Lewis-base Adducts of Group 11 Metal(I) Compounds. Part 28.[1] Solid-state Phosphorus-31 Cross-polarization Magic-angle Spinning Nuclear Magnetic Resonance and Structural Studies * on the Mononuclear 3:1 Adducts of Triphenylphosphine with Copper(I) Halides

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Solid-state cross-polarization magic-angle spinning ^{31}P n.m.r. data and single-crystal *X*-ray diffraction structure determinations are reported for solvated and unsolvated 3:1 adducts of triphenylphosphine with copper(I) halides, [Cu(PPh$_3$)$_3$X]. The structures of the unsolvated bromide and iodide complexes are isomorphous with the previously studied chloride analogue, crystallizing in the trigonal space group *P*3 with three independent molecules each disposed about a crystallographic three-fold symmetry axis. Two of the molecules are related by a pseudo-inversion centre. The PPh$_3$ ligands adopt a skewed conformation about Cu–P with respect to Cu–X [X–Cu–P–C(/11) angles 30.6—34.1°]. The Cu–P distances are not halide dependent [Br, 2.351(4), 2.340(4), and 2.369(4) Å; I, 2.362(3), 2.346(5), and 2.357(5) Å] and all P–Cu–P angles are close to the tetrahedral value. Solid-state ^{31}P n.m.r. spectra of each halide reveal two symmetric quartets in an intensity ratio of 2:1; average chemical shifts overall are −10, −13, and −17 p.p.m. for X = Cl, Br, and I respectively. The splittings within each quartet are also halide independent ranging between 900 and 940 Hz. The high intensity quartet is assigned to the two enantiomerically related molecules. The acetone solvated structures crystallize in the triclinic space group *P*$\bar{1}$ with the bromide and iodide isomorphous. Solvation changes the conformation of the PPh$_3$ ligands about Cu–P from skewed to staggered, with X–Cu–P–C(/11) 45.5—56.3°. The potential increase in back strain because of this conformational change is relieved by an increase of ~5° in the P–Cu–P angles. The Cu–P and P–Cu–P bond lengths and angles again do not change significantly with halogen within the series. The solid-state ^{31}P n.m.r. spectra each reveal a single quartet shifted downfield by 6—10 p.p.m.; the quartets are slightly more asymmetric than in the trigonal phase with splitting values lying in the range 890—980 Hz.

In the preceding paper[1] we described the results of our investigations into the structural and solid-state ^{31}P n.m.r. characteristics of the 2:1 monomeric adducts of triphenylphosphine with copper(I) and gold(I) halides, [M(PPh$_3$)$_2$X]. With bases in the ratio 3:1, monomeric adducts are obtained in which the co-ordination geometry of the Group 11 metal(I) cation ranges between trigonal planar and tetrahedral extremes. *X*-Ray diffraction studies on [Cu(PPh$_3$)$_3$Cl][2] show that the molecular geometry for M = Cu closely approaches ideal tetrahedral symmetry with Cu–P 2.348(2)—2.355(2), Cu–Cl 2.320(4)—2.350(4) Å, P–Cu–P 109.12(6)—110.51(6), and Cl–Cu–P 108.41(7)—109.83(6)°; in the analogous silver compound,[3] while M–P and M–Cl distances are again comparable, considerable angular distortion exists: Ag–P 2.520(1)—2.552(1), Ag–Cl 2.552(1) Å, P–Ag–P 113.41(4)—117.09(4), and Cl–Ag–P 96.66(5)—109.72(5)°. In [Au(PPh$_3$)$_3$Cl],[4] the Au–Cl bond length is considerably lengthened by comparison with Au–P and the angular distortion is even greater with the P–Au–P angles approaching the value of 120° expected for a trigonal planar species: Au–P 2.395(2)—2.431(2), Au–Cl 2.710(2) Å, P–Au–P 116.1(1)—119.6(1), and Cl–Au–P 92.0(1)—107.7(1)°.

In the copper compounds changes in the symmetry of the ligand environment about the metal atom from tetrahedral have been shown to result in asymmetric quartets in the solid-state ^{31}P cross-polarization magic-angle spinning (c.p.m.a.s.) n.m.r. spectra.[1,5,6] Thus for [Cu(PPh$_3$)$_3$Cl][5] which has nearly perfect tetrahedral symmetry for the P$_3$CuCl core, these secondary effects are negligible, whereas for the less symmetrical [Cu(PPh$_3$)$_3$(CH$_3$CN)]ClO$_4$ and [Cu(PPh$_3$)$_4$]ClO$_4$ differences in splitting values are *ca.* 100 Hz[7] and for the trigonal planar compounds [Cu(PPh$_3$)$_2$X], these differences increase to *ca.* 500 Hz.[1]

For the 2:1 adducts we have shown that within each halide series the structural and solid-state ^{31}P n.m.r. parameters of the molecules are independent of halogen and it was to ascertain whether this was also the case for the sterically more crowded [Cu(PPh$_3$)$_3$X] system that led us to determine the previously unreported crystal structures for X = Br or I and record their solid-state ^{31}P n.m.r. spectra. During the course of the work we found that these two compounds and the chloride could be isolated in two phases: (*a*) an unsolvated phase, crystallizing in the trigonal lattice already reported for the chloride, and (*b*) a solvated triclinic phase, acetone being the solvent, which for all three halides gave homogeneous samples adequate for solid-state n.m.r. experiments and crystals suitable for *X*-ray diffraction studies.

Experimental

Preparation of Compounds.—[Cu(PPh$_3$)$_3$X] [X = Cl, Br, *or* I (*trigonal form*)]. These complexes were prepared according to literature methods.[8,9] Stoicheiometric quantities of CuX and PPh$_3$ were refluxed for 2—4 h in chloroform and the hot, clear

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* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

Table 1. Non-hydrogen atom co-ordinates for [Cu(PPh$_3$)$_3$Br]

Molecule *l*	1			2			3		
Atom	*x*	*y*	*z*	*x*	*y*	*z*	*x*	*y*	*z*
Br(*l*)	0	0	0.235 1(2)	$-\frac{1}{3}$	$\frac{1}{3}$	0.527 1(2)	$\frac{1}{3}$	$-\frac{1}{3}$	0.300 8(2)
Cu(*l*)	0	0	0	$-\frac{1}{3}$	$\frac{1}{3}$	0.293 7(3)	$\frac{1}{3}$	$-\frac{1}{3}$	0.534 0(2)
Ligand									
P(*l*)	−0.106 8(2)	−0.123 6(2)	−0.069 6(3)	−0.299 0(2)	0.239 4(2)	0.221 1(3)	0.372 3(2)	−0.425 8(2)	0.604 3(3)
C(*l*11)	−0.199 5(7)	−0.178 3(7)	0.024 4(10)	−0.229 8(8)	0.217 1(7)	0.305 5(11)	0.346 6(7)	−0.519 1(7)	0.515 3(11)
C(*l*12)	−0.203 2(7)	−0.153 9(8)	0.145 0(11)	−0.213 4(8)	0.236 4(8)	0.431 8(11)	0.317 0(7)	−0.528 0(7)	0.396 5(12)
C(*l*13)	−0.271 2(9)	−0.198 6(9)	0.216 8(11)	−0.165 1(9)	0.213 9(9)	0.498 9(12)	0.301 3(9)	−0.596 4(9)	0.332 2(13)
C(*l*14)	−0.335 2(7)	−0.263 8(8)	0.170 7(13)	−0.132 4(9)	0.172 5(9)	0.442 5(17)	0.315 7(10)	−0.652 6(9)	0.377 2(15)
C(*l*15)	−0.331 6(8)	−0.290 3(8)	0.054 8(13)	−0.146 0(9)	0.155 3(9)	0.318 2(13)	0.349 2(10)	−0.641 4(9)	0.496 8(13)
C(*l*16)	−0.264 4(8)	−0.247 1(8)	0.018 2(11)	−0.194 4(9)	0.176 4(8)	0.248 9(11)	0.362 8(9)	−0.576 5(8)	0.565 1(12)
C(*l*21)	−0.079 6(6)	−0.203 1(6)	−0.083 5(10)	−0.387 3(7)	0.138 1(7)	0.216 1(11)	0.483 5(6)	−0.378 8(6)	0.608 0(10)
C(*l*22)	−0.026 6(7)	−0.201 1(8)	0.008 8(11)	−0.442 7(9)	0.115 6(9)	0.317 9(12)	0.524 5(7)	−0.322 8(7)	0.520 7(11)
C(*l*23)	−0.002 8(9)	−0.260 3(10)	0.004 6(14)	−0.508 0(9)	0.038 9(9)	0.324 3(15)	0.608 1(8)	−0.281 2(8)	0.519 1(12)
C(*l*24)	−0.030 5(10)	−0.315 8(9)	−0.093 6(18)	−0.519 9(9)	−0.015 3(9)	0.232 5(18)	0.647 5(8)	−0.303 6(9)	0.604 4(14)
C(*l*25)	−0.081 8(10)	−0.317 1(9)	−0.180 2(14)	−0.467 4(9)	0.003 0(9)	0.131 8(15)	0.606 7(9)	−0.360 4(9)	0.691 9(14)
C(*l*26)	−0.109 1(7)	−0.261 4(7)	−0.176 1(11)	−0.401 8(9)	0.079 3(9)	0.127 6(13)	0.521 7(8)	−0.399 7(8)	0.697 7(12)
C(*l*31)	−0.142 4(7)	−0.115 4(6)	−0.226 1(9)	−0.258 6(8)	0.260 2(7)	0.059 9(10)	0.337 6(7)	−0.463 8(7)	0.765 4(11)
C(*l*32)	−0.099 7(7)	−0.111 3(6)	−0.335 7(10)	−0.308 7(8)	0.240 5(8)	−0.046 4(12)	0.376 6(8)	−0.413 2(7)	0.866 4(10)
C(*l*33)	−0.119 7(9)	−0.096 2(7)	−0.449 7(11)	−0.278 6(11)	0.261 7(10)	−0.162 2(11)	0.345 4(10)	−0.438 5(10)	0.988 8(12)
C(*l*34)	−0.183 5(10)	−0.084 7(8)	−0.462 9(11)	−0.193 2(10)	0.307 1(10)	−0.178 9(12)	0.276 1(11)	−0.510 3(10)	1.004 4(13)
C(*l*35)	−0.228 8(8)	−0.088 9(8)	−0.355 8(12)	−0.144 7(8)	0.328 4(8)	−0.080 4(13)	0.239 6(9)	−0.559 4(8)	0.904 8(12)
C(*l*36)	−0.210 2(7)	−0.106 0(8)	−0.235 8(10)	−0.173 5(7)	0.305 3(7)	0.043 2(12)	0.269 9(7)	−0.535 7(7)	0.786 8(10)

solutions filtered. On slow cooling and evaporation of the solvent, the products separated as colourless crystals whose identity as the trigonal phase was subsequently confirmed by comparisons of powder *X*-ray diffraction data with theoretical patterns calculated from single-crystal data.

[Cu(PPh$_3$)$_3$X] [X = Cl, Br *or* I (*acetone solvate*)]. Dissolution of each of the above compounds (0.5 g) in acetone (50—80 cm^3), followed by slow cooling and evaporation, gave well formed, multifaceted crystals of the acetone solvate forms of these complexes. Crystal integrity was rapidly lost in the absence of mother-liquor. The quality of the solid-state ^{31}P n.m.r. data was consequently less than desirable. *X*-Ray powder and ^{31}P n.m.r. data on dried samples were identical to those of the orginal trigonal form.

Physical Measurements.—Powder *X*-ray diffraction data were obtained using a Phillips Debye-Scherrer camera. Theoretical powder patterns were calculated from single-crystal data using the LAZY-PULVERIX program package,[10] adapted for a VAX 780 computing system. Solid-state ^{31}P n.m.r. spectra were obtained on a Bruker CXP-300 spectrometer at 121.47 MHz as described previously.[7]

Crystallography.—General details are given in the preceding paper.[1]

Crystal data. [Cu(PPh$_3$)$_3$Br]. $C_{54}H_{45}BrCuP_3$, M = 930.3, trigonal, space group $P3$ (C_3^1, no. 143), a = 19.225(8), c = 10.610(3) Å, U = 3 397(2) Å^3, D_m = 1.37(1), D_c (Z = 3) = 1.37 g cm^{-3}, $F(000)$ = 1 434, μ_{Mo} = 15.1 cm^{-1}. Specimen: irregular, approximated as a sphere, 0.18-mm diameter for absorption correction; $2\theta_{max.}$ = 50°; N = 4 402, N_o = 2 632; R = 0.050, R' = 0.051.

[Cu(PPh$_3$)$_3$I]. $C_{54}H_{45}CuIP_3$, M = 977.3, trigonal, space group $P3$, a = 19.025(6), c = 10.915(6) Å, U = 3 421(3) Å^3, D_m = 1.43(1), D_c (Z = 3) = 1.42 g cm^{-3}, $F(000)$ = 1 488, μ_{Mo} = 13.2 cm^{-1}. Specimen: 0.07 × 0.12 × 0.18 mm; $2\theta_{max.}$ = 45°; N = 2 795, N_o = 2 225; R = 0.043, R' = 0.045.

[Cu(PPh$_3$)$_3$Cl]·2Me$_2$CO. $C_{60}H_{57}ClCuO_2P_3$, M = 1 002.0, triclinic, space group $P\bar{1}$ (C_i^1, no. 2), a = 20.24(4), b = 13.06(2), c = 10.88(2) Å, α = 92.3(1), β = 105.4(1), γ = 106.5(1)°, U = 2 638(4) Å^3, D_m = 1.25(2), D_c (Z = 2) = 1.26(1) g cm^{-3}, $F(000)$ = 1 048, μ_{Mo} = 6.2 cm^{-1}. Specimen: 0.07 × 0.20 × 0.25 mm; $2\theta_{max.}$ = 40°; N = 4 604, N_o = 3 092; R = 0.092, R' = 0.080.

[Cu(PPh$_3$)$_3$Br]·2Me$_2$CO. $C_{60}H_{57}BrCuO_2P_3$, M = 1 046.5, triclinic, space group $P\bar{1}$, a = 14.565(3), b = 14.412(4), c = 13.262(4) Å, α = 87.82(2), β = 83.82(2), γ = 71.80(2)°, U = 2 629(1) Å^3, D_m = 1.27(2), D_c (Z = 2) = 1.32 g cm^{-3}, $F(000)$ = 1 084, μ_{Mo} = 13.7 cm^{-1}. Specimen: 0.1 × 0.2 × 0.3 mm (irregular); $2\theta_{max.}$ = 45°; N = 6 908, N_o(2σ level) = 4 714; R = 0.060, R' = 0.064.

[Cu(PPh$_3$)$_3$I]·'C$_9$'. $C_{63}H_{45}CuIP_3$, M = 1 085.4, triclinic, space group $P\bar{1}$, a = 14.646(5), b = 14.471(6), c = 13.249(5) Å, α = 87.91(3), β = 84.28(3), γ = 71.85(3)°, U = 2 655(1) Å^3, D_m = 1.30(2), D_c (Z = 2) = 1.36 g cm^{-3}, $F(000)$ = 1 100, μ_{Mo} = 11.5 cm^{-1}. Specimen: 0.34 × 0.30 × 0.14 mm; $2\theta_{max.}$ = 50°; N = 9 379, N_o = 5 650; R = 0.042, R' = 0.050.

Abnormal features. As with the previously studied chloride, accessible data was limited for the trigonal bromide and iodide structures. The co-ordinate setting follows that of the chloride with *x* and *y* interchanged in accord with the measured data. In no case could absolute configurations be meaningfully assigned. In the solvates data were also weak and/or limited in extent and in the refinement high thermal motion (and incipient solvent disorder?) caused problems in modelling the solvent appropriately; it is likely that the ascribed population of 2 may represent an upper limit rather than an actual population. In the chloride, one of the solvent groups defined could not be described meaningfully in terms of acetone; in the bromide, the second group was highly distorted pyramidally,

Table 2. Non-hydrogen atom co-ordinates for [Cu(PPh$_3$)$_3$I]

Molecule *l*	1			2			3		
Atom	*x*	*y*	*z*	*x*	*y*	*z*	*x*	*y*	*z*
I(*l*)	0	0	0.245 9(2)	$-\frac{1}{3}$	$\frac{1}{3}$	0.536 3(2)	$\frac{1}{3}$	$-\frac{1}{3}$	0.294 2(2)
Cu(*l*)	0	0	0	$-\frac{1}{3}$	$\frac{1}{3}$	0.292 6(3)	$\frac{1}{3}$	$-\frac{1}{3}$	0.538 1(2)
Ligand									
P(*l*)	−0.110 3(2)	−0.124 2(2)	−0.068 1(3)	−0.296 6(2)	0.239 7(2)	0.221 7(3)	0.374 0(2)	−0.425 2(2)	0.606 4(3)
C(*l*11)	−0.205 3(9)	−0.178 1(9)	0.023 4(11)	−0.224 0(8)	0.219 3(8)	0.300 8(11)	0.348 7(8)	−0.519 7(8)	0.522 5(12)
C(*l*12)	−0.209 2(9)	−0.147 7(9)	0.136 2(12)	−0.209 8(8)	0.237 2(8)	0.425 2(11)	0.316 4(9)	−0.532 2(10)	0.408 2(14)
C(*l*13)	−0.276 4(11)	−0.190 0(11)	0.206 4(13)	−0.161 0(11)	0.214 2(11)	0.489 7(14)	0.301 6(10)	−0.600 3(10)	0.340 8(15)
C(*l*14)	−0.342 7(10)	−0.261 2(10)	0.170 0(14)	−0.124 2(11)	0.174 8(11)	0.430 5(18)	0.320 3(12)	−0.654 7(9)	0.386 9(20)
C(*l*15)	−0.335 5(9)	−0.289 0(9)	0.057 0(15)	−0.140 9(10)	0.157 1(11)	0.309 0(15)	0.353 5(12)	−0.642 8(10)	0.501 6(19)
C(*l*16)	−0.269 4(10)	−0.251 6(9)	−0.013 2(15)	−0.188 2(9)	0.179 3(9)	0.245 7(12)	0.370 5(10)	−0.574 1(10)	0.572 2(12)
C(*l*21)	−0.085 8(7)	−0.205 9(8)	−0.084 0(11)	−0.384 7(7)	0.136 2(8)	0.217 2(11)	0.484 1(7)	−0.378 3(7)	0.612 5(10)
C(*l*22)	−0.036 0(8)	−0.206 9(9)	0.004 4(12)	−0.440 9(11)	0.115 5(10)	0.311 8(13)	0.527 8(9)	−0.322 7(8)	0.520 2(11)
C(*l*23)	−0.012 9(10)	−0.266 5(12)	0.001 6(14)	−0.507 0(10)	0.037 7(12)	0.322 6(15)	0.613 3(9)	−0.282 0(9)	0.517 5(13)
C(*l*24)	−0.032 9(13)	−0.316 4(11)	−0.093 2(20)	−0.518 1(11)	−0.016 9(10)	0.233 5(21)	0.652 7(9)	−0.300 7(11)	0.604 2(13)
C(*l*25)	−0.087 9(11)	−0.318 4(9)	−0.179 9(16)	−0.465 2(10)	0.002 7(10)	0.138 1(15)	0.611 7(11)	−0.356 8(11)	0.693 3(15)
C(*l*26)	−0.113 1(9)	−0.260 9(9)	−0.178 3(11)	−0.398 6(9)	0.078 9(9)	0.129 5(13)	0.527 1(9)	−0.396 2(9)	0.698 1(11)
C(*l*31)	−0.145 2(8)	−0.115 5(8)	−0.219 0(10)	−0.255 9(8)	0.261 5(8)	0.067 2(10)	0.339 7(9)	−0.463 1(8)	0.762 1(10)
C(*l*32)	−0.102 6(7)	−0.111 2(8)	−0.323 6(13)	−0.308 1(9)	0.239 5(9)	−0.037 3(13)	0.377 7(8)	−0.412 8(8)	0.861 2(10)
C(*l*33)	−0.121 2(10)	−0.097 1(8)	−0.438 4(11)	−0.277 7(11)	0.262 2(10)	−0.152 5(11)	0.351 7(10)	−0.434 7(11)	0.978 5(12)
C(*l*34)	−0.184 7(11)	−0.083 5(9)	−0.448 3(11)	−0.195 6(11)	0.305 5(10)	−0.172 5(12)	0.283 0(11)	−0.510 4(11)	1.000 5(13)
C(*l*35)	−0.231 7(8)	−0.086 0(9)	−0.346 2(13)	−0.143 0(9)	0.328 5(10)	−0.071 8(14)	0.245 1(10)	−0.560 1(9)	0.904 5(14)
C(*l*36)	−0.211 7(8)	−0.103 1(8)	−0.233 6(10)	−0.171 4(8)	0.306 9(8)	0.045 4(12)	0.272 3(7)	−0.537 4(8)	0.785 4(11)

Table 3. Non-hydrogen atom co-ordinates for [Cu(PPh$_3$)$_3$Cl]·2Me$_2$CO

Ligand *l*	1			2			3		
Atom	*x*	*y*	*z*	*x*	*y*	*z*	*x*	*y*	*z*
Cl	0.212 3(3)	0.555 3(4)	0.582 2(5)						
Cu	0.255 2(1)	0.643 1(2)	0.793 6(2)						
Ligand									
P(*l*)	0.159 5(3)	0.578 5(4)	0.878 7(5)	0.272 2(3)	0.822 8(4)	0.762 5(5)	0.355 3(3)	0.587 5(4)	0.881 5(5)
C(*l*11)	0.126 6(11)	0.429 5(16)	0.860 8(22)	0.323 9(11)	0.874 8(17)	0.652 3(19)	0.417 8(12)	0.602 2(15)	0.788 4(21)
C(*l*12)	0.129 5(12)	0.369 6(18)	0.758 4(21)	0.373 7(13)	0.828 0(17)	0.637 5(22)	0.392 4(11)	0.569 9(17)	0.654 5(24)
C(*l*13)	0.103 7(15)	0.262 1(20)	0.742 7(25)	0.413 7(12)	0.866 7(22)	0.550 0(27)	0.438 9(15)	0.584 3(18)	0.578 9(20)
C(*l*14)	0.073 9(16)	0.206 9(19)	0.826 0(32)	0.401 4(15)	0.955 0(24)	0.483 4(24)	0.513 1(14)	0.630 7(18)	0.635 0(25)
C(*l*15)	0.071 6(15)	0.263 4(21)	0.935 0(30)	0.353 1(16)	1.000 0(21)	0.503 1(27)	0.539 6(12)	0.663 0(17)	0.764 2(25)
C(*l*16)	0.096 2(12)	0.376 2(20)	0.949 9(23)	0.314 5(12)	0.964 6(19)	0.589 0(24)	0.492 4(14)	0.647 2(14)	0.841 5(20)
C(*l*21)	0.077 6(11)	0.609 4(18)	0.798 3(21)	0.189 1(11)	0.858 9(18)	0.694 0(21)	0.332 8(11)	0.446 0(15)	0.902 1(20)
C(*l*22)	0.067 3(12)	0.705 8(20)	0.831 7(21)	0.138 4(13)	0.784 4(16)	0.591 1(22)	0.290 6(11)	0.405 9(17)	0.981 7(20)
C(*l*23)	0.005 1(19)	0.731 6(26)	0.770 7(31)	0.076 4(12)	0.806 2(20)	0.523 4(21)	0.271 4(11)	0.300 1(21)	1.001 1(21)
C(*l*24)	−0.048 7(22)	0.666 0(35)	0.675 5(43)	0.065 8(15)	0.901 8(23)	0.562 5(28)	0.294 8(15)	0.229 6(19)	0.940 5(26)
C(*l*25)	−0.038 0(18)	0.570 4(28)	0.639 1(33)	0.115 3(16)	0.974 5(22)	0.664 3(28)	0.336 4(14)	0.266 6(22)	0.862 3(25)
C(*l*26)	0.024 3(15)	0.540 6(18)	0.696 9(27)	0.176 5(16)	0.951 7(16)	0.727 5(22)	0.354 7(12)	0.376 3(19)	0.839 0(20)
C(*l*31)	0.178 7(14)	0.624 0(15)	1.049 6(19)	0.316 4(12)	0.920 0(15)	0.907 8(19)	0.412 0(11)	0.647 4(17)	1.041 5(19)
C(*l*32)	0.250 5(13)	0.656 6(18)	1.119 9(23)	0.287 0(12)	0.906 7(16)	1.009 0(23)	0.424 6(11)	0.755 9(18)	1.071 8(19)
C(*l*33)	0.264 8(14)	0.689 8(21)	1.246 9(30)	0.319 6(14)	0.970 3(20)	1.121 7(22)	0.468 0(13)	0.809 7(16)	1.190 5(25)
C(*l*34)	0.213 5(22)	0.694 3(21)	1.305 9(23)	0.384 1(16)	1.044 8(19)	1.140 8(21)	0.500 2(11)	0.751 9(22)	1.282 9(19)
C(*l*35)	0.144 5(16)	0.661 9(23)	1.235 5(32)	0.417 0(12)	1.060 6(17)	1.043 6(26)	0.485 2(12)	0.643 6(20)	1.249 9(23)
C(*l*36)	0.126 0(13)	0.626 5(18)	1.105 4(25)	0.382 3(12)	0.997 4(18)	0.924 1(20)	0.441 9(11)	0.592 2(16)	1.130 5(21)
Solvent									
C(1)	0.239 8(15)	0.268 1(18)	0.495 4(26)	0.117 8(23)	0.027 8(31)	0.187 0(41)			
C(2)	0.262 3(13)	0.357 6(23)	0.356 8(25)	0.082 0(19)	0.067 0(28)	0.216 1(38)			
C(3)	0.306 4(15)	0.273 7(21)	0.419 8(31)	0.152 7(18)	−0.017 8(26)	0.289 8(36)			
C(4)				0.126 4(21)	0.001 8(32)	0.066 4(32)			

Table 4. Non-hydrogen atom co-ordinates for $[Cu(PPh_3)_3Br]\cdot2Me_2CO$

Ligand *l*	1			2			3		
Atom	*x*	*y*	*z*	*x*	*y*	*z*	*x*	*y*	*z*
Br	0.381 1(1)	0.180 1(1)	0.233 8(1)						
Cu	0.213 3(1)	0.169 3(1)	0.228 0(1)						
Ligand									
P(*l*)	0.236 8(2)	0.006 5(2)	0.273 6(2)	0.129 0(2)	0.288 6(2)	0.347 4(2)	0.171 2(2)	0.201 1(2)	0.061 0(2)
C(*l*11)	0.296 5(8)	−0.032 3(7)	0.391 9(8)	0.146 2(7)	0.405 7(8)	0.314 5(9)	0.191 9(8)	0.307 5(7)	−0.001 5(8)
C(*l*12)	0.397 0(9)	−0.061 2(9)	0.386 2(9)	0.124 5(9)	0.444 1(8)	0.217 9(9)	0.277 8(9)	0.324 8(8)	0.009 3(9)
C(*l*13)	0.442 7(8)	−0.085 3(10)	0.472 8(10)	0.136 8(10)	0.532 6(10)	0.188 4(10)	0.300 5(9)	0.404 2(10)	−0.040 2(11)
C(*l*14)	0.392 2(10)	−0.082 4(10)	0.565 8(10)	0.168 3(10)	0.584 5(10)	0.251 7(12)	0.234 8(12)	0.467 0(9)	−0.098 3(11)
C(*l*15)	0.293 3(10)	−0.054 0(10)	0.571 5(9)	0.190 0(11)	0.548 2(11)	0.347 6(11)	0.148 6(11)	0.451 3(10)	−0.104 3(11)
C(*l*16)	0.244 2(8)	−0.026 4(9)	0.486 0(9)	0.178 2(10)	0.457 9(9)	0.377 9(10)	0.127 1(9)	0.373 0(9)	0.058 4(9)
C(*l*21)	0.317 7(8)	−0.082 4(8)	0.182 1(8)	0.157 8(8)	0.271 7(7)	0.479 4(8)	0.235 8(8)	0.103 4(8)	−0.029 1(8)
C(*l*22)	0.387 4(8)	−0.055 0(8)	0.122 7(9)	0.247 7(8)	0.209 2(8)	0.503 8(9)	0.208 0(8)	0.020 3(8)	−0.026 3(7)
C(*l*23)	0.452 1(8)	−0.119 8(9)	0.051 4(9)	0.269 0(9)	0.198 5(10)	0.603 5(11)	0.256 9(10)	−0.057 3(9)	−0.090 8(10)
C(*l*24)	0.445 2(9)	−0.211 6(10)	0.042 2(10)	0.203 7(10)	0.250 5(10)	0.680 8(9)	0.332 7(10)	−0.050 8(9)	−0.156 7(9)
C(*l*25)	0.375 4(10)	−0.239 9(8)	0.102 8(11)	0.116 5(9)	0.310 0(8)	0.658 7(8)	0.362 2(8)	0.031 3(10)	−0.162 2(9)
C(*l*26)	0.311 7(8)	−0.174 9(9)	0.172 5(9)	0.093 7(8)	0.321 1(8)	0.560 5(9)	0.312 3(9)	0.108 2(8)	−0.097 4(9)
C(*l*31)	0.128 4(8)	−0.032 1(8)	0.291 7(8)	−0.003 0(8)	0.316 5(8)	0.364 7(8)	0.045 5(8)	0.217 7(7)	0.038 0(9)
C(*l*32)	0.047 4(9)	0.023 0(8)	0.243 2(8)	−0.039 7(9)	0.239 6(9)	0.384 8(8)	−0.027 1(9)	0.257 7(8)	0.115 3(8)
C(*l*33)	−0.036 2(9)	−0.002 6(10)	0.248 4(10)	−0.138 9(12)	0.254 3(12)	0.396 1(12)	−0.123 9(9)	0.275 2(9)	0.101 5(9)
C(*l*34)	−0.044 0(9)	−0.081 6(11)	0.304 7(11)	−0.203 5(10)	0.346 9(13)	0.385 6(11)	−0.148 0(9)	0.252 0(9)	0.012 7(11)
C(*l*35)	0.033 6(11)	−0.138 5(9)	0.354 7(9)	−0.167 3(10)	0.424 1(11)	0.366 4(10)	−0.077 0(10)	0.211 3(9)	−0.065 1(9)
C(*l*36)	0.118 1(9)	−0.112 6(9)	0.349 2(9)	−0.068 2(9)	0.410 3(8)	0.355 7(9)	0.019 2(8)	0.194 5(8)	−0.051 5(9)
Solvent fragments (modelled as carbon atoms with unit population)									
C(*l*01)	0.547 2(25)	0.378 6(37)	0.193 2(37)	0.454 8(28)	0.379 9(21)	0.568 4(37)			
C(*l*02)	0.594 8(29)	0.390 5(31)	0.129 2(31)	0.569 3(15)	0.348 3(16)	0.593 1(17)			
C(*l*03)	0.554 9(35)	0.332 7(27)	0.280 2(36)	0.426 7(16)	0.460 6(17)	0.621 7(22)			
C(*l*04)	0.445 9(17)	0.444 3(15)	0.182 9(19)	0.443 4(17)	0.335 5(18)	0.687 4(19)			

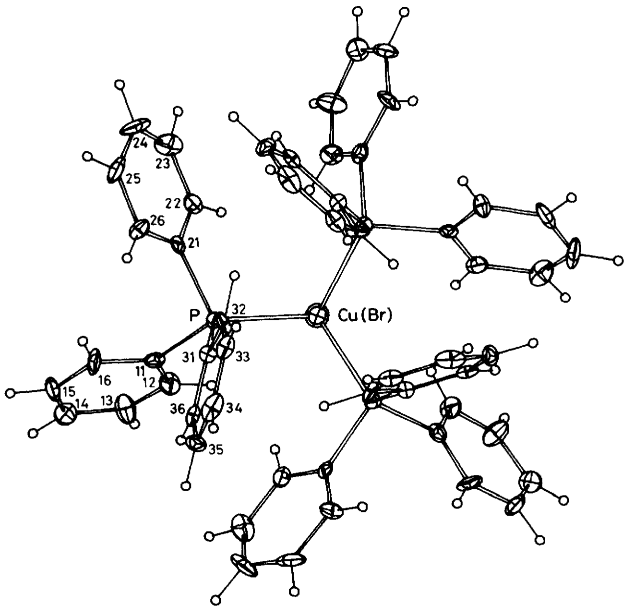


Figure 1. A single molecule of trigonal $[Cu(PPh_3)_3Br]$ viewed down *c*. 20% Thermal ellipsoids are shown for the non-hydrogen atoms; hydrogen atoms have an arbitrary radius of 0.1 Å

and in the iodide, an additional peak was resolved and refinable, all peaks being modelled as 'carbon'.

Atom co-ordinates are given in Tables 1—5 and geometrical details in Tables 6 and 7. Single molecules of $[Cu(PPh_3)_3Br]$ and $[Cu(PPh_3)_3Br]\cdot2Me_2CO$ are shown in Figures 1 and 2 respectively. The atom-numbering scheme adopted for the phenyl rings of each triphenylphosphine ligand follows the scheme defined in ref. 1: the three digits of C(*lmn*) denote respectively ligand, ring, and atom numbers. The *ortho* carbon atoms on the same side of the C(*l*11)–C(*l*21)–C(*l*31) plane as the co-ordinated metal atom are defined as C(*lm*2). In the trigonal compounds, only one PPh_3 ligand on each molecule is crystallographically independent. In this case the number *l* refers to the molecule under consideration. Where structural data have been taken or calculated from published work, the atom labelling has been adjusted to conform with the present scheme.

Results and Discussion

The structural determinations of the unsolvated forms of $[Cu(PPh_3)_3X]$ (X = Br or I) confirm the isomorphism of the structures with the previously published chloride structure. This structural type is well known for species of this composition and can accommodate a wide range of sizes and electronic configurations of M and X.[11] Three independent molecules occupy the unit cell, each with the M–X bond located on a crystallographic three-fold axis, and with the ligand chiralities of two of the molecules the same and opposite to the third. Molecules 1 and 3 are related by a pseudo-inversion centre. A major contributing factor to the conformation adopted by the triphenylphosphine ligands in each molecule appears to be close intramolecular contact distances between the halogen and H(*l*12): 2.6_6, 2.7_4, 2.7_4 (Cl); 2.7_9, 2.7_9, 2.7_4 (Br); and 2.9_0, 2.8_6, 2.8_5 Å (I). These close X···H distances constrain the triphenylphosphine ligands to adopt a skewed conformation about M–P with respect to M–X,

Table 5. Non-hydrogen atom co-ordinates for $[Cu(PPh_3)_3I]\cdot$'C_9'

Ligand *l*	1			2			3		
Atom	*x*	*y*	*z*	*x*	*y*	*z*	*x*	*y*	*z*
I	0.386 73(3)	0.187 60(3)	0.240 55(3)						
Cu	0.210 97(5)	0.169 39(5)	0.229 99(5)						
Ligand									
P(*l*)	0.236 1(1)	0.006 7(1)	0.273 8(1)	0.126 6(1)	0.287 3(1)	0.350 4(1)	0.169 0(1)	0.202 0(1)	0.062 1(1)
C(*l*11)	0.294 1(4)	−0.031 6(4)	0.390 8(4)	0.143 9(4)	0.405 0(4)	0.316 4(4)	0.190 3(4)	0.308 3(4)	−0.001 9(4)
C(*l*12)	0.394 2(4)	−0.060 5(5)	0.386 8(4)	0.125 1(5)	0.441 9(4)	0.221 5(5)	0.278 4(5)	0.323 7(5)	0.004 1(5)
C(*l*13)	0.440 6(4)	−0.085 2(5)	0.475 3(5)	0.139 8(5)	0.528 5(5)	0.188 5(5)	0.300 0(5)	0.401 6(5)	−0.045 0(6)
C(*l*14)	0.388 2(5)	−0.081 1(5)	0.567 6(5)	0.171 8(6)	0.579 8(5)	0.254 9(6)	0.231 6(6)	0.465 2(5)	−0.099 5(6)
C(*l*15)	0.289 2(5)	−0.051 3(5)	0.572 0(5)	0.189 6(7)	0.545 2(5)	0.350 2(6)	0.145 0(5)	0.452 8(5)	−0.104 2(5)
C(*l*16)	0.242 3(4)	−0.025 6(5)	0.484 9(4)	0.175 3(6)	0.458 1(5)	0.381 4(5)	0.122 6(5)	0.375 1(5)	−0.055 1(5)
C(*l*21)	0.317 3(4)	−0.083 1(4)	0.183 3(4)	0.154 4(4)	0.270 6(4)	0.483 4(4)	0.233 4(4)	0.103 5(4)	−0.027 2(4)
C(*l*22)	0.387 5(4)	−0.055 2(4)	0.122 6(4)	0.241 4(4)	0.208 1(4)	0.508 5(4)	0.205 3(4)	0.019 9(4)	−0.023 0(4)
C(*l*23)	0.452 2(4)	−0.120 6(5)	0.054 3(5)	0.263 3(5)	0.198 7(5)	0.608 6(5)	0.253 8(5)	−0.057 9(4)	−0.087 1(5)
C(*l*24)	0.445 1(5)	−0.212 4(5)	0.045 8(5)	0.198 8(5)	0.252 6(5)	0.683 5(4)	0.329 3(5)	−0.052 1(5)	−0.154 4(5)
C(*l*25)	0.375 9(5)	−0.239 9(5)	0.105 9(5)	0.112 1(5)	0.314 8(4)	0.659 8(4)	0.357 9(5)	0.029 5(5)	−0.157 8(5)
C(*l*26)	0.311 4(4)	−0.175 9(4)	0.174 6(5)	0.089 7(4)	0.323 6(4)	0.559 5(4)	0.311 2(4)	0.106 4(4)	−0.095 5(5)
C(*l*31)	0.127 9(4)	−0.032 0(4)	0.292 0(4)	−0.004 1(4)	0.316 4(4)	0.366 3(4)	0.043 6(4)	0.218 8(4)	0.039 6(4)
C(*l*32)	0.049 2(4)	0.020 9(4)	0.243 6(4)	−0.042 0(5)	0.238 7(5)	0.388 3(5)	−0.028 1(4)	0.257 9(4)	0.116 3(4)
C(*l*33)	−0.035 8(4)	−0.005 3(5)	0.251 1(5)	−0.139 9(5)	0.255 4(6)	0.398 3(5)	−0.124 0(4)	0.276 8(5)	0.101 6(5)
C(*l*34)	−0.041 8(5)	−0.085 5(5)	0.306 6(5)	−0.203 6(5)	0.348 5(6)	0.388 7(5)	−0.149 9(4)	0.255 5(5)	0.009 8(5)
C(*l*35)	0.037 4(5)	−0.139 3(5)	0.354 8(5)	−0.167 4(5)	0.424 7(6)	0.367 9(5)	−0.079 7(5)	0.215 6(5)	−0.066 0(5)
C(*l*36)	0.121 9(5)	−0.113 7(5)	0.347 6(5)	−0.069 2(4)	0.408 1(5)	0.357 6(5)	0.016 6(4)	0.198 0(5)	−0.053 1(4)
Solvent fragments (modelled as carbon atoms, with unit population*)									
C(*l*01)	0.547(1)	0.402(1)	0.167(1)	0.473(1)	0.383(1)	0.613(1)			
C(*l*02)	0.595(1)	0.409(1)	0.088(1)	0.579(1)	0.341(1)	0.594(1)			
C(*l*03)	0.588(1)	0.334(1)	0.234(1)	0.418(1)	0.470(1)	0.625(1)			
C(*l*04)	0.445(1)	0.458(1)	0.175(1)	0.411(4)	0.318(1)	0.695(1)			
C(*l*05)				0.428(2)	0.371(2)	0.506(2)			

* Isotropic thermal parameters for C(101—4) are (10^3U/Å^2): 176(5), 205(6), 167(5), and 155(5) and for C(201—5) 244(8), 201(6), 227(7), 253(8), and 297(10).

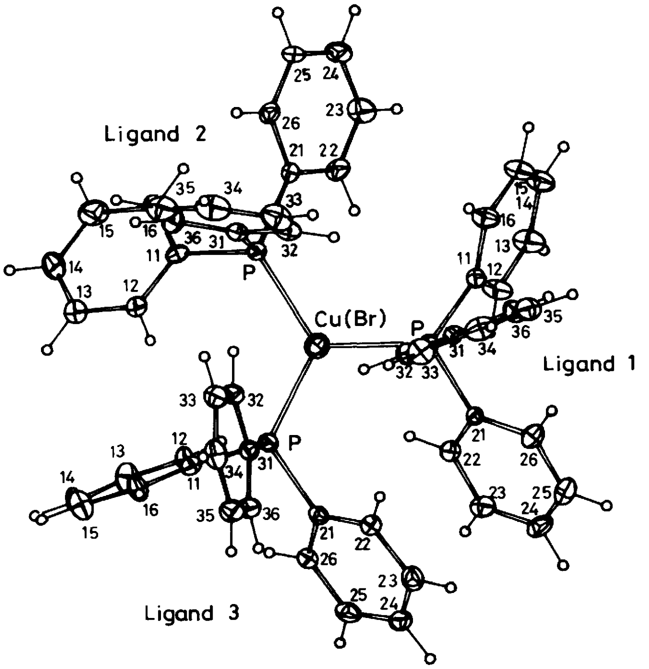


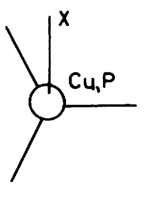
Figure 2. A single molecule of $[Cu(PPh_3)_3Br]\cdot 2Me_2CO$, projected down the Cu–Br bond

with an average conformation angle, Cu–P(*l*)–C(*l*11)–C(*l*12), of 32° (Table 6). In each molecule, the conformation angle, X–Cu–P(*l*)–C(*l*11), of phenyl ring 1 is opposite in sign to the other two angles and is twisted towards the halogen atom. This contrasts with the more normal conformational structure of triphenylphosphine as found for $[M(PPh_3)_2X]$ [1] and $[Au(PPh_3)X]$ [12] where each phenyl ring forms the 'blade' of a chiral propeller.

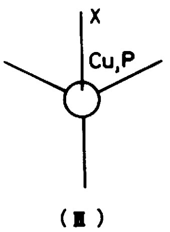
The solid-state ^{31}P n.m.r. spectra of each of these compounds reveals two symmetric quartets in an intensity ratio of 2:1 as has been previously reported for the chloride.[5] This result indicates that two of the molecules in the unit cell occupy equivalent sites and is consistent with the structural results which show that while molecules 1 and 3 are crystallographically distinguishable, they, in fact, form a chemically equivalent enantiomeric pair. The splittings within each quartet are remarkably constant, falling within the range 900—940 Hz for the entire series (Table 8). The Cu–P distances and P–Cu–P angles are also halide independent with average Cu–P values of 2.351(4), 2.353(14), and 2.355(8) Å for Cl, Br, and I respectively and all the P–Cu–P angles assuming values close to the tetrahedral angle of 109.6°.

Structure determination on the crystalline products obtained from recrystallization of the trigonal compounds from acetone show that while the molecular composition of $[Cu(PPh_3)_3X]$ remains unaltered, the conformational angles of the PPh_3 ligands and the P_3CuX core geometries both change significantly, with an array of less symmetrically disposed H $\cdots$ O and H $\cdots$ X contact distances between the halide anion, solvated acetone, and the phenyl hydrogens: Cl $\cdots$ H(124) ($x,y,z-1$) 2.9_6; Cl $\cdots$ H(135) ($\bar{x},1-y,1-z$) 2.9_6; Cl $\cdots$ C(11,21) (solvent) 4.0_5, 4.0_0; Br $\cdots$ C(101,103) (solvent) 4.2_6, 3.9_3; and I $\cdots$ C(103,104) (solvent) 4.1_2, 4.2_9 Å. The net result is a rotation of the PPh_3 ligands about Cu–P to approach the staggered conformation (**II**) rather than the skewed conformation (**I**).

The potential increase in back strain that would result from this conformation change (Figure 2) is relieved by an increase in the P–Cu–P angles by an average of ~5°, there being only small, and, given the imprecision of the structure determinations on the solvated complexes, probably insignificant changes in both the Cu–X and Cu–P distances, with Cu–P decreasing by *ca.* 0.01—0.02 Å and Cu–X increasing by *ca.* 0.01—0.03 Å. The



(I)



(II)

Table 6. Conformational angles (°) for $[Cu(PPh_3)_3X]$

		X–Cu–P(*l*)–C(*lm*1)			Cu–P(*l*)–C(*lm*1)–C(*lm*2)		
X	*l*	*m* = 1	*m* = 2	*m* = 3	*m* = 1	*m* = 2	*m* = 3
Trigonal phase (unsolvated)							
Cl[a]	1	−30.8	86.0	−153.8	11.5	−33.9	−75.7
	2	33.0	−84.0	156.1	−19.2	39.3	79.0
	3	31.9	−84.6	156.8	−10.7	31.9	74.3
Br	1	−30.6	87.1	−153.6	9.7	−36.3	−76.7
	2	32.8	−84.2	157.3	−19.2	40.6	78.6
	3	32.9	−84.0	156.7	−11.5	32.5	74.8
I	1	−30.9	87.9	−153.9	4.3	−38.3	−75.4
	2	34.1	−83.9	157.0	−22.2	36.9	79.5
	3	33.6	−84.7	157.0	−10.3	36.8	74.7
Triclinic phase (solvated)							
Cl	1	−53.4	61.9	−175.2	32.0	85.8	22.7
	2	50.5	−68.3	172.8	27.5	43.8	54.5
	3	−50.1	68.7	−173.6	45.2	61.0	39.6
Br	1	−51.6	65.5	−174.1	84.5	−27.5	−22.8
	2	−56.3	63.2	−175.2	−54.5	−21.9	−53.0
	3	48.1	−71.9	170.1	−43.2	−75.5	−30.8
I	1	−51.1	66.4	−172.2	85.3	−26.8	−24.3
	2	−56.1	63.9	−173.8	−53.0	−20.5	−55.1
	3	45.5	−74.4	167.9	−46.2	−74.6	−30.7
Fluoride (solvated)[b]							
	1	−41.5	78.3	−169.3	12.8	−33.1	−87.8
	2	−32.7	83.6	−154.6	14.3	−49.0	−71.5
	3	−31.5	87.0	−155.4	15.4	−33.4	−77.2

[a] Ref. 2. [b] Ref. 14.

Table 8. Solid state c.p.m.a.s. ^{31}P n.m.r. data for $[Cu(PPh_3)_3X]$ compounds *

	δ_1	δ_2	δ_3	δ_4	$\langle\delta\rangle$	$\Delta\nu_1$	$\Delta\nu_2$	$\Delta\nu_3$	$\Delta\nu_{ij}$
X	p.p.m.					Hz			
Trigonal phase (unsolvated)									
Cl	0.3	−7.4	−15.1	−22.5	−11.2	940	940	900	40
	2.5	−5.2	−12.9	−20.5	−9.0	940	940	920	20
Br	−2.6	−10.3	−18.1	−25.7	−14.2	930	940	930	10
	−0.5	−7.8	−15.5	−23.3	−11.8	900	930	940	10
I	−7.5	−14.9	−22.9	−30.3	−18.8	900	930	930	30
	−4.4	−11.7	−19.4	−27.1	−15.6	900	930	920	30
Triclinic phase (solvated)									
Cl	8.4	0.7	−7.4	−15.4	−3.4	930	980	970	50
Br	6.5	−1.0	−9.0	−16.8	−5.1	900	960	950	60
I	3.3	−4.1	−11.4	−18.9	−7.8	900	890	910	20
	5.9	−1.5	−9.4	−17.2	−5.6	900	960	940	60

* δ_i are chemical shift values (±0.5 p.p.m.) with respect to 85% H_3PO_4. δ (solid PPh_3) = −9.9 p.p.m.; $\langle\delta\rangle$ is the average chemical shift for each quartet; $\Delta\nu_i$ is the spin–spin coupling interaction in Hz (±30) between each of the four peaks of the quartet; $\Delta\nu_{ij} = \Delta\nu_i(\text{max.}) - \Delta\nu_i(\text{min.})$ is defined here as the asymmetry parameter of the quartet.

Table 7. Core geometries for $[Cu(PPh_3)_3X]$

	Trigonal			Triclinic		
X	Cl	Br	I	Cl	Br	I
Distances/Å						
Cu–P(*l*)	2.348(2) 2.351(2) 2.355(2)	2.351(4) 2.340(4) 2.369(4)	2.362(3) 2.346(5) 2.357(5)	2.327(8) 2.327(7) 2.326(7)	2.335(4) 2.335(4) 2.355(4)	2.327(2) 2.340(2) 2.358(2)
Mean	2.351(4)	2.353(14)	2.355(8)	2.326(1)	2.342(11)	2.342(15)
Cu–X	2.336(4) 2.320(4) 2.350(4)	2.494(3) 2.478(4) 2.478(5)	2.684(3) 2.661(4) 2.662(4)			
Mean	2.335(15)	2.481(5)	2.669(13)	2.349(6)	2.510(3)	2.686(1)
Angles/°						
P–Cu–P	109.83(6) 109.12(6) 110.51(6)	110.6(2) 109.5(2) 110.5(2)	110.6(2) 109.7(2) 110.5(2)	111.1(3) 115.1(3) 118.9(2)	117.7(1) 111.9(1) 116.0(1)	118.00(6) 111.80(7) 116.08(6)
Mean	109.8(7)	110.2(6)	110.3(5)	115(4)	115(3)	115(3)
P–Cu–X	109.11(6) 109.83(6) 108.41(7)	108.3(1) 109.2(1) 108.3(1)	108.3(1) 109.2(1) 108.4(1)	104.0(2) 102.5(2) 102.7(2)	100.9(1) 99.2(1) 108.5(1)	102.03(4) 97.56(5) 108.80(5)
Mean	109.1(7)	108.6(5)	108.6(5)	103(1)	103(5)	103(6)

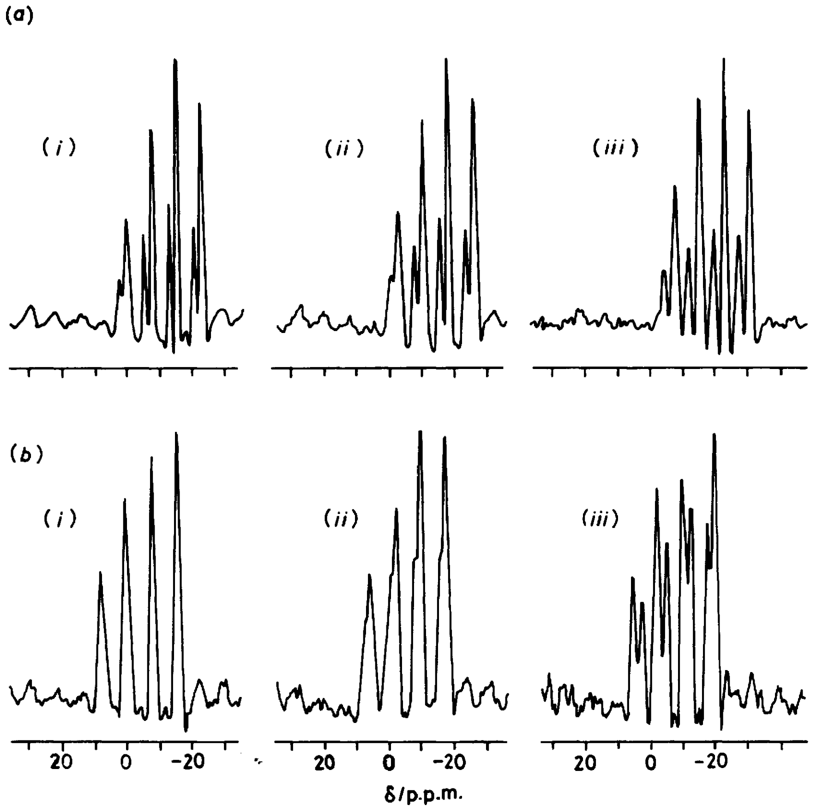


Figure 3. ^{31}P Solid-state n.m.r. spectra of trigonal (*a*) and triclinic solvated (*b*); (*i*) [Cu(PPh$_3$)$_3$Cl], (*ii*) [Cu(PPh$_3$)$_3$Br], and (*iii*) [Cu(PPh$_3$)$_3$I]

Table 9. Average core geometries for [CuL$_3$X] compounds (L = nitrogen or phosphorus base); distances in Å, angles in °

	Ligand		
Parameter	3Me-py[a]	3,5Me$_2$-py[b]	PPh$_2$Me[c]
Cu–Cl	2.451(4)	2.412(9)	2.336(4)
Cu–L	2.029(10)	2.08(1)	2.282(4)—2.294(4)
L–Cu–L	113.1(4)	113.7(6)	108.3(1)—118.1(1)
Cl–Cu–L	105.5(2)	104.8(6)	101.7(1)—104.8(1)
Cu–Br	2.585(6)	2.51(1)	
Cu–N	2.032(13)	2.02(1)	
L–Cu–L	114.0(5)	111.7(5)	
Br–Cu–L	104.4(3)	107.1(5)	
Cu–I	2.710(3)	2.683(3)	
Cu–N	2.046(14)	1.98(2)—2.15(4)	
L–Cu–L	112.8(4)	106(1)—122(2)	
I–Cu–L	105.9(2)	104(1)—107(1)	

[a] Ref. 15. [b] Ref. 16. [c] Ref. 2.

resulting geometry of the [Cu(PPh$_3$)$_3$]$^+$ moiety, surprisingly, more closely resembles that found in the analogous ClO$_4$[11] and BF$_4$[13] structures where, unlike the present compounds, the anion is very weakly co-ordinated indeed.

The solid-state ^{31}P n.m.r. spectra for each of these complexes, while affected by poor signal quality as a result of lattice disorder induced by solvent loss during the n.m.r. experiments and less than optimal sample quality, showed a single quartet for the chloride structure and two quartets for the isomorphous bromide and iodide structures, although for the bromide these are not well resolved (Figure 3). The spectra of fully desolvated samples were identical to those of the trigonal phase. Solvation, with associated conformational changes in the PPh$_3$ ligands results in a small but significant downfield chemical shift of 6—10 p.p.m. by comparison with the trigonal structures. The splittings within each quartet are slightly more asymmetric than in the trigonal phase, falling in the range 890—980 Hz, possibly reflecting the lower symmetry of the copper atom in these compounds. By comparison, in [Cu(PPh$_3$)$_3$(CH$_3$CN)] where the [P$_3$Cu]$^+$ core geometry is similar [Cu–P 2.332(4), 2.321(5), and 2.338(5) Å; P–Cu–P 114.1(2), 119.3(2), and 113.0(2)°] the splittings range from 920 to 1 060 Hz.[7]

Structural data are also available for the fluoride complex as its ethanol solvate.[14] Despite close F $\cdots$ H(solvent) contact distances of 2.63(2) and 2.60(2) Å the conformation of the triphenylphosphine ligands and the structure of the P$_3$CuF core is quite similar to the trigonal phase of the Cl, Br, and I compounds, with each PPh$_3$ ligand adopting a skewed conformation with F–Cu–P(*l*)–C(*l*11) = −41.5, −32.7, and −31.5°, and average Cu–P(*l*)–C(*l*11)–C(*l*12) angles of +14, −38, and −79° [*cf.* trigonal structures: 10, −36, −76° (consistent chirality assumed)]. The P–Cu–P angles for this compound fall into a narrow range close to the tetrahedral value [111.2(1), 113.5(1), and 111.1(1)°] and the Cu–P distances are short with values of 2.325(3), 2.310(3), and 2.316(2) Å. The Cu–F bond length is 2.062(6) Å.

The halide independence of both the [P$_3$Cu]$^+$ core geometry and the spin–spin coupling interactions in both series of halides, and the small changes observed on passing to the fluoride, are similar to the results obtained for the [M(PPh$_3$)$_2$X] molecules[1] and its seems reasonable to assume again that the relative percentages of ionic *versus* covalent character are not significant factors in determining the cation geometry of these compounds. Here, even more than in the 2:1 adducts, the steric requirements of the triphenylphosphine ligands and the anion–dipole X $\cdots$ H interactions play an important and obvious role in determining the detailed structure of the cation. In this context it is also useful to compare the present results with data available for the analogous [CuL_3X] systems where L are the tertiary aromatic nitrogen bases 3-methylpyridine (3Me-py)[15] or 3,5-dimethylpyridine (3,5Me_2-py)[16] and the phosphorus base methyldiphenylphosphine[2] (for X = Cl). Geometric parameters for these molecules are collated in Table 9 and show that the Cu–X distances are not dramatically affected by either changing the steric profile of the P base or introducing N bases with major differences in both steric and electronic profiles, the L–Cu–L and L–Cu–X angles often showing greater variation within each base series than between series.

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