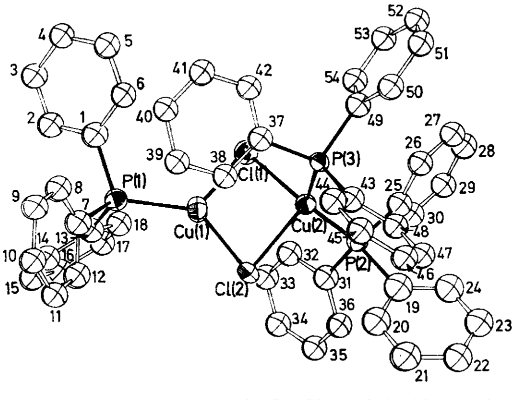

FIGURE 1 View of the molecule $Cu_2Cl_2(PPh_3)_3$ (drawn by use of ORTEP) in the monoclinic crystal (thermal ellipsoids at 40% probability). The symbols for carbon atoms have been omitted for clarity

DESCRIPTION OF THE STRUCTURE AND DISCUSSION

The molecular structure of $Cu_2Cl_2(PPh_3)_2$ is schematically represented in Figure 1, and the relevant distances and angles are reported in Table 3. The structure of the molecule in the present crystal (I) is essentially the same as in (II). Two copper atoms are held together by two bridging chloride ions, and the phosphine ligands are bonded one to the Cu(1) atom and two to the Cu(2) atom, so that the co-ordination around Cu(1) is approximately planar trigonal and that round Cu(2) approximately tetrahedral. The packing of molecules is shown in Figure 2. An important feature of the molecular packing is the tendency of phenyl rings belonging to different molecules to form almost parallel couples which generate *quasi*-graphitic interactions. Two of such interactions between molecules related by the inversion centre at

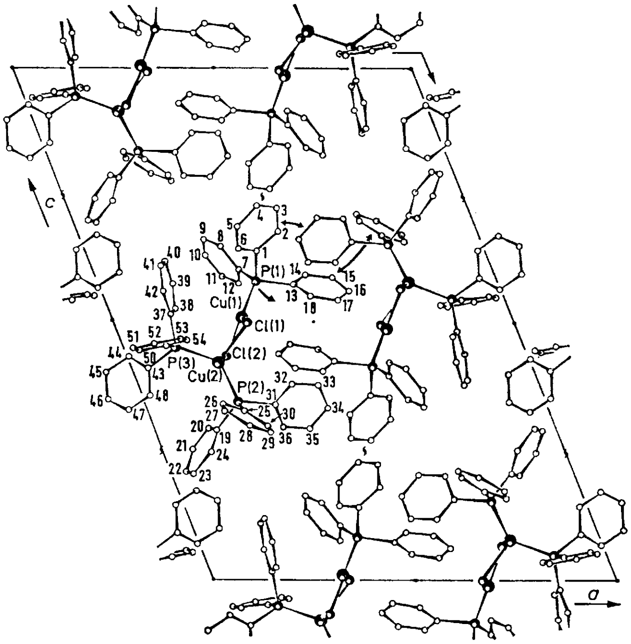

FIGURE 2 Crystal packing of monoclinic $Cu_2Cl_2(PPh_3)_3$, projected down the b axis (a right-handed system of axes is used and therefore the b axis is pointing downwards). Double arrows indicate the *quasi*-graphitic interactions (see text). A single arrow indicates the displacement direction of P(1) from the ' ideal ' position

(1/2,0,1/2) are indicated in Figure 2 by double arrows. A number of similar interactions have been observed with phenyl rings belonging to the upper and lower cells.

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* For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20.

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TABLE 2

Derived atomic co-ordinates and estimated standard deviations for the phenyl group atoms

Atom	*x*/*a*	*y*/*b*	*z*/*c*
C(1)	4303(6)	2111(10)	6402(3)
C(2)	4991(5)	2332(10)	6812(4)
C(3)	5215(4)	1503(9)	7263(3)
C(4)	4752(5)	454(8)	7303(3)
C(5)	4063(4)	235(9)	6892(3)
C(6)	3839(4)	1064(10)	6440(3)
C(7)	3645(9)	4747(12)	6055(4)
C(8)	3418(8)	4655(8)	6485(4)
C(9)	3064(4)	5756(11)	6616(3)
C(10)	2937(7)	6949(10)	6315(3)
C(11)	3163(6)	7041(8)	5885(3)
C(12)	3517(5)	5939(12)	5755(3)
C(13)	4860(4)	3736(13)	5751(4)
C(14)	5241(5)	4945(11)	5947(4)
C(15)	5916(5)	5213(8)	5888(3)
C(16)	6210(4)	4268(11)	5633(3)
C(17)	5827(5)	3059(9)	5438(3)
C(18)	5153(5)	2793(9)	5497(4)
C(19)	1561(6)	886(14)	2867(4)
C(20)	1366(5)	2235(13)	2906(3)
C(21)	762(6)	2818(9)	2498(4)
C(22)	354(5)	2052(12)	2048(3)
C(23)	549(5)	703(11)	2010(3)
C(24)	1152(7)	118(10)	2418(5)
C(25)	2391(7)	−1610(7)	3250(4)
C(26)	1945(5)	−2532(10)	3389(4)
C(27)	1944(5)	−3902(9)	3256(3)
C(28)	2389(5)	−4353(7)	2985(3)
C(29)	2837(4)	−3431(10)	2846(3)
C(30)	2838(5)	−2060(9)	2980(4)
C(31)	3197(5)	901(25)	3377(4)
C(32)	3872(6)	666(15)	3801(3)
C(33)	4536(4)	1161(13)	3779(3)
C(34)	4527(4)	1890(19)	3335(3)
C(35)	3852(5)	2124(11)	2912(3)
C(36)	3188(4)	1630(18)	2932(3)
C(37)	1511(6)	942(10)	5171(2)
C(38)	1648(5)	2333(10)	5248(3)
C(39)	1829(5)	2897(7)	5754(3)
C(40)	1872(5)	2070(9)	6183(2)
C(41)	1735(4)	678(8)	6107(3)
C(42)	1555(6)	113(7)	5600(4)
C(43)	405(7)	1118(20)	4094(4)
C(44)	−1(5)	1903(12)	4319(2)
C(45)	−674(6)	2498(13)	3995(3)
C(46)	−940(5)	2307(15)	3444(3)
C(47)	−532(5)	1521(9)	3219(2)
C(48)	139(7)	927(17)	3544(4)
C(49)	1063(5)	−1498(7)	4523(4)
C(50)	337(5)	−1938(9)	4433(4)
C(51)	190(4)	−3321(10)	4447(3)
C(52)	765(5)	−4267(7)	4548(3)
C(53)	1489(4)	−3828(9)	4637(3)
C(54)	1639(4)	−2443(10)	4624(4)
H(2)	5351(8)	3150(14)	6781(6)
H(3)	5752(4)	1673(14)	7584(4)
H(4)	4927(8)	−191(12)	7653(4)
H(5)	3702(7)	−579(13)	6925(5)
H(6)	3304(5)	894(15)	6118(4)
H(8)	3516(12)	3725(10)	6718(5)
H(9)	2887(7)	5685(17)	6952(4)
H(10)	2661(12)	7808(15)	6416(5)
H(11)	3063(10)	7969(10)	5652(5)
H(12)	3693(8)	6010(19)	5419(4)
H(14)	5014(7)	5678(15)	6145(6)
H(15)	6212(8)	6156(10)	6040(5)
H(16)	6735(5)	4474(17)	5586(5)
H(17)	6055(8)	2324(15)	5239(6)
H(18)	4855(10)	1850(15)	5344(7)
H(20)	1685(7)	2833(18)	3255(4)
H(21)	609(10)	3869(10)	2530(6)
H(22)	−112(8)	2506(17)	1729(5)
H(23)	229(7)	106(15)	1662(5)
H(24)	1304(11)	−933(11)	2387(7)
H(26)	1597(8)	−2182(14)	3600(5)
H(27)	1595(7)	−4620(13)	3363(5)
H(28)	2387(9)	−5421(8)	2883(5)
H(29)	3183(7)	−3780(14)	2634(5)
H(30)	3187(8)	−1341(13)	2874(6)
H(32)	3881(9)	98(23)	4147(4)
H(33)	5061(5)	979(23)	4110(4)
H(34)	5045(6)	2274(35)	3317(5)
H(35)	3844(8)	2695(18)	2567(4)
H(36)	2663(4)	1813(28)	2600(4)
H(38)	1614(7)	2979(13)	4914(4)
H(39)	1936(8)	3981(7)	5813(5)
H(40)	2012(8)	2510(12)	6576(3)
H(41)	1768(7)	34(11)	6441(4)
H(42)	1449(9)	−969(8)	5540(5)
H(44)	205(7)	2050(17)	4747(2)
H(45)	−991(9)	3108(22)	4171(5)
H(46)	−1463(9)	2770(28)	3191(4)
H(47)	−739(7)	1372(14)	2791(3)
H(48)	455(11)	314(27)	3368(5)
H(50)	−109(6)	−1201(12)	4351(6)
H(51)	−372(4)	−3661(14)	4378(5)
H(52)	650(7)	−5346(7)	4559(5)
H(53)	1937(5)	−4566(12)	4717(5)
H(54)	2202(5)	−2102(14)	4693(6)

All values $\times 10^4$. Hydrogen atoms are numbered according to the carbon atoms to which they are bonded. The mean isotropic temperature factors (Å^2) of the nine phenyl rings in the same order as the above listing are: 4·5(1), 4·6(1), 4·5(1), 6·2(1), 4·9(1), 4·9(1), 4·1(1), 4·8(1), and 4·4(1).

TABLE 3

Bond lengths (Å) and angles (deg.) in the $Cu_2Cl_2P_3$ moiety with estimated standard deviations. The corresponding values for the triclinic form (II) taken from ref. 9 are given in square brackets

(*a*) Distances

Cu(1) · · · Cu(2)	2·909(2)	[3·14]
Cl(1) · · · Cl(2)	3·656(5)	[3·51]
Cu(1)–Cl(1)	2·298(4)	[2·30]
Cu(1)–Cl(2)	2·247(4)	[2·26]
Cu(2)–Cl(1)	2·418(4)	[2·44]
Cu(2)–Cl(2)	2·454(4)	[2·47]
Cu(1)–P(1)	2·183(4)	[2·19]
Cu(2)–P(2)	2·236(5)	[2·25]
Cu(2)–P(3)	2·245(5)	[2·27]

(*b*) Angles

Cl(1)–Cu(1)–P(1)	118·8(2)	[123·6]
Cl(2)–Cu(1)–P(1)	133·5(2)	[134·8]
Cl(1)–Cu(1)–Cl(2)	107·1(2)	[101·6]
Cl(1)–Cu(2)–Cl(2)	97·3(2)	[91·6]
Cu(1)–Cl(1)–Cu(2)	76·1(2)	[82·9]
Cu(1)–Cl(2)–Cu(2)	76·3(2)	[82·9]
Cl(1)–Cu(2)–P(2)	113·4(3)	[117·0]
Cl(1)–Cu(2)–P(3)	102·4(3)	
Cl(2)–Cu(2)–P(2)	102·4(3)	
Cl(2)–Cu(2)–P(3)	103·9(3)	[103·9]
P(2)–Cu(2)–P(3)	131·8(2)	[130·4]

The interactions shown in Figure 2 may explain the deformations found in the bonding pattern of the three-co-ordinate Cu(1) atom. The best overlap of the phenyl rings is achieved by a displacement (0·25 Å) of the P(1) atom out of the Cl(1), Cu(1), Cl(2) plane, and by a deformation of the Cl(1)–Cu(1)–P(1) and Cl(2)–Cu(1)–P(1) angles, which become quite different. The displacement of P(1) from its ' ideal ' position is directed towards the phenyl rings of the centrosymmetrical molecule, as indicated by the arrow in Figure 2. A similar deformation in the co-ordination pattern of Cu(1), though less pronounced, is also present in (II) (Table 3), and therefore a similar centrosymmetric coupling of molecules

TABLE 4

Bond lengths (Å) and selected angles (deg.) with estimated standard deviations for the triphenylphosphine ligands

(*a*) Distances

P(1)–C(1)	1·82(1)	P(2)–C(31)	1·83(1)
P(1)–C(7)	1·84(1)	P(3)–C(37)	1·83(1)
P(1)–C(13)	1·82(1)	P(3)–C(43)	1·84(1)
P(2)–C(19)	1·84(1)	P(3)–C(49)	1·83(1)
P(2)–C(25)	1·83(1)		

(*b*) Angles

P(1)–C(1)–C(4)	178(1)	Cu(2)–P(2)–C(31)	113·5(5)
P(1)–C(7)–C(10)	173(1)	Cu(2)–P(3)–C(37)	112·8(5)
P(1)–C(13)–C(16)	175(1)	Cu(2)–P(3)–C(43)	115·7(5)
P(2)–C(19)–C(22)	177(1)	Cu(2)–P(3)–C(49)	113·8(5)
P(2)–C(25)–C(28)	177(1)	C(1)–P(1)–C(7)	103·4(7)
P(2)–C(31)–C(34)	177(1)	C(1)–P(1)–C(13)	103·8(6)
P(3)–C(37)–C(40)	176(1)	C(7)–P(1)–C(13)	106·3(7)
P(3)–C(43)–C(46)	177(1)	C(19)–P(2)–C(25)	104·2(7)
P(3)–C(49)–C(52)	177(1)	C(19)–P(2)–C(31)	105·8(7)
Cu(1)–P(1)–C(1)	114·8(5)	C(25)–P(2)–C(31)	102·7(9)
Cu(1)–P(1)–C(7)	117·3(5)	C(37)–P(3)–C(43)	104·0(7)
Cu(1)–P(1)–C(13)	109·9(5)	C(37)–P(3)–C(49)	104·9(7)
Cu(2)–P(2)–C(19)	111·4(5)	C(43)–P(3)–C(49)	104·6(8)
Cu(2)–P(2)–C(25)	118·0(5)		

very probably exists in the triclinic crystal. Analogous interactions between phenyl rings have been observed in ReH$_3$(PPh$_3$)$_2$(Ph$_2$P·[CH$_2$]$_2$·PPh$_2$),[17] Pt(PPh$_3$)$_3$,[18] and Ir(NO)(PPh$_3$)$_3$.[19] Apart from being a source of considerable deformations of molecular parameters, these interactions have been shown to determine special packing effects (see ref. 19 and refs. therein).

The main structural differences between the molecules (I) and (II) are in the Cu$_2$Cl$_2$ group, which is folded around the Cl(1) · · · Cl(2) axis, the dihedral angle being 158·7 in (I) and 168·3° in (II). Correspondingly, the Cu(1) · · · Cu(2) distance in (I) is 0·23 Å shorter and the Cl(1) · · · Cl(2) distance 0·15 Å longer, whereas the Cl–Cu–Cl and Cu–Cl–Cu angles are increased and decreased respectively by *ca.* 6°. All these effects can only be due to packing forces.

The other parts of the molecule exhibit only small differences in the two structures. The Cu–P [20–22] and Cu–Cl [23] distances are within the range of those found in a number of copper(I) compounds. The Cu–P distance in the three-co-ordinate copper atom is 0·06 Å shorter than the corresponding interactions in the four-co-ordinate atom. The variation can be accounted for in terms of different covalent radii and steric repulsions. On the other hand, the Cu–Cl distances involving Cu(1) are, on the average, 0·16 Å shorter than those involving Cu(2), the difference being 2·5 times greater than that observed in the Cu–P distances. A bond-order effect, resulting from p_π–p_π overlap, may account for the shortening in the Cu(1)–Cl interactions observed.

Cu(2) is co-ordinated in a distorted tetrahedral manner. The planes containing Cl(1), Cu(2), Cl(2), and P(2), Cu(2), P(3) form a dihedral angle of 86·2(3)°. A more marked departure from an idealized tetrahedral geometry is present in the Cl(1)–Cu(2)–Cl(2) and P(2)–Cu(2)–P(3) angles, which are 97·3 and 131·8°. The former value is clearly fixed by the strains which characterize the four-membered ring, the latter merits further discussion. A similar deformation, besides being present in (II), has been observed in a number of tetrahedral copper(I) complexes.[20–22] Lippard and Melmed [22] have shown that in a series of copper(I) complexes the P–Cu–P angle increases with the increase of the electronegativity of the other ligands. This trend, valid for the complexes considered by these authors, is not of general application, as will be seen later. For the same class of compounds, Messmer and Palenik [21] have suggested that both Cu–P distances and P–Cu–P angles depend on the donor properties of the other ligands. This statement is convincing, and a possible interpretation of the two effects could be that the shortening of the Cu–P distances increases the steric repulsions between the phosphorus atoms, so that the P–Cu–P angle is forced to larger values. If this were the case, the two effects would be correlated; however, as the authors themselves have shown,[21] a variety of P–Me–P angles is possible in tetrahedral complexes, without apparent correlation with the metal–phosphorus distances. Further examples are 2·31 Å, 101° in Ir(NO)(PPh$_3$)$_3$,[19] 2·34 Å, 111° in monoclinic Pt(CO)(PPh$_3$)$_3$,[24] 2·36 Å, 105° in trigonal Pt(CO)(PPh$_3$)$_3$,[25] and 2·36 Å, 98° in Pt(CO)$_2$(PPh$_2$Et)$_2$.[26] In the last-named molecule the lowering of the P–Pt–P angle to 98°, and the corresponding widening of the C–Pt–C angle to 117°,[26] show a clear inversion of tendency with respect to the copper(I) compounds. A similar situation is present in the recently reported structure of Fe(NO)$_2$(Ph$_2$PC$_5$F$_6$PPh$_2$),[27] in which the value of the N–Fe–N angle is 125·4°. In the light of these results we would suggest that, in addition to other co-operative factors, the π-bonding effects play an important role in determining such angular distortions. The observed enlargement in the ligand–metal–ligand angles can be considered as the consequence of non-bonding repulsions between the ligand orbitals which receive electron density from the metal atom *via* π back-

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donation. In the group of copper compounds, the value of the P–Cu–P angle would seem to be an increasing function of the electronic population on the phosphorus 3*d* orbitals, and, therefore, of the donor properties of the other ligands. When ligands with more pronounced acceptor properties are present together with phosphine groups, the P–M–P angle becomes the lower, as can be seen from the values reported above for the complexes $Pt(CO)_2(PPh_2Et)_2$ (ref. 26) and $Fe(NO)_2(Ph_2PC_5F_6PPh_2)$.[27] In the former the better π-acceptor properties of the carbonyl ligands are responsible for a scanty population of the phosphorus atom *d* orbitals and an appreciable population on the π* molecular orbitals of the carbonyl groups; the P–Pt–P angle is therefore smaller and the C–Pt–C angle larger than the tetrahedral value. In the iron complex, in which the π* orbitals of the nitrosyl groups are probably more populated than the corresponding carbonyl orbitals, the effect is even more apparent. An extreme angular value has been found in the cation $[Ir(NO)_2(PPh_3)_2]^+$ with N–Ir–N 154·2, and P–Ir–P 116·3°.[28] Although this complex should be considered a borderline case, since other causes may have determined the flattening of the molecule, we emphasize that the above angular values do in fact fall into line with the suggested interpretation.

With regard to bonding parameters within the phosphine ligands, the P–C distances are substantially equivalent within experimental error, mean 1·83 Å. The Cu–P–C angles are, as usual, larger than the tetrahedral angle (mean 114·3°), and the C–P–C angles correspondingly smaller (mean 104·4°). All these parameters are consistent with those commonly found in the co-ordinated ligand and in triphenylphosphine itself.[29]

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