Lewis-base Adducts of Group 1B Metal(I) Compounds. Part 13.[1] Crystal Structure Determinations of Tetrakis(triphenylphosphine)copper(I) and -silver(I) Perchlorates, Bis(pyridine)bis(triphenylphosphine)copper(I) Perchlorate, (2,2′-Bipyridyl)bis(triphenylphosphine)copper(I) Perchlorate, and Tetrahydroboratobis(triphenylphosphine)copper(I)–Pyridine (1/0.5) †

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The crystal structures of $[Cu(PPh_3)_4]ClO_4$ (1) and $[Ag(PPh_3)_4]ClO_4$ (2) have been determined by single-crystal *X*-ray diffraction methods at 295 K, being refined by least-squares methods to residuals of 0.10 and 0.08 for 591 and 1 294 independent 'observed' reflections respectively. The two compounds are isomorphous (rhombohedral, space group $R\bar{3}$, and $Z = 2$) with $a = 19.02(2)$ Å, $\alpha = 44.06(6)°$ and $a = 19.085(5)$ Å, $\alpha = 43.90(1)°$ respectively; the cation lies on a site of 3 symmetry, while the anion is disordered about a site of $\bar{3}$ symmetry. The metal-atom geometry is pseudo-tetrahedral [Cu–P = 2.60(1), 2.52(1) Å; Ag–P = 2.668(5), 2.650(2) Å, with all P–M–P angles lying between 109.3 and 109.7°]. For the structure determination of $[Cu(PPh_3)_2(py)_2]ClO_4$ (3) obtained by the recrystallization of $[Cu(PPh_3)_4]ClO_4$ from pyridine (py), 2 843 'observed' reflections were refined to a residual of 0.052. Crystals are triclinic, space group $P\bar{1}$, with $a = 15.599(4)$, $b = 13.413(4)$, $c = 10.982(4)$ Å, $\alpha = 79.51(3)$, $\beta = 70.47(3)$, $\gamma = 86.03(3)°$, and $Z = 2$. Cu–P = 2.271(4), 2.295(3) Å and Cu–N = 2.102(7), 2.115(8) Å in a pseudo-tetrahedral copper(I) environment, with P–Cu–P = 115.85(9)° and N–Cu–N = 101.5(2)°. The 2,2′-bipyridyl (bipy) analogue $[Cu(PPh_3)_2(bipy)]ClO_4$ (4) is monoclinic, space group $P2_1/c$, with $a = 10.210(3)$, $b = 15.085(4)$, $c = 28.455(9)$ Å, $\beta = 109.13(2)°$, and $Z = 4$. Cu–P = 2.246(3), 2.256(3) Å and Cu–N = 2.056(8), 2.113(9) Å, with P–Cu–P = 125.4(1) and N–Cu–N = 79.6(4)°. *R* was 0.081 for 2 605 reflections. $[Cu(BH_4)(PPh_3)_2]$, by contrast, yields a hemipyridine solvate, (5), on recrystallization from pyridine; crystals are triclinic, space group $P\bar{1}$, with $a = 12.849(6)$, $b = 10.319(5)$, $c = 13.618(6)$ Å, $\alpha = 102.91(4)$, $\beta = 101.91(4)$, $\gamma = 73.42(4)°$, and $Z = 2$. The structure was refined to a residual of 0.051 for 3 633 independent 'observed' reflections, and is isomorphous with the hemibenzene solvates of $[CuX(PPh_3)_2]$ (X = Cl or Br) and $[AuCl(PPh_3)_2]$.

Previous papers in the present series have been concerned with the synthesis and structure determination of nitrogen-base adducts of copper(I) and silver(I) halides; in extending this work within the framework of pyridine (py) and later, phosphine complexes of this type, it became desirable to acquire a series of reference distances for copper(I) and silver(I) in two-, three-, and four-co-ordinate environments of the base in question. In the previous paper,[1] by establishing the structures of some bis(substituted pyridine)-copper(I) and -silver(I) species this has been achieved for $CuL_{2,3,4}$, and $AgL_{2,4}$ (L = pyridine base). For phosphine base systems with these metals, such data are even more sparse, being restricted to the sterically crowded two-co-ordinate complex bis(trimesitylphosphine)silver(I) hexafluorophosphate.[2] In the present report we describe the structure determinations of the previously recorded [3] tetrakis(triphenylphosphine)-copper(I) and -silver(I) perchlorates, (1) and (2), confirming the four-co-ordinate nature of the metal atom environment; both complexes were prepared and recrystallized as described previously. In addition, by recrystallization of the copper(I) derivative (1) from pyridine, we find the formation of the (symmetrically) mixed-ligand complex, bis(pyridine)bis(triphenylphosphine)-copper(I) perchlorate, (3), as well formed colourless crystals; its structure has also been determined and is reported, together with that of the 2,2′-bipyridyl (bipy) analogue, (4), for comparison. By contrast, recrystallization of (tetrahydroborato)bis(triphenylphosphine)copper(I) from pyridine yields a hemipyridine adduct, (5), characterized crystallographically and shown to be isomorphous with the series $[CuX(PPh_3)_2]\cdot0.5C_6H_6$ (X = halide).

Experimental

Crystallography.—General details are given in an accompanying paper.[4]

$[Cu(PPh_3)_4]ClO_4$ (1). $C_{72}H_{60}ClCuO_4P_4$, $M = 1\,212$, rhombohedral, space group $R\bar{3}$ (C_{3i}^2, no. 148), $a = 19.02(2)$ Å, $\alpha = 44.06(6)°$, $U = 3\,024(4)$ Å^3, $D_m = 1.34(1)$, D_c ($Z = 2$) = 1.33 g cm^{-3}, $F(000) = 1\,244$, $\mu_{Mo} = 5$ cm^{-1}. Specimen: 0.28 × 0.20 × 0.05 mm; $2\theta_{max.} = 40°$; N,N_o = 2 151, 591; R,R' = 0.10, 0.10.

$[Ag(PPh_3)_4]ClO_4$ (2). $C_{72}H_{60}AgClO_4P_4$, $M = 1\,257$, rhombohedral, space group $R\bar{3}$, $a = 19.085(5)$ Å, $\alpha = 43.90(1)°$, $U = 3\,035(8)$ Å^3, $D_m = 1.36(1)$, D_c ($Z = 2$) = 1.38 g cm^{-3}, $F(000) = 1\,296$, $\mu_{Mo} = 5.3$ cm^{-1}. Specimen: 0.25 × 0.25 × 0.25 mm; $2\theta_{max.} = 40°$; N,N_o = 2 200, 1 294; R,R' = 0.077, 0.088.

$[Cu(PPh_3)_2(py)_2]ClO_4$ (3). $C_{46}H_{40}ClCuN_2O_4P_2$, $M = 845.8$, triclinic, space group $P\bar{1}$ (C_i^1, no. 2), $a = 15.599(4)$, $b = 13.413(4)$, $c = 10.982(4)$ Å, $\alpha = 79.51(3)$, $\beta = 70.47(3)$, $\gamma = 86.03(3)°$, $U = 2\,129(1)$ Å^3, $D_m = 1.31(1)$, D_c ($Z = 2$) = 1.32

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† *Supplementary data available* (No. SUP 56059, 29 pp.): thermal parameters, H-atom co-ordinates, ligand geometries, least-squares planes. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

Table 1. Non-hydrogen atomic co-ordinates for complexes (1) and (2)

	Complex (1) (M = Cu)			Complex (2) (M = Ag)		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
M	0.251 5(2)	0.251 5(2) *	0.251 5(2) *	0.252 23(4)	0.252 23(4) *	0.252 23(4) *
Axial PPh$_3$ ligand						
P	0.202 4(3)	0.202 4(3) *	0.202 4(3) *	0.200 9(1)	0.200 9(1) *	0.200 9(1) *
C(1)	0.286(2)	0.216(2)	0.059(1)	0.285(1)	0.216(1)	0.056(1)
C(2)	0.295(2)	0.313(2)	−0.024(2)	0.300(1)	0.313(1)	−0.028(1)
C(3)	0.357(2)	0.332(2)	−0.137(2)	0.359(2)	0.328(2)	−0.135(2)
C(4)	0.391(2)	0.258(2)	−0.159(2)	0.396(1)	0.254(1)	−0.161(1)
C(5)	0.376(2)	0.160(2)	−0.077(2)	0.382(1)	0.156(1)	−0.078(1)
C(6)	0.325(2)	0.136(2)	0.036(2)	0.329(2)	0.132(1)	0.031(2)
Off-axis PPh$_3$ ligand						
P	0.129 5(7)	0.215 3(7)	0.460 8(7)	0.126 0(4)	0.215 5(4)	0.466 4(4)
C(A1)	−0.016(2)	0.303(2)	0.489(2)	−0.022(1)	0.304(1)	0.495(1)
C(A2)	−0.102(2)	0.269(2)	0.577(2)	−0.105(1)	0.270(1)	0.582(1)
C(A3)	−0.215(2)	0.345(2)	0.590(3)	−0.213(2)	0.344(2)	0.593(2)
C(A4)	−0.233(3)	0.451(3)	0.514(3)	−0.240(2)	0.452(2)	0.518(2)
C(A5)	−0.156(2)	0.493(3)	0.432(2)	−0.160(2)	0.492(2)	0.433(2)
C(A6)	−0.043(3)	0.417(2)	0.419(3)	−0.048(2)	0.416(2)	0.421(2)
C(B1)	0.126(2)	0.080(2)	0.562(2)	0.122(1)	0.080(1)	0.572(1)
C(B2)	0.135(2)	0.017(2)	0.543(2)	0.140(1)	0.016(1)	0.545(1)
C(B3)	0.124(2)	−0.079(2)	0.624(2)	0.125(1)	−0.079(1)	0.622(2)
C(B4)	0.098(2)	−0.118(2)	0.729(2)	0.098(2)	−0.119(2)	0.730(2)
C(B5)	0.089(2)	−0.065(2)	0.758(2)	0.091(2)	−0.066(2)	0.759(1)
C(B6)	0.105(2)	0.036(2)	0.676(2)	0.103(1)	0.034(1)	0.683(1)
C(C1)	0.161(2)	0.240(2)	0.513(2)	0.152(1)	0.243(1)	0.519(1)
C(C2)	0.267(2)	0.208(2)	0.476(2)	0.262(1)	0.212(1)	0.482(1)
C(C3)	0.296(2)	0.212(2)	0.521(2)	0.293(2)	0.219(2)	0.521(2)
C(C4)	0.218(2)	0.251(3)	0.598(3)	0.211(2)	0.255(2)	0.600(2)
C(C5)	0.104(3)	0.283(3)	0.644(3)	0.098(2)	0.286(2)	0.647(2)
C(C6)	0.077(3)	0.281(3)	0.593(3)	0.069(2)	0.283(2)	0.599(2)
Anions (oxygen population: 0.5)						
Cl(1)	$\frac{1}{2}$*	$\frac{1}{2}$*	$\frac{1}{2}$*	$\frac{1}{2}$ *	$\frac{1}{2}$ *	$\frac{1}{2}$ *
O(1)	0.567(3)	0.428(3)	0.461(3)	0.574(2)	0.433(3)	0.447(3)
Cl(2)	0*	0*	0*	0 *	0 *	0 *
O(2)	0.023(3)	−0.046(3)	0.075(3)	0.016(5)	−0.049(4)	0.082(4)

* Parameter constrained by symmetry.

Table 2. Non-hydrogen atomic co-ordinates for complex (3)

	Ligand A			Ligand B		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
Cu	0.258 91(6)	0.281 58(7)	0.041 69(9)			
Triphenylphosphine ligand						
P	0.251 6(1)	0.363 6(2)	0.208 6(2)	0.230 5(2)	0.110 8(1)	0.098 7(2)
C(11)	0.151 6(5)	0.325 8(5)	0.350 1(7)	0.262 8(5)	0.040 3(5)	0.235 2(7)
C(12)	0.073 6(5)	0.386 4(6)	0.382 0(8)	0.211 7(5)	−0.039 9(6)	0.321 4(7)
C(13)	−0.005 3(5)	0.350 4(7)	0.480 8(9)	0.239 7(6)	−0.093 6(6)	0.421 5(8)
C(14)	−0.008 2(6)	0.235 2(7)	0.548 2(9)	0.317 5(7)	−0.068 2(7)	0.438 7(8)
C(15)	0.067 0(6)	0.194 0(9)	0.518 3(8)	0.368 2(6)	0.011 9(7)	0.356 0(9)
C(16)	0.147 0(6)	0.228 2(6)	0.420 7(7)	0.340 4(5)	0.066 5(6)	0.254 4(8)
C(21)	0.243 6(4)	0.502 0(5)	0.181 5(7)	0.289 6(5)	0.039 0(5)	−0.033 7(7)
C(22)	0.247 2(5)	0.557 9(6)	0.274 5(8)	0.276 3(6)	0.072 6(6)	−0.152 2(8)
C(23)	0.240 9(6)	0.660 9(6)	0.250 9(9)	0.321 9(7)	0.024 1(8)	−0.260 0(9)
C(24)	0.232 4(6)	0.711 3(6)	0.136 6(10)	0.377 5(6)	−0.057 1(8)	−0.245 8(9)
C(25)	0.230 7(6)	0.657 2(6)	0.040 0(8)	0.390 7(6)	−0.089 7(7)	−0.128 0(9)
C(26)	0.235 4(5)	0.552 6(6)	0.063 5(7)	0.347 4(6)	−0.041 0(6)	−0.021 2(8)
C(31)	0.347 4(5)	0.340 0(6)	0.270 4(8)	0.112 7(5)	0.076 2(6)	0.140 7(7)
C(32)	0.433 6(6)	0.347 9(7)	0.179 7(9)	0.085 5(6)	−0.012 0(7)	0.111 5(8)
C(33)	0.511 8(6)	0.333 5(8)	0.218 1(12)	−0.007 3(7)	−0.034 5(8)	0.152 3(9)
C(34)	0.499 0(7)	0.308 6(8)	0.349 7(13)	−0.069 8(6)	0.030 7(10)	0.217 1(9)
C(35)	0.416 3(8)	0.302 2(9)	0.441 1(12)	−0.044 8(6)	0.116 8(9)	0.247 1(9)
C(36)	0.339 6(6)	0.318 2(7)	0.401 4(10)	0.046 0(5)	0.138 9(7)	0.207 9(8)

Table 2 (*continued*)

	Ligand A			Ligand B		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
Pyridine ligands						
N	0.382 9(4)	0.304 1(4)	−0.113 0(6)	0.164 5(4)	0.338 0(5)	−0.055 2(6)
C(2)	0.449 3(5)	0.235 0(6)	−0.129 6(8)	0.179 7(6)	0.332 5(6)	−0.180 5(8)
C(3)	0.529 4(6)	0.250 0(7)	−0.230 5(9)	0.112 5(6)	0.345 5(7)	−0.237 9(8)
C(4)	0.544 3(6)	0.339 4(8)	−0.315 6(9)	0.025 2(6)	0.367 9(7)	−0.163 6(9)
C(5)	0.477 8(6)	0.411 5(7)	−0.300 3(9)	0.008 6(6)	0.376 3(7)	−0.036 1(8)
C(6)	0.396 5(6)	0.390 8(6)	−0.196 0(8)	0.078 4(5)	0.360 8(6)	0.014 4(8)

Perchlorate ion

	x	*y*	*z*
Cl	0.766 3(2)	0.373 9(2)	0.335 1(3)
O(1)	0.810 9(10)	0.416 6(8)	0.219 3(9)
O(2)	0.726 1(8)	0.281 7(8)	0.345 9(14)
O(3)	0.707 7(10)	0.443 6(10)	0.387 4(17)
O(4)	0.808 8(12)	0.351 1(12)	0.409 4(18)

Table 3. Non-hydrogen atomic co-ordinates for complex (4)

	Ligand A			Ligand B		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
Cu	0.237 4(1)	0.259 1(1)	0.370 01(5)			
Phosphine ligand						
P	0.193 4(3)	0.113 6(2)	0.372 6(1)	0.445 7(3)	0.318 7(2)	0.377 2(1)
C(11)	0.035(1)	0.072 6(7)	0.327 4(4)	0.570(1)	0.296 1(8)	0.438 5(4)
C(12)	0.002(1)	0.1049 (7)	0.278 9(5)	0.577(1)	0.210 8(8)	0.455 2(5)
C(13)	−0.115(1)	0.072 7(10)	0.241 7(5)	0.667(1)	0.189 2(9)	0.501 0(6)
C(14)	−0.194(1)	0.010 2(11)	0.251 1(6)	0.755(1)	0.251 7(11)	0.531 6(5)
C(15)	−0.164(1)	−0.023 0(9)	0.298 4(6)	0.744(1)	0.334 9(10)	0.514 9(5)
C(16)	−0.048(1)	0.007 9(9)	0.336 0(4)	0.653(1)	0.358 3(8)	0.468 4(5)
C(21)	0.173(1)	0.092 9(7)	0.433 1(4)	0.527(1)	0.278 0(6)	0.334 8(4)
C(22)	0.055(1)	0.119 3(8)	0.441 0(5)	0.666(1)	0.253 7(8)	0.346 7(4)
C(23)	0.048(2)	0.117 7(10)	0.488 9(7)	0.721(1)	0.224 0(8)	0.310 3(5)
C(24)	0.156(2)	0.088 7(12)	0.528 4(6)	0.631(1)	0.219 7(8)	0.261 4(5)
C(25)	0.274(2)	0.062 7(10)	0.520 7(5)	0.493(1)	0.242 7(9)	0.248 1(4)
C(26)	0.286(1)	0.064 8(8)	0.473 6(6)	0.444(1)	0.273 5(7)	0.285 6(4)
C(31)	0.312(1)	0.030 1(7)	0.366 6(4)	0.461(1)	0.436 7(7)	0.371 4(4)
C(32)	0.413(1)	0.054 1(7)	0.346 1(4)	0.556(1)	0.476 6(8)	0.353 1(4)
C(33)	0.504(1)	−0.007 3(10)	0.337 1(5)	0.572(1)	0.566 2(10)	0.351 9(5)
C(34)	0.494(1)	−0.093 7(10)	0.350 7(5)	0.493(2)	0.619 4(8)	0.370 0(5)
C(35)	0.394(2)	−0.118 8(8)	0.370 8(5)	0.392(2)	0.586 4(10)	0.387 3(5)
C(36)	0.307(1)	−0.058 8(9)	0.377 2(4)	0.381(1)	0.492 9(9)	0.388 4(4)
Bipyridyl ligand						
N	0.069 1(8)	0.332 4(6)	0.328 9(4)	0.182 3(7)	0.320 7(5)	0.427 6(3)
C(2)	0.008(1)	0.382 8(9)	0.355 1(4)	0.066(1)	0.370 0(7)	0.409 4(4)
C(3)	−0.097(1)	0.441 5(10)	0.334 9(7)	0.007(1)	0.405 6(11)	0.443 5(6)
C(4)	−0.148(1)	0.443 8(10)	0.283 6(8)	0.068(2)	0.386 8(14)	0.495 1(7)
C(5)	−0.093(1)	0.391 0(10)	0.253 8(5)	0.187(2)	0.341 1(10)	0.510 3(6)
C(6)	0.018(1)	0.338 1(8)	0.279 2(6)	0.238(1)	0.308 7(8)	0.475 8(4)
Anion						
Cl	0.090 8(4)	0.281 9(3)	0.648 7(1)			
O(1)	0.158 7(9)	0.310 2(7)	0.696 2(3)			
O(2)	0.046 1(10)	0.351 5(6)	0.615 2(3)			
O(3)	−0.023 2(10)	0.233 8(9)	0.650 4(4)			
O(4)	0.181 4(13)	0.229 4(8)	0.633 4(4)			

g cm^{-3}, $F(000) = 876$, $\mu_{Mo} = 5.9$ cm^{-1}. Specimen: 0.20 × 0.10 × 0.07 mm; $2\theta_{max.} = 45°$; $N,N_o = 5\,549,\ 2\,843$; $R,R' = 0.052,\ 0.054$.

[Cu(PPh$_3$)$_2$(bipy)]ClO$_4$ (4). $C_{46}H_{38}ClCuN_2O_4P_2$, $M = 848.8$, monoclinic, space group $P2_1/c$ (C^5_{2h}, no. 14), $a = 10.210(3)$, $b = 15.085(4)$, $c = 28.455(9)$ Å, $\beta = 109.13(2)°$, $U = 4\,140(2)$ Å^3, $D_m = 1.34(1)$, D_c ($Z = 4$) $= 1.35$ g cm^{-3}, $F(000) = 1\,744$, $\mu_{Mo} = 7.4$ cm^{-1}. Specimen: 0.27 × 0.20 × 0.06 mm; $2\theta_{max.} = 40°$; $N,N_o = 3\,812,\ 2\,605$; $R,R' = 0.081,\ 0.038$.

[Cu(BH$_4$)(PPh$_3$)$_2$]·0.5py (5). $C_{36}H_{34}BCuP_2\cdot(C_5H_5N)_{0.5}$, $M = 642.5$, triclinic, space group $P\bar{1}$, $a = 12.849(6)$, $b = 10.319(5)$,

Table 4. Non-hydrogen atomic co-ordinates for complex (5) (tetrahydroborate hydrogen-atom co-ordinate estimates are included)

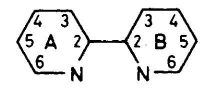
	Ligand A			Ligand B		
Atom	x	y	z	x	y	z
Cu	0.123 16(6)	0.292 66(7)	0.253 75(6)			
Tetrahydroborate ligand						
B	0.149 2(7)	0.441 1(8)	0.174 8(7)			
H(1)	0.107(—)	0.473(—)	0.240(—)			
H(2)	0.173(—)	0.331(—)	0.157(—)			
H(3)	0.219(—)	0.477(—)	0.195(—)			
H(4)	0.091(—)	0.487(—)	0.119(—)			
Pyridine solvent						
C(1)	0.420(2)	0.105(3)	−0.016(3)			
C(2)	0.489(3)	0.115(3)	0.070(2)			
C(3)	0.433(2)	−0.008(5)	−0.081(1)			
Triphenylphosphine ligands						
P	0.275 1(1)	0.188 9(2)	0.354 7(1)	−0.041 4(1)	0.240 7(2)	0.230 7(1)
C(11)	0.270 7(5)	0.205 4(6)	0.489 6(5)	−0.045 2(5)	0.065 2(6)	0.168 0(5)
C(12)	0.175 8(5)	0.199 7(7)	0.520 4(6)	0.035 6(6)	−0.042 7(7)	0.202 6(6)
C(13)	0.168 2(6)	0.212 6(7)	0.621 9(6)	0.036 2(6)	−0.177 6(7)	0.160 0(6)
C(14)	0.253 4(7)	0.237 0(8)	0.696 4(6)	−0.042 9(7)	−0.206 5(7)	0.081 6(6)
C(15)	0.348 5(7)	0.241 9(8)	0.668 7(7)	−0.122 6(8)	−0.101 1(9)	0.047 4(7)
C(16)	0.355 9(5)	0.228 1(7)	0.567 6(6)	−0.123 3(6)	0.033 8(8)	0.089 2(7)
C(21)	0.403 4(5)	0.233 5(6)	0.356 7(5)	−0.162 1(5)	0.348 9(6)	0.164 2(5)
C(22)	0.503 4(5)	0.137 4(6)	0.359 2(5)	−0.267 5(5)	0.352 6(7)	0.176 9(6)
C(23)	0.599 4(5)	0.177 1(8)	0.369 0(6)	−0.359 2(5)	0.433 3(8)	0.126 2(6)
C(24)	0.597 9(5)	0.312 1(8)	0.376 1(6)	−0.345 8(6)	0.512 1(8)	0.064 2(6)
C(25)	0.499 7(6)	0.407 7(7)	0.372 7(6)	−0.241 8(7)	0.509 3(8)	0.050 3(6)
C(26)	0.401 3(5)	0.371 9(7)	0.362 2(6)	−0.150 0(5)	0.428 2(7)	0.100 3(5)
C(31)	0.309 2(5)	0.004 4(6)	0.305 9(5)	−0.084 8(4)	0.259 6(6)	0.353 7(4)
C(32)	0.317 7(6)	−0.038 7(7)	0.205 2(6)	−0.098 0(5)	0.388 4(6)	0.415 6(5)
C(33)	0.336 7(7)	−0.176 1(9)	0.161 0(6)	−0.122 7(6)	0.411 9(7)	0.510 9(6)
C(34)	0.347 2(6)	−0.273 2(8)	0.220 7(8)	−0.131 6(5)	0.305 5(8)	0.552 6(5)
C(35)	0.339 5(6)	−0.232 4(7)	0.321 5(7)	−0.118 8(5)	0.176 9(7)	0.494 0(5)
C(36)	0.321 0(5)	−0.093 2(7)	0.367 5(5)	−0.096 9(5)	0.152 0(6)	0.395 1(5)

$c = 13.618(6)$ Å, $\alpha = 102.91(4)$, $\beta = 101.91(4)$, $\gamma = 73.42(4)°$, $U = 1\ 667(1)$ Å^3, D_c ($Z = 2$) $= 1.28$ g cm^{-3}, $F(000) = 670$, $\mu_{Mo} = 8.0$ cm^{-1}. Specimen: $0.30 \times 0.30 \times 0.10$ mm (capillary); $2\theta_{max.} = 50°$; $N,N_o = 5\ 280,\ 3\ 633$; $R,R' = 0.051$, 0.055.

Abnormal features. In complexes (1) and (2) data quality was poor and the data limited in extent, with the added difficulty of disordered perchlorate (or lower space group symmetry). In both of these structures, only isotropic thermal parameters could be meaningfully refined for atoms other than the metal, Cl, and P. In (4) also, weak data are responsible for a rather high R, although R' is satisfactory.

For complex (5) the crystal was enclosed in a capillary. Data were weak and the 3 633 ' observed ' reflections include 1 042 with intensities calculating greater than the 3σ threshold. The pyridine group is centrosymmetric about the origin and, given the unlikelihood of obtaining meaningful refinement in a lower symmetry space group, and no meaningful identification of the nitrogen atom in terms of thermal parameters or molecular geometry, all atoms were modelled as carbon. Tetrahydroborate hydrogen atoms were located in difference maps; the remaining hydrogen atoms were estimated. No absorption correction was applied to the data. Refinement of the solvent population showed no significant deviation from unity, and the latter constraint was restored.

Non-hydrogen atom labelling within the bipyridyl ligand of (4) is as shown.



Atomic co-ordinates for complexes (1) and (2) are given in Table 1 and those for (3)—(5) in Tables 2—4 respectively.

Discussion

Complexes $[Cu(PPh_3)_4]ClO_4$ (1) *and* $[Ag(PPh_3)_4]ClO_4$ (2).—The structure determinations confirm the isostructural nature of the copper(I) and silver(I) analogues, $[M(PPh_3)_4]ClO_4$, together with the assignment of stoicheiometry. The cations are disposed about crystallographic three-fold axes, the metal atom lying on a special position of symmetry 3 and co-ordinated by two independent ligand types (see Figures 1 and 2). One of these (axial) lies with its phosphorus atom on the same 3 axis as the associated atom; only one of the phenyl rings is crystallographically independent. The other, the off-axis ligand, is totally independent, three symmetry-related off-axis phosphorus atoms completing the co-ordination environment of the metal atom. Two independent chlorine atoms are found; both lie on special positions of symmetry $\bar{3}$. The oxygen atom disposition as modelled, although consistent with noisy difference maps and high thermal motion, is not fully compatible with disorder, adopting $\bar{3}$ symmetry

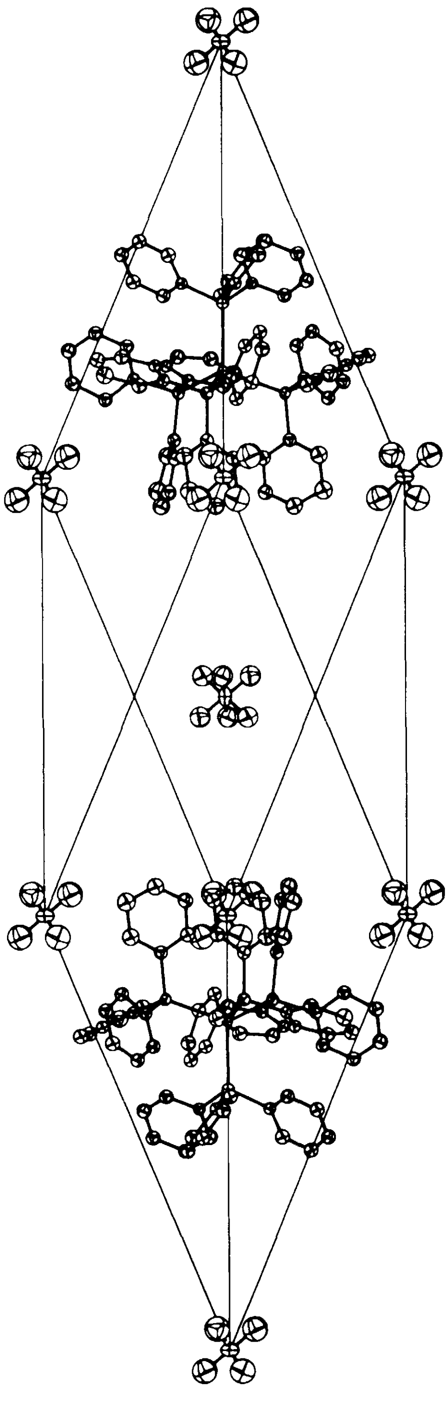


Figure 1. Unit-cell contents of (2) projected normal to the three-fold axis. 20% Thermal 'ellipsoids' are shown, anisotropic for the metal, phosphorus, and chlorine atoms and isotropic for the remainder

about the chlorine; attempts to improve the model were fruitless. No evidence for superlattice formation was evident from photographs; it may be that the space group is non-centrosymmetric, but in view of the lack of good data, and the reasonable definition of the cations, which embody most features of interest of the structure, no attempt has been made to pursue the possibility of a model in terms of a non-centrosymmetric/alternative space group. The possibility of true disorder of the anions seems real enough, however, as there is a dearth of perchlorate oxygen–ligand contacts, and the anion environment in the lattice is sparse.

About both copper(I) and silver(I) metal species, the angular environment is a very good approximation to tetrahedral: P(axial)–M–P(off-axis) are 109.6(4) (Cu) and 109.3(2)° (Ag), while P(off-axis)–M–P(off-axis) are 109.3(4) (Cu) and 109.4(2)° (Ag). Consideration of the bond lengths shows a similar equivalence between the two independent metal–axial and –off-axis phosphorus distances in the silver(I) derivative [2.650(2), 2.668(5) Å], with a rather larger discrepancy in the copper(I) complex [2.524(6), 2.605(11) Å].

In $[\{AgCl(PPh_3)\}_4]$,[5] $[\{AgCl(PPh_3)_2\}_2]$,[6] $[AgCl(PPh_3)_3]$,[7] and $[Ag(PPh_3)_4]^+$, the silver atom environment changes from one containing three chlorine atoms and one phosphorus to one containing all phosphorus atoms. Because of the polynuclear and binuclear arrays of the first two members, any trend observed must be regarded circumspectly; nevertheless, it is of interest to observe the regular increase in silver–phosphorus distance as chlorine atoms are supplanted by phosphorus atoms in the co-ordination environment. [The values, respectively, are 2.376(3), 2.388(3);[5] 2.467(2), 2.472(2);[6] 2.520(1)—2.556(1);[7] and 2.650(2), 2.668(2) Å (present work).] For the corresponding copper(I) series, $[\{CuCl(PPh_3)\}_4]$ [8] is also polynuclear, $[CuCl(PPh_3)_2]$ [9] mononuclear, as are $[CuCl(PPh_3)_3]$ [10] and $[Cu(PPh_3)_4]^+$. The respective values are 2.192(2), 2.193(2);[8] 2.272(2), 2.260(2);[9] 2.348(2)—2.355(2);[10] and 2.524(6), 2.605(11) Å (this work). In the copper(I) series, the discrepancy between the last two members is considerably greater than in the silver(I) series and out of keeping with the otherwise regular monotonic trends. It has been noted elsewhere [7] that the angular geometry of $[CuCl(PPh_3)_3]$ about the metal is much more regular than in the silver(I) analogue [range 108.41(7)—110.51(6), *cf.* 96.66(5)—109.72(5) (Cl–Ag–P) and 113.41(4)—117.09(4)° (P–Ag–P)] and the suggestion has been made that the greater degree of regularity in the copper(I) derivative is consequent upon a higher degree of steric crowding in the metal environment. Such crowding should be enhanced even more in the tetrakis(triphenylphosphine)metal(I) species, and, in fact, the regularity of the tetrahedral angular geometry in the present cations is quite striking, as is the agreement between the distances in the silver complex. The significance of the apparent disagreement between the two independent distances in the $[Cu(PPh_3)_4]^+$ species is open to question in view of the poor precision of the structure, and becomes even more questionable in the light of the structure determination of $[Pd^0(PPh_3)_4]$, in which regular tetrahedral angular geometry [108.8(3), 110.2(2)°] about the metal is associated with more nearly equivalent *shorter* distances [2.427(5), 2.458(5) Å] about a metal atom on a 3 site.[11] Nevertheless, the point is of interest because ^{65}Cu n.m.r. measurements on the present complex [12] reveal that it is 'n.m.r. silent,' suggesting that the copper environment is significantly distorted from tetrahedral geometry and the signal broadened by quadrupolar effects. As low-temperature facilities become accessible, it will be of interest to redetermine the structure; it has been suggested elsewhere [13] that for phosphine complexes generally the difference in distances to copper(I) and silver(I) is ~0.20 Å. The present difference appears to be appreciably less.

In passing from four-co-ordinate $[Ag(PPh_3)_4]^+$ to the two-co-ordinate $[Ag\{P(C_6H_2Me_3\text{-}2,4,6)_3\}_2]^+$ structure,[2] Ag–P decreases by ~0.20 Å to 2.461 Å. This decrease is very similar, when steric crowding effects are allowed for, to the decrease in Ag–N distance in passing from $[Ag(py)_4]^+$ to $[Ag(2,6Me_2\text{-}py)_2]^+$ [4] (from 2.322 to 2.166, difference 0.156 Å).

Complex $[Cu(PPh_3)_2(py)_2]ClO_4$ (3).—Single-crystal structure determination assigns the stoicheiometry of the complex

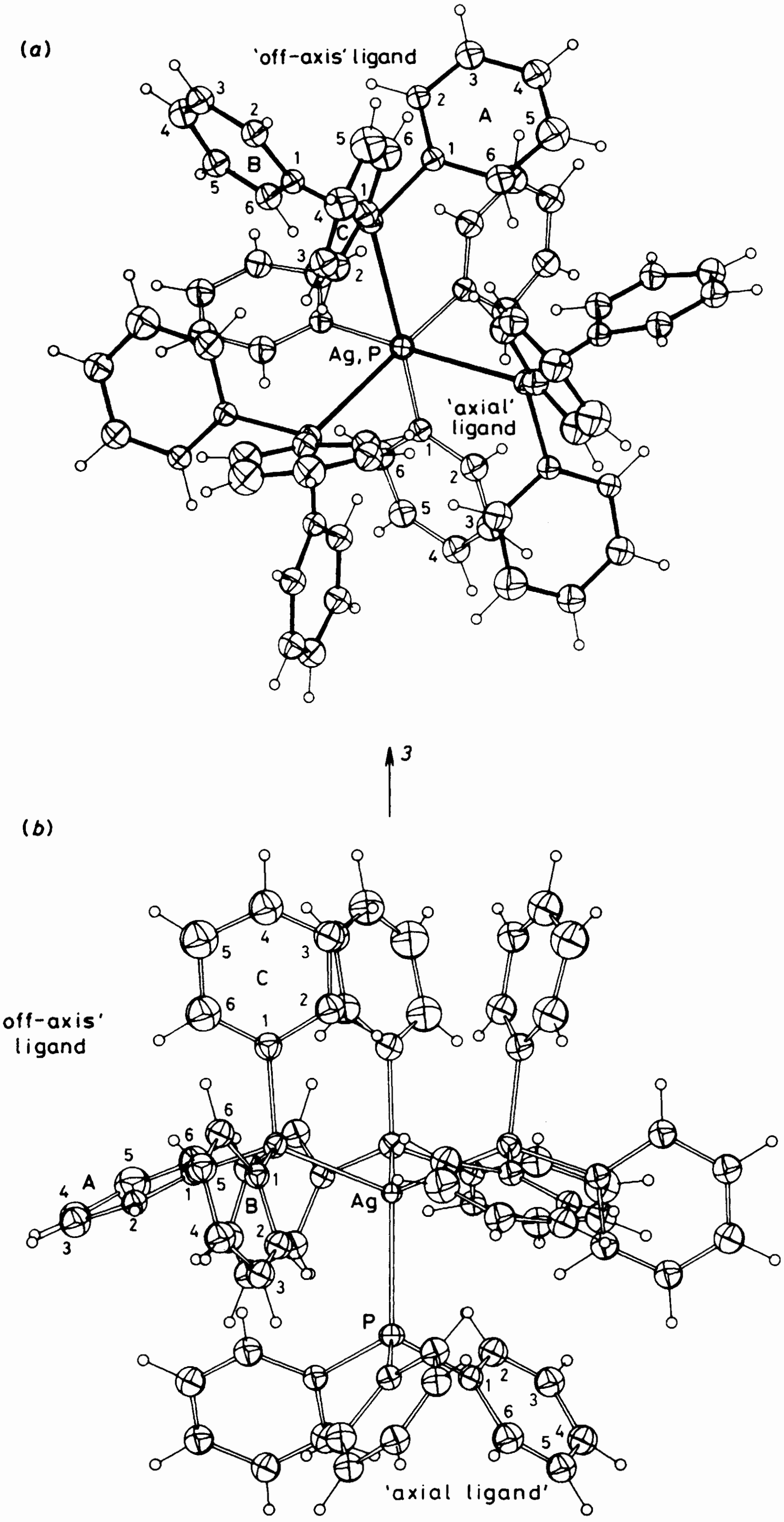


Figure 2. The cation of (2) projected (*a*) down and (*b*) normal to the three-fold axis

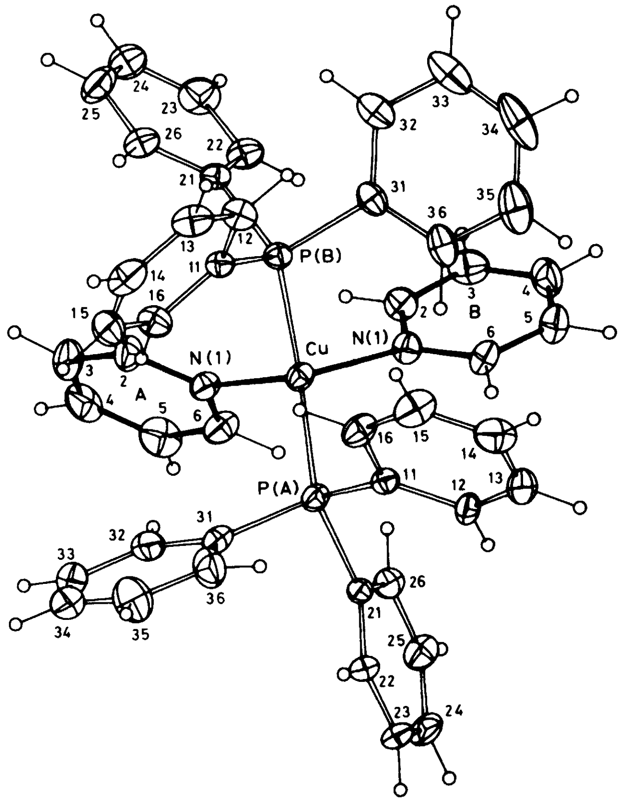


Figure 3. The cation of (3) projected down the bisector of the P–Cu–P angle. Hydrogen atoms have an arbitrary radius of 0.1 Å

obtained by pyridine recrystallization of tetrakis(triphenylphosphine)copper(I) perchlorate as bis(pyridine)bis(triphenylphosphine)copper(I) perchlorate, a mononuclear cation, $[Cu(PPh_3)_2(py)_2]^+$ in association with a perchlorate anion. The structure is well ordered (Figure 3) and more precisely determined than those of (1) and (2). The copper atom co-ordination environment is pseudo-tetrahedral, but with angular distortions much greater than those of (1) and (2). The copper–nitrogen distances, 2.102(7) and 2.115(8) Å (Table 5), are longer than those found in the $[Cu(py)_4]^+$ cation [2.05(1) Å (room temperature),[14] and 2.046(4) Å (260 K) [13]], with the diminished N–Cu–N angle 101.5(2)° suggestive of weaker bonding or steric crowding relative to the phosphine ligands. The phosphine geometries are similar to these observed in mononuclear complexes of the type $[CuX(PPh_3)_2]$ {complex (3); Cu–P, 2.271(4), 2.295(3) Å and P–Cu–P, 115.85(9)°; $[CuCl(PPh_3)_2]$: 2.272, 2.260(2) Å and 125.48(7)°;[9] $[Cu(NO_3)(PPh_3)_2]$: 2.256(3) Å and 131.2° [15]}. Although N–Cu–N is less than the tetrahedral angle the effect of steric crowding is again reflected in the low value of the P–Cu–P angle when compared with other bisubstituted triphenylphosphine complexes.

Table 5. The copper environment of $[Cu(PPh_3)_2(py)_2]ClO_4$ (3); distances (Å) and angles (°)

Cu–N(A,B)	2.102(7), 2.115(8)
Cu–P(A,B)	2.271(4), 2.295(3)
P(A)–Cu–P(B)	115.85(9)
N(A)–Cu–N(B)	101.5(2)
P(A)–Cu–N(A)	112.8(2)
P(A)–Cu–N(B)	113.1(2)
P(B)–Cu–N(A)	108.5(2)
P(B)–Cu–N(B)	103.8(2)

Table 6. The copper environment of $[Cu(PPh_3)_2(bipy)]ClO_4$ (4); distances (Å) and angles (°)*

Cu–N(A,B)	2.056(8), 2.113(9)
Cu–P(A,B)	2.246(3), 2.256(3)
P(A)–Cu–P(B)	125.4(1)
N(A)–Cu–N(B)	79.6(4)
P(A)–Cu–N(A)	113.9(3)
P(A)–Cu–N(B)	107.3(2)
P(B)–Cu–N(A)	115.1(3)
P(B)–Cu–N(B)	103.7(2)

* N(A) ··· N(B) = 2.67(1) Å.

Complex $[Cu(PPh_3)_2(bipy)]ClO_4$ (4).—Single-crystal structure determination assigns the stoicheiometry of the complex obtained by the recrystallization of tetrakis(triphenylphosphine)copper(I) perchlorate with an equimolar quantity of 2,2′-bipyridyl from acetonitrile [16,*] as that of (2,2′-bipyridyl)bis(triphenylphosphine)copper(I) perchlorate, a mononuclear cation $[Cu(PPh_3)_2(bipy)]^+$ in association with a perchlorate anion. The structure is well ordered (Figure 4, Table 6). The cation geometry may be compared with that of (3). The Cu–P [2.246(3), 2.256(3) Å] bond lengths are shorter than in (3) [2.271(4), 2.295(3) Å], consistent with the larger P–Cu–P angle [125.4(1), *cf.* 115.85(9)°], consequent upon the constraint of the smaller 'bite' angle [79.6(4), *cf.* 101.5(2)°] subtended by the two pyridine rings by virtue of their incorporation into the 2,2′-bipyridyl ligand. There is some asymmetry in the bipyridyl co-ordination [Cu–N(A,B), 2.056(8), 2.113(9) Å], the longer distance being comparable with the Cu–N(pyridine) distances of (3).

Complex $[Cu(BH_4)(PPh_3)_2]\cdot 0.5py$ (5).—Single-crystal structure determination assigns the stoicheiometry of the material obtained by the recrystallization of (tetrahydroborato)bis(triphenylphosphine)copper(I) from pyridine to be simply the hemisolvate; the asymmetric unit of the structure is a single molecule of the complex and one-half of the pyridine which is disposed about the crystallographic centre of symmetry (Figure 5). The solvent nitrogen atom is seemingly disordered over the available sites, and the solvent molecule itself is subject to high thermal motion in consequence of its lack of close contacts to other species.

The structure of the parent complex molecule has been previously determined.[17] In the parent structure the molecule has crystallographically imposed 2 symmetry; this is also true of iodobis(triphenylphosphine)copper(I).[9] In the present structure and also in chlorobis(triphenylphosphine)copper(I) hemibenzene solvate,[9] although the crystallographic symmetry constraint is lost, the molecular conformation retains a very high degree of pseudo-symmetry. The present compound, in fact, is isomorphous with $[CuX(PPh_3)_2]\cdot 0.5C_6H_6$ (X = Cl or Br),[18] the setting of the present structure conforming to these; also isomorphous is $[AuCl(PPh_3)_2]\cdot 0.5C_6H_6$,[19] refined in an alternative setting.

The copper environment in the present study is closely comparable with that of the unsolvated parent: in the latter, Cu–P,B are 2.276(1), 2.184(9) Å, with P–Cu–P,B 123.26(6), 118.4(1)°. In the present study, Cu–P,P,B are 2.282(2), 2.271(2), and 2.189(11) Å, with P–Cu–P, B–Cu–P,P 123.02(9), 114.9(2), and 122.0(2)°, a significant asymmetry being observed in the latter angles.

The present structure determination is of considerable value

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* Ref. 16 reports the preparation of the nitrate analogue; the perchlorate salts may be obtained by similar procedures.

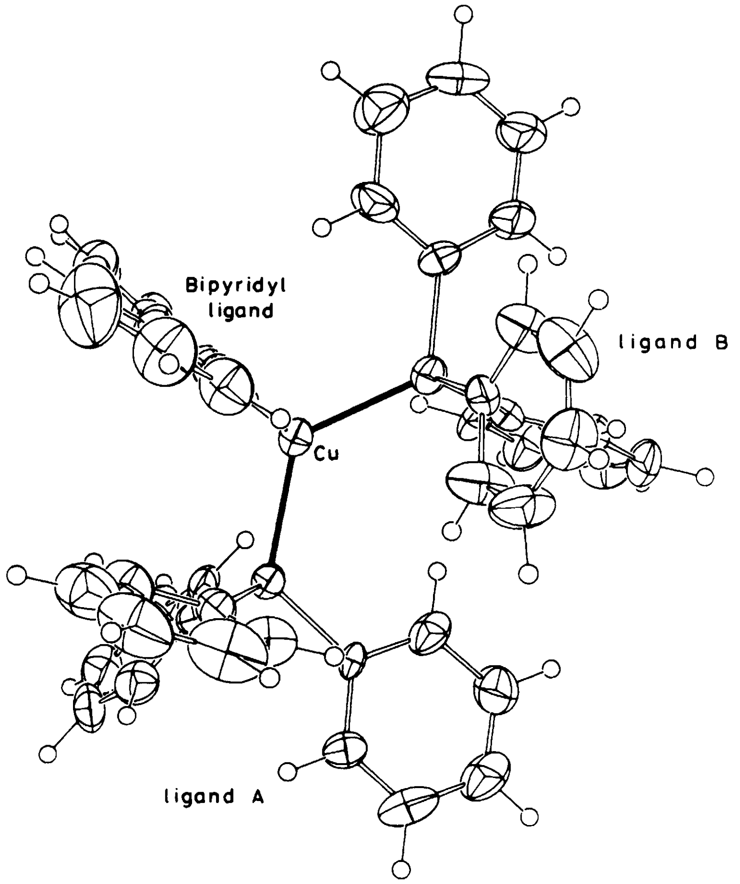

Figure 4. The complex cation of (4), projected normal to the CuP_2 plane

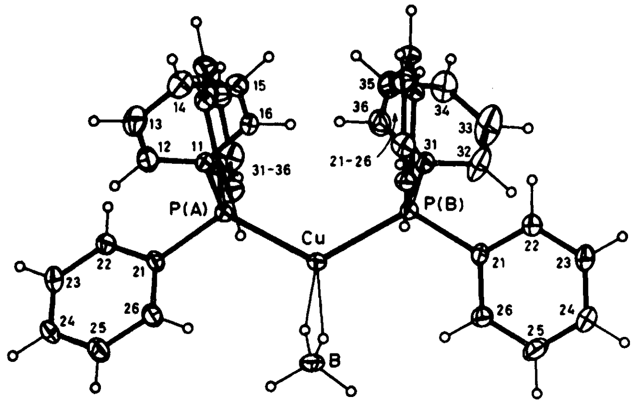

Figure 5. The complex molecule of (5), projected normal to the CuP_2 plane

as a null experiment (the substitution of pyridine was expected but not obtained), in the context of the existence of (3) in particular. Given the various species present with which the pyridine nitrogen atom *might* potentially interact, it is of interest that, in fact, it interacts with none of them, but remains as an isolated molecule in the lattice.

The above observations highlight the utility of the $[Cu(PPh_3)_4]^+$ cation in the preparation of mixed-ligand complexes (*e.g.* ref. 16) where the lability of two of the triphenylphosphine groups and the steric constraints of the $[Cu(PPh_3)_2]^+$ system imposes quite stringent restrictions on the nature of the incoming ligands. For example, while reaction of $[Cu(PPh_3)_4]^+$ with 1,10-phenanthroline (phen) or 2,2'-bipyridyl gives rise to well characterized complexes, *e.g.* $[Cu(PPh_3)_2(phen)]^+$,[16] interaction with the sterically crowded 2,9-dimethylphenanthroline ligand gives no well defined products, apart from bis(α,α-di-imine)copper(I) salts.

Acknowledgements

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