Synthetic, Spectroscopic and X-Ray Crystallographic Studies on Phenylcyanamidocopper(I) Complexes *

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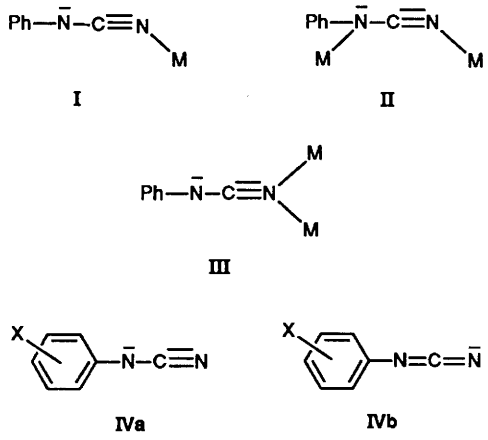
The preparations of phenylcyanamidocopper(I) complexes of the types $[Cu_2(dppe)_3L_2]\cdot 2Me_2CO$ [dppe = 1,2-bis(diphenylphosphino)ethane, L = a phenylcyanamide ion] and $[\{Cu(PPh_3)_2L\}_2]$ are described. The crystal structures of two of the complexes, namely $[Cu_2(dppe)_3(4\text{-}ClC_6H_4NCN)_2]\cdot 2Me_2CO$ (4-ClC_6H_4NCN = 4-chlorophenylcyanamide) and $[\{Cu(PPh_3)_2(4\text{-}MeC_6H_4NCN)\}_2]$ (4-MeC_6H_4NCN = 4-methylphenylcyanamide) have been determined by X-ray diffraction techniques. Crystals of $[Cu_2(dppe)_3(4\text{-}ClC_6H_4NCN)_2]\cdot 2Me_2CO$ are orthorhombic, space group *Pbca*, with a = 22.397(14), b = 18.970(7), c = 20.341(5) Å and Z = 4. The complex contains centrosymmetric dppe-bridged dinuclear molecules. Each copper atom has a distorted tetrahedral geometry with the cyano nitrogen from a terminally bound $[4\text{-}ClC_6H_4NCN]^-$ ligand [Cu–N 1.967(5) Å], two phosphorus atoms from a chelating dppe and one from the bridging dppe making up the co-ordination sphere. Crystals of $[\{Cu(PPh_3)_2(4\text{-}MeC_6H_4NCN)\}_2]$ are monoclinic, space group $P2_1/n$, with a = 15.003(2), b = 13.844(2), c = 18.711(2) Å, β = 101.22(1)° and Z = 2. This complex is a centrosymmetric dimer with the $[4\text{-}MeC_6H_4NCN]^-$ ligands bridging in a μ-1,3 fashion. Each copper atom has a distorted tetrahedral geometry, being bound to two PPh_3 phosphorus atoms, a terminal cyano nitrogen atom from a $[4\text{-}MeC_6H_4NCN]^-$ ligand [Cu–N 2.045(2) Å] and an amido nitrogen from the centrosymmetrically related $[4\text{-}MeC_6H_4NCN]^-$ ligand [Cu–N 2.095(2) Å]. The ν(CN) stretching vibration for the co-ordinated phenylcyanamides occurs in the 2125–2175 cm^{-1} range. Solid-state cross-polarisation magic-angle-spinning (CP-MAS) ^{31}P NMR spectra at 121.47 MHz for the complexes $[\{Cu(PPh_3)_2L\}_2]$ (L = XC_6H_4NCN; X = 4-Me, 4-Cl or H) consist of two well resolved quartets of doublets arising from each of the crystallographically independent phosphorus nuclei. The doublet structure is a consequence of homonuclear phosphorus–phosphorus two-bond coupling $[^2J(P^1\text{–}P^2)$ = 120 Hz]. Available structural data for phenylcyanamidocopper complexes are summarised and comparison made with related pseudohalide complexes.

Recently we reported the first X-ray structural characterisation of anionic phenylcyanamido ligand complexes.[1,2] It was established that, when bound to copper(II), phenylcyanamido ligands can exhibit three different co-ordination modes, namely **I** terminal, binding through the cyano nitrogen; **II** μ-1,3-bridging, through the amido and cyano nitrogens and **III** μ-1,1-bridging, through the cyano nitrogen. In this respect the phenylcyanamido ion resembles pseudohalides which also show similar ambidentate behaviour, *e.g.* the azido ion, N_3^-.[3] In order to investigate further the extent to which the anionic phenylcyanamides **IV** behave as pseudohalides, we have examined their interaction with copper(I). In this paper the synthesis and characterisation of two series of phenylcyanamidocopper(I) complexes which incorporate the phosphines 1,2-bis(diphenylphosphino)ethane (dppe) and triphenylphosphine as coligands is reported. The X-ray crystal structures of two compounds, $[Cu_2(dppe)_3(4\text{-}ClC_6H_4NCN)_2]\cdot 2Me_2CO$ and $[\{Cu(PPh_3)_2(4\text{-}MeC_6H_4NCN)\}_2]$ are also presented and compared with previously reported halide and pseudohalide complexes.



X = H, 4-Cl, 3-Cl, 4-Br, 4-F, 4-Me or 4-MeO

Experimental

Infrared spectra were recorded on a Pye Unicam SP3-300 spectrometer. Solid-state cross-polarisation magic-angle-spinning (CP-MAS) ^{31}P NMR spectra were obtained at room temperature on a Bruker CXP-300 spectrometer at 121.47 MHz as described previously[4] using ^1H–^{31}P cross-polarisation with radio-frequency fields of 8 and 20 G for ^1H and ^{31}P respectively. Chemical shifts were referenced to solid triphenylphosphine [$\delta(PPh_3)$ −9.9 ppm with respect to 85% H_3PO_4]. Microanalyses (Table 1) were by Professor A. D. Campbell, University of Otago.

* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, xviii–xxii.

Table 1 Analytical and IR spectral data for the complexes (L = XC_6H_4NCN)

Complex	X	Analysis[a] (%) C	H	N	X[d]	ν(CN)[b]/cm^{-1}
$[Cu_2(dppe)_3L_2]$[c]	H	70.2 (70.4)	5.6 (5.6)	4.1 (3.4)		2165, 2126
	4-Cl	67.6 (67.3)	5.3 (5.4)	3.2 (3.1)	4.1 (4.2)	2166, 2140
	3-Cl	67.1 (67.6)	5.0 (5.3)	3.5 (3.2)	4.9 (4.1)	2163, 2139
	4-Br	64.1 (64.3)	5.1 (5.0)	3.0 (3.1)	9.1 (8.3)	2159, 2137
	4-F	67.3 (68.7)	5.6 (5.4)	3.3 (3.3)	2.0 (2.2)	2177, 2132
$[\{Cu(PPh_3)_2L\}_2]$	H	72.95 (73.3)	5.35 (5.0)	4.0 (4.0)		2163
	4-Cl	69.9 (69.8)	4.8 (4.6)	3.8 (3.8)	5.0 (4.8)	2173
	3-Cl	69.8 (69.8)	4.9 (4.6)	3.7 (3.8)	4.9 (4.8)	2153
	4-Br	65.6 (65.9)	4.6 (4.4)	3.3 (3.6)		2174
	4-F	71.4 (71.1)	4.7 (5.0)	3.9 (4.0)		2161
	4-Me	73.5 (73.5)	5.35 (5.2)	3.9 (3.9)		2174, 2167
	4-MeO	71.6 (71.9)	5.3 (5.1)	3.7 (3.8)		2167

[a] Calculated values in parentheses. [b] Recorded as Nujol mulls. [c] These compounds contain two molecules of Me_2CO per dinuclear molecule. [d] X = Halogen.

Preparation of the Phenylcyanamides.—These were prepared from the appropriate anilines *via* phenylthioureas following the literature method[5] for the unsubstituted compound or directly using cyanogen bromide.[6] M.p. and IR data have been listed previously.[2] A typical preparation using cyanogen bromide follows.

Preparation of 4-methoxyphenylcyanamide. To a stirred, ice-cooled solution of 4-methoxyaniline (23.0 g, 0.19 mol) dissolved in ethanol (50 cm^3)–water (50 cm^3) was added dropwise cyanogen bromide (10.6 g, 0.10 mol) in ethanol (50 cm^3). The reaction mixture was stirred for a further 30 min and then poured slowly into water (500 cm^3). The resulting precipitate was dissolved in chloroform and the solution filtered and dried over anhydrous magnesium sulphate. Pentane was added to initiate crystallisation of the product. M.p. 87–89 °C, yield 5.3 g (36%).

Preparation of the Copper Complexes.—$[Cu_2(dppe)_3L_2]$·2-Me_2CO (L = XC_6H_4NCN; X = H, 4-Cl, 3-Cl, 4-Br *or* 4-F). The appropriate phenylcyanamide, HL (1 mmol), in acetone (15 cm^3) was deprotonated by reaction with sodium (0.02 g, 1 mmol) dissolved in ethanol (5 cm^3). The resulting solution was added to $[Cu(MeCN)_4]ClO_4$[7] (0.33 g, 1 mmol) and dppe (0.60 g, 1.5 mmol) in acetone (30 cm^3). After immediate filtration the product began to crystallise. It was washed with acetone and air dried. Yields 70–80%.

$[\{Cu(PPh_3)_2L\}_2]$ (L = XC_6H_4NCN; X = H, 4-Cl, 3-Cl, 4-Br, 4-F, 4-Me *or* 4-MeO). The appropriate phenylcyanamide (2 mmol) was deprotonated by reaction with sodium (0.05 g, 2 mmol) in ethanol (10 cm^3). The resulting solution was added to $[Cu(PPh_3)_2(NO_3)]$ (1.30 g, 2 mmol) in CH_2Cl_2 (40 cm^3) and the reaction mixture heated gently for 30 min. The precipitate of $NaNO_3$ which formed was filtered off and hexane added to the filtrate until crystallisation of the product began. It was washed with hexane and dried *in vacuo*. Yields 30–75%.

Crystal Structure Determination of μ-1,2-*Bis(diphenylphosphino)ethane*-κP:κP′-*bis*{[1,2-*bis(diphenylphosphino)ethane*-κ^2P,P′](4-*chlorophenylcyanamido*-κN^3)*copper*(I)}–*Acetone* (1/2), $[Cu_2(dppe)_3(4\text{-}ClC_6H_4NCN)_2]$·2$Me_2CO$.—Colourless plate-like crystals of the complex were obtained by the slow evaporation of an acetone solution.

Crystal data. $C_{92}H_{80}Cl_2Cu_2N_4P_6$·$C_6H_{12}O_2$, M = 1740, orthorhombic, space group *Pbca*, a = 22.397(14), b = 18.970(7), c = 20.341(5) Å, U = 8642(8) Å^3 (by least-squares refinement on diffractometer angles of 16 automatically centred reflections), Mo-Kα radiation, λ = 0.710 69 Å, D_m = 1.31 g cm^{-3}, Z = 4, D_c = 1.34 g cm^{-3}, F(000) = 3624. Crystal dimensions 0.54 × 0.40 × 0.20 mm, μ(Mo-Kα) = 6.64 cm^{-1}.

Data collection and processing. Nicolet R3M diffractometer at 153 K, ω–2θ scan mode with graphite-monochromated Mo-Kα radiation, scan range 1.2°, scan speed 4.88° min^{-1}, 6407 reflections measured ($5 \leqslant 2\theta \leqslant 45°$, h,k,l), 5628 unique [merging R = 0.016 after data corrected for Lorentz and polarisation effects and absorption correction applied (maximum, minimum transmission factors = 0.774, 0.722)] giving 3604 with $I > 3\sigma(I)$.

Structure analysis and refinement. Patterson and Fourier methods. Full-matrix least-squares refinement with anisotropic thermal motion assumed for all non-hydrogen atoms. Hydrogen atoms in calculated positions (C–H 1.08 Å). The lattice acetone molecules were extensively disordered and could not be refined satisfactorily; in the final model acetone was treated as two partially overlapped half-weight molecules. At convergence R and R' were 0.047 and 0.048 respectively for the 495 parameters refined. The function minimised was $\Sigma w(|F_o| - |F_c|)^2$ with $w = 1.8619/[\sigma^2(F) + 0.000\,398F^2]$. Computations were with the SHELX 76[8] and SHELXTL 86[9] programs, with atomic scattering factors as given therein. Positional parameters for non-hydrogen atoms are given in Table 2, and selected bond lengths and angles in Table 4.

Crystal Structure Determination of Bis(μ-4-*methylphenylcyanamido*)-1:2κ^{2}N^1:N^3; 1:2κ^{2}N^3:N^1-*bis*[*bis*(*triphenylphosphine*-κP)*copper*(I)], $[\{Cu(PPh_3)_2(4\text{-}MeC_6H_4NCN)\}_2]$.—Colourless crystals of the complex were obtained from dichloromethane solution.

Crystal data. $C_{88}H_{74}Cu_2N_4P_4$, M = 1438.6, monoclinic,

Table 2 Fractional atomic coordinates for $[Cu_2(dppe)_3(4\text{-}ClC_6H_4NCN)_2]\cdot 2Me_2CO$ with estimated standard deviations (e.s.d.s) in parentheses *

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Cu	0.029 81(3)	0.170 91(3)	0.048 32(3)	C(32)	−0.108 5(3)	0.213 8(3)	0.148 8(3)
P(1)	0.040 90(7)	0.097 56(7)	−0.039 74(7)	C(33)	−0.143 9(3)	0.231 0(4)	0.202 7(3)
P(2)	0.083 39(6)	0.274 06(8)	0.055 90(7)	C(34)	−0.169 9(3)	0.296 3(4)	0.208 6(3)
P(3)	−0.054 78(6)	0.235 59(8)	0.028 59(7)	C(35)	−0.160 7(3)	0.346 1(4)	0.158 9(3)
Cl	−0.116 60(8)	0.023 01(9)	0.456 12(8)	C(36)	−0.126 1(3)	0.329 3(3)	0.104 4(3)
N(1)	0.033 7(2)	0.121 6(2)	0.133 3(2)	C(111)	0.020 2(2)	0.135 3(3)	−0.118 9(2)
N(2)	0.058 4(2)	0.071 0(2)	0.241 8(2)	C(112)	−0.016 3(3)	0.102 2(3)	−0.164 3(3)
C(1)	0.042 4(3)	0.098 7(3)	0.185 0(3)	C(113)	−0.028 2(3)	0.134 4(4)	−0.224 6(4)
C(2)	0.015 1(3)	0.060 7(3)	0.289 5(3)	C(114)	−0.005 2(3)	0.199 7(4)	−0.239 3(3)
C(3)	0.033 2(3)	0.030 7(3)	0.350 2(3)	C(115)	0.030 8(3)	0.233 1(3)	−0.194 0(3)
C(4)	−0.006 0(3)	0.019 8(3)	0.400 2(3)	C(116)	0.043 9(3)	0.201 0(3)	−0.134 4(3)
C(5)	−0.065 5(3)	0.037 8(3)	0.392 0(3)	C(211)	0.119 9(2)	0.295 7(3)	0.133 7(3)
C(6)	−0.085 1(3)	0.067 8(3)	0.334 4(3)	C(212)	0.122 0(3)	0.363 7(3)	0.158 4(3)
C(7)	−0.044 5(3)	0.079 2(3)	0.283 1(3)	C(213)	0.147 8(3)	0.377 9(4)	0.219 1(3)
C(8)	−0.006 7(2)	0.019 7(3)	−0.032 0(3)	C(214)	0.173 4(3)	0.323 0(4)	0.255 1(3)
C(9)	0.026 1(2)	0.342 8(3)	0.046 6(3)	C(215)	0.172 9(3)	0.255 8(4)	0.229 9(3)
C(10)	−0.023 2(2)	0.318 7(3)	−0.000 6(3)	C(216)	0.145 1(2)	0.241 4(3)	0.169 7(3)
C(11)	0.114 1(3)	0.059 2(3)	−0.057 8(3)	C(311)	−0.113 5(2)	0.213 4(3)	−0.029 8(2)
C(12)	0.161 5(3)	0.077 0(4)	−0.017 6(4)	C(312)	−0.140 6(3)	0.147 8(3)	−0.022 8(3)
C(13)	0.218 3(3)	0.049 9(5)	−0.031 5(6)	C(313)	−0.189 0(3)	0.129 2(3)	−0.063 4(3)
C(14)	0.226 9(4)	0.007 2(5)	−0.083 6(6)	C(314)	−0.209 5(3)	0.175 3(4)	−0.110 2(3)
C(15)	0.180 0(4)	−0.011 9(4)	−0.123 1(4)	C(315)	−0.181 8(3)	0.240 7(3)	−0.117 3(3)
C(16)	0.122 9(3)	0.015 3(4)	−0.111 1(3)	C(316)	−0.134 1(2)	0.259 1(3)	−0.078 5(3)
C(21)	0.138 4(2)	0.296 4(3)	−0.007 1(3)	C(A1)	0.179 2	−0.026 9	0.173 9
C(22)	0.126 9(3)	0.343 4(3)	−0.058 0(3)	C(A2)	0.202 7	−0.004 8	0.228 4
C(23)	0.168 2(3)	0.353 3(3)	−0.108 7(3)	C(A3)	0.234 7	0.052 9	0.189 8
C(24)	0.221 4(3)	0.317 4(4)	−0.107 8(3)	C(A4)	0.219 7	0.066 5	0.131 3
C(25)	0.233 7(3)	0.271 1(5)	−0.057 4(4)	O(A1)	0.173 8	0.031 9	0.271 7
C(26)	0.192 6(3)	0.260 5(4)	−0.007 0(3)	O(A2)	0.267 1	0.095 8	0.231 1
C(31)	−0.099 3(2)	0.263 2(3)	0.099 7(3)				

* Coordinates are related to the other half of the dinuclear molecule by symmetry. Atoms C(A1) to O(A2) are for the disordered acetone; C(A2) and C(A3) are full weight, the others are half weight.

Table 3 Fractional atomic coordinates for $[\{Cu(PPh_3)_2(4\text{-}MeC_6H_4NCN)\}_2]$ with e.s.d.s in parentheses

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Cu	0.378 72(2)	0.108 87(3)	0.038 89(2)	C(131)	0.375 5(2)	0.361 8(2)	0.085 2(2)
P(1)	0.424 82(5)	0.266 00(5)	0.037 99(4)	C(132)	0.344 8(3)	0.448 3(3)	0.052 9(3)
P(2)	0.230 82(4)	0.069 23(5)	0.028 49(4)	C(133)	0.309 7(4)	0.518 6(4)	0.091 4(4)
N(1)	0.573 6(2)	0.936 9(2)	0.050 6(1)	C(134)	0.301 6(4)	0.502 3(4)	0.163 5(4)
N(2)	0.468 0(2)	0.023 2(2)	0.112 7(1)	C(135)	0.332 6(4)	0.415 8(4)	0.197 1(3)
C(1)	0.525 0(2)	0.975 7(2)	0.082 2(1)	C(136)	0.369 7(3)	0.347 8(3)	0.157 3(2)
C(2)	0.486 6(2)	0.031 3(2)	0.188 8(1)	C(211)	0.208 8(2)	−0.059 1(2)	0.042 3(2)
C(3)	0.425 1(2)	0.079 6(3)	0.222 6(2)	C(212)	0.134 3(2)	−0.107 7(2)	0.000 7(2)
C(4)	0.443 4(3)	0.092 9(4)	0.297 6(2)	C(213)	0.120 1(3)	−0.204 4(3)	0.013 9(3)
C(5)	0.520 2(4)	0.055 7(4)	0.341 3(2)	C(214)	0.178 3(3)	−0.253 1(3)	0.067 6(3)
C(6)	0.579 9(4)	0.006 1(5)	0.307 6(2)	C(215)	0.252 7(4)	−0.204 8(3)	0.110 0(3)
C(7)	0.563 4(3)	−0.006 4(4)	0.233 1(2)	C(216)	0.267 8(3)	−0.108 7(3)	0.096 0(3)
C(8)	0.545 3(6)	0.077 2(6)	0.424 0(3)	C(221)	0.167 3(2)	0.091 9(2)	−0.063 6(2)
C(111)	0.546 4(2)	0.286 5(2)	0.068 9(2)	C(222)	0.082 8(2)	0.134 3(3)	−0.078 8(2)
C(112)	0.603 8(2)	0.209 3(3)	0.069 1(3)	C(223)	0.041 8(3)	0.154 1(4)	−0.150 0(3)
C(113)	0.698 2(3)	0.220 6(3)	0.092 0(3)	C(224)	0.082 3(3)	0.128 9(4)	−0.207 1(2)
C(114)	0.733 3(2)	0.310 5(3)	0.114 4(3)	C(225)	0.164 6(3)	0.083 5(4)	−0.192 9(2)
C(115)	0.675 0(3)	0.388 1(3)	0.114 0(2)	C(226)	0.207 4(2)	0.065 1(3)	−0.120 7(2)
C(116)	0.582 0(2)	0.376 4(2)	0.091 6(2)	C(231)	0.162 4(2)	0.129 3(2)	0.086 5(2)
C(121)	0.404 4(2)	0.306 0(2)	−0.056 4(2)	C(232)	0.104 1(3)	0.078 8(3)	0.122 6(2)
C(122)	0.317 8(3)	0.294 5(4)	−0.098 4(3)	C(233)	0.051 3(4)	0.128 6(4)	0.164 8(3)
C(123)	0.299 3(4)	0.319 5(4)	−0.172 0(3)	C(234)	0.059 9(4)	0.227 3(5)	0.171 4(3)
C(124)	0.369 8(5)	0.353 4(4)	−0.203 6(3)	C(235)	0.116 8(3)	0.279 2(4)	0.134 3(3)
C(125)	0.451 6(5)	0.371 2(5)	−0.162 5(3)	C(236)	0.167 8(3)	0.229 5(3)	0.091 9(3)
C(126)	0.470 7(3)	0.343 5(4)	−0.090 0(2)				

space group $P2_1/n$, a = 15.003(2), b = 13.844(2), c = 18.711(2) Å, β = 101.22(1)°, U = 3812(2) Å^3 (by least-squares refinement of diffractometer angles of 25 automatically centred reflections), Cu-Kα radiation, λ = 1.5418 Å, D_m = 1.24 g cm^{-3}, Z = 2, D_c = 1.25 g cm^{-3}, F(000) 1496. Crystal dimensions 0.30 × 0.40 × 0.30 mm, μ(Cu-Kα) = 18.3 cm^{-1}.

Data collection and processing. Enraf Nonius CAD-4 diffractometer at 293 K, ω–2θ scan mode with Cu-Kα radiation, scan range (1.0 + 0.14tanθ)°, variable scan speed 1.1–8.2° min^{-1}, 8498 reflections measured ($0 \leqslant 2\theta \leqslant 130°$, $\pm h, k, l$). The intensities of three standard reflections were monitored every hour of X-ray exposure time and showed an average total loss of intensity of 10.5%. This loss of intensity was compensated for by applying a linear decay correction (minimum, maximum

Table 4 Selected bond lengths (Å) and angles (°) for $[Cu_2(dppe)_3(4\text{-}ClC_6H_4NCN)_2]\cdot 2Me_2CO$ with e.s.d.s in parentheses

Cu–N(1)	1.967(5)	P(1)–C(8)	1.828(6)
Cu–P(1)	2.282(2)	P(2)–C(9)	1.839(5)
Cu–P(2)	2.301(2)	P(3)–C(10)	1.827(5)
Cu–P(3)	2.293(2)	C(8)–C(8′)	1.532(10)
N(1)–C(1)	1.156(8)	C(9)–C(10)	1.533(7)
N(2)–C(1)	1.319(8)	Cu · · · Cu′	6.906(2)
N(2)–C(2)	1.385(7)		
N(1)–Cu–P(1)	113.2(1)	Cu–N(1)–C(1)	170.7(5)
N(1)–Cu–P(2)	108.8(1)	N(1)–C(1)–N(2)	173.5(6)
N(1)–Cu–P(3)	116.4(1)	C(1)–N(2)–C(2)	118.6(5)
P(1)–Cu–P(2)	121.0(1)	N(2)–C(2)–C(3)	117.7(5)
P(1)–Cu–P(3)	106.2(1)	N(2)–C(2)–C(7)	124.9(5)
P(2)–Cu–P(3)	89.3(1)	P(1)–C(8)–C(8′)	110.6(4)
Cu–P(1)–C(8)	111.2(2)	P(2)–C(9)–C(10)	110.8(4)
Cu–P(2)–C(9)	103.4(2)	P(3)–C(10)–C(9)	109.4(4)
Cu–P(3)–C(10)	101.5(2)		

Table 5 Selected bond lengths (Å) and angles (°) for $[\{Cu(PPh_3)_2(4\text{-}MeC_6H_4NCN)\}_2]$ with e.s.d.s in parentheses

Cu–N(1′)	2.045(2)	N(1)–C(1)	1.152(4)
Cu–N(2)	2.095(2)	C(1)–N(2)	1.296(4)
Cu–P(1)	2.284(1)	N(2)–C(2)	1.402(3)
Cu–P(2)	2.257(1)	Cu · · · Cu′	5.149(1)
N(1′)–Cu–N(2)	94.7(1)	C(1)–N(1)–Cu′	156.8(2)
P(1)–Cu–P(2)	121.7(1)	N(1)–C(1)–N(2)	175.2(3)
P(1)–Cu–N(1′)	97.7(1)	Cu–N(2)–C(1)	112.9(4)
P(1)–Cu–N(2)	112.9(1)	Cu–N(2)–C(2)	126.8(2)
P(2)–Cu–N(1′)	110.4(1)	C(1)–N(2)–C(2)	118.0(2)
P(2)–Cu–N(2)	114.3(1)		

correction = 1.000, 1.057). Of the reflections measured, 7850 were unique (merging $R = 0.042$ after data corrected for Lorentz and polarisation effects, no absorption corrections applied) giving 6148 reflections with $I > 3\sigma(I)$.

Structure analysis and refinement. Patterson and Fourier methods. Full-matrix least-squares refinement with anisotropic thermal motion assumed for all non-hydrogen atoms. Hydrogen atoms in calculated positions (C–H 1.08 Å). At convergence R and R' were 0.051 and 0.060 respectively for the 450 parameters refined. The weighting function minimised was $\Sigma w(|F_o| - |F_c|)^2$ with $w = 2.7498/[\sigma^2(F) + 0.001\,884F^2]$. Positional parameters for non-hydrogen atoms are given in Table 3, and selected bond lengths and angles in Table 5.

For both structures additional material available from the Cambridge Crystallographic Data Centre comprises hydrogen atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

The phenylcyanamidocopper(I) complexes, $[Cu_2(dppe)_3L_2]\cdot 2Me_2CO$ (L = XC_4H_6NCN; X = H, 4-Cl, 3-Cl, 4-Br or 4-F), were prepared from the reaction of the appropriate deprotonated phenylcyanamide with $[Cu(MeCN)_4]ClO_4$ in the presence of dppe, whereas the triphenylphosphine coligand complexes, $[\{Cu(PPh_3)_2L\}_2]$ (L = XC_6H_4NCN; X = H, 4-Cl, 3-Cl, 4-Br, 4-F, 4-Me or 4-MeO), were synthesised by anion displacement from $[Cu(PPh_3)_2(NO_3)]$. The complexes were obtained as air-stable crystalline solids, although a number of them were light sensitive, becoming blue or green on standing. The dinuclear formulations for both series of compounds are proposed on the basis of the single crystal X-ray structures for $[Cu_2(dppe)_3(4\text{-}ClC_6H_4NCN)_2]\cdot 2Me_2CO$ and $[\{Cu(PPh_3)_2(4\text{-}MeC_6H_4NCN)\}_2]$ (see below). In each case the reaction products were independent of the copper-to-phosphine ratio used. For example, attempts to replace the anions in the tris(triphenylphosphine) complexes, $[Cu(PPh_3)_3X]$ (X = BF_4 or NO_3), with $[4\text{-}MeOC_6H_4NCN]^-$ yielded only the complex $[\{Cu(PPh_3)_2(4\text{-}MeOC_6H_4NCN)\}_2]$. The dppe complexes join a class of dinuclear copper(I) compounds of common stoichiometry $[Cu_2(dppe)_3A_2]$, where A is a monoanion such as Cl,[10] N_3,[11] OPh,[12] 2-(5-perfluoromethyltetrazolate)[13] or benzo-1,3-thiazole-2-thiolate.[14]

Crystal Structure of $[Cu_2(dppe)_3(4\text{-}ClC_6H_4NCN)_2]\cdot 2Me_2CO$.—The complex contains centrosymmetric dinuclear molecules with the centre of symmetry lying between the two methylene carbons of the bridging dppe ligand. There are two disordered acetone solvate molecules associated with each dinuclear molecule. A view of the complex is shown in Fig. 1 and selected bond lengths and angles are given in Table 4.

Each copper atom is in a distorted tetrahedral co-ordination environment, being bound to a cyano nitrogen from the monodentate 4-chlorophenylcyanamide (as in **I**), two phosphorus atoms from the chelating dppe ligand and one phosphorus from the bridging dppe ligand. The Cu–N(1) bond length of 1.967(5) Å is significantly less than the mean value of Cu^I–N distances (2.04 Å) for four-co-ordinate copper(I) complexes and in fact is similar to the mean Cu^I–N distance (1.967 Å) given for three-co-ordinate copper(I).[15] The Cu–N(1) distance is also shorter than the Cu–N distance in the structurally related azido complex $[Cu_2(dppe)_3(N_3)_2]$ [Cu–N 2.040(13) Å].[11] The Cu–P distances (mean 2.292 Å) are comparable with those found in other copper(I) complexes containing three Cu–P bonds.[10–14] Deviation from an ideal tetrahedral geometry arises from the geometrical constraints imposed by the small bite angle [P(2)–Cu–P(3) 89.3(1)°]. The N(1)–Cu–P(2) bond angle at 108.8(1)° is close to tetrahedral whereas the N(1)–Cu–P(1) and N(1)–Cu–P(3) bond angles are larger [113.2(1) and 116.4(1)° respectively]. This suggests that the geometry about the copper atom can be described as a distortion from tetrahedral in which the dppe ligands are pushed away from the $[4\text{-}ClC_6H_4NCN]^-$ ligand.

The 4-chlorophenylcyanamido ligand is terminally bound in the same fashion as that found for one of the $[PhNCN]^-$ ligands in the copper(II) complex $[\{Cu(bipy)(PhNCN)_2\}_2]$ (bipy = 2,2′-bipyridine). The main difference is that the Cu–N(1)–C(1) bond angle, 170.7(5)°, in $[Cu_2(dppe)_3(4\text{-}ClC_6H_4NCN)_2]$ indicates an approximately linear end-on co-ordination for the cyanamide moiety whereas in the copper(II) complex the analogous angle is considerably smaller (mean value 140.8°).[2] The N(1)–C(1), C(1)–N(2) and N(2)–C(2) bond lengths are 1.156(8), 1.319(8) and 1.385(7) Å respectively indicating that the resonance structure **IVa** predominates in the bond description for the $[4\text{-}ClC_6H_4NCN]^-$ anion, although the contribution from structure **IVb** may not be negligible. Thus the value of 1.156(8) Å compares closely with that expected for a CN triple bond (1.16 Å)[16] and 1.319(8) Å is closer to the value expected for a CN double (1.29 Å) rather than a single bond (1.47 Å).[16] The phenyl ring of the $[4\text{-}ClC_6H_4NCN]^-$ ligand is planar (within the limits of experimental error) and the substituent chlorine atom is coplanar with this ring.

Crystal Structure of $[\{Cu(PPh_3)_2(4\text{-}MeC_6H_4NCN)\}_2]$.—The complex is a centrosymmetric, 4-methylphenylcyanamide-bridged dimer with the cyanamide bonding in mode **II**. The structure is shown in Fig. 2 and selected bond parameters are given in Table 5.

Each copper atom has a distorted tetrahedral co-ordination sphere consisting of two triphenylphosphine phosphorus atoms, a terminal cyano nitrogen from the $[4\text{-}MeC_6H_4NCN]^-$ ligand and an amido nitrogen from the symmetry related $[4\text{-}MeC_6H_4NCN]^-$ ligand. Angles around the copper atom range from 94.7(1) to 121.7(1)°, with the largest being the P(1)–Cu–P(2) angle. For tetrahedral bis(triphenylphosphine)-copper(I) centres, P–Cu–P angles of greater than 120° are

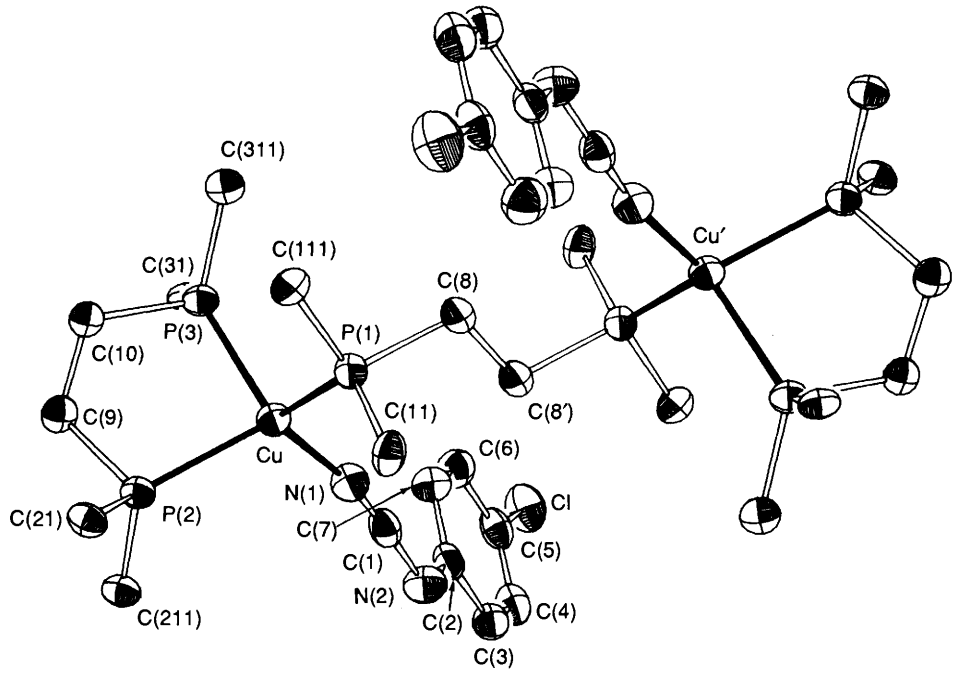


Fig. 1 The structure of the complex $[Cu_2(dppe)_3(4\text{-}ClC_6H_4NCN)_2]$, showing the numbering system used. Ellipsoids are drawn at the 50% probability level. Only the first atoms of the phenyl rings of the dppe ligands are shown, the remainder having been omitted for clarity

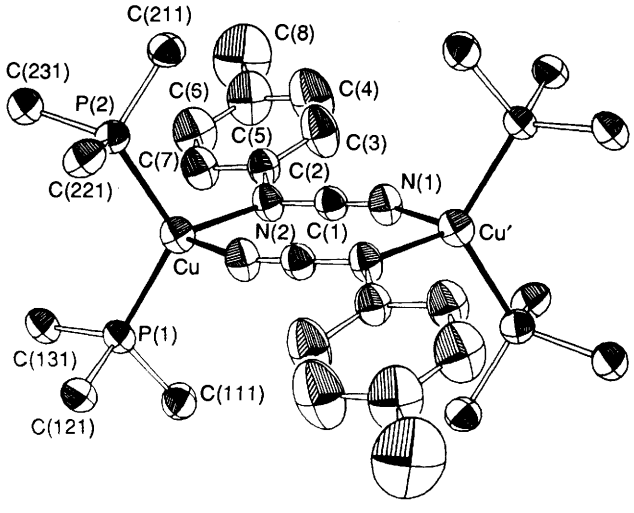


Fig. 2 The structure of the complex $[\{Cu(PPh_3)_2(4\text{-}MeC_6H_4NCN)\}_2]$, showing the numbering system used. Ellipsoids are drawn at the 50% probability level. Only the first atoms of the phenyl rings of the PPh_3 ligands are shown, the remainder having been omitted for clarity

commonly found (for 50 structures reported in the Cambridge Crystallographic Data File, 1987, the mean P–Cu–P angle is 124.7°) and must arise in part from repulsions between the phenyl rings of the PPh_3 ligands. The copper to cyano nitrogen distance, Cu–N(1′) at 2.045(2) Å, is the same as the average Cu–N distance (2.04 Å) quoted for four-co-ordinate copper(I) complexes[15] and is longer than the copper–cyano nitrogen distance in $[Cu_2(dppe)_3(4\text{-}ClC_6H_4NCN)_2]\cdot 2Me_2CO$ [1.967(5) Å].

The longer copper–cyano nitrogen distance found in $[\{Cu(PPh_3)_2(4\text{-}MeC_6H_4NCN)\}_2]$ can be correlated with the fact that the deviation of the Cu′–N(1)–C(1) bond angle from linearity is considerably greater [156.8(2) *cf.* 170.7(5)°]. The copper to amido nitrogen distance, Cu–N(2) at 2.095(2) Å, is longer than Cu–N(1′). The Cu–P distances [2.284(1) and 2.257(1) Å] are close to the average value of 2.26 Å found for complexes of this type (Cambridge Crystallographic Data File, 1987).

The 4-methylphenylcyanamido ligand bond parameters are similar to those found for the bridging $[PhNCN]^-$ ligand in the copper(II) complex $[\{Cu(bipy)(PhNCN)_2\}_2]$,[2] which also is μ-1,3-bridged. The N(1)–C(1), C(1)–N(2) and N(2)–C(2) bond distances [1.152(4), 1.296(4) and 1.402(3) Å respectively] again point to the importance of the resonance structure **IVa**. The phenyl ring is essentially planar but the methyl group is displaced by 0.1 Å from the plane.

Spectroscopic Studies.—IR spectra. The IR spectra of the complexes (Table 1) all show intense bands in the 2125–2175 cm^{-1} range assignable to ν(CN) stretching frequencies. As found for the phenylcyanamidocopper(II) complexes,[2] there does not appear to be a correlation between the ν(CN) frequencies and the nature of the substituent on the phenyl ring. From the limited amount of structural data it does not appear that it is possible to distinguish between the different bonding modes **I**, **II** or **III** by IR spectroscopy. All the dppe complexes displayed a strong band at *ca.* 1710 cm^{-1} consistent with the ν(CO) frequency of acetone.

Solid-state ^{31}P *NMR spectra.* The CP-MAS ^{31}P NMR spectra for the complexes $[\{Cu(PPh_3)_2L\}_2]$ (L = XC_6H_4NCN; X = 4-Me, 4-Cl or H) are shown in Fig. 3 and chemical shift and line spacing data for each compound tabulated in Table 6. The spectrum for each complex consists of two well resolved quartets of doublets, arising from each of the crystallographically independent phosphorus nuclei. The doublet structure is a consequence of homonuclear phosphorus–phosphorus two-bond coupling with a value for $^2J(P^1\text{–}P^2)$ in each compound of 120 Hz. This is the first such coupling observed in solid-state copper(I) phosphine complexes and is comparable with values reported for $[HgX_2(PPh_3)_2]$ (X = halide).[17] As described previously,[18,19] the quartet structure is due to spin–spin coupling of the phosphorus nuclei to the copper nucleus (^{63}Cu, ^{65}Cu; $I = \frac{3}{2}$). Nuclear quadrupole coupling interactions between the copper nucleus and its surroundings result in unequal line spacings, $\Delta\nu_i$, between the four lines of each quartet with the asymmetry in these line spacings represented by the ratio $\Delta\nu_3/\Delta\nu_1$. This ratio is exactly

Table 6 Solid-state CP-MAS ^{31}P NMR parameters for $[\{Cu(PPh_3)_2L\}_2]$ ($L = XC_6H_4NCN$)*

X	δ_1	δ_2	δ_3	δ_4	$\langle\delta\rangle$	$\Delta\nu_1$	$\Delta\nu_2$	$\Delta\nu_3$	$\langle\Delta\nu_i\rangle$	$\Delta\nu_3/\Delta\nu_1$
4-*Me*	20.63	12.26	3.42	−5.47	7.7	1.017	1.073	1.080	1.06	1.06
	19.86	11.29	2.44	−6.49	6.8	1.041	1.075	1.085	1.07	1.04
	16.15	6.25	−4.01	−14.49	1.0	1.202	1.246	1.273	1.24	1.06
	15.14	5.25	−5.02	−15.52	0.0	1.201	1.247	1.275	1.24	1.07
4-Cl	21.67	13.06	4.08	−5.01	8.5	1.046	1.091	1.104	1.08	1.06
	20.70	12.09	3.11	−5.99	7.5	1.046	1.091	1.105	1.08	1.06
	17.00	7.11	−3.22	−13.81	1.8	1.201	1.255	1.286	1.25	1.07
	16.00	6.19	−4.18	−14.79	0.8	1.192	1.260	1.289	1.25	1.08
H	17.38	8.94	0.28	−8.42	4.5	1.025	1.052	1.057	1.04	1.03
	16.30	7.89	−0.77	−9.45	3.5	1.022	1.052	1.054	1.04	1.03
	16.30	6.25	−4.18	−14.95	0.9	1.221	1.227	1.308	1.25	1.07
	15.12	5.20	−5.22	−16.02	−0.2	1.205	1.266	1.312	1.26	1.09

* δ_i are the chemical shifts (ppm), $\langle\delta\rangle$ is the average chemical shift for each quartet, $\Delta\nu_i$ is the splitting in kHz between each of the four peaks of the quartet and $\langle\Delta\nu_i\rangle$ is the average of $\Delta\nu_i$ for each quartet.

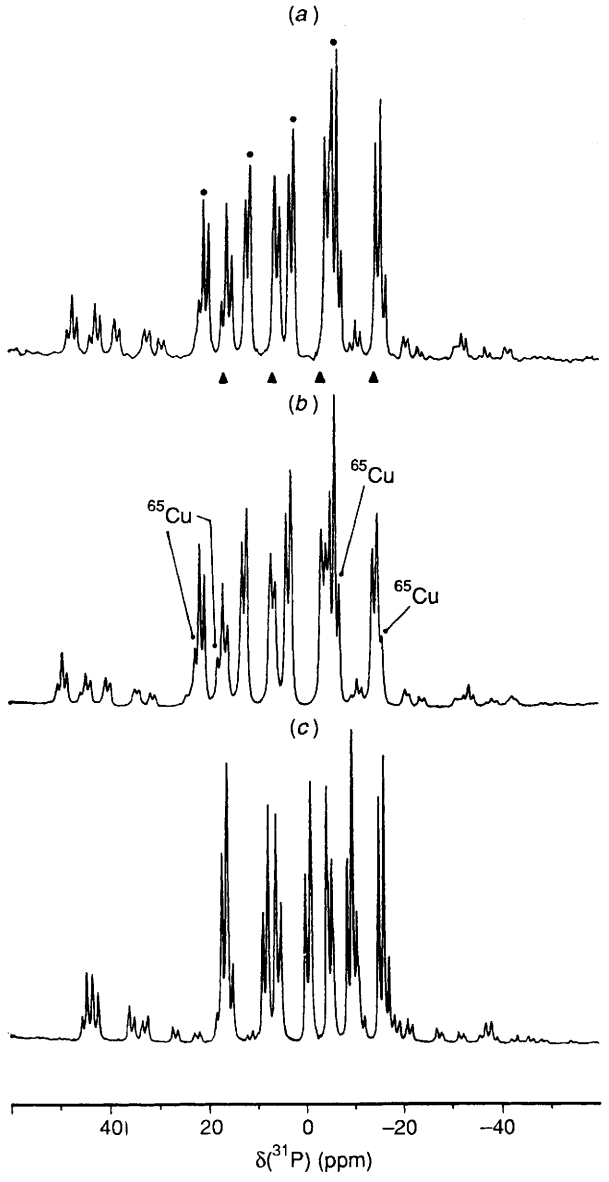


Fig. 3 Solid-state CP-MAS ^{31}P NMR spectra of $[\{Cu(PPh_3)_2L\}_2]$, L = (*a*) $4\text{-}MeC_6H_4NCN$, (*b*) $4\text{-}ClC_6H_4NCN$ and (*c*) PhNCN. For (*a*) ● indicates the quartet of doublets assigned to P(1) and ▲ the quartet assigned to P(2). The spinning side bands observed on either side of the main envelope indicate the existence of considerable ^{31}P chemical shift anisotropy

1.0 for copper atoms in a symmetrical tetrahedral environment and is greater than 1.0 for lower symmetry. The average line spacings $\langle\Delta\nu_i\rangle$ are generally inversely proportional to the Cu–P distances and therefore increase with the numbers of co-ordinated triphenylphosphine molecules. Values in the ranges 1.6–1.8, 1.2–1.3 and 0.9–1.0 kHz are usually found for one, two and three molecules respectively.[19]

The spectra of the $[4\text{-}MeC_6H_4NCN]^-$ and $[4\text{-}ClC_6H_4NCN]^-$ compounds are essentially identical, implying similar crystal lattices for both compounds. Values for $\Delta\nu_3/\Delta\nu_1$ of 1.03–1.06 are indicative of four-co-ordinate, nearly tetrahedral co-ordination sites for the copper nuclei, consistent with the structural results. However, two distinctly different line spacings are observed with average values of 1.07 and 1.25 kHz respectively. The Cu–P distances of 2.284(1) Å for Cu–P(1) and 2.257(1) Å for Cu–P(2) in the $[4\text{-}MeC_6H_4NCN]^-$ compound support the assignment of the quartet ($\langle\delta\rangle$ = 7.7, 6.8 ppm) with the smaller spacing to P(1) and the upfield quartet ($\langle\delta\rangle$ = 1.0, 0.0 ppm) to P(2). The spectrum of the unsubstituted $[PhNCN]^-$ compound is similar, with four distinct quartets. The average chemical shift of the first pair of quartets is, however, shifted *ca.* 3 ppm upfield to 3.5, 4.5 ppm, suggesting a variation in the lattice structure of this compound from that found for the $[4\text{-}MeC_6H_4NCN]^-$ and $[4\text{-}ClC_6H_4NCN]^-$ compounds.

Comparison with Pseudohalides.—Their ambidentate nature and ability to act as bridging ligands are important features of the pseudohalides.[3] That phenylcyanamides behave similarly is emphasized by the fact that there is an exact parallel between the copper(I) complexes reported in this paper and those which have been reported for the azide ion. Hence both $[Cu_2(dppe)_3(4\text{-}ClC_6H_4NCN)_2]\cdot 2Me_2CO$ and $[Cu_2(dppe)_3(N_3)_2]$[11] contain centrosymmetric dinuclear molecules with terminally co-ordinated $[4\text{-}ClC_6H_4NCN]^-$ and azido ligands respectively, and both $[\{Cu(PPh_3)_2(4\text{-}MeC_6H_4NCN)\}_2]$ and $[\{Cu(PPh_3)_2(N_3)\}_2]$[20] contain μ-1,3-anionic ligands (as in mode **II**). The parallel continues for copper(II) in that both $[\{Cu(bipy)(PhNCN)_2\}_2]$ and $[\{Cu(tmen)(N_3)_2\}_2]$ (tmen = *N,N,N',N'*-tetramethylethylenediamine)[21] contain terminal and unsymmetrically μ-1,3-bridged anions (mode **II**). An example of μ-1,1-bridging for the azide ion in a copper(II) complex is seen in $[\{CuL_2(N_3)\}_2][ClO_4]_2$ (L = 4-*tert*-butylpyridine),[22] thus providing an analogy with the phenylcyanamide ligand in $[\{Cu(phen)(3\text{-}ClC_6H_4NCN)(CH_3CO_2)\}_2]\cdot 2H_2O$ (phen = 1,10-phenanthroline).[2] A related result concerns the series of complex anions $[ML_4]^{2-}$ (M = Co, Ni, Cu or Zn; L = 2-chloro- or 2,4,6-trichloro-phenylcyanamide ion) prepared by Hollebone and Nyholm.[23] On the basis of magnetic and electronic spectral data, four-co-ordinate tetrahedral structures

were proposed similar to those formed by halides and pseudohalides.

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