Synthesis, Characterization, Structures and Reactivities of Dinuclear Copper(I) Complexes of Three New Binucleating Hexadentate Ligands Having N_2P_4 or N_2As_4 Donor Sites†

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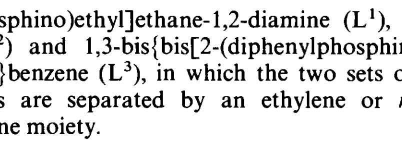
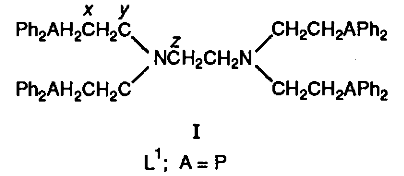
Three new binucleating hexadentate ligands having N_2P_4 or N_2As_4 donor sites, *viz.* *N,N,N′,N′*-tetrakis[2-(diphenylphosphino)ethyl]ethane-1,2-diamine (L^1), its arsine analogue (L^2) and 1,3-bis{bis[2-(diphenylphosphino)ethyl]aminomethyl}benzene (L^3) have been prepared. The ligands react with $[Cu(PPh_3)_3Cl]$ to give the dinuclear four-co-ordinate copper(I) complexes $[Cu_2(L^1)(PPh_3)_2Cl_2]$, $[Cu_2(L^2)(PPh_3)_2Cl_2]$ and $[Cu_2(L^3)Cl_2]$. With $[Cu(NCMe)_4][ClO_4]$ the ligands yielded the three-co-ordinate dinuclear complexes $[Cu_2L][ClO_4]_2$ ($L = L^1$, L^2 or L^3), which on treatment with NaN_3, NH_4NCS, KOH or $NaBH_4$ ($L = L^1$ or L^3) gave dinuclear four-co-ordinate copper(I) complexes $[Cu_2L(X)_2]$ ($X = N_3$, NCS, OH or BH_4) *via* elimination of perchlorate and co-ordination of X. For the tetrahydroborato complexes, two hydrogen atoms of each BH_4^- ligand were co-ordinated to separate copper(I) centres. All the new ligands and complexes were characterized on the basis of elemental analysis, molar conductivity, IR spectra and ^1H, $^{13}C-\{^1H\}$, $^{11}B-\{^1H\}$ and $^{31}P-\{^1H\}$ NMR spectral data. The molecular structures of $[Cu_2(L^1)(PPh_3)_2Cl_2]$ **1** and $[Cu_2(L^3)Cl_2]$ **3** were established by single-crystal X-ray diffraction [crystal data: **1**, $C_{94}H_{90}Cl_2Cu_2N_2P_6$, triclinic, space group $P\bar{1}$, $a = 11.711(2)$, $b = 18.731(3)$, $c = 10.080(1)$ Å, $\alpha = 91.22(1)$, $\beta = 107.45(1)$, $\gamma = 78.11(1)°$, $Z = 1$, final R factor 0.040 ($R' = 0.046$) for 3715 observed reflections; **3** $C_{64}H_{64}Cl_2Cu_2N_2P_4$, triclinic, space group $P\bar{1}$, $a = 12.922(4)$, $b = 19.161(1)$, $c = 12.777(3)$ Å, $\alpha = 93.11(1)$, $\beta = 111.85(2)$, $\gamma = 84.69(1)°$, $Z = 2$, final R factor 0.042 ($R' = 0.046$) for 5684 observed reflections].

The synthesis and characterization of copper(I) complexes with ligands of π-acceptor character has attracted much attention over the past two decades owing to their interesting structural chemistry,[1–5] reactivity towards small molecules[6] and catalytic activity.[7,10] In most of these studies monodentate tertiary phosphine and halide ligands were used. However, in a few cases bidentate tertiary phosphine ligands, such as 1,2-bis(diphenylphosphino)ethane and bis(diphenylphosphino)methane,[11–13] and tri- and tetra-dentate ligands, *e.g.* 1,1,1-tris[2-(diphenylphosphino)ethyl]ethane and tris[2-(diphenylphosphino)ethyl]amine,[6] respectively, have been used.

With copper(I), monodentate tertiary phosphine ligands form mononuclear complexes of co-ordination number two,[5] three[1,2] or four[1,3] as well as dinuclear complexes containing halogen bridges between two Cu^I centres of co-ordination number three[14] or four.[1,15] The structural characterization of such mono- and di-nuclear complexes has also been extensively reported.[1–5,14–16] Very little is known, however, about the copper(I) chemistry of polydentate ligands containing both soft (P/As) and hard (N) donor atoms. These ligands may form copper(I) complexes with various co-ordination numbers and stereochemistries. Further, the complexes should display a greater chemical robustness relative to their monodentate phosphine anologues; the latter often undergo complicated dissociative equilibria in solution[17,18] which do not occur with the chelated phosphines complexes. With a view to synthesizing stable chelated copper(I) complexes and studying their reactivity we have therefore synthesized three new hexadentate ligands with N_2P_4 or N_2As_4 donors, *viz.* *N,N,N′,N′*-tetrakis[2-(diphenylphosphino)ethyl]ethane-1,2-diamine (L^1), its arsine analogue (L^2) and 1,3-bis{bis[2-(diphenylphosphino)ethyl]aminomethyl}benzene (L^3), in which the two sets of NP_2 or NAs_2 donors are separated by an ethylene or *m*-phenylenedimethylene moiety.



I
L^1; A = P
L^2; A = As



II
L^3

We report herein the synthesis of these ligands and the dinuclear copper(I) complexes formed by their reaction with $[Cu(PPh_3)_3Cl]$ and $[Cu(NCMe)_4][ClO_4]$, together with the reactivity of some of the complexes towards small anionic species (N_3^-, NCS^-, OH^- or BH_4^-). The molecular structures of $[Cu_2(L^1)(PPh_3)_2Cl_2]$ and $[Cu_2(L^3)Cl_2]$ have also been determined by X-ray crystallography.

Experimental

Materials.—1,2-Dibromoethane[19] and 1,3-bis(bromometh-

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† *Supplementary data available.* See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xviii–xxiii.

yl)benzene[20] were prepared from published procedures. Diethanolamine, thionyl chloride, sodium carbonate, potassium carbonate and hydrated copper(II) acetate were purchased from S.D. Fine-Chem. Potassium metal was obtained from Robert–Johnson. Triphenylphosphine, triphenylarsine, copper(II) chloride, sodium azide, ammonium thiocyanate, potassium hydroxide and sodium tetrahydroborate were obtained from Aldrich. The compounds $[Cu(PPh_3)_3Cl]$,[21] $[Cu(NCMe)_4][ClO_4]$,[22] $KPPh_2$[23] and $KAsPh_2$[23] were prepared by published procedures.

All organic solvents used were of reagent grade and were purified and dried by standard procedures before use. All the preparations were carried out in an atmosphere of dry nitrogen or argon.

Physical Measurements.—Carbon, H and N analyses were performed on a model 1106 Carlo Erba Elemental Analyser. A model D1-909 Digisun Electronics digital conductivity meter was used for conductivity measurements. Magnetic measurements were carried out with a PAR model 155 vibrating-sample magnetometer. Infrared spectra were recorded on a Carl Zeiss Specord M80 spectrometer, as KBr pellets or in Nujol mulls. NMR spectra were recorded on a JEOL FX-100 FT NMR instrument. For ^{13}C, ^{11}B and ^{31}P NMR spectra 10 mm tubes with a capillary of deuterium oxide for the internal lock were used. The UV/VIS spectra were recorded on a Shimadzu UV-160 spectrometer.

Synthesis of Ligands.—N,N,N′,N′-*Tetrakis*[2-(*diphenylphosphino*)*ethyl*]*ethane*-1,2-*diamine* (L^1). To a refluxing mixture of diethanolamine (10.5 g, 0.1 mol) and potassium carbonate (6.91 g, 0.05 mol) in absolute ethanol (200 cm^3) 1,2-dibromoethane (9.4 g, 0.05 mol) was added slowly and refluxing continued for 40 h. After removing KBr, which had deposited during reflux, the solvent was removed by rotary evaporation. The residue, $[CH_2N(CH_2CH_2OH)_2]_2$, was dissolved in chloroform (80 cm^3) and excess thionyl chloride (20 cm^3) in chloroform (50 cm^3) was added dropwise in cold conditions (5 °C) with stirring. After complete addition the reaction mixture was heated to 60 °C for 6 h. Chloroform and excess thionyl chloride were then removed and the semi-solid mass, $[CH_2N(CH_2CH_2Cl)_2]_2{\cdot}2HCl$, dissolved in water (50 cm^3) and Na_2CO_3 added slowly at room temperature with stirring. The free amine $[CH_2N(CH_2CH_2Cl)_2]_2$ which separated as an insoluble oil was extracted with diethyl ether, dried and used immediately for the next step. The free amine (9.3 g, 0.03 mol) thus obtained was dissolved in dry tetrahydrofuran (thf) (20 cm^3) and added dropwise to a cold (5–10 °C) solution of $KPPh_2$ (0.12 mol) in 1,4-dioxane (100 cm^3). After complete addition, the reaction mixture was heated slowly and finally refluxed for 1 h. The solution was then allowed to reach room temperature, poured into twice its volume of ice-cold water and kept in a refrigerator for 24 h. The white solid that separated was collected by filtration and recrystallized from dichloromethane–ethanol (1:1); yield 45% (calculated on the basis of 1,2-dibromoethane used in the first step).

N,N,N′,N′-*Tetrakis*[2-(*diphenylarsino*)*ethyl*]*ethane*-1,2-*diamine* (L^2) *and* 1,3-*bis*{*bis*[2-(*diphenylphosphino*)*ethyl*]-*aminomethyl*}*benzene* (L^3). These ligands were synthesized following the same procedure as described for L^1 but using $KAsPh_2$ instead of $KPPh_2$ for L^2 and 1,3-bis(bromomethyl)benzene in place of 1,2-dibromoethane for L^3; yields 45% (L^2) and 40% (L^3).

Synthesis of Metal Complexes.—$[Cu_2(L^1)(PPh_3)_2Cl_2]$ **1** *and* $[Cu_2(L^2)(PPh_3)_2Cl_2]$ **2**. To a boiling solution of $[Cu(PPh_3)_3Cl]$ (0.5 mmol) in dry acetone (40 cm^3) L^1 or L^2 (0.25 mmol) dissolved in benzene (10 cm^3) was added dropwise and refluxing continued for 4 h. The white compound which separated during reflux was isolated by filtration and washed with benzene and acetone. Recrystallization of **1** from chloroform–ethanol (2:1) gave white crystals; yield 80%. Compound **2** was recrystallized from dimethylformamide (dmf); yield 75%.

$[Cu_2(L^3)Cl_2]$ **3**. This compound was prepared following the same procedure as described for complex **1** except that the compound did not precipitate during reflux. After completion of the reaction the volume of the solution was reduced to *ca.* 10 cm^3 and on adding diethyl ether (40 cm^3) a white precipitate separated. The compound was isolated by filtration, washed with benzene and hot methanol and finally recrystallized from chloroform–ethanol (1:1); yield 64%.

$[Cu_2L][ClO_4]_2$ ($L = L^1$, **4**; L^2, **5**; or L^3, **6**. To a refluxing solution of $[Cu(NCMe)_4][ClO_4]$ (0.5 mmol) in acetone (25 cm^3) the appropriate ligand L (0.25 mmol) dissolved in benzene (5 cm^3) was added dropwise and refluxing continued for 3 h. The volume of the solution thus obtained was reduced to *ca.* 10 cm^3 by rotary evaporation and after adding diethyl ether (10 cm^3) the solution was kept at room temperature overnight. The white compound which precipitated was isolated by filtration and recrystallized from acetonitrile–ethanol (2:1); yield 70–80%.

$[Cu_2L(X)_2]$ ($L = L^1$; $X = N_3^-$, **7**; NCS^-, **9**; OH^-, **11**; or BH_4^-, **13**; $L = L^3$; $X = N_3^-$, **8**; NCS^-, **10**; OH^-, **12**; or BH_4^-, **14**). These complexes were synthesized by a similar procedure to that described above. To an acetonitrile solution (10 cm^3) of $[Cu_2L][ClO_4]_2$ ($L = L^1$ or L^3) an aqueous solution (3 cm^3) of NaN_3 or NH_4NCS or an ethanolic solution of KOH or $NaBH_4$ (2 mmol, fourfold excess) was added dropwise at room temperature with stirring. After stirring for 1 h the solution was dried by rotary evaporation and the solid mass was extracted with dichloromethane. The volume of the dichloromethane solution was reduced to *ca.* 5 cm^3 and on slow addition of hexane (25 cm^3) a white product separated. Recrystallization from dichloromethane–ethanol (1:1) gave a white crystalline compound; yield 80–85%.

Structure Determinations of Complexes **1** *and* **3**.—Preliminary data on space group and unit-cell dimensions as well as intensity data were collected using a crystal of suitable size on an Enraf-Nonius CAD4/PDP-11/73 system with graphite monochromatized Cu-Kα radiation in the θ range 2–65°. Accurate unit-cell dimensions were obtained using 25 arbitrarily chosen higher-order reflections ($28 < \theta < 30°$). After correcting for Lorentz and polarization factors, the intensities were corrected for absorption using an empirical absorption correction method[24] with three reflections near $\chi = 90°$. The structures were solved by direct methods using MULTAN[25], which gave the positions of the metal and phosphorus atoms unambiguously and were developed by alternating least-squares refinement and difference Fourier maps. Hydrogen atoms for the phenyl rings and methylene groups were generated by stereochemical constraints. Anisotropic refinement of the non-hydrogen atoms was by a block-diagonal matrix method using two blocks with hydrogens held fixed by stereochemical constraints or in positions in the difference maps. A unit weighing scheme and Dunitz–Seiler factor[26] resulted in convergence. The scattering factors for Cu, Cl, P, O, C and N atoms were taken from ref. 27 while those of hydrogens were from ref. 28. All computations were carried out using the SDP package of the Enraf-Nonius system available with PDP-11/73.[29] The structure of complex **3** was refined by two blocks, with 39 atoms selected for each of the blocks. Atoms Cu(1), Cu(2), P(45) and P(60) were overlapped during the refinement. At the end of the refinement the maximum shift-to-error ratio was 0.10. The final R and R' values were calculated using the equations $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{\frac{1}{2}}$.

Crystal data. For Complex **1**: $C_{94}H_{90}Cl_2Cu_2N_2P_6$, $M = 1631.60$, triclinic, space group $P\bar{1}$, $a = 11.711(2)$, $b = 18.731(3)$, $c = 10.080(1)$ Å, $\alpha = 91.22(1)$, $\beta = 107.45(1)$, $\gamma = 78.11(1)°$, $U = 2061.9(4)$ Å^3, $Z = 1$, $D_c = 1.313$ g cm^{-3}, specimen $0.18 \times 0.24 \times 0.31$ mm, Cu-Kα radiation ($\lambda = 1.54184$ Å),

Table 1 Analytical and selected IR spectral data for the ligands and their copper(I) complexes[a]

Compound	Analysis[a] (%)			
	C	H	N	IR[b]/cm^{-1}
L^1	76.1 (76.6)	65.0 (6.60)	2.90 (3.10)	
L^2	64.3 (64.2)	5.45 (5.55)	2.50 (2.60)	
L^3	77.8 (78.0)	6.65 (6.55)	2.70 (2.85)	
1 $[Cu_2(L^1)(PPh_3)_2Cl_2]$	69.0 (69.2)	5.60 (5.50)	1.65 (1.70)	218m [ν(Cu–Cl)]
2 $[Cu_2(L^2)(PPh_3)_2Cl_2]$	62.2 (62.4)	5.05 (5.00)	1.35 (1.55)	232m [ν(Cu–Cl)]
3 $[Cu_2(L^3)Cl_2]$	65.1 (65.0)	5.35 (5.40)	2.20 (2.35)	248m, 264m [ν(Cu–Cl)]
4 $[Cu_2L^1][ClO_4]_2$	56.6 (56.4)	4.75 (4.85)	2.15 (2.25)	1100br [$\nu_3(ClO_4^-)$], 625m [$\nu_4(ClO_4^-)$]
5 $[Cu_2L^2][ClO_4]_2$	49.2 (49.4)	4.40 (4.25)	1.85 (2.00)	1100br [$\nu_3(ClO_4^-)$], 625m [$\nu_4(ClO_4^-)$]
6 $[Cu_2L^3][ClO_4]_2$	58.5 (58.6)	4.95 (4.90)	2.05 (2.15)	1100br [$\nu_3(ClO_4^-)$], 625m [$\nu_4(ClO_4^-)$]
7 $[Cu_2(L^1)(N_3)_2]$	62.4 (62.2)	5.25 (5.35)	9.90 (10.0)	2050s [$\nu_{asym}(N_3)$]
8 $[Cu_2(L^3)(N_3)_2]$	64.0 (64.3)	5.10 (5.35)	9.10 (9.35)	2050s [$\nu_{asym}(N_3)$]
9 $[Cu_2(L^1)(NCS)_2]$	62.4 (62.6)	5.35 (5.20)	4.65 (4.85)	2080s [$\nu_{asym}(NCS)$]
10 $[Cu_2(L^3)(NCS)_2]$	64.7 (64.5)	5.25 (5.20)	4.40 (4.55)	2080s [$\nu_{asym}(NCS)$]
11 $[Cu_2(L^3)(OH)_2]$	65.3 (65.1)	5.65 (5.80)	2.50 (2.60)	3600s [ν(OH)]
12 $[Cu_2(L^3)(OH)_2]$	67.2 (67.1)	5.65 (5.75)	2.30 (2.45)	3600m [ν(OH)]
13 $[Cu_2(L^1)(BH_4)_2]$	65.3 (65.4)	6.45 (6.40)	2.40 (2.65)	2365s [$\nu(B-H_t)$], 2010 [$\nu(B-H_b)$]
14 $[Cu_2(L^3)(BH_4)_2]$	67.5 (67.3)	6.20 (6.50)	2.30 (2.45)	2365 [$\nu(B-H_t)$], 2010s [$\nu(B-H_b)$]

[a] Calculated values are given in parentheses, [b] In KBr disc or in Nujol mull (for lower region), s = strong, m = medium, w = weak and br = broad.

Table 2 Proton ^{13}C-{^1H} and ^{31}P-{^1H} NMR spectral data for the ligands and their copper(I) complexes[a]

	^1H (δ)[b]				^{13}C-{^1H} (δ)[b]				
Compound	Solvent	x-CH_2[d]	y-CH_2	z-CH_2	Solvent	x-CH_2	y-CH_2	z-CH_2	^{31}P-{^1H} (δ)[c]
L^1	$CDCl_3$	1.88 (m)	2.22 (m)	2.37 (s)	$CHCl_3$	25.57 (d)[e]	50.33 (d)[f]	52.06 (d)	−19.01 (s)
L^2	$CDCl_3$	1.94 (t)	2.26 (t)	2.44 (s)	$CHCl_3$	25.54 (s)	50.57 (s)	52.21 (s)	
L^3	$CDCl_3$	2.09 (m)	2.56 (m)	3.52 (s)	$CHCl_3$	25.92 (d)[g]	49.98 (d)[h]	58.58 (s)	−20.89 (s)
1	$CDCl_3$	2.24 (m)	2.30 (m)	2.42 (s)	$CHCl_3$	28.13	50.52	52.12	−17.44, −4.18
2	[$^2H_6$]dmso	2.18 (t)	2.32 (t)	2.41 (s)	dmso	28.23	50.80	52.26	−3.63 (s)
3	$CDCl_3$	2.30 (m)	2.72 (m)	4.09 (s)	$CHCl_3$	28.56	50.88	59.63	−17.62 (s)
4	[$^2H_6$]dmso	2.25 (m)	2.42 (m)	2.63 (s)	MeCN	26.48	50.85	53.29	−12.47 (s)
5	[$^2H_6$]dmso	2.27 (t)	2.41 (t)	2.55 (s)	MeCN	26.41	51.12	53.38	—
6	[$^2H_6$]dmso	2.34 (m)	2.74 (m)	3.88 (s)	MeCN	26.57	51.45	59.74	−12.11 (s)
7	$CDCl_3$	2.28 (m)	2.47 (m)	2.65 (s)	$CHCl_3$	26.50	50.77	53.01	−14.56 (s)
8	$CDCl_3$	2.30 (m)	2.71 (m)	3.79 (s)	$CHCl_3$	26.72	50.96	59.03	−14.89 (s)
9	$CDCl_3$	2.21 (m)	2.55 (m)	2.74 (s)	$CHCl_3$	27.63	50.68	52.89	−14.96 (s)
10	$CDCl_3$	2.33 (m)	2.72 (m)	3.97 (s)	$CHCl_3$	28.48	50.65	59.52	−14.95 (s)
11	$CDCl_3$	2.25 (m)	2.58 (m)	2.78 (s)	$CHCl_3$	26.56	50.70	53.12	−14.50 (s)
12	$CDCl_3$	2.34 (m)	2.77 (m)	3.89 (s)	$CHCl_3$	27.89	50.94	59.25	−14.92 (s)
13	$CDCl_3$	2.16 (m)	2.34 (m)	2.40 (s)	$CHCl_3$	28.04	50.92	52.14	−15.68 (s)
14	$CDCl_3$	2.31 (m)	2.60 (m)	3.61 (s)	$CHCl_3$	28.12	50.64	58.56	−15.56 (s)

[a] Proton and ^{13}C-{^1H} NMR spectral data due to the aromatic moieties appear in the ranges δ 7.12–7.52 and δ 127.31–141.08, respectively. [b] Relative to $SiMe_4$. [c] Relative to 85% H_3PO_4. [d] See structures **I** and **II** for labelling of CH_2, s = singlet, d = doublet, t = triplet and m = multiplet. [e] J_{CP} = 13.43 Hz. [f] J_{CP} = 23.20 Hz. [g] J_{CP} = 12.20 Hz. [h] J_{CP} = 23.20 Hz.

$N = 5182$, $N_o = 3715$, parameters refined 316, $\mu = 26.9$ cm^{-1}, $F(000) = 850$, $R = 0.040$ and $R' = 0.046$.

For complex **2** $C_{64}H_{64}Cl_2Cu_2N_2P_4$, $M = 1183.12$, triclinic, space group $P\bar{1}$, $a = 12.922(4)$, $b = 19.161(1)$, $c = 12.777(3)$ Å, $\alpha = 93.11(1)°$, $\beta = 111.85(2)$, $\gamma = 84.69(1)°$, $U = 2922.9(5)$ Å^3, $Z = 2$, $D_c = 1.344$ g cm^{-3}, specimen 0.22 × 0.37 × 0.18 mm, Cu-Kα radiation (λ = 1.54184 Å), $N = 7209$, $N_o = 5684$, parameters refined 352 and 352 (in blocks), $\mu = 31.057$ cm^{-1}, $F(000) = 1228$, $R = 0.042$ and $R' = 0.046$.

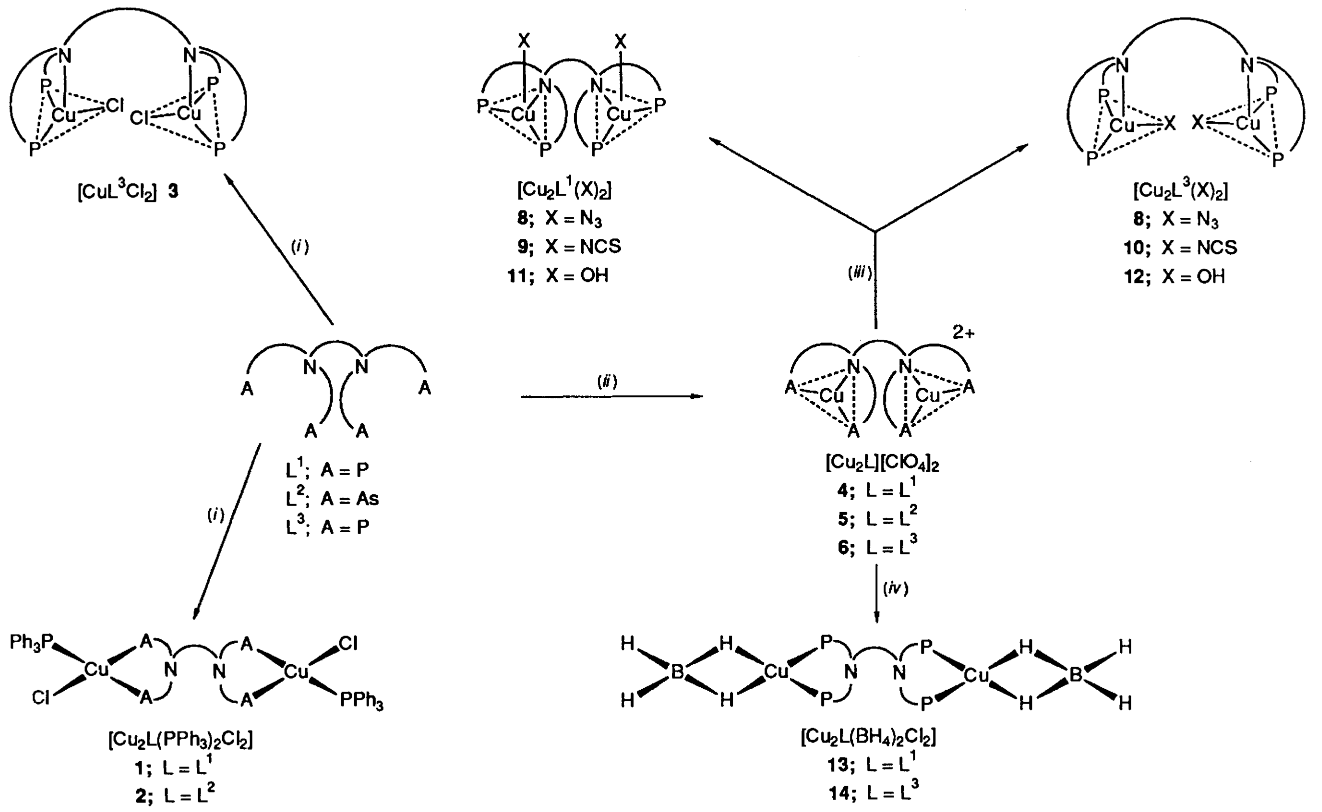
Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

Ligands.—The ligands L^1–L^3 were characterized by elemental and IR analysis (Table 1) and by ^1H, ^{13}C and ^{31}P NMR spectroscopy (Table 2). The ^1H NMR spectra of L^1 and L^2 exhibit singlets at δ 2.37 and 2.44, respectively, which can be assigned to the z-CH_2 protons (see structure **I**). Two multiplets at δ 1.88 and 2.22 for L^1 and two triplets at δ 1.94 and 2.26 for L^2 arise from the x- and y-CH_2 protons respectively. For L^2 these signals appear as triplets owing to coupling between two nonequivalent CH_2 groups whereas for L^1 multiplets are observed owing to further coupling with ^{31}P. The phenyl protons of L^1 and L^2 give signals at δ 7.16 and 7.28, respectively.

The ligand L^3 exhibits a similar ^1H NMR spectrum to L^1. However the benzyl CH_2 protons appear at δ 3.52 and the phenyl protons give rise to two resonances at δ 7.14 and 7.27.

In the ^{13}C-{^1H} NMR spectra the carbon atoms of the x- and y-CH_2 groups of L^1 and L^3 appear as doublets centred at δ 25.57 (J_{CP} 13.43), 50.33 (J_{CP} 23.2) and at 25.92 (J_{CP} 12.2), 49.98 (J_{CP} 23.2 Hz), respectively. The appearance of doublets is due to coupling of the carbon atom to the phosphorus nucleus and the coupling constants are in good agreement with literature values.[30] For L^2 the carbon atoms of the x- and y-CH_2 groups appear as singlets at δ 25.54 and 50.57, respectively. The resonances due to the z-CH_2 carbons of L^1–L^3 appear as singlets at δ 52.06, 52.21 and 58.58, respectively. The aromatic carbons appear in the ranges δ 128.85–138.84, 128.56–141.08 and 127.98–139.14 for L^1–L^3, respectively. The ^{31}P-{^1H} NMR spectra of L^1 and L^3 exhibit singlets at δ −19.01 and −20.89, respectively, indicating that all four phosphorus atoms in each ligand are magnetically equivalent.



Scheme 1 (*i*) $[Cu(PPh_3)_3Cl]$; (*ii*) $[Cu(NCMe)_4][ClO_4]$; (*iii*) X^-; (*iv*) $NaBH_4$

Table 3 Selected bond distances (Å) and angles (°) for complexes **1** and **3**

Complex				
1	Cu(1)–Cl(2)	2.347(2)	Cl(2)–Cu(1)–P(3)	100.09(4)
	Cu(1)–P(3)	2.299(2)	Cl(2)–Cu(1)–P(21)	113.31(4)
	Cu(1)–P(21)	2.319(1)	Cl(2)–Cu(1)–P(35)	105.59(4)
	Cu(1)–P(35)	2.327(1)	P(3)–Cu(1)–P(21)	110.71(4)
			P(3)–Cu(1)–P(35)	112.58(4)
			P(21)–Cu(1)–P(35)	113.70(3)
3	Cu(1)–Cl(1)	2.246(1)	Cl(1)–Cu(1)–P(3)	117.99(5)
	Cu(1)–P(3)	2.242(1)	Cl(1)–Cu(1)–P(21)	125.30(5)
	Cu(1)–P(21)	2.244(1)	P(3)–Cu(1)–P(21)	116.50(5)
	Cu(1)–N(18)	2.416(5)	N(18)–Cu(1)–Cl(1)	104.6(1)
	Cu(2)–Cl(2)	2.234(2)	N(18)–Cu(1)–P(3)	85.2(1)
	Cu(2)–P(45)	2.223(1)	N(18)–Cu(1)–P(21)	84.3(1)
	Cu(2)–P(60)	2.242(1)	Cl(2)–Cu(2)–P(45)	122.16(7)
	Cu(2)–N(42)	2.630(5)	Cl(2)–Cu(2)–P(60)	122.36(6)
			P(45)–Cu(2)–P(60)	114.83(6)
			N(42)–Cu(2)–Cl(2)	113.16(9)
			N(42)–Cu(2)–P(45)	80.41(10)
			N(42)–Cu(2)–P(60)	82.99(9)

Metal Complexes.—The reaction of $[Cu(PPh_3)_3Cl]$ with L^1–L^3 resulted in the formation of the dinuclear complexes $[Cu_2(L^1)(PPh_3)_2Cl_2]$ **1**, $[Cu_2(L^2)(PPh_3)_2Cl_2]$ **2** and $[Cu_2(L^3)Cl_2]$ **3**. It is noteworthy that under identical conditions the reaction gave complexes of different composition. The difference in co-ordination can be attributed to the greater flexibility of the ethylene chain of L^1 or L^2 compared to that of the *m*-phenylenedimethylene moiety of L^3. The steric constraints imparted by the *m*-phenylenedimethylene moiety leads to a smaller Cu ··· Cu separation and does not allow the bulky PPh_3 moiety to co-ordinate to Cu^I.

The reaction of the ligands L^1–L^3 with $[Cu(NCMe)_4][ClO_4]$ yielded complexes of composition $[Cu_2L][ClO_4]_2$ ($L = L^1$, **4**; L^2, **5**; or L^3, **6**). These complexes exhibit three-co-ordinated copper and react with anions X ($X = N_3^-$, NCS^-, OH^- or BH_4^-) according to equation (1). All the reactions are summarized in Scheme 1. The compositions of all the complexes

$$[Cu_2L][ClO_4]_2 + 2X^- \longrightarrow [Cu_2L(X)_2] + 2ClO_4^- \quad (1)$$

were confirmed by elemental analysis (Table 1). They are white, diamagnetic (d^{10} configuration), and show no d–d bands in the visible region of their electronic spectra.

Conductivity measurements in dmf show that all the complexes, except **4**–**6**, are non-electrolytes with Λ_M in the range 4–12 $ohm^{-1}\ cm^2\ mol^{-1}$. Complexes **4**–**6** correspond to 1:2 electrolytes with Λ_M in the range 135–146 $ohm^{-1}\ cm^2\ mol^{-1}$. This shows that the perchlorate anions are not co-ordinated to Cu^I but that other anionic species (Cl^-, N_3^-, NCS^-, OH^- or BH_4^-) do co-ordinate to the metal ion.

The IR spectra (Table 1) of complexes **1**–**3** exhibit bands at 218 **1**, 232 **2** and 248 and 264 cm^{-1} **3** which can be assigned to ν(Cu–Cl).[2,5] The appearance of two bands for ν(Cu–Cl) in complex **3** may be due to the different Cu–Cl distances (Table 2). Complexes **4**–**6** exhibit a strong broad band centered at 1100 cm^{-1} and a sharp band at 625 cm^{-1} which can be assigned to the ν_3 and ν_4 modes of unco-ordinated perchlorate.[31] A strong band at 2050 cm^{-1} in **7** and **8** and at 2080 cm^{-1} in **9** and **10** are due to $\nu_{asym}(N_3)$ and $\nu_{asym}(NCS)$, respectively, of co-ordinated N_3^- and NCS^-.[32] Complexes **11** and **12** exhibit a medium intensity band at 3600 cm^{-1} which can be assigned to ν(OH) of co-ordinated OH^-.[33] The IR spectra of complexes **13** and **14** exhibit two broad bands at 2365 and 2010 cm^{-1} due to terminal and bridging ν(B–H) of co-ordinated BH_4^-.[34] These two compounds also show a sharp intense band at 1120 cm^{-1} in the range expected for BH_2-deformation of a two co-ordinate BH_4^- moiety,[34] indicating that two hydrogen atoms of BH_4^- are co-ordinated to Cu^I.

For all the complexes both the ^1H and $^{13}C-\{^1H\}$ NMR spectra show the resonance from *x*-CH_2 (see structures **I** and **II** for labelling) to be significantly deshielded compared to that of the free ligand as a result of co-ordination of the adjacent phosphorus or arsenic atom to Cu^I. Similar notable

Table 4 Positional parameters of non-hydrogen atoms and their estimated standard deviations (e.s.d.s) for complex **1**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Cu(1)	0.978 95(4)	0.218 84(3)	0.207 74(5)	C(27)	1.304 8(4)	0.184 5(2)	0.541 6(4)
Cl(2)	0.978 15(9)	0.218 27(6)	−0.025 38(8)	C(28)	1.254 6(3)	0.082 4(2)	0.285 5(4)
P(3)	0.785 42(7)	0.200 15(5)	0.180 85(9)	C(29)	1.268 8(3)	0.109 4(2)	0.166 0(4)
P(21)	1.125 66(7)	0.125 74(4)	0.346 23(8)	C(30)	1.366 3(4)	0.077 7(3)	0.118 0(4)
P(35)	1.001 48(8)	0.335 21(4)	0.280 96(9)	C(31)	1.448 1(4)	0.016 7(3)	0.186 1(6)
N(18)	0.946 9(3)	0.033 1(2)	0.152 8(3)	C(32)	1.436 2(5)	−0.011 5(3)	0.307 1(6)
C(4)	0.739 7(3)	0.189 0(2)	0.336 8(4)	C(33)	1.340 9(4)	0.021 2(3)	0.355 6(4)
C(5)	0.814 8(4)	0.202 6(2)	0.464 3(4)	C(34)	0.948 9(4)	−0.006 1(2)	0.025 6(4)
C(6)	0.785 5(6)	0.191 8(3)	0.586 0(5)	C(36)	1.161 2(4)	0.345 5(2)	0.334 7(5)
C(7)	0.682 3(5)	0.167 4(3)	0.579 1(5)	C(37)	1.212 8(5)	0.385 5(3)	0.443 4(6)
C(8)	0.605 2(4)	0.153 0(3)	0.451 2(6)	C(38)	1.338 6(7)	0.387 9(4)	0.474(1)
C(9)	0.633 4(4)	0.164 6(3)	0.330 9(5)	C(39)	1.407 2(6)	0.349 5(5)	0.395(1)
C(10)	0.664 4(3)	0.273 8(2)	0.077 4(5)	C(40)	1.354 0(6)	0.312 2(4)	0.287(1)
C(11)	0.643 3(6)	0.277 8(3)	−0.065 4(6)	C(41)	1.232 3(4)	0.308 1(3)	0.255 6(6)
C(12)	0.558 9(7)	0.334 8(4)	−0.146 2(8)	C(42)	0.925 1(4)	0.414 3(2)	0.162 1(4)
C(13)	0.494 9(7)	0.389 5(4)	−0.082(1)	C(43)	0.840 2(5)	0.404 9(3)	0.039 1(5)
C(14)	0.516 3(6)	0.385 5(4)	0.058(1)	C(44)	0.776 3(6)	0.464 7(3)	−0.054 8(6)
C(15)	0.601 6(5)	0.327 8(3)	0.140 9(7)	C(45)	0.803 3(6)	0.532 3(3)	−0.022 6(8)
C(16)	0.746 9(3)	0.119 0(2)	0.086 4(4)	C(46)	0.885 0(7)	0.542 0(3)	0.099(1)
C(17)	0.823 7(3)	0.049 0(2)	0.167 0(4)	C(47)	0.948 1(7)	0.482 8(3)	0.194 4(9)
C(19)	1.038 6(3)	−0.004 5(2)	0.275 2(4)	C(48)	0.949 0(5)	0.359 8(2)	0.432 8(5)
C(20)	1.072 3(3)	0.046 1(2)	0.393 7(4)	C(49)	1.017 3(6)	0.326 3(3)	0.562 4(5)
C(22)	1.204 7(3)	0.152 1(2)	0.520 2(4)	C(50)	0.972 3(9)	0.330 1(4)	0.671 9(6)
C(23)	1.162 1(4)	0.146 1(3)	0.634 3(4)	C(51)	0.859(1)	0.368 4(5)	0.656 5(9)
C(24)	1.216 2(5)	0.171 9(3)	0.761 8(5)	C(52)	0.787(1)	0.405 4(5)	0.533(1)
C(25)	1.316 6(6)	0.203 0(3)	0.779 3(5)	C(53)	0.830 6(8)	0.399 7(4)	0.411 2(8)
C(26)	1.361 7(4)	0.209 5(3)	0.670 4(5)				

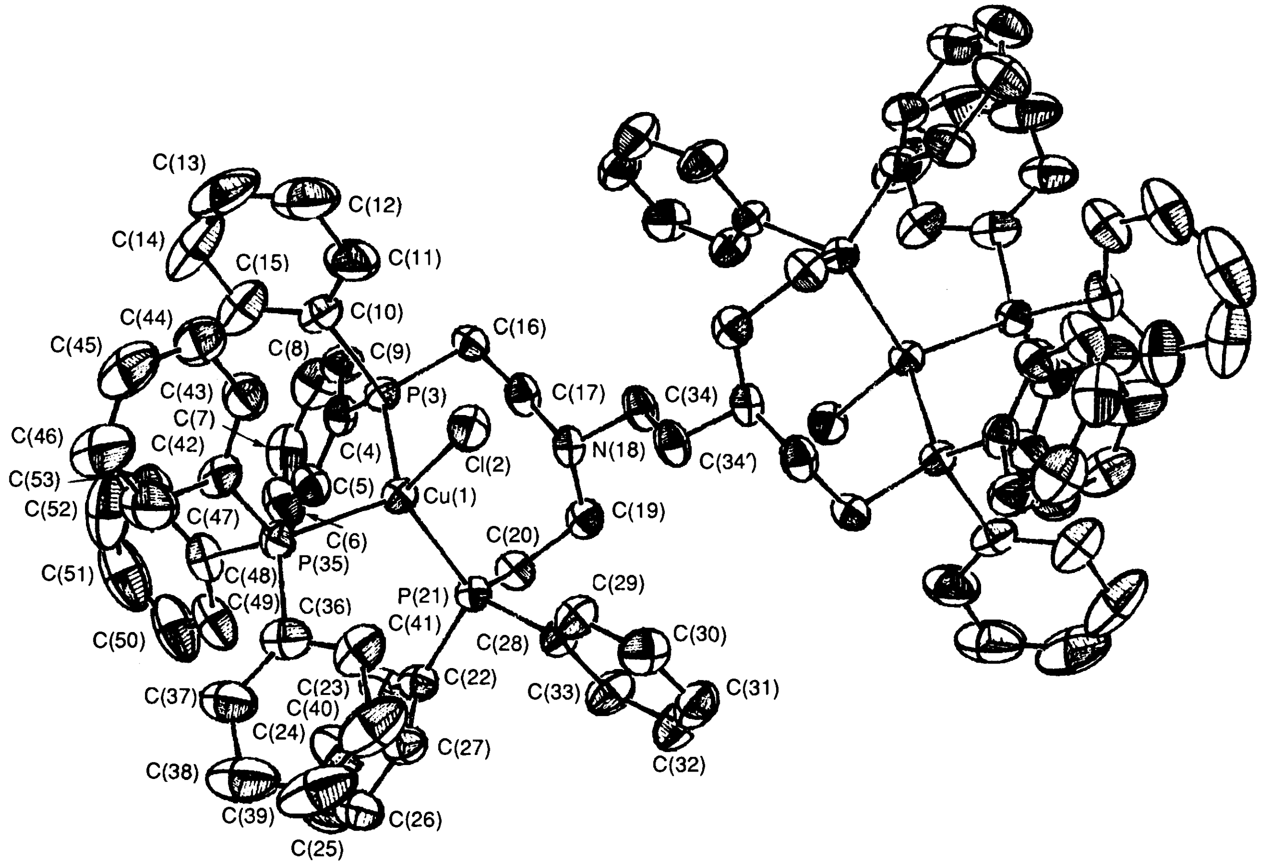


Fig. 1 ORTEP diagram of $[Cu_2(L^1)(PPh_3)_2Cl_2]$ **1**, showing the atom labelling scheme

deshieldings for *z*-CH_2 were observed for complexes **3**–**12**, indicating that the nitrogen atoms of the ligands in these complexes are also co-ordinated. The *y*-CH_2 moiety is also deshielded significantly upon co-ordination in all the complexes. The resonances due to the phenyl protons and carbons appear in the expected regions.

The $^{11}B\text{-}\{^1H\}$ NMR spectra of complexes **13** and **14** exhibit singlets at δ −52.48 and −52.37, respectively, a significant low-

Table 5 Positional parameters of non-hydrogen atoms and their e.s.d.s for complex **3**

Atom	*x*	*y*	*z*
Cu(1)	0.151 83(5)	0.208 49(3)	0.453 83(5)
Cu(2)	−0.483 38(6)	0.284 73(4)	0.215 89(6)
Cl(1)	0.133 5(1)	0.321 63(6)	0.407 6(1)
Cl(2)	−0.341 9(1)	0.212 73(7)	0.203 7(1)
P(3)	0.260 6(1)	0.179 15(7)	0.630 5(1)
P(21)	0.082 0(1)	0.119 93(6)	0.333 7(1)
P(45)	−0.458 8(1)	0.392 21(7)	0.290 4(1)
P(60)	−0.662 4(1)	0.260 63(7)	0.130 8(1)
N(18)	−0.002 5(3)	0.195 8(2)	0.513 3(3)
N(42)	−0.523 4(3)	0.268 0(2)	0.400 0(3)
C(4)	0.307 2(4)	0.086 6(3)	0.649 7(4)
C(5)	0.364 0(4)	0.055 7(3)	0.583 4(4)
C(6)	0.398 4(5)	−0.015 2(3)	0.591 0(5)
C(7)	0.375 2(5)	−0.056 0(3)	0.664 0(5)
C(8)	0.318 8(5)	−0.026 6(3)	0.728 6(5)
C(9)	0.285 5(5)	0.044 2(3)	0.723 1(5)
C(10)	0.377 5(4)	0.224 7(3)	0.728 6(4)
C(11)	0.457 3(5)	0.192 8(3)	0.823 6(4)
C(12)	0.538 4(5)	0.232 1(4)	0.899 9(5)
C(13)	0.541 8(5)	0.301 3(4)	0.881 9(5)
C(14)	0.464 8(5)	0.332 4(3)	0.787 8(5)
C(15)	0.382 6(4)	0.294 1(3)	0.710 6(4)
C(16)	0.157 7(4)	0.194 6(3)	0.699 0(4)
C(17)	0.047 5(4)	0.164 0(3)	0.625 6(4)
C(19)	−0.078 5(4)	0.148 6(3)	0.430 3(4)
C(20)	−0.014 9(4)	0.087 7(3)	0.392 7(4)
C(22)	−0.007 9(4)	0.141 5(3)	0.189 2(4)
C(23)	−0.044 3(5)	0.211 0(3)	0.165 3(5)
C(24)	−0.116 0(6)	0.229 3(4)	0.056 3(6)
C(25)	−0.147 4(5)	0.178 1(4)	−0.026 7(5)
C(26)	−0.110 4(5)	0.110 1(3)	−0.004 0(5)
C(27)	−0.041 0(5)	0.091 3(3)	0.103 9(4)
C(28)	0.162 3(4)	0.040 3(2)	0.314 8(4)
C(29)	0.143 1(4)	−0.026 7(3)	0.336 7(5)
C(30)	0.210 3(5)	−0.084 5(3)	0.325 3(5)
C(31)	0.297 7(5)	−0.077 1(3)	0.291 9(4)
C(32)	0.317 5(4)	−0.011 7(3)	0.267 5(4)
C(33)	0.250 5(4)	0.046 4(3)	0.278 8(4)
C(34)	−0.058 3(4)	0.267 1(3)	0.517 0(4)
C(35)	−0.147 0(4)	0.270 8(2)	0.567 4(4)
C(36)	−0.120 7(4)	0.292 6(3)	0.679 4(4)
C(37)	−0.198 6(5)	0.293 8(3)	0.729 9(4)
C(38)	−0.304 4(4)	0.273 5(3)	0.669 3(4)
C(39)	−0.333 7(4)	0.251 8(2)	0.557 6(4)
C(40)	−0.254 0(4)	0.251 3(2)	0.507 3(4)
C(41)	−0.446 6(4)	0.224 4(3)	0.494 7(4)
C(43)	−0.544 4(4)	0.339 5(3)	0.440 8(4)
C(44)	−0.465 9(5)	0.390 1(3)	0.431 7(5)
C(46)	−0.567 4(4)	0.457 9(3)	0.214 0(5)
C(47)	−0.575 4(5)	0.472 5(3)	0.107 2(5)
C(48)	−0.662 5(6)	0.518 4(4)	0.038 7(6)
C(49)	−0.738 5(6)	0.549 3(3)	0.077 8(7)
C(50)	−0.731 9(7)	0.534 7(4)	0.183 9(8)
C(51)	−0.646 0(6)	0.490 0(3)	0.253 2(7)
C(52)	−0.328 7(4)	0.433 1(3)	0.318 2(5)
C(53)	−0.248 2(5)	0.396 8(3)	0.284 0(6)
C(54)	−0.144 2(5)	0.423 6(4)	0.309 7(7)
C(55)	−0.123 5(6)	0.485 4(4)	0.368 5(7)
C(56)	−0.201 4(7)	0.521 9(4)	0.401 7(6)
C(57)	−0.306 4(5)	0.496 2(3)	0.376 7(6)
C(58)	−0.628 0(4)	0.231 0(3)	0.352 3(4)
C(59)	−0.714 4(4)	0.262 5(3)	0.247 1(4)
C(61)	−0.763 6(4)	0.319 8(3)	0.028 2(4)
C(62)	−0.741 6(5)	0.335 1(3)	−0.064 9(5)
C(63)	−0.812 6(6)	0.380 9(3)	−0.145 4(5)
C(64)	−0.905 8(5)	0.411 7(3)	−0.132 7(6)
C(65)	−0.930 6(5)	0.397 7(4)	−0.041 8(7)
C(66)	−0.859 4(5)	0.351 6(4)	0.039 3(6)
C(67)	−0.695 0(4)	0.173 9(3)	0.067 2(4)
C(68)	−0.607 7(5)	0.123 9(3)	0.076 4(5)
C(69)	−0.629 3(6)	0.056 0(3)	0.035 4(6)
C(70)	−0.737 5(6)	0.038 5(3)	−0.016 7(5)
C(71)	−0.824 7(6)	0.087 8(3)	−0.028 5(5)
C(72)	−0.805 2(5)	0.155 2(3)	0.012 7(5)

field shifting of the boron resonance compared to that of $NaBH_4$ (δ −61.00), and arise from co-ordination of some of the hydrogen atoms of BH_4^- to Cu^I. However, an interaction between copper and boron cannot be ruled out as suggested in the compound $[Cu(PPh_3)_2(BH_4)]$.[35]

The $^{31}P-\{^1H\}$ NMR spectral data are useful for geometrical assignment. Except for complexes **1**, **2** and **4** all the complexes exhibit a singlet in the range δ −12.11 to −17.62, significantly upfield relative to the free ligands. Complex **1** exhibits two resonances at δ −17.44 and −4.18 and **2** shows a singlet at δ −3.63. These data suggest that (*i*) in all the complexes there are no free PPh_2 groups; (*ii*) in complex **1** two types of co-ordinated phosphorus atoms are present with the resonance at δ −4.18 assigned to the phosphorus atom of co-ordinated PPh_3, by comparison with the resonance at δ −3.63 for complex **2**; (*iii*) in each complex the co-ordinated PPh_2 groups are magnetically equivalent, *i.e.* the geometry of both copper(I) centres in each compound are identical. In complex **1** the P–P coupling, expected from the non-equivalent phosphorus atoms, could not be observed at room temperature. The upfield shifting of the phosphorus (PPh_2) resonance with different anions lie in the order ClO_4^- (un-co-ordinated) > N_3^- ≈ NCS^- ≈ OH^- > BH_4^- > Cl^- which indicates that the Cu–P bond strength in these complexes decreases in the same order.

Geometry.–Considering all the data discussed above, it is clear that the perchlorate complexes **4**–**6** are three-co-ordinate with an NP_2 core and that all the other complexes are four-co-ordinate. In these systems three-co-ordination permits only a trigonal-planar geometry but for four-co-ordination two possible geometries, tetrahedral or trigonal pyramidal, can occur. Single-crystal X-ray analysis of complex **1** shows that Cu^I possesses a slightly distorted tetrahedral geometry and one can expect a similar geometry for complex **2**. However for complex **3** the geometry as established by X-ray studies is trigonal pyramidal with a P_2Cl trigonal basal plane and a nitrogen atom co-ordinated apically. For four-co-ordinate complexes of L^3 molecular models show that apical co-ordination of nitrogen, in a trigonal pyramidal geometry, is most favoured in agreement with the crystal structure of **3**. A similar geometry is therefore proposed for the four-co-ordinate complexes **8**, **10** and **12** (Scheme 1). By contrast, for complexes of L^1 molecular models indicate that it is difficult for nitrogen to co-ordinate in a similar manner due to steric overcrowding from the phenyl rings of co-ordinated PPh_2 groups and now co-ordination of nitrogen in the basal plane is favoured. Therefore, for complexes **7**, **9** and **11**, a trigonal-pyramidal geometry with an NP_2 basal plane and apically co-ordinated ligand X is proposed (Scheme 1). For complexes **13** and **14** a tetrahedral geometry with a P_2H_2 core is suggested, although a significant distortion cannot be ruled out due to the differing nature of the donor atoms.

Description of Structures.—$[Cu_2(L^1)(PPh_3)_2Cl_2]$ **1**. An ORTEP view[36] of complex **1** is shown in Fig. 1. Selected bond distances and angles are presented in Table 3 and positional parameters in Table 4..

The crystal structure analysis shows that complex **1** has an inversion centre located at the mid-point of the C(34)–C(34′) bond, thus dividing the molecule into identical halves. The Cu

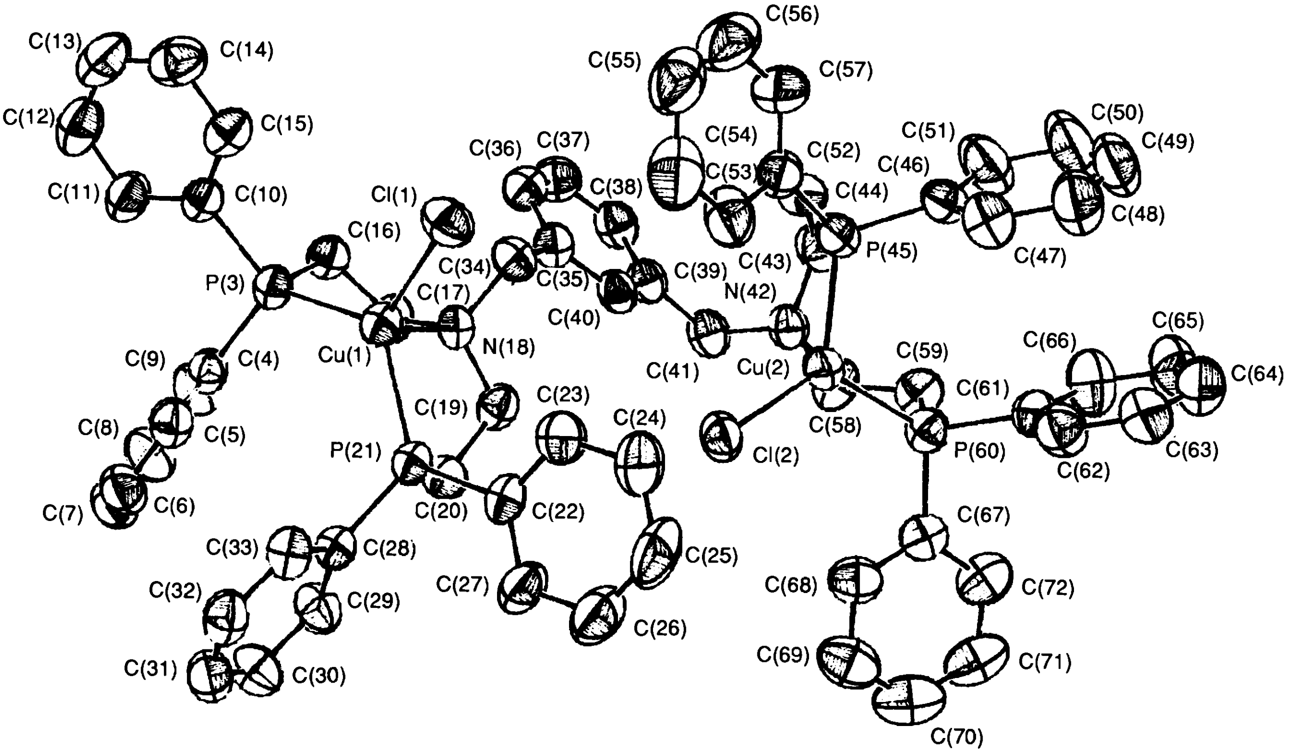


Fig. 2 ORTEP diagram of [$Cu_2(L^3)Cl_2$] **3**, showing the atom labelling scheme

atom has a slightly distorted tetrahedral disposition with ligation to a chloride ion and to three phosphorus atoms, two from PPh_2 groups, and one from PPh_3. The interligand angles in the co-ordination sphere are in the range 100.09(4)–113.70(3)° (Table 2). The distortion is a consequence of the differing Cu–P and Cu–Cl bond lengths with the latter being significantly longer. The presence of bulky PPh_2 groups on the ligand in combination with PPh_3 prevents co-ordination of the nitrogen atom [Cu • • • N 3.588(2) Å] through apparently it is in a favourable position to co-ordinate to form a stable five-membered ring. This demonstrates that steric overcrowding determines the co-ordination in the molecular structure. The dihedral angles are Cu(1)–P(3)–P(21)/Cu(1)–P(35)–Cl(2) 95.19(4), Cu(1)–P(21)–P(35)/Cu(1)–P(3)–Cl(2) 93.62(3) and Cu(1)–P(3)–P(35)/Cu(1)–P(35)–Cl(2) 71.76(4)°. The Cu(1) atom lies 0.65 Å above the P(3)–P(21)–P(35) plane, 0.89 Å below the P(3)–P(35)–Cl(2) plane, 0.72 Å below the P(21)–P(35)–Cl(2) plane and 0.82 Å below the P(3)–P(21)–Cl(2) plane. The Cu • • • Cu separation is 9.116 Å.

The Cu–P distances of 2.299(2), 2.319(1) and 2.327(1) Å and the Cu–Cl distance of 2.347(2) Å compare well with other reported values for tetrahedral copper(I) complexes containing tertiary phosphine and chloride ligands.[1–3]

[$Cu_2(L^3)Cl_2$] **3**. Fig 2 displays a perspective view of complex **3** along with the atom-numbering scheme. Selected bond distances and angles are listed in Table 3 and final positional parameters in Table 5.

The centre of symmetry found in **1** is absent in **3** because of the presence of the *m*-phenylenedimethylene moiety and the compound has two Cu centres separated by 6.777(2) compared to 9.116 Å in **1**. The smaller separation in **3** can be attributed to two distinct factors: (*i*) it need not accommodate the bulky PPh_3 ligand, which obviously increases the span of the molecule; and (*ii*) the *m*-phenylenediomethylene moiety is constrained and does not have the same flexibility as the ethylene bridge. The tertiary amine nitrogen, which is not involved in co-ordination to Cu^I in **1** owing to the severe steric factors, is now able to co-ordinate in **3** with the formation of a stable five-membered chelate ring now outweighing any steric factors. The bond angles around both Cu centres suggest trigonal-pyramidal geometry, in which two phosphorus atoms and chloride form the basal trigonal plane and a nitrogen atom occupies a position apical to the trigonal base. The interligand angles in the basal plane (Table 2) are all within 5.3° of the ideal value of 120°. The three angles sum to 359.8° for Cu(1) and 359.4° for Cu(2) consistent with very small displacement of either Cu atom from the basal trigonal plane [0.006 for Cu(1) and 0.10 Å for Cu(2)]. A further reason for the difference in co-ordination geometry between complexes **1** and **3** may be the presence of a stacking interaction of the xylene phenyl ring with the phosphine phenyl rings.

The Cu–P and Cu–Cl distances for the two Cu centres in **3** are similar but are considerably shorter than those found in **1**. This arises because the PPh_3 group, co-ordinated to the Cu atom in **1**, does not allow other bulky co-ordinating groups to approach the Cu. The Cu–N distances in **3** are long at 2.416(2) and 2.630(2) Å for Cu(1) and Cu(2) respectively. Similar long Cu–N distances (2.31–2.73 Å) with tertiary amine nitrogen atoms in some copper(I) complexes have also been reported recently.[3,7] It is noteworthy that the Cu–N distances differ significantly, although the reason for this is not clear. The angles between the apex and the basal plane are not exactly 90°, and may be attributed to the steric restraints imposed by the system.

The new hexadentate ligands, therefore, form dinuclear complexes with trigonal-planar, trigonal-pyramidal or tetrahedral geometries with mixed soft (P) as well as hard (N) donor atoms and the complexes thus obtained are stable in the solid state as well as in solution for extended periods.

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