Mono- and Bi-dentate Phosphaalkene Ligands: Structures of their Copper(I) Chloride Complexes†

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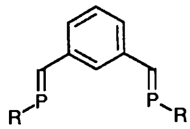
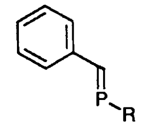
While the reaction of the monophosphaalkene [(2,4,6-tri-*tert*-butylphenyl)phosphanediylmethyl]-benzene (L^2) with copper(I) chloride led to a dimeric complex $[Cu_2Cl_2L^2_2(NCMe)_2]$ **1**, use of the diphosphaalkene 1,3-bis[(2,4,6-tri-*tert*-butylphenyl)phosphanediylmethyl]benzene (L^1) gave rise to a tetrameric complex $[Cu_4Cl_4L^1_2]\cdot 3EtOH$ **2**. The crystal structures of the complexes have been determined and indicate that **1** is a centrosymmetric dimer with tetrahedrally co-ordinated copper(I) centres, whereas **2** adopts a 'cubane-like' structure with pairs of copper atoms bridged by different L^1 units.

Since the first synthesis[1] of a stable phosphaalkene in 1978, compounds containing a trivalent dico-ordinated phosphorus atom have been intensively investigated. These molecules exhibit particularly interesting chemical reactivities[2] and are known to form σ and η^2 complexes[3] with a large variety of transition metals. In this context, we have previously shown that 1,3-bis[(2,4,6-tri-*tert*-butylphenyl)phosphanediylmethyl]-benzene,[4] L^1, is a specially interesting compound which can act as a terdentate chelate when reacting with palladium(II) and platinum(II) ions. However, the type of complexes that it can form with metals that are not likely to give rise to orthometallation (*e.g.* Cu^I) remains unknown. Surprisingly, whereas the literature on the complexation of Cu^+ ions by phosphines is particularly abundant,[5] to our knowledge no phosphaalkene complex of Cu^I has ever been reported. We will first show that such a σ bond can indeed be formed between Cu^I and the monodentate [(2,4,6-tri-*tert*-butylphenyl)phosphanediylmethyl]benzene,[6] L^2, and will then describe the 1:2 L^1 : copper(I) chloride complex, which, to our knowledge, is the first $Cu_4X_4L_2$ 'cubane-like' structure with bridging ligands.

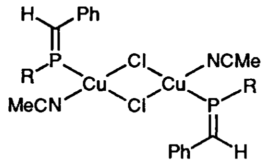


L^1



L^2

R = $C_6H_2Bu^t_3$-2, 4, 6



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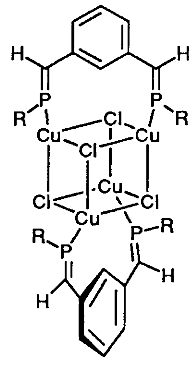

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Results and Discussion

The binuclear complex **1** was obtained as a yellow solid by treating stoichiometric quantities of L^2 with CuCl in CH_2Cl_2–MeCN. It is air-stable for many weeks when stored at 5 °C. This complex is a centrosymmetric dimer with copper(I) centres tetrahedrally co-ordinated to a phosphorus atom, two chlorine atoms and a solvent molecule (Fig. 1). The Cu_2Cl_2 core has an irregular diamond shape with two slightly different Cu–Cl bonds (Table 1). A similar chloride-bridged dimeric structure has recently been reported for a phosphine complex[7] $[(Ph_3P)(py)CuCl_2Cu(py)(PPh_3)]$ (py = pyridine); a notable difference between these two structures lies in the Cu_2Cl_2 unit in which the bond angles are closer to 90° for the phosphaalkene complex (Table 1) than for the phosphine complex[7] (Cl–Cu–Cl 105.05, Cu–Cl–Cu 74.4 and 75.5°).

The reaction of compound L^1 with CuCl or $CuCl_2$ in CH_2Cl_2 at 40 °C leads to the yellow crystalline complex **2**. The crystal structure indicates that, as for the 1:1 triphenylphosphine: copper(I) chloride complex,[8] a cubane-like structure is formed (Fig. 2). In **2**, however, two faces of the Cu_4Cl_4 core contain two copper atoms which are σ bonded to the two phosphaalkene groups of the same L^1 ligand. These 'bridged faces' (Cu_2Cl_2) are planar (maximum deviations = 0.047 and 0.048 Å) and parallel (0.6°). Moreover, the two phosphaalkene bonds of each bridging ligand are coplanar and the corresponding planes of the two L^1 entities are perpendicular to each other (90.1°) and almost perpendicular to the 'bridged face' (89.4 and 86.2° respectively). Although the Cu_4Cl_4 core of the molecule is largely distorted from an idealized cube, all geometrical

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

Table 1 Selected bond lengths (Å) and angles (°) for complexes **1** and **2**

		1	**2**[a]
Cu···Cu	*b*	3.1659(9)	3.058(3)
	c		3.218(11)
Cl···Cl	*b*	3.553(2)	3.836(6)
	c		3.530(21)
Cu–Cl	*b*	2.355(2), 2.404(2)	2.453(16)
	c		2.354(18)
Cu–N		2.041(6)	—
Cu–P		2.205(1)	2.167(4)
$P–C_{alkene}$		1.663(5)	1.66(1)
$P–C_{aryl}$		1.840(5)	1.85(1)
Cl–Cu–Cl	*b*	96.59(5)	102.9(8)
	c		94.5(4)
Cu–Cl–Cu	*b*	83.41(6)	77.1(3)
	c		84.0(6)
Cl–Cu–P	*b*	121.56(7), 112.52(6)	114(2)
	c		131.2(6)
Cl–Cu–N		105.2(2), 104.4(2)	—
P–Cu–N		114.1(1)	—
$Cu–P–C_{alkene}$		130.8(2)	126.8(5)
$Cu–P–C_{aryl}$		127.4(2)	131(1)

[a] Mean values. [b] In the 'bridged face'. [c] Out of the 'bridged face'.

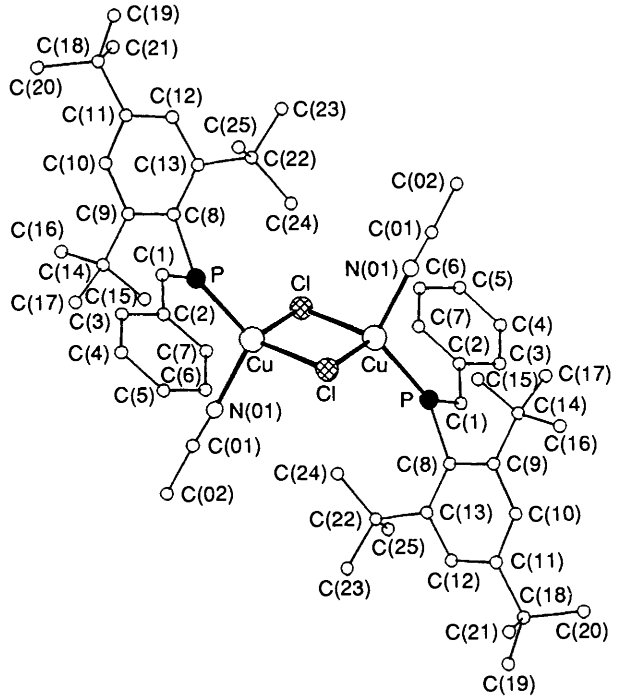

Fig. 1 Molecular structure of complex **1**

parameters (Table 1) show excellent correlations if we distinguish the two 'bridged faces' from the four others. The presence of the bridging ligand acts as an ordering factor of the Cu_4Cl_4 core, contrary to the soft structure observed in the analogous triphenylphosphine complex.[8] Owing to the presence of the bridging ligand, the Cu···Cu distances of the 'bridged faces' [3.060(3) and 3.056(4) Å] are smaller than in the other faces [mean 3.218(11) Å]. Consequently, the Cu–Cl–Cu angles decrease and the Cl–Cu–Cl angles increase significantly.

It should be noted that, even if no stacking interaction were observed, the benzene rings of the two ligands are not similarly oriented. Thus, one L^1 unit is almost planar (angles between the benzene ring and the plane of each P=C–C moiety are 6°), whereas for the second L^1 the corresponding angles are equal to 22°.

Table 2 Summary of crystal data, intensity measurements and structure refinements for complexes **1** and **2** *

	1	**2**
Formula	$C_{54}H_{76}Cl_2Cu_2N_2P_2$	$C_{88}H_{128}Cl_4Cu_4P_4\cdot 3C_2H_6O$
M	1013.2	1844.1
a/Å	9.238(1)	15.420(2)
b/Å	11.463(2)	19.101(3)
c/Å	14.116(4)	19.932(5)
α/°	110.38(1)	108.93(1)
β/°	101.94(1)	96.74(1)
γ/°	94.73(1)	111.76(1)
$U/Å^3$	1351.3(5)	4965(2)
Z	1	2
F(000)	536	1956
$D_c/g\ cm^{-3}$	1.25	1.23
$\mu(Mo\text{-}K\alpha)/mm^{-1}$	0.981	1.062
$[(\sin\theta)/\lambda]_{max}/Å^{-1}$	0.55	0.49
No. measured reflections	3763	9222
No. observed reflections $[\lvert F_o\rvert > 4\sigma(F_o)]$	3277	5635
No. parameters	281	954
Weighting scheme, *w*	$1/\sigma^2(F_o)$	1
Maximum and minimum $\Delta\rho/e\ Å^{-3}$	0.78, −0.68	1.21, −0.91
S	3.61	4.97
R, *R′*	0.060, 0.049	0.076, 0.076

* Details in common: crystal size 0.2 × 0.2 × 0.2 mm; triclinic, space group $P\bar{1}$; full-matrix least-squares refinement on *F*.

Such 'cubane-like' $Cu_4X_4L_2$ edifices are quite unusual. As recently reported for the 1,2-bis(diphenylphosphino)methane ligand,[9,10] in the presence of two bidentate ligands, the Cu_4X_4 core adopts a 'step' structure; the present cubane-like geometry is likely to be due to the phosphaalkene moieties which increase the rigidity of the ligands.

As shown by ^1H and ^{31}P NMR spectroscopy, in solution the two L^1 ligands in complex **2** are equivalent; it is therefore probable that the difference observed in the crystal is due to a matrix effect. A noticeable difference between the spectra obtained for L^1 and **2** concerns the chemical shift of the aromatic proton located between the two phosphaalkene groups. This chemical shift passes from δ 7.52 (L^1) to 9.68 (**2**) (for L^2, δ 7.6; for **1**, δ 7.76); the chemical shifts of the protons *ortho* to the C=P bonds remain similar to that measured for L^1. The variation probably reflects the fact that, in **2**, in contrast to the other three molecules, there is no free rotation around the C(phosphaalkene)–C(phenyl) bond; the two magnetic susceptibility tensors associated with the phosphaalkene double bonds are therefore parallel and fixed with respect to the *o*-proton.

Experimental

All experiments were performed under a nitrogen atomosphere in carefully dried glassware. Reagents were purchased from Fluka and used as received. Solvents were dried, where necessary, by standard methods before use. NMR spectra were recorded at room temperature using a Bruker AC-F200 spectrometer (^1H, 200 MHz; ^{31}P, 81 MHz).

Syntheses.—$[Cu_2Cl_2L^2{}_2(NCMe)_2]$ **1**. A solution containing CuCl (0.027 g, 0.2 mmol) in MeCN (2 cm^3) was added to a solution of compound L^2 (0.1 g, 0.2 mmol) in CH_2Cl_2 (5 cm^3) and refluxed for 30 min. After filtration of unreacted CuCl, yellow crystalline **1** was obtained by slow evaporation of the solution, m.p. 174 °C (decomp.). NMR: $^{31}P\text{-}\{^1H\}$ ($CDCl_3$, external reference H_3PO_4), δ 205.9; $^1H(CD_2Cl_2$, internal reference $SiMe_4$), δ 1.4 (s, 18 H), 1.6 (s, 36 H), 1.97 (s, 6 H), 7.28

Table 3 Non-hydrogen positional parameters

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Complex **1**							
Cu	0.364 93(8)	0.389 00(6)	0.429 86(5)	C(14)	0.255 1(6)	−0.015 0(5)	0.359 9(5)
Cl	0.423 3(2)	0.593 7(1)	0.431 5(1)	C(15)	0.296(1)	0.092 2(7)	0.461 9(6)
P	0.342 4(2)	0.219 6(1)	0.288 4(1)	C(16)	0.227(1)	−0.129 5(7)	0.383 6(8)
C(1)	0.240 6(6)	0.180 8(5)	0.166 7(4)	C(17)	0.103 3(8)	−0.000 2(9)	0.299 5(6)
C(2)	0.140 1(6)	0.254 0(5)	0.126 1(4)	C(18)	0.600 8(7)	−0.275 9(5)	0.178 8(4)
C(3)	0.030 6(7)	0.194 3(5)	0.033 3(4)	C(19)	0.688(1)	−0.287 3(6)	0.099 0(6)
C(4)	−0.070 3(7)	0.260 3(7)	−0.003 4(5)	C(20)	0.471 6(9)	−0.382 0(6)	0.136 0(7)
C(5)	−0.059 3(8)	0.389 7(7)	0.049 3(6)	C(21)	0.697 5(9)	−0.293 0(7)	0.270 9(6)
C(6)	0.049 6(8)	0.449 6(6)	0.138 0(5)	C(22)	0.655 6(7)	0.181 1(5)	0.217 3(5)
C(7)	0.151 2(7)	0.382 7(5)	0.177 7(4)	C(23)	0.816 4(8)	0.168 1(7)	0.230 1(7)
C(8)	0.438 4(5)	0.082 6(4)	0.276 9(4)	C(24)	0.652 2(9)	0.313 4(6)	0.285 4(7)
C(9)	0.376 7(5)	−0.019 7(5)	0.300 4(4)	C(25)	0.605 5(9)	0.171 9(8)	0.105 2(7)
C(10)	0.433 8(6)	−0.132 5(5)	0.267 8(4)	N(01)	0.186 0(5)	0.393 9(4)	0.494 3(4)
C(11)	0.547 1(6)	−0.147 1(5)	0.216 0(4)	C(01)	0.092 2(7)	0.389 4(5)	0.534 0(5)
C(12)	0.611 8(6)	−0.043 7(5)	0.202 5(4)	C(02)	−0.025 8(7)	0.390 3(7)	0.591 6(6)
C(13)	0.563 3(6)	0.072 9(5)	0.233 6(4)				
Complex **2**							
Cu(1)	0.731 6(1)	0.330 6(1)	0.181 2(1)	C(02)	0.378 3(9)	0.236 5(7)	0.289 9(7)
Cu(2)	0.745 7(1)	0.476 9(1)	0.312 2(1)	C(03)	0.381 3(9)	0.213 4(8)	0.349 3(7)
Cu(3)	0.534 6(1)	0.346 5(1)	0.201 1(1)	C(04)	0.310(1)	0.211(1)	0.385 8(9)
Cu(4)	0.631 8(1)	0.294 2(1)	0.305 9(1)	C(05)	0.240(1)	0.231(1)	0.365(1)
Cl(1)	0.673 0(3)	0.434 0(2)	0.180 5(2)	C(06)	0.233(1)	0.250(1)	0.303 9(9)
Cl(2)	0.795 7(3)	0.368 4(2)	0.311 6(2)	C(07)	0.296 2(9)	0.277 3(8)	0.203 8(8)
Cl(3)	0.578 2(3)	0.229 6(2)	0.171 9(2)	C(08)	0.318(1)	0.332 8(9)	0.091 9(7)
Cl(4)	0.598 0(3)	0.414 5(2)	0.336 0(2)	C(09)	0.279(1)	0.272 1(9)	0.019 6(9)
P(1)	0.832 8(3)	0.323 8(2)	0.115 0(2)	C(010)	0.218(1)	0.282 0(9)	−0.029 7(8)
P(2)	0.861 1(3)	0.600 7(2)	0.365 7(2)	C(011)	0.197(1)	0.348 1(9)	−0.014 3(9)
C(1)	0.981 0(9)	0.486 1(8)	0.175 1(7)	C(012)	0.243(1)	0.408 7(9)	0.055 9(9)
C(2)	0.945 1(9)	0.518 2(8)	0.232 9(7)	C(013)	0.304(1)	0.405 1(9)	0.109 8(8)
C(3)	0.991(1)	0.601 6(8)	0.277 3(7)	C(014)	0.458(1)	0.192 9(8)	0.377 2(7)
C(4)	1.072(1)	0.651 6(9)	0.263 1(9)	C(015)	0.620(1)	0.176 2(9)	0.418 5(7)
C(5)	1.108(1)	0.618(1)	0.206 2(9)	C(016)	0.626(1)	0.100 3(9)	0.382 8(8)
C(6)	1.062(1)	0.536(1)	0.162 3(8)	C(017)	0.648(1)	0.062 7(9)	0.428 2(9)
C(7)	0.935 4(9)	0.399 6(8)	0.123 4(7)	C(018)	0.663(1)	0.097(1)	0.503 9(9)
C(8)	0.826(1)	0.235 0(8)	0.036 5(8)	C(019)	0.667(1)	0.173(1)	0.534 8(8)
C(9)	0.776(1)	0.217 9(9)	−0.036 0(9)	C(020)	0.649(1)	0.216 4(9)	0.495 9(9)
C(10)	0.784(1)	0.156 8(9)	−0.094 1(8)	C(021)	0.294(2)	0.194(1)	−0.009(1)
C(11)	0.833(1)	0.113 2(9)	−0.083 1(8)	C(022)	0.398(2)	0.209(2)	0.013(2)
C(12)	0.875(1)	0.128 5(9)	−0.012 2(8)	C(023)	0.258(2)	0.148(1)	−0.091(1)
C(13)	0.873(1)	0.188 0(9)	0.049 4(7)	C(024)	0.239(3)	0.131(1)	0.019(1)
C(14)	0.959(1)	0.640 5(8)	0.338 7(8)	C(025)	0.135(1)	0.358(1)	−0.069 5(9)
C(15)	0.881(1)	0.690 6(8)	0.449 0(8)	C(026)	0.095(3)	0.293(2)	−0.139(2)
C(16)	0.848(1)	0.748 3(9)	0.440 1(7)	C(027)	0.176(2)	0.422(3)	−0.091(3)
C(17)	0.891(1)	0.825(1)	0.495 8(9)	C(028)	0.056(3)	0.362(4)	−0.050(2)
C(18)	0.962(1)	0.849 3(8)	0.559 1(8)	C(029)	0.344(1)	0.478(1)	0.186(1)
C(19)	0.982(1)	0.786 7(9)	0.568 8(7)	C(030)	0.446(1)	0.501(1)	0.224(1)
C(20)	0.940(1)	0.707 2(9)	0.516 2(8)	C(031)	0.282(2)	0.463(1)	0.237(1)
C(21)	0.717(1)	0.262(1)	−0.057 2(8)	C(032)	0.346(2)	0.557(1)	0.177(1)
C(22)	0.780(2)	0.348(1)	−0.045(1)	C(033)	0.609(1)	0.059 4(9)	0.300 3(8)
C(23)	0.645(2)	0.264(2)	−0.013(1)	C(034)	0.619(1)	−0.022(1)	0.276 9(9)
C(24)	0.658(1)	0.219(1)	−0.138(1)	C(035)	0.508(1)	0.036(1)	0.253 3(8)
C(25)	0.835(2)	0.046(1)	−0.149(1)	C(036)	0.690(1)	0.118(1)	0.277 5(9)
C(26)	0.818(3)	0.054(2)	−0.218(1)	C(037)	0.690(1)	0.055(1)	0.552(1)
C(27)	0.917(2)	0.028(2)	−0.136(1)	C(038)	0.796(2)	0.092(1)	0.586(1)
C(28)	0.753(3)	−0.030(2)	−0.162(2)	C(039)	0.663(2)	−0.035(1)	0.508(1)
C(29)	0.922(1)	0.197(1)	0.125 5(8)	C(040)	0.636(2)	0.056(2)	0.609(2)
C(30)	0.944(2)	0.124(1)	0.119(1)	C(041)	0.662(1)	0.305 7(9)	0.544 4(8)
C(31)	0.856(2)	0.198(1)	0.176(1)	C(042)	0.744(2)	0.342(1)	0.613(1)
C(32)	1.020(1)	0.269(1)	0.160(1)	C(043)	0.690(1)	0.364 4(9)	0.506 8(9)
C(33)	0.769(1)	0.733(1)	0.376(1)	C(044)	0.569(1)	0.300(1)	0.569(1)
C(34)	0.813(2)	0.749(2)	0.317(1)	C(101)	0.399(2)	−0.024(1)	0.035(1)
C(35)	0.720(1)	0.789(1)	0.396 8(9)	C(102)	0.400(2)	−0.025(2)	−0.032(2)
C(36)	0.696(2)	0.651(2)	0.341(2)	C(103)	0.435(2)	0.012(1)	−0.067(1)
C(37)	1.016(1)	0.937 3(8)	0.619 9(9)	C(104)	0.522(3)	0.036(2)	−0.046(2)
C(38)	0.957(1)	0.984(1)	0.620(1)	C(201)	0.435(2)	0.416(2)	0.522(1)
C(39)	1.042(2)	0.940(1)	0.696 6(9)	C(202)	0.420(2)	0.441(2)	0.468(2)
C(40)	1.107(1)	0.980(1)	0.602(1)	C(203)	0.402(2)	0.470(2)	0.423(1)
C(41)	0.963(1)	0.643(1)	0.537 0(9)	C(204)	0.484(4)	0.535(3)	0.463(3)
C(42)	0.983(2)	0.667(1)	0.619(1)	C(301)	0.538(2)	0.468(2)	0.036(2)
C(43)	1.054(2)	0.640(2)	0.517(1)	C(302)	0.545(2)	0.425(2)	0.013(1)
C(44)	0.887(2)	0.558(1)	0.501(1)	C(303)	0.557(5)	0.518(5)	0.072(3)
P(01)	0.382 4(3)	0.316 2(2)	0.165 0(2)	C(304)	0.460(5)	0.433(3)	−0.024(4)
P(02)	0.568 3(3)	0.219 7(2)	0.364 8(2)	O(01)	0.578(2)	0.647(1)	0.120(1)
C(01)	0.305(1)	0.254 5(8)	0.265 8(7)				

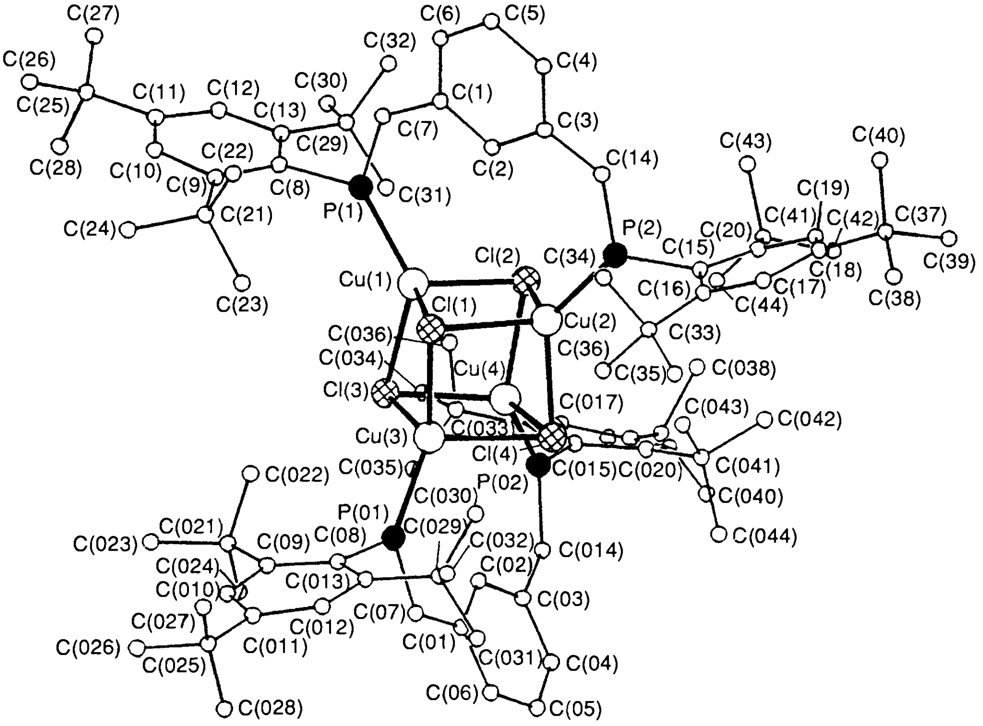

Fig. 2 Molecular structure of complex **2**

(m, 6 H), 7.52 (d, 4 H, 2 Hz), 7.76 (m, 4 H) and 7.83 (d, 2 H, 27 Hz).

$[Cu_4Cl_4L^1{}_2]\cdot 3EtOH$ **2**. A solution containing CuCl (0.03 g, 0.3 mmol) in MeCN (2 cm^3) was added to a solution of compound L^1 (0.1 g, 0.15 mmol) in CH_2Cl_2 (5 cm^3) and refluxed for 30 min. The solvent of the resulting pale yellow solution was removed under reduced pressure. Stable yellow crystals of complex **2** were obtained by slow evaporation of a $CHCl_3$–EtOH (7:3) solution, m.p. 242–244 °C (decomp.). NMR: $^{31}P-\{^1H\}$ ($CDCl_3$), δ 199.35; ^1H($CDCl_3$), δ 1.37 (s, 36 H), 1.62 (s, 72 H), 6.84 (m, 4 H), 7.1 (t, 2 H, 8 Hz), 7.5 (d, 8 H, 1.8 Hz), 7.56 (d, 4 H, 26 Hz) and 9.68 (t, 2 H, 5 Hz).

Crystallography.—The cell parameters and diffracted intensities were measured at room temperature on Nonius CAD4 (**1**) and Philips PW1100 (**2**) diffractometers with graphite-monochromated Mo-Kα radiation (λ = 0.710 69 Å). Two reference reflections showed variations of less than $3.2\sigma(I)$ for complex **1** and about 16% for **2**; all intensities were corrected for this drift. Data were corrected for Lorentz and polarization effects but not for absorption. The structures were solved by direct methods using MULTAN 87,[11] all other calculations used the XTAL[12] system and ORTEP.[13] Atomic scattering factors and anomalous dispersion terms were taken from ref. 14. All hydrogen-atom coordinates were calculated. The three molecules of EtOH observed in the crystal structure of **2** are disordered. A summary of the crystal data, intensity measurements and structure refinements is given in Table 2, final atomic coordinates in Table 3.

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

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