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Structural and Solid-state ^{31}P Nuclear Magnetic Resonance Studies on 1:1:1 Mixed Nitrogen and Phosphine Base Complexes with Copper(I) Halides *

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1:1:1 Adducts of copper(I) halides with phosphine and amine donor ligands, $[\{CuX[PPh_2(C_6H_4Me\text{-}o)](cpy)\}_2]$ and $[\{CuX(PPh_3)(pip)\}_2]$ (cpy = 4-cyanopyridine, pip = piperidine; X = Cl, Br or I) have been synthesized as crystalline dihalide-bridged binuclear complexes and characterized by single-crystal structure determinations and solid-state ^{31}P cross-polarization magic angle spinning (CPMAS) NMR spectroscopy. The $[\{CuX[PPh_2(C_6H_4Me\text{-}o)](cpy)\}_2]$ complexes are isomorphous with their PPh_3 analogues, crystallizing as centrosymmetric dimers in space group $P2_1/n$ with $a \approx 15..5$, $b \approx 8.0$, $c \approx 18.7$ Å, $\beta \approx 104°$ ($Z = 2$ dimers). Introduction of the *o*-tolyl group into the phosphine ligand increases all of the Cu–P, Cu–N and Cu–X bond distances by 1–2% with the increase in Cu–X accommodated primarily by an increase in the Cu···Cu distances by 2–6%. For $[\{CuX(PPh_3)(pip)\}_2]$ the chloride and bromide complexes are isomorphous, crystallizing in space group *Pbca* with $a \approx 16.5$, $b \approx 18.0$, $c \approx 14.6$ Å ($Z = 4$ dimers). The monomer/asymmetric units are disposed close to a centre of symmetry but the two Cu–X distances at each copper site differ by over 0.3 Å and the resultant 'dimers' are better described as associated monomers with three- rather than four-co-ordinate copper. The iodide complex crystallizes in space group $P\bar{1}$, with $a = 17.442(9)$, $b = 16.532(6)$, $c = 13.801(3)$ Å, $\alpha = 92.78(2)$, $\beta = 112.08(3)$, $\gamma = 112.65(3)°$ ($Z = 3$ dimers). The unit cell contains independent centro- and non-centro-symmetric dimers with significant differences in the geometric parameters of the two. Differences in the Cu–X distances are much smaller than for the X = Cl and Br complexes. The piperidine ligand co-ordinates through the nitrogen lone pair with the Cu–N bond approximately perpendicular to the Cu_2X_2 plane and is disposed away from the Cu_2X_2 plane and towards the phosphine ligand for all dimers except the centrosymmetric iodide dimer. The Cu···Cu distances are 7–11% longer than those of the corresponding pyridine base complexes, but are shorter than those in complexes with acetonitrile as the base. The solid-state ^{31}P CP MAS NMR spectra of the complexes at $B = 9.4$ T show well resolved asymmetric quartets arising from a combination of scalar and dipolar coupling between the quadrupolar spin-$\frac{3}{2}$ copper and the spin-$\frac{1}{2}$ phosphorus nuclei. The structural and spectroscopic data are discussed in relation to steric and electronic properties of the donor ligands and the influence of these on the size and shape of the Cu_2X_2 core.

Recrystallization of 1:1 mixtures of tertiary arylphosphines (PR_3) and copper(I) halides (CuX; X = Cl, Br or I) from solutions containing nitrogen-base donors L can yield 1:1:1 mixed-ligand complexes[1] which have been characterized by X-ray diffraction techniques as dihalide-bridged binuclear species, $[\{CuX(PR_3)L\}_2]$, with distorted tetrahedral CuX_2PN copper co-ordination.[2-6] These compounds may be considered as derivatives of $(PCuX)_2$ dimers, known in cases where the phosphine is sterically hindered,[6-10] in which the dihalide-bridged structures have three-co-ordinate copper sites. These $(PCuX)_2$ and $(PNCuX)_2$ dimers are interesting because of the considerable variation that is possible in the steric and donor properties of the ligands which, in turn, influences the bonding and steric interactions within the Cu_2X_2 core. However, the list of structurally characterized compounds for this class is not extensive with results available only for complexes with triphenylphosphine or tris(*o*-tolyl)phosphine as the P-donor ligands and acetonitrile or pyridine bases as the N-donor ligands. As part of our studies into the structural and spectroscopic properties of copper(I) phosphine complexes we were interested in extending the available data set for these $(PNCuX)_2$ dimers to include complexes incorporating a phosphine ligand with an intermediate steric profile between those of PPh_3 and $P(C_6H_4Me\text{-}o)_3$ and a nitrogen-base ligand having a tetrahedral rather than a planar or linear nitrogen geometry. To this end we synthesized the six complexes $[\{CuX[PPh_2(C_6H_4Me\text{-}o)](cpy)\}_2]$ (cpy = 4-cyanopyridine) and $[\{CuX(PPh_3)(pip)\}_2]$ (pip = piperidine) (X = Cl, Br or I) and characterized them by both X-ray diffraction analyses and solid-state ^{31}P NMR spectroscopy. These results, together with those published previously on related complexes, demonstrate that changes in the character of the N-donor can result in quite profound changes in the structural and bonding parameters and that an almost continuous variation in core geometries and the distribution of electronic charge about the copper(I) nucleus is possible through suitable choice of the phosphine, amine and halide ligands.

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* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

Experimental

Preparation of Compounds.—Di-μ-halogeno-bis[(4-*cyanopyridine*)(*diphenyl*-o-*tolylphosphine*)*copper*(I)], [{CuX[$PPh_2(C_6H_4Me$-*o*)](cpy)}$_2$] (X = Cl, Br *or* I). Dissolution of CuX (2.0 mmol) and $PPh_2(C_6H_4Me$-*o*) (2.0 mmol, 0.56 g) in a solution of an excess of 4-cyanopyridine [X = Cl or Br, 0.5 g (5 mmol); X = I, 1.0 g (10 mmol)] in refluxing acetonitrile (100 cm^3) under atmospheric conditions resulted in clear yellow to orange solutions which yielded yellow-orange acicular crystals of the appropriate complex on cooling. X = Cl **1**: m.p. 189–201 °C (Found: C, 62.40; H, 4.40; N, 5.80. $C_{50}H_{42}Cl_2Cu_2N_4P_2$ requires C, 62.40; H, 4.40; N, 5.85%); ν(CN) 2232 cm^{-1}. X = Br **2**: m.p. 207–210 °C (Found: C, 57.30; H, 4.00; N, 5.30. $C_{50}H_{42}Br_2Cu_2N_4P_2$ requires C, 57.30; H, 4.05; N, 5.35%); ν(CN) 2232 cm^{-1}. X = I **3**: m.p. 203–205 °C (Found: C, 52.5; H, 3.70; N, 4.80. $C_{50}H_{42}Cu_2I_2N_4P_2$ requires C, 52.60; H, 3.70; N, 4.90%); ν(CN) 2231 cm^{-1}.

Di-μ-halogeno-bis[(*piperidine*)(*triphenylphosphine*)*copper*(I)], [{CuX(PPh_3)(pip)}$_2$] (X = Cl, Br *or* I). Dissolution of CuX (0.1 mmol) in a solution of PPh_3 (0.1 mmol, 0.26 g) in refluxing piperidine (10 cm^3) under an argon atmosphere (rapid oxidation of the reaction mixture occurred in the presence of air) gave clear reaction mixtures which formed crystalline precipitates on cooling. These were filtered off under argon and dried for 1 h under vacuum. The crystals were routinely stored under argon as they decompose slowly in air to green oxidation products. X = Cl **4**: m.p. 195–200 °C (decomp.) (Found: C, 62.00; H, 6.00; Cl, 8.20; N, 3.10. $C_{23}H_{26}ClCuNP$ requires C, 61.90; H, 5.85; Cl, 7.95; N, 3.15%). X = Br **5**: m.p. 186–190 °C (decomp.) (Found: C, 56.60; H, 5.5; Br, 16.20; N, 2.80. $C_{23}H_{26}BrCuNP$ requires C, 56.30; H, 5.35; Br, 16.30; N, 2.85%). X = I **6**: m.p. 159–163 °C (decomp.) (Found: C, 51.40; H, 5.00; I, 23.50; N, 2.60. $C_{23}H_{26}CuINP$ requires C, 51.35; H, 4.85; I, 23.60; N, 2.60%).

Structure Determinations.—Unique data sets were measured at *ca.* 295 K using an Enraf–Nonius CAD-4 four-circle diffractometer (scan mode 2θ–θ; monochromatic Mo-Kα radiation, λ = 0.7107_3 Å), yielding *N* independent reflections, N_o with $I > 3\sigma(I)$ being considered 'observed' and used in the full-matrix least-squares refinements after analytical absorption corrections. Anisotropic thermal parameters were refined for the non-hydrogen atoms; $(x, y, z, U_{iso})_H$ were included, constrained at estimated values. Conventional residuals at convergence, *R*, *R′* on |*F*| are quoted, statistical reflection weights derivative of $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\sigma^4(I_{diff})$ being used. Neutral-atom complex scattering factors were used; computation used the XTAL 3.2 program system implemented by S. R. Hall.[11] Pertinent results are presented in Figs. 1–3 and Tables 1–5. Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters, and remaining bond lengths and angles.

Crystal/refinement data. $C_{50}H_{42}Cl_2Cu_2N_4P_2$ **1**, *M* = 958, monoclinic, space group $P2_1/n$ (C_{2h}^5, no. 14, variant), *a* = 15.414(6), *b* = 8.093(4), *c* = 18.57(1) Å, β = 105.04(4)°, *U* = 2237 Å^3, D_c (*Z* = 2 dimers) = 1.42 g cm^{-3}, *F*(000) = 984, μ_{Mo} = 11.8 cm^{-1}. Specimen: 0.085 × 0.43 × 0.085 mm. $A^*_{min,max}$ = 1.08, 1.13, $2\theta_{max}$ = 45°. *N* = 2931, N_o = 1467. *R* = 0.061, *R′* = 0.062. n_v = 271.

$C_{50}H_{42}Br_2Cu_2N_4P_2$ **2**, *M* = 1047, monoclinic, space group $P2_1/n$, *a* = 15.501(4), *b* = 8.118(2), *c* = 18.724(3) Å, β = 104.49(2)°, *U* = 2281 Å^3, D_c (*Z* = 2 dimers) = 1.53 g cm^{-3}, *F*(000) = 1056, μ_{Mo} = 28.0 cm^{-1}. Specimen: 0.19 × 0.25 × 0.05 mm. $A^*_{min,max}$ = 1.13, 1.74, $2\theta_{max}$ = 50°. *N* = 4018, N_o = 2090. *R* = 0.046, *R′* = 0.042. n_v = 271.

$C_{50}H_{42}Cu_2I_2N_4P_2$, **3**, *M* = 1141, monoclinic, space group $P2_1/n$, *a* = 15.683(3), *b* = 8.132(3), *c* = 18.82(1) Å, β = 103.20(5)°, *U* = 2336 Å^3, D_c (*Z* = 2 dimers) = 1.62 g cm^{-3}, *F*(000) = 1128, μ_{Mo} = 23.4 cm^{-1}. Specimen: 0.12 × 0.36 × 0.08 mm. $A^*_{min,max}$ = 1.18, 1.39, $2\theta_{max}$ = 50°. *N* = 3591, N_o = 2354. *R* = 0.040, *R′* = 0.040. n_v = 271.

$C_{46}H_{52}Cl_2Cu_2N_2P_2$ **4**, *M* = 892.4, orthorhombic, space group *Pbca* (D_{2h}^{15}, no. 61), *a* = 16.447(5), *b* = 18.046(3), *c* = 14.629(5) Å, *U* = 4342 Å^3, D_c (*Z* = 4 dimers) = 1.37 g cm^{-3}, *F*(000) = 1856, μ_{Mo} = 12.1 cm^{-1}. Specimen: 0.37 × 0.27 × 0.37 mm. $A^*_{min,max}$ = 1.35, 1.55, $2\theta_{max}$ = 50°. *N* = 3675, N_o = 2506. *R* = 0.040, *R′* = 0.049, n_v = 244.

$C_{46}H_{52}Br_2Cu_2N_2P_2$ **5**, *M* = 981.3, orthorhombic, space group *Pbca*, *a* = 16.558(6), *b* = 18.301(7), *c* = 14.613(3) Å, *U* = 4428 Å^3, D_c = 1.47 g cm^{-3}, *F*(000) = 2000, μ_{Mo} = 28.6 cm^{-1}. Specimen: 0.30 × 0.15 × 0.40 mm. $A^*_{min,max}$ = 1.69, 2.19, $2\theta_{max}$ = 60°. *N* = 3359, N_o = 1606. *R* = 0.055, *R′* = 0.053. n_v = 244.

$C_{46}H_{52}Cu_2I_2N_2P_2$ **6**, *M* = 1075.3, triclinic, space group $P\bar{1}$ (C_i^1, no. 2), *a* = 17.442(9), *b* = 16.532(6), *c* = 13.801(3) Å, α = 92.78(2), β = 112.08(3), γ = 112.65(3)°, *U* = 3315 Å^3, D_c (*Z* = 3 dimers) = 1.62 g cm^{-3}, *F*(000) = 1608, μ_{Mo} = 24.6 cm^{-1}. Specimen: 0.18 × 0.19 × 0.14 mm. $A^*_{min,max}$ = 1.30, 1.51, $2\theta_{max}$ = 50°. *N* = 11 663, N_o = 7178. *R* = 0.038, *R′* = 0.036. n_v = 731.

Spectroscopy.—Solid-state ^{31}P NMR spectra were recorded utilizing conventional cross-polarization (CP) and magic-angle-spinning (MAS) techniques, coupled with spin-temperature alternation to eliminate spectral artifacts. These experiments were implemented on a Bruker MSL 400 spectrometer at a field strength of *B* = 9.4 T, using a Bruker 4 mm double-air-bearing probe in which MAS frequencies of 12 kHz were achieved. A recycle time of 30 s, contact period of 10 ms and ^1H π/2 pulse length of 3 μs were common to all CP MAS spectra. All ^{31}P chemical shifts were externally referenced to solid triphenylphosphine which has a shift of δ −9.9. with respect to 85% H_3PO_4. Infrared spectra were recorded at 2 cm^{-1} resolution as Nujol mulls between NaCl plates in the range 4000–600 cm^{-1} on a Perkin-Elmer 1725 FTIR spectrometer.

Results and Discussion

Crystal Structures of [{CuX[$PPh_2(C_6H_4Me$-*o*)](cpy)}$_2$].—The structures of the three complexes are isomorphous, crystallizing in space group $P2_1/n$ as discrete dihalide-bridged dimeric species disposed about a crystallographic centre of symmetry such that the asymmetric unit constitutes one half of the dimer. The complexes are isomorphous also with the analogous triphenylphosphine complexes, [{CuX(PPh_3)(cpy)}$_2$],[3] and are presented in that setting, the change in phosphine ligand from PPh_3 to $PPh_2(C_6H_4Me$-*o*) increasing the cell volumes by *ca.* 4%. The orientations of the phenyl groups in both sets of compounds are similar with the largest differences occurring, as might be expected, for the *o*-tolyl group (Table 4). Small differences occur in the disposition of the 4-cyanopyridine ring (which co-ordinates through the pyridine N) in the two sets of complexes. For [{CuX(PPh_3)(cpy)}$_2$] both the copper and nitrile atoms lie in the pyridine plane. This is not the case for the $PPh_2(C_6H_4Me$-*o*) complexes where the copper atoms lie 0.34(2), 0.35(1) and 0.28(1) Å out of this plane for X = Cl, Br and I respectively. In both sets of complexes the two independent Cu–X bond distances differ by only 2–3%. The change from PPh_3 to $PPh_2(C_6H_4Me$-*o*) expands the copper co-ordination sphere, with each of the Cu–P, Cu–X and Cu–N bond distances increasing by 1–2%. This result suggests that the lattice forces controlling the crystal-packing geometries play an indirect but significant role in the determination of the geometries of the copper co-ordination sphere and the Cu_2X_2 core. The X ··· X distances remain essentially constant for the chloride complexes and decrease by *ca.* 2% for both the bromide and iodide complexes. Thus, the observed increases in Cu–X bond distances are accommodated primarily within the Cu_2X_2 core by increases in the Cu ··· Cu distances (2% for X = Cl, 3% for Br and 6% for I).

Crystal Structures of [{CuX(PPh_3)(pip)}$_2$].—The chloride and bromide complexes in this series are isomorphous, crystal-

Table 1 Non-hydrogen coordinates for [{CuX[PPh$_2$(C$_6$H$_4$Me-*o*)](cpy)}$_2$]

	X = Cl			X = Br			X = I		
Atom	*x*	*y*	*z*	*x*	*y*	*z*	*x*	*y*	*z*
Cu	0.087 9(1)	−0.033 6(2)	0.475 74(9)	0.088 25(6)	−0.038 9(1)	0.473 34(5)	0.089 33(6)	−0.044 4(1)	0.471 35(5)
X	0.033 4(2)	−0.142 1(4)	0.578 5(2)	0.034 50(5)	−0.156 3(1)	0.581 35(5)	0.032 07(3)	−0.177 41(7)	0.583 31(3)
N(1)	0.064 0(7)	−0.234(1)	0.402 6(6)	0.063 7(4)	−0.235 8(8)	0.399 2(3)	0.066 9(4)	−0.233 6(8)	0.394 4(3)
C(2)	0.087(1)	−0.384(2)	0.429 2(8)	0.093 1(5)	−0.386(1)	0.422 0(5)	0.104 6(5)	−0.379(1)	0.411 9(4)
C(3)	0.086 9(9)	−0.519(2)	0.383 7(9)	0.093 4(5)	−0.515(1)	0.376 1(5)	0.104 6(5)	−0.507(1)	0.362 5(5)
C(4)	0.061 6(9)	−0.497(2)	0.309 8(9)	0.061 1(5)	−0.493(1)	0.301 6(5)	0.062 3(5)	−0.482(1)	0.291 4(5)
C(5)	0.034(1)	−0.344(2)	0.279 4(8)	0.028 6(6)	−0.340(1)	0.276 3(4)	0.022 5(6)	−0.333(1)	0.272 7(5)
C(6)	0.036(1)	−0.220(2)	0.330 0(9)	0.029 9(5)	−0.218(1)	0.327 0(5)	0.025 9(5)	−0.214(1)	0.325 0(5)
C(41)	0.064(1)	−0.638(3)	0.259(1)	0.061 2(6)	−0.625(1)	0.250 4(6)	0.061 3(6)	−0.612(1)	0.238 3(6)
N(41)	0.063(1)	−0.739(2)	0.217 0(9)	0.062 5(6)	−0.729(1)	0.210 7(6)	0.060 6(6)	−0.716(1)	0.199 1(5)
P	0.227 3(2)	0.057 6(4)	0.517 0(2)	0.226 8(1)	0.054 9(2)	0.514 4(1)	0.226 9(1)	0.049 0(2)	0.511 6(1)
C(11)	0.243 8(9)	0.183(1)	0.602 5(7)	0.241 0(5)	0.178 7(9)	0.598 1(4)	0.240 2(5)	0.172(1)	0.594 9(4)
C(12)	0.172(1)	0.280(2)	0.607 1(8)	0.171 6(5)	0.279(1)	0.604 1(5)	0.172 7(6)	0.275(1)	0.602 8(5)
C(13)	0.180(1)	0.375(2)	0.670(1)	0.179 6(7)	0.374(1)	0.666 5(7)	0.181 1(7)	0.372(1)	0.665 3(6)
C(14)	0.258(2)	0.370(2)	0.728(1)	0.255 8(9)	0.369(1)	0.723 3(5)	0.256 0(8)	0.361(1)	0.719 6(5)
C(15)	0.328(1)	0.279(2)	0.721 6(8)	0.324 6(7)	0.271(1)	0.717 0(5)	0.322 5(7)	0.262(1)	0.712 0(4)
C(16)	0.320 8(9)	0.184(2)	0.658 2(8)	0.317 7(5)	0.177 8(9)	0.654 0(4)	0.315 6(6)	0.167(1)	0.649 3(4)
C(21)	0.313 0(8)	−0.103(1)	0.546 4(6)	0.311 6(5)	−0.104 3(8)	0.543 8(4)	0.311 2(5)	−0.109 1(9)	0.539 4(4)
C(22)	0.293 0(9)	−0.230(2)	0.589 2(7)	0.292 7(5)	−0.233(1)	0.587 3(4)	0.293 3(5)	−0.233(1)	0.583 1(4)
C(23)	0.356(1)	−0.350(2)	0.615 9(8)	0.356 0(5)	−0.352(1)	0.613 2(4)	0.355 8(6)	−0.352 6(9)	0.609 7(4)
C(24)	0.437(1)	−0.346(2)	0.600 3(8)	0.436 6(5)	−0.351(1)	0.596 8(5)	0.434 5(6)	−0.351(1)	0.590 5(5)
C(25)	0.458 1(9)	−0.221(2)	0.558 4(9)	0.455 9(5)	−0.226(1)	0.553 9(5)	0.453 8(5)	−0.229(1)	0.547 2(5)
C(26)	0.395 4(9)	−0.099(1)	0.530 7(8)	0.394 1(5)	−0.102 9(9)	0.527 6(5)	0.391 7(6)	−0.107(1)	0.521 1(4)
C(31)	0.271 3(8)	0.192(1)	0.454 6(7)	0.271 8(4)	0.186 2(9)	0.452 8(4)	0.271 3(4)	0.183(1)	0.450 0(3)
C(32)	0.272 0(9)	0.139(2)	0.382 9(7)	0.272 1(5)	0.136(1)	0.381 5(4)	0.270 4(5)	0.131(1)	0.379 2(4)
C(321)	0.247(1)	−0.037(2)	0.357 7(8)	0.243 9(6)	−0.036(1)	0.353 7(5)	0.240 8(6)	−0.037(1)	0.352 0(5)
C(33)	0.297 1(9)	0.248(2)	0.335 0(7)	0.298 1(5)	0.244(1)	0.333 3(4)	0.299 3(6)	0.241(1)	0.332 5(4)
C(34)	0.322(1)	0.406(2)	0.356 9(9)	0.324 6(6)	0.403(1)	0.356 2(5)	0.328 3(5)	0.395(1)	0.354 6(5)
C(35)	0.324 8(9)	0.454(2)	0.427 2(8)	0.326 7(5)	0.452(1)	0.425 4(5)	0.329 0(5)	0.447(1)	0.423 8(4)
C(36)	0.299 2(9)	0.350(2)	0.476 1(7)	0.300 8(5)	0.346(1)	0.473 7(4)	0.301 8(5)	0.340 5(9)	0.471 7(4)

Table 2 Non-hydrogen coordinates for $[\{CuX(PPh_3)(pip)\}_2]$

	X = Cl			X = Br		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
Cu	−0.044 01(4)	0.058 05(3)	0.070 83(4)	−0.044 65(9)	0.061 74(9)	0.068 5(1)
X	−0.088 42(8)	−0.062 48(6)	0.038 28(9)	−0.093 42(7)	−0.063 99(7)	0.039 08(9)
P	0.001 48(8)	0.080 42(6)	0.208 04(9)	0.000 8(2)	0.081 1(2)	0.207 7(2)
N	−0.105 4(2)	0.114 5(2)	−0.031 4(3)	−0.106 9(6)	0.117 2(5)	−0.031 2(7)
C(2)	−0.193 4(4)	0.100 5(3)	−0.037 8(4)	−0.194 9(8)	0.104 2(7)	−0.036 0(9)
C(3)	−0.235 1(3)	0.136 7(3)	0.042 6(4)	−0.235 0(7)	0.138 8(8)	0.043(1)
C(4)	−0.218 1(4)	0.218 2(3)	0.045 9(4)	−0.217 8(8)	0.220 5(7)	0.047(1)
C(5)	−0.127 7(4)	0.233 7(3)	0.040 7(4)	−0.127 7(8)	0.235 8(6)	0.042(1)
C(6)	−0.089 7(3)	0.194 4(3)	−0.038 7(4)	−0.092 8(8)	0.195 6(7)	−0.037(1)
C(11)	0.074 6(3)	0.011 2(2)	0.247 9(3)	0.072 4(7)	0.012 7(6)	0.247 1(8)
C(12)	0.049 1(3)	−0.062 7(3)	0.249 0(4)	0.048 5(8)	−0.061 3(8)	0.249 8(8)
C(13)	0.101 2(4)	−0.117 7(3)	0.278 8(4)	0.099(1)	−0.115 5(7)	0.277 6(9)
C(14)	0.178 1(4)	−0.100 5(3)	0.306 4(4)	0.175 0(9)	−0.099 1(9)	0.303(1)
C(15)	0.204 8(3)	−0.028 6(3)	0.304 4(4)	0.202 6(8)	−0.026 0(9)	0.302(1)
C(16)	0.153 0(3)	0.027 7(3)	0.276 2(4)	0.150 8(8)	0.028 2(7)	0.271 1(9)
C(21)	0.052 5(3)	0.169 6(2)	0.221 6(3)	0.051 4(7)	0.168 0(6)	0.224(1)
C(22)	0.079 0(3)	0.206 0(3)	0.144 1(4)	0.078 3(8)	0.206 1(7)	0.149(1)
C(23)	0.113 4(3)	0.275 8(3)	0.150 7(5)	0.112 0(9)	0.274 1(8)	0.156(1)
C(24)	0.122 7(4)	0.309 2(3)	0.233 3(6)	0.121 8(9)	0.305 5(9)	0.241(2)
C(25)	0.098 1(4)	0.273 5(3)	0.311 7(5)	0.097 3(9)	0.268 2(8)	0.318(1)
C(26)	0.062 6(3)	0.204 0(3)	0.306 4(4)	0.063 4(8)	0.200 2(8)	0.310 3(9)
C(31)	−0.073 6(3)	0.082 6(3)	0.300 6(3)	−0.073 9(7)	0.081 6(7)	0.300(1)
C(32)	−0.141 0(3)	0.127 9(3)	0.288 8(4)	−0.139(1)	0.125 5(9)	0.290 6(9)
C(33)	−0.201 2(4)	0.131 4(4)	0.353 8(5)	−0.200 4(9)	0.130(1)	0.355(1)
C(34)	−0.196 4(4)	0.089 1(4)	0.430 9(6)	−0.193(1)	0.087(1)	0.432(1)
C(35)	−0.131 0(5)	0.045 0(4)	0.444 6(5)	−0.129(1)	0.046(1)	0.445(1)
C(36)	−0.068 7(4)	0.040 5(3)	0.379 1(4)	−0.065 6(9)	0.041 2(9)	0.383(1)

Table 3 Non-hydrogen coordinates for $[\{CuI(PPh_3)(pip)\}_2]$

Atom	*x*	*y*	*z*
I(1)	0.817 54(3)	0.417 12(3)	1 076 39(4)
I(2)	0.522 13(3)	0.282 89(3)	0.961 77(3)
Cu(1)	0.684 20(6)	0.358 06(5)	1.146 33(7)
Cu(2)	0.652 64(6)	0.325 92(5)	0.892 74(7)
P(1)	0.687 1(1)	0.252 8(1)	1.238 4(1)
P(2)	0.651 3(1)	0.418 6(1)	0.781 8(1)
N(1)	0.693 3(4)	0.486 7(4)	1.187 9(4)
N(2)	0.674 1(4)	0.211 3(4)	0.868 8(5)
C(111)	0.684 8(4)	0.153 6(4)	1.169 9(5)
C(112)	0.753 2(5)	0.167 0(4)	1.137 1(6)
C(113)	0.760 0(5)	0.096 5(5)	1.090 7(6)
C(114)	0.697 4(5)	0.010 3(5)	1.076 3(6)
C(115)	0.628 7(6)	−0.004 5(5)	1.107 2(7)
C(116)	0.621 6(5)	0.066 9(5)	1.153 1(7)
C(121)	0.789 6(4)	0.280 3(4)	1.363 9(5)
C(122)	0.868 6(4)	0.357 2(4)	1.385 8(5)
C(123)	0.948 1(5)	0.375 3(4)	1.476 7(6)
C(124)	0.949 6(5)	0.318 2(5)	1.544 2(6)
C(125)	0.871 4(5)	0.241 6(5)	1.523 7(6)
C(126)	0.792 3(5)	0.222 2(5)	1.432 8(6)
C(131)	0.590 0(4)	0.209 6(4)	1.273 9(5)
C(132)	0.502 0(5)	0.163 5(5)	1.192 1(5)
C(133)	0.425 9(5)	0.136 4(5)	1.212 6(6)
C(134)	0.435 0(5)	0.156 1(5)	1.314 6(6)
C(135)	0.521 6(5)	0.203 1(5)	1.398 3(6)
C(136)	0.598 3(4)	0.230 5(5)	1.376 2(5)
C(211)	0.547 4(4)	0.377 0(4)	0.654 7(5)
C(212)	0.471 0(5)	0.303 3(4)	0.647 5(5)
C(213)	0.390 7(5)	0.267 9(5)	0.552 1(5)
C(214)	0.386 0(5)	0.305 5(5)	0.465 9(5)
C(215)	0.462 2(5)	0.378 6(5)	0.472 2(5)
C(216)	0.542 6(4)	0.414 9(4)	0.567 3(5)
C(221)	0.747 5(4)	0.448 1(4)	0.745 3(5)
C(222)	0.835 7(5)	0.502 1(5)	0.826 1(5)
C(223)	0.912 4(5)	0.517 1(5)	0.808 0(6)
C(224)	0.903 4(5)	0.478 6(5)	0.711 8(6)
C(225)	0.817 9(5)	0.424 3(5)	0.632 1(6)
C(226)	0.740 3(4)	0.409 3(4)	0.648 5(5)
C(231)	0.662 1(4)	0.528 9(4)	0.831 9(5)
C(232)	0.633 3(5)	0.535 8(4)	0.910 8(5)
C(233)	0.635 9(5)	0.615 5(5)	0.949 0(6)
C(234)	0.667 9(5)	0.689 7(5)	0.900 5(6)
C(235)	0.696 1(5)	0.683 4(5)	0.829 9(6)
C(236)	0.692 4(5)	0.602 7(4)	0.790 8(5)
C(12)	0.777 8(5)	0.547 0(5)	1.288 5(7)
C(13)	0.763 3(7)	0.519 1(7)	1.383 1(6)
C(14)	0.680 6(8)	0.519 6(8)	1.385 4(7)
C(15)	0.595 5(6)	0.462 7(6)	1.276 6(8)
C(16)	0.613 1(6)	0.493 0(6)	1.185 7(7)
C(22)	0.604 0(6)	0.122 3(6)	0.852 4(7)
C(23)	0.530 1(6)	0.095 6(6)	0.742 7(7)
C(24)	0.566 4(7)	0.096 7(6)	0.660 1(7)
C(25)	0.642 7(6)	0.185 9(6)	0.680 0(7)
C(26)	0.716 1(5)	0.211 2(5)	0.791 4(7)
I(3)	0.857 17(3)	−0.032 89(3)	0.944 96(4)
Cu(3)	0.997 06(6)	0.063 91(6)	0.904 22(7)
P(3)	0.978 9(1)	0.020 3(1)	0.739 5(1)
N(3)	1.060 7(4)	0.199 6(4)	0.982 7(5)
C(311)	0.970 3(4)	−0.091 5(4)	0.704 5(5)
C(312)	0.894 3(5)	−0.164 5(5)	0.700 5(7)
C(313)	0.882 8(6)	−0.251 0(5)	0.676 7(7)
C(314)	0.949 0(6)	−0.267 0(5)	0.660 4(6)
C(315)	1.024 4(5)	−0.196 7(5)	0.663 9(6)
C(316)	1.034 8(5)	−0.108 8(5)	0.686 3(6)
C(321)	0.875 6(4)	0.012 6(4)	0.629 4(5)
C(322)	0.814 0(5)	0.032 1(5)	0.654 6(6)
C(323)	0.731 6(5)	0.021 4(5)	0.570 5(7)
C(324)	0.714 6(5)	−0.003 7(5)	0.466 7(7)
C(325)	0.774 5(5)	−0.022 7(5)	0.441 9(6)
C(326)	0.855 1(5)	−0.016 3(5)	0.523 0(6)
C(331)	1.074 7(4)	0.095 8(4)	0.714 3(5)
C(332)	1.162 5(5)	0.114 0(5)	0.791 0(5)
C(333)	1.239 1(5)	0.175 4(5)	0.782 7(6)
C(334)	1.230 7(5)	0.219 4(5)	0.701 0(7)
C(335)	1.144 5(5)	0.202 6(5)	0.626 6(6)
C(336)	1.067 8(5)	0.142 1(4)	0.633 9(6)
C(32)	1.016 2(7)	0.230 8(5)	1.037 0(7)
C(33)	0.942 3(6)	0.244 5(6)	0.959 1(8)
C(34)	0.972 6(6)	0.309 6(6)	0.892 9(8)
C(35)	1.025 8(6)	0.280 9(6)	0.846 5(7)
C(36)	1.099 3(6)	0.267 8(6)	0.926 1(7)

Table 4 Core geometries (distances in Å, angles in °) for [{CuX[PPh$_2$(C$_6$H$_4$Me-*o*)](cpy)}$_2$] and [{CuX(PPh$_3$)(cpy)}$_2$]

	X = Cl		X = Br		X = I	
	PPh$_2$(C$_6$H$_4$Me-*o*)	PPh$_3$	PPh$_2$(C$_6$H$_4$Me-*o*)	PPh$_3$	PPh$_2$(C$_6$H$_4$Me-*o*)	PPh$_3$
Cu–X	2.357(4)	2.361(2)	2.491(1)	2.486(2)	2.654(1)	2.642(1)
Cu–X′	2.439(4)	2.417(2)	2.557(1)	2.542(2)	2.698(2)	2.683(1)
Cu–P	2.212(4)	2.192(2)	2.227(2)	2.216(2)	2.249(2)	2.233(2)
Cu–N	2.08(1)	2.069(4)	2.089(6)	2.065(7)	2.087(6)	2.079(6)
Cu ··· Cu′	3.119(3)	3.057(2)	3.201(2)	3.106(2)	3.304(2)	3.104(2)
X ··· X′	3.645(5)	3.627(2)	3.904(1)	3.996(2)	4.211(2)	4.281(2)
P–Cu–X	122.6(1)	119.37(7)	119.75(7)	117.26(8)	116.67(7)	114.72(9)
P–Cu–X′	110.5(1)	110.32(6)	109.36(7)	109.15(7)	109.70(7)	109.63(6)
P–Cu–N	118.5(3)	117.7(1)	119.4(2)	117.6(2)	118.6(2)	116.3(2)
N–Cu–X	101.8(3)	103.5(1)	102.7(2)	104.3(2)	103.9(2)	105.3(2)
N–Cu–X′	101.0(4)	103.0(1)	101.5(2)	103.6(2)	102.3(2)	102.9(2)
X–Cu–X′	98.9(1)	110.43(7)	101.30(5)	103.72(6)	103.76(4)	107.00(5)
Cu–X–Cu′	81.1(1)	79.57(5)	78.70(4)	76.28(5)	76.24(4)	72.99(4)
Torsion angles (reduced to a common chirality)						
Cu–P–C(11)–C(12)	35(1)	35.2(5)	36.8(7)	36.5(7)	37.2(7)	37.5(7)
Cu–P–C(21)–C(22)	44(1)	48.1(5)	44.5(7)	46.3(7)	46.1(7)	44.1(7)
Cu–P–C(31)–C(32)	56(1)	47.8(3)	54.0(6)	50.9(6)	53.9(6)	51.4(6)
Deviations (Å) from the Cu(μ-X)$_2$XCu plane						
δ(P)	1.592(4)	1.645(2)	1.671(2)	1.699(3)	1.728(2)	1.723(2)
δ(N)	−1.985(1)	−1.932(5)	−1.917(7)	−1.901(7)	−1.941(7)	−1.897(6)

Table 5 Core geometries (distances in Å, angles in °) for [{CuX(PPh$_3$)(pip)}$_2$]

	X = Cl	Br	I (centric)	I (non centric)	
Cu–X	2.343(1)	2.476(2)	2.635(2)	2.706(2)	2.654(2)
Cu–X′	2.701(2)	2.775(2)	2.862(2)	2.756(1)	2.789(1)
Cu–P	2.180(2)	2.198(4)	2.216(2)	2.210(2)	2.218(2)
Cu–N	2.072(4)	2.05(1)	2.093(6)	2.104(7)	2.102(8)
Cu ··· Cu′	3.283(1)	3.362(2)	3.460(2)	3.314(2)	
X ··· X′	3.847(2)	4.045(2)	4.276(3)	4.324(2)	
P–Cu–X	117.75(5)	115.0(1)	114.24(6)	114.74(8)	116.07(8)
P–Cu–X′	105.18(5)	103.9(1)	109.20(8)	107.47(5)	106.14(5)
P–Cu–N	137.8(1)	138.5(3)	122.4(2)	131.3(2)	123.1(1)
N–Cu–X	99.1(1)	99.9(3)	112.6(2)	94.5(5)	107.9(2)
N–Cu–X′	87.2(1)	90.2(3)	91.5(2)	101.0(2)	94.7(1)
X–Cu–X′	99.13(5)	100.61(7)	102.10(5)	104.67(5)	105.19(5)
Cu–X–Cu′	80.87(4)	79.39(6)	77.90(5)	75.51(5)	74.15(5)
Torsion angles					
Cu–P–C(11)–C(12)	−56.7(4)	−58(1)	−65.6(6)	−57.4(5)	25.9(5)
Cu–P–C(21)–C(22)	−17.9(4)	−18(1)	1.6(6)	13.7(8)	−14.7(8)
Cu–P–C(31)–C(32)	−52.0(5)	−52(1)	−50.9(7)	−64.9(6)	68.6(8)
Deviations (Å) from the Cu(μ-X)$_2$XCu plane					
δ(P)	1.781(2)	1.862(4)	1.788(2)	1.931(2)	1.611(2)
δ(N)	−2.045(4)	−2.02(1)	−1.919(8)	−1.947(8)	−2.075(7)

lizing in the centrosymmetric orthorhombic space group *Pbca* with half the dimeric unit constituting the asymmetric unit of the crystal (Fig. 1). Unlike the complexes with pyridine bases as the N-donor ligand, the Cu–X distances differ by 0.3–0.4 Å and the system is better described as pairs of associated monomers. It seems apparent that in these complexes one halide ion is 'pushed' out of the copper co-ordination sphere such that the copper environment is three- rather than four-co-ordinate with a weakly associated halide atom. This can be seen also from the sum of the P–Cu–X, P–Cu–N and N–Cu–X angles which range between 350 and 355°, the X–Cu–P,N,X angles which are each close to 90° and the copper atoms which lie only 0.27, 0.29 (X = Cl) and 0.26, 0.37 Å (Br) out of the NPX(1) plane. The piperidine ring is disposed away from the Cu$_2$X$_2$ plane such that P–Cu–N–C(4) is 33.8 for X = Cl and 31.2° for Br. The Cu–P distances 2.180(2) and 2.198(4) Å for the chloride and bromide complexes are shorter than the values found for the pyridine complexes (Table 6) (consistent with the decrease in co-ordination number about the copper) and are comparable to the Cu–P distances for three-co-ordinate (PCuX$_2$)$_2$ complexes.[6] As would be expected with the increase in the Cu–X distances and the disaggregation of the Cu$_2$X$_2$ core in these compounds, the Cu ··· Cu distances of 3.283(1) and 3.362(2) Å are considerably longer than those found for the pyridine base complexes (Table 6).

The structure of the iodide complex is unusual in that the asymmetric unit consists of one complete dimer and half a second dimer which is located about a crystallographic centre of symmetry (Figs. 2 and 3). The structures of the two dimers are different. For the non-centric dimer major differences are present in the respective Cu–P–C(*n*1)–C(*n*2) torsion angles (Table 5) and ring 2 of the PPh$_3$ ligand is twisted in the opposite sense to the other two rings. However, the differences in the Cu–X distances and P–Cu–X angles are much smaller than

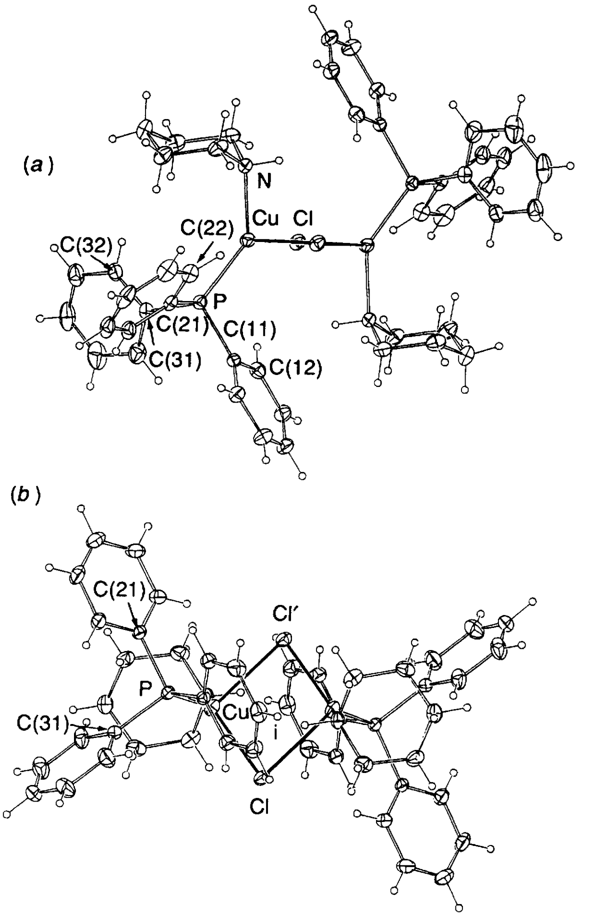

Fig. 1 The molecule of [{CuCl(PPh$_3$)(pip)}$_2$] projected (*a*) along a line in the CuCl$_2$Cu plane, perpendicular to the Cu $\cdots$ Cu line, and (*b*) normal to this plane. 20% Thermal ellipsoids are shown for the non-hydrogen atoms. Hydrogen atoms have arbitrary radii of 0.1 Å

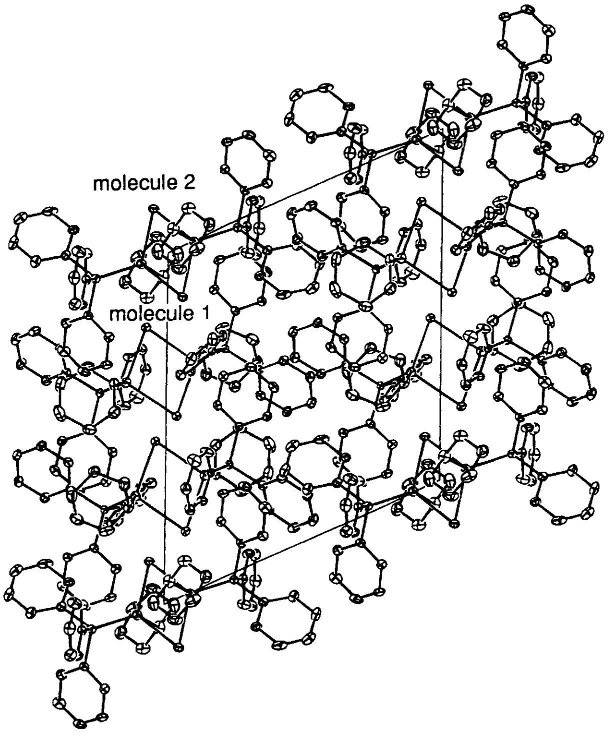

Fig. 2 Unit-cell diagram of [{CuI(PPh$_3$)(pip)}$_2$] projected onto the *ac* plane

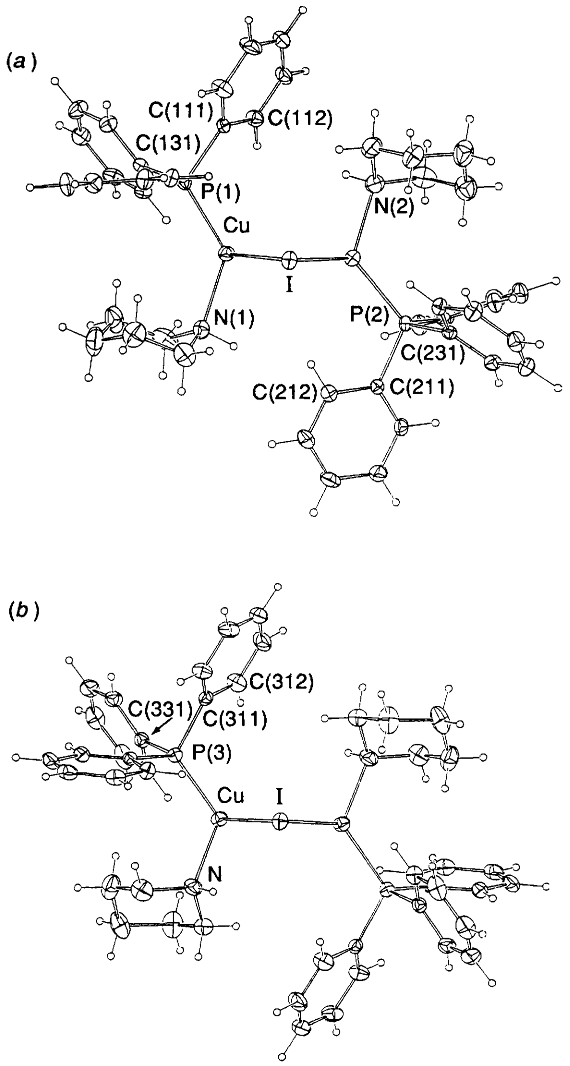

Fig. 3 Structure of (*a*) the non-centric dimer (molecule 1) and (*b*) the centric dimer (molecule 2) of [{CuI(PPh$_3$)(pip)}$_2$]

those found for the chloride and bromide complexes and the geometry is more closely aligned to the tetrahedral co-ordination about the copper found for the pyridine and nitrile base complexes. A feature of the centrosymmetric dimer is the rotation of the piperidine ring away from the phosphine ligand with P–Cu–N–C(4) −64.2°, resulting in the P–Cu–N angle decreasing to 122.4(2)°. The Cu $\cdots$ Cu distance of 3.314(2) Å for the non-centric dimer is similar to those found for the chloride and bromide complexes. For the centrosymmetric dimer this distance increases to 3.460(2) Å, the largest observed for this series of complexes although not as large as the value of 3.543(1) Å found for the corresponding MeCN adduct with P(C$_6$H$_4$Me-*o*)$_3$ as the P-donor ligand.[6]

These results, together with those published previously for related systems, are summarized in Table 6. They provide a useful range of structural data for (PNCuX)$_2$ complexes in which P represents a range of phosphine-donor ligands with a variety of steric profiles and N represents nitrogen-containing ligands in the form of a linear nitrile, a planar heterocyclic aromatic amine or a tetrahedral aliphatic amine. Considering these complexes as products of the reaction of the N-donor with the three-co-ordinate (PCuX)$_2$ dimer, addition of this ligand to the copper co-ordination sphere will cause a distortion away from trigonal co-ordination, and it would be expected that, as the ligand approaches the Cu atom from above the PCuX$_2$CuP plane, the P–Cu–N angle would increase from the value of 90°,

Table 6 Summary of average bond lengths (Å) and angles (°) for dimeric $PNCuX_2CuNP$ species

P-donor	N-donor	Cu–P	Cu–N	Cu–X	Cu–X′	X···X	Cu···Cu	Cu–X–Cu	X–Cu–X	Ref.
X = Cl										
PPh_3	pip	2.18_0	2.07_2	2.34_3	2.70_1	3.84_7	3.28_3	$80._9$	$99._1$	*a*
PPh_3	py	2.18_9	2.08_3	2.40_9	2.38_1	3.80_2	2.91_5	$75._2$[b]	$105._1$	3
PPh_3	cpy	2.19_2	2.06_9	2.41_7	2.36_1	3.62_7	2.98_3	$79._6$	$100._4$	3
PPh_3	mpy[c]	2.19_6	2.06_1	2.39_5	2.40_2	3.75_6	2.98_3	$76._9$	$103._1$	4
		2.19_7	2.06_0	2.42_0	2.38_6	3.67_8	3.09_3	$80._1$	$100._0$	
$PPh_2(C_6H_4Me\text{-}o)$	cpy	2.21_2	2.08	2.35_7	2.43_9	3.64	3.11_9	$81._1$	$98._9$	*a*
X = Br										
PPh_3	pip	2.19_8	2.05	2.47_6	2.77_5	4.04_5	3.36_2	$79._4$	$100._6$	*a*
PPh_3	py	2.20_9	2.05_3	2.50_7	2.53_8	4.09_5	2.94_8	$71._5$[b]	$108._5$	2
PPh_3	cpy	2.21_6	2.06_5	2.48_6	2.54_2	3.99_6	3.10_6	$76._3$	$103._7$	3
$PPh_2(C_6H_4Me\text{-}o)$	MeCN	2.22_8	2.00_8	2.46_5	2.56_9	3.87_5	3.21_5	$79._3$	$100._6$	6
$PPh_2(C_6H_4Me\text{-}o)$	cpy	2.22_7	2.08_9	2.49_1	2.55_7	3.90_4	3.20_1	$78._7$	$101._3$	*a*
$P(C_6H_4Me\text{-}o)_3$	MeCN	2.24_2	2.10	2.51_5	2.51_0	3.81_7	3.26_8	$81._3$	$98._7$	6
$P(C_6H_4Me\text{-}o)_3$	MeCN	2.25_2	2.15_1	2.47_1	2.53_7	3.76_7	3.30_2	$82._5$	$97._5$	6
X = I										
PPh_3	pip	2.21_6	2.09_3	2.63_5	2.86_2	4.28	3.46_0	$77._9$	$102._1$	*a*
PPh_3	pip	2.21_0	2.10_4	2.70_6	2.75_6	4.32	3.31_4	$74._1$	$104._7$	*a*
		2.21_8	2.10_2	2.65_4	2.78_9			$75._5$	$105._2$	
PPh_3	py	2.24_0	2.05_3	2.69_2	2.67_7	4.46_8	2.97_6	$67._3$[b]	$112._7$	3
PPh_3	cpy	2.23_3	2.07_9	2.68_3	2.64_2	4.28_1	3.10_4	$73._0$	$107._0$	3
$PPh_2(C_6H_4Me\text{-}o)$	cpy	2.24_9	2.08_7	2.65_4	2.69_8	4.21	3.30_4	$76._2$	$103._8$	*a*
$P(C_6H_4Me\text{-}o)_3$	MeCN	2.26_9	2.04_1	2.70_8	2.70_4	4.09_1	3.54_3	$81._8$	$98._7$	6

[a] This work. [b] Average of two values. [c] mpy = 4-methylpyridine.

representing no interaction, to a value which should depend on the σ-donor strength of the N-donor ligand; *i.e.* variations in the P–Cu–N angle with variations in the N-donor ligand should be indicative of the relative σ-donor strengths of these ligands. These angles lie in the following ranges for the ligands indicated: 104–115 (acetonitrile),[6] 116–120 (pyridine bases) and 122–140° (piperidine). This suggests that the relative order of σ-donor strengths is acetonitrile < pyridine base < piperidine and this corresponds to the change in the pK_a values of the conjugate acids which range from −10 for acetonitrile to 2–6 for the pyridine bases to 11 for piperidine.[12] If this interpretation is correct, then the increasing degree of σ donation along this series should also be accompanied by a weakening of the Cu–X bonds and this agrees well with the overall trend in the observed Cu–X bond lengths. This is particularly evident, of course, for the piperidine complexes where the degree of interaction is such that one halide atom is essentially ejected from the copper co-ordination sphere.

The X–Cu–X angles remain relatively unchanged for these complexes and so the Cu···Cu distance is determined primarily by the Cu–X bond lengths. This, therefore, provides a straightforward explanation for the increase in the Cu···Cu distance in going from the pyridine to the piperidine complexes but also further highlights the unusually long Cu···Cu distances which have been observed in each of the previously reported acetonitrile complexes. Molecular orbital calculations on some model systems have predicted that the Cu···Cu distance in $PCuX_2CuP$ systems should increase if a terminal π-acceptor ligand is added to each of the copper atoms.[9] The reason given for such an increase is that the π-bonding ligand removes from the copper atoms some of the π-electron density which is responsible for Cu···Cu bonding which is postulated in these complexes. Acetonitrile should be a better π acceptor than are the other amine ligands so, according to this hypothesis, the unusually long Cu···Cu distances in these complexes can be attributed to the disruption of Cu···Cu bonding. As we have noted previously,[6] the postulate of metal–metal bonding in multinuclear copper(I) complexes is controversial, but it is difficult to see any other explanation for this unusual result.

It was stated above that the σ-donor strength was an important factor in determining changes in the P–Cu–N angle with changes in the N-donor ligand. However, there is evidence from the present results that steric factors also play a role. In the centrosymmetric $[\{CuI(PPh_3)(pip)\}_2]$ complex the fact that each piperidine ring is rotated away from the phosphine ligand on the same copper atom should reduce the steric interactions between these two ligands. Consistent with this, the P–Cu–N angles show an overall decrease from 131.3(2) and 123.1(1)° in the non-centrosymmetric dimer to 122.4(2)° in the less sterically crowded centrosymmetric dimer (Table 5).

Solid-state ^{31}P *NMR Spectroscopy*.—Solid-state ^{31}P NMR spectroscopy of copper(I) phosphine complexes has proved to be a valuable tool in the investigation of the structural and electronic properties of these complexes and can provide good estimates of both the magnitude of the scalar coupling constant, $^1J(Cu-P)$, and the symmetry of the charge distribution about the copper site. The spectra generally consist of a quartet of lines for each crystallographically independent phosphorus atom in which the line spacings are determined primarily by the magnitude of the scalar $^1J(Cu-P)$ interactions; differences between the three values arise from quadrupolar perturbations by the spin-$\frac{3}{2}$ $^{63,65}Cu$ nuclei. The high-field line spacing ($\Delta\nu_3$) increases and the low-field spacing ($\Delta\nu_1$) decreases in magnitude as a function of increasing asymmetry in the charge distribution about the copper while the central line spacing ($\Delta\nu_2$) remains unchanged.[13–16] Thus, the ratio $\Delta\nu_3 : \Delta\nu_1$ can be used to monitor trends in the asymmetry of the charge distribution about the copper[17] while $\Delta\nu_2$ reflects the magnitude of $^1J(Cu-P)$. The CP MAS ^{31}P NMR spectra at $B = 9.4$ T of $[\{CuX(PPh_3)(cpy)\}_2]$, $[\{CuI[PPh_2(C_6H_4Me\text{-}o)](cpy)\}_2]$ and $[\{CuX(PPh_3)(pip)\}_2]$ are presented in Fig. 4. Chemical shift and line-spacing data for these complexes are presented in Table 7, together with comparative data recorded at this field strength for the acetonitrile complexes $[\{CuX[P(C_6H_4Me\text{-}o)_3](MeCN)\}_2]$ (X = Br or I), the three-co-ordinate dimers $[\{CuX(PR_3)\}_2]$ [X = Cl, Br or I; $PR_3 = P(C_6H_4Me\text{-}o)_3$ or $PPh(C_6H_2Me_3\text{-}2,4,6)_2$] and the 'cubane' $[\{CuX(PPh_3)\}_4]$ complexes (X = Cl, Br or I), the synthesis and crystal structures of these compounds

Table 7 Solid-state CP MAS ^{31}P NMR chemical shifts (with respect to PPh_3) and line spacings at B = 9.4 T for three- and four-co-ordinate compounds with $CuPX_2$, $CuPX_2N$ and $CuPX_3$ co-ordination

			Line spacing/kHz			
Compound	Cu–P/Å	δ	$\Delta\nu_1$	$\Delta\nu_2$	$\Delta\nu_3$	$\Delta\nu_3:\Delta\nu_1$
$[\{CuCl(PPh_3)(cpy)\}_2]$	2.19_2	2.7_3	1.578	1.671	1.709	1.08
$[\{CuCl[PPh_2(C_6H_4Me\text{-}o)](cpy)\}_2]$	2.21_2	1.6_8	1.578	1.709	1.746	1.11
$[\{CuCl(PPh_3)(pip)\}_2]$	2.18_0	4.9_3	1.596	1.821	1.934	1.21
$[\{CuCl(PPh_3)\}_4]$	2.19_3	1.0_5	1.784	1.972	2.085	1.17
	2.19_3	3.6_0	1.803	1.991	2.085	1.16
$[\{CuCl[P(C_6H_4Me\text{-}o)_3]\}_2]$	2.19_1	-9.7_4	1.634	1.972	2.122	1.30
$[\{CuCl[PPh(C_6H_2Me_3\text{-}2,4,6)_2]\}]$	2.20_2	-10.6_7	1.636	1.987	2.150	1.31
$[\{CuBr(PPh_3)(cpy)\}_2]$	2.21_6	0.5_8	1.540	1.615	1.671	1.09
$[\{CuBr[PPh_2(C_6H_4Me\text{-}o)](cpy)\}_2]$	2.22_7	-1.2_8	1.540	1.653	1.709	1.11
$[\{CuBr[P(C_6H_4Me\text{-}o)_3](MeCN)\}_2]$	2.52_2	-4.2_9	1.521	1.653	1.690	1.11
$[\{CuBr(PPh_3)(pip)\}_2]$	2.19_8	3.5_4	1.540	1.822	1.878	1.22
$[\{CuBr(PPh_3)\}_4]$	2.20_9	0.7_0	1.690	1.897	1.972	1.17
	2.20_6	4.2_4	1.671	1.897	1.953	1.17
$[\{CuBr[PPh(C_6H_2Me_3\text{-}2,4,6)_2]\}_2]$	2.19_7	-11.3_0	1.621	1.934	2.051	1.26
$[\{CuBr[P(C_6H_4Me\text{-}o)_3]\}_2]$	2.20_8	-7.5_9	1.577	1.897	2.047	1.30
$[\{CuI(PPh_3)(cpy)\}_2]$	2.23_3	-4.4_7	1.409	1.521	1.540	1.09
$[\{CuI[PPh_2(C_6H_4Me\text{-}o)](cpy)\}_2]$	2.24_9	-6.9_5	1.446	1.521	1.506	1.10
$[\{CuI[P(C_6H_4Me\text{-}o)_3](MeCN)\}_2]$	2.69_9	-6.4_4	1.427	1.559	1.596	1.12
$[\{CuI(PPh_3)(pip)\}_2]$	2.21_0	-7.4_9	1.446	1.634	1.652	1.14
	2.21_6	-4.8_7	1.446	1.696	1.709	1.18
$[\{CuI(PPh_3)\}_4]$	2.25	-10.0_9	1.427	1.578	1.634	1.15
	2.25	-14.8_4	1.502	1.634	1.728	1.15
$[\{CuI[PPh(C_6H_2Me_3\text{-}2,4,6)_2]\}_2]$	2.23_0	-5.5_0	1.430	1.706	1.836	1.28
$[\{CuI[P(C_6H_4Me\text{-}o)_3]\}_2]$	2.38_8	-5.3_3	1.446	1.728	1.878	1.30

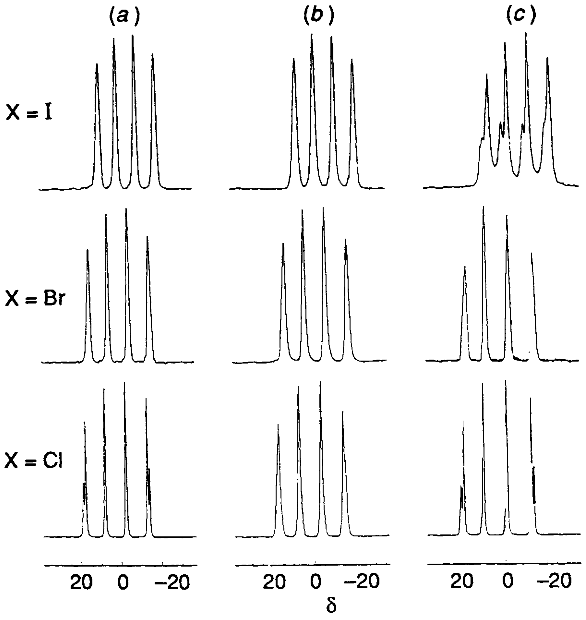

Fig. 4 Solid-state ^{31}P CP MAS NMR spectra of (*a*) $[\{CuX(PPh_3)(cpy)\}_2]$, (*b*) $[\{CuX[PPh_2(C_6H_4Me\text{-}o)](cpy)\}_2]$ and (*c*) $[\{CuX(PPh_3)(pip)\}_2]$ for X = I, Br or Cl. Chemical shifts are with reference to solid PPh_3 [δ(PPh_3) −9.9 with respect to 85% H_3PO_4]

having been previously reported.[6,12,18,21] The trends in $\Delta\nu_2$ observed for the present series of complexes are similar to those found for related complexes[6] and show a decrease in values along the series Cl > Br > I for a given phosphine and nitrogen donor. For a given halide the values of $\Delta\nu_2$ for $(PNCuX)_2$ complexes lie within a narrow range for nitrile or pyridine bases (1.671–1.709 for X = Cl, 1.615–1.653 for Br and 1.521–1.559 kHz for I). Changing the N-donor to piperidine increases this line spacing by approximately 10% to 1.82 kHz for X = Cl and Br and 1.64, 1.70 kHz for X = I, reflecting the transition towards three-co-ordination observed for this set of compounds.

As noted above, the ratio $\Delta\nu_3:\Delta\nu_1$ can be used to monitor trends in the asymmetry of the charge distribution about the copper. Perfectly tetrahedral complexes have a zero quadrupole coupling constant and the spacings between the lines of the quartet are equal ($\Delta\nu_3:\Delta\nu_1$ = 1:1). For three-co-ordinate complexes, however, the quadrupole coupling constant is of the order of 50–60 MHz[22,23] and $\Delta\nu_3:\Delta\nu_1$ at B = 9.40 T increases to 1.25–1.30 (Table 7). For the three sets of complexes $[\{CuX(PPh_3)(cpy)\}_2]$, $[\{CuX[PPh_2(C_6H_4Me\text{-}o)](cpy)\}_2]$ and $[\{CuX[P(C_6H_4Me\text{-}o)_3](MeCN)\}_2]$, the addition of the N-donor ligand to the $(PCuX)_2$ 'parent' complex results in values of $\Delta\nu_3:\Delta\nu_1$ ranging from 1.08 to 1.12:1. This can be explained in terms of the N-donor acting to reduce the asymmetry of the charge distribution about the three-co-ordinate copper site by donation of electron density to the copper atom which produces a relatively more balanced distribution of charge in the copper 4p orbitals. Within this data set, the larger values of $\Delta\nu_3:\Delta\nu_1$ correlate with increasing steric hindrance of the phosphine ligand, PPh_3 < $PPh_2(C_6H_4Me\text{-}o)$ < $P(C_6H_4Me\text{-}o)_3$, and while the significance of this trend should not be overestimated it does reflect the level of sensitivity of this parameter to small changes in the structural environment about the copper sites. In the case of piperidine as the N-donor ligand the structural results described above suggest that so much charge is donated by co-ordination of the piperidine that one halide is forced to reduce its contribution so that the p-orbital becomes unbalanced again and similar to the $CuPX_2$ three-co-ordinate case but with CuPNX co-ordination instead. Consistent with this view, $\Delta\nu_3:\Delta\nu_1$ for these two complexes increases to 1.21–1.22:1 which is only slightly less than the range of values observed for the three-co-ordinate $CuPX_2$ complexes. For the iodide complex, where the donation of electron density to the copper is expected to be the greatest for the halides and where differences in the Cu–X bond lengths for these complexes are the smallest, the increase in $\Delta\nu_3:\Delta\nu_1$ would be expected to be less and this is confirmed with observed values lying in the range 1.14–1.18:1.

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