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Structure of Chloro[1,1,1-tris(diphenylphosphinomethyl)ethane]copper(I)

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Abstract. $[CuCl(C_{41}H_{39}P_3)]$, $M_r = 723.6$, orthorhombic, $Pna2_1$, $a = 20.704\ (16)$, $b = 10.287\ (6)$, $c = 16.982\ (8)$ Å, $V = 3617\ (4)$ Å^3, $Z = 4$, $D_x = 1.329$ g cm^{-3}, $\lambda(\text{Mo}\ K\alpha) = 0.71073$ Å, $\mu = 8.37$ cm^{-1}, $F(000) = 1504$, $T = 296$ K, $R = 0.050$ for 1754 independent observed reflections with $I > 2.0\sigma(I)$. The copper(I) complex, $Cu(p_3)Cl$, of the tridentate ligand 1,1,1-tris(diphenylphosphinomethyl)ethane, $[(C_6H_5)_2PCH_2]_3CCH_3$ (p_3), has been prepared and characterized by complete X-ray crystal structure analysis. The ligand is tridentate. Angles at Cu range from 92 to 126°.

Introduction. Arylphosphine complexes of copper(I) halides have shown excellent properties as photochemical triplet sensitizers (Fife, Moore & Morse, 1984*a*, 1985). However, the monodentate ligands have shown considerable ligand dissociation in solution (Fife, Moore & Morse, 1984*b*). The complexes that were not fully coordinated lost considerable efficiency as sensitizers; tridentate ligands seemed to offer a possibility of solution stability. The [1,1,1-tris(diphenylphosphinomethyl)ethane]copper(I) complex, $[(\{(C_6H_5)_2PCH_2\}_3CCH_3)CuCl]$, has been synthesized previously with a suggested probable pseudotetrahedral structure (Sacconi & Midollini, 1972). This suggested structure was based on spectral data being similar to those of other tetrahedral complexes.

Preliminary photosensitizer results with the $Cu(p_3)Cl$ complex compared to the tris monodentate complex tris(methyldiphenylphosphine)copper(I) chloride shows considerable loss of efficiency as a triplet sensitizer. The strain in the P—Cu—P angles shown in the crystal structure of $Cu(p_3)Cl$ in comparison with the monodentate complex (Gill, Mayerle, Welcker, Lewis, Ucko, Barton, Stowens & Lippard, 1976) may suggest a possible explanation.

Experimental. Chloro[1,1,1-tris(diphenylphosphinomethyl)ethane]copper(I) was prepared as previously described for the monodentate ligands (Fife, Moore & Morse, 1984*b*). The compound crystallizes as colorless thin plates. The specimen selected for X-ray analysis had approximate dimensions 0.02 × 0.40 × 0.40 mm. Data collection: Siemens *R*3*m*/*V* four-circle diffractometer, graphite-monochromated Mo *Kα* radiation; cell parameters refined with 25 strong reflections ($15 < 2\theta < 25°$); ω scan, scan speed 2.93 to 14.63° min^{-1}. The intensities of two standard reflections (040 and 221) showed no significant variations. Of 2642 reflections collected, 1754 independent reflections ($3.5 \leq 2\theta \leq 45°$; $0 \leq h \leq 22$, $0 \leq k \leq 11$, $0 \leq l \leq 18$) with $|F_o| > 4\sigma(F_o)$ were used for the analysis; $R_{\text{int}} = 0.032$; data corrected for Lorentz and polarization effects, face-indexed numerical absorption corrections applied (minimum/maximum transmission 0.7855/0.9826).

All crystallographic calculations were carried out with the Siemens *SHELXTL-Plus* software package (Sheldrick, 1990) on a Digital Equipment VAXStation 3100/30 computer system. The structure was solved by direct methods and refined by full-matrix least-squares techniques. Coordinates for the 46 non-H atoms along with anisotropic thermal parameters for the Cu, P, Cl and five C atoms and isotropic thermal parameters for the remaining 36 phenyl C atoms (235 parameters), and the inclusion of 39 H atoms bonded to C atoms riding in idealized positions yielded $R = 0.050$ and $wR = 0.041$ for 1754 data measured $[|F| > 4\sigma(F)]$ and $R = 0.078$ and $wR = 0.045$ for all 2400 independent reflections within the $2\theta = 45°$ sphere. The weighting scheme used was $w = 1/[\sigma^2(|F_o|) + g(|F_o|)^2]$ with $g = 0.0002$. The isotropic

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Table 1. *Atomic coordinates* (× 10^4) *and equivalent isotropic displacement coefficients* (Å^2 × 10^3)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	*y*	*z*	U_{eq}
Cu(1)	9326 (1)	758 (1)	225	50 (1)
Cl(1)	8889 (2)	−61 (3)	1338 (2)	83 (2)
P(1)	9386 (2)	−271 (3)	−966 (2)	43 (1)
C(1)	10027 (5)	−1475 (11)	−1105 (7)	44 (4)
C(2)	10164 (5)	−2289 (11)	−473 (7)	49 (5)
C(3)	10621 (7)	−3266 (12)	−558 (10)	77 (6)
C(4)	10951 (7)	−3440 (14)	−1251 (11)	86 (7)
C(5)	10802 (8)	−2600 (17)	−1876 (11)	100 (8)
C(6)	10368 (7)	−1660 (14)	−1817 (8)	79 (6)
C(7)	8704 (5)	−1073 (10)	−1453 (7)	45 (4)
C(8)	8635 (7)	−1174 (12)	−2252 (7)	68 (6)
C(9)	8117 (8)	−1774 (15)	−2585 (10)	78 (7)
C(10)	7663 (8)	−2337 (14)	−2126 (12)	86 (8)
C(11)	7705 (7)	−2264 (16)	−1337 (12)	90 (7)
C(12)	8230 (6)	−1607 (12)	−982 (8)	66 (5)
C(13)	9587 (5)	1059 (9)	−1654 (6)	38 (4)
P(2)	8982 (2)	2724 (3)	−268 (2)	45 (1)
C(14)	8259 (5)	2852 (11)	−882 (7)	48 (5)
C(15)	7847 (7)	1812 (12)	−943 (8)	67 (6)
C(16)	7310 (7)	1901 (16)	−1452 (11)	86 (7)
C(17)	7200 (8)	3018 (18)	−1862 (11)	96 (9)
C(18)	7595 (7)	4052 (15)	−1810 (8)	76 (6)
C(19)	8120 (6)	3955 (13)	−1329 (8)	62 (5)
C(20)	8860 (5)	4082 (10)	390 (7)	40 (4)
C(21)	9039 (5)	5351 (11)	240 (9)	58 (4)
C(22)	8910 (6)	6328 (12)	761 (8)	65 (5)
C(23)	8590 (6)	6087 (14)	1453 (8)	65 (6)
C(24)	8393 (6)	4855 (14)	1603 (7)	62 (5)
C(25)	8525 (6)	3843 (12)	1087 (7)	49 (5)
C(26)	9637 (5)	3271 (10)	−943 (7)	46 (4)
P(3)	10402 (1)	1306 (3)	182 (2)	47 (1)
C(27)	10665 (7)	2738 (11)	725 (7)	57 (5)
C(28)	10310 (7)	3157 (13)	1354 (8)	70 (6)
C(29)	10492 (10)	4172 (17)	1827 (11)	108 (9)
C(30)	11063 (12)	4761 (17)	1695 (12)	118 (11)
C(31)	11445 (9)	4417 (15)	1066 (10)	101 (8)
C(32)	11253 (7)	3380 (13)	593 (8)	67 (6)
C(33)	11023 (6)	132 (11)	451 (6)	44 (4)
C(34)	11644 (6)	65 (11)	156 (9)	62 (5)
C(35)	12088 (6)	−817 (12)	413 (8)	64 (5)
C(36)	11928 (8)	−1674 (13)	986 (9)	77 (7)
C(37)	11316 (8)	−1629 (13)	1314 (9)	76 (6)
C(38)	10868 (6)	−722 (12)	1044 (8)	63 (5)
C(39)	10592 (6)	1693 (10)	−856 (6)	46 (4)
C(40)	10011 (6)	2168 (11)	−1375 (6)	42 (4)
C(41)	10320 (5)	2797 (12)	−2110 (6)	55 (5)

Table 2. *Selected bond lengths* (Å) *and angles* (°)

Cu(1)—Cl(1)	2.260 (4)	P(3)—C(39)	1.850 (11)
Cu(1)—P(2)	2.302 (4)	C(40)—C(41)	1.544 (15)
P(1)—C(1)	1.831 (11)	Cu(1)—P(1)	2.287 (4)
P(1)—C(13)	1.846 (10)	Cu(1)—P(3)	2.297 (4)
C(1)—C(6)	1.412 (18)	P(1)—C(7)	1.832 (12)
C(3)—C(4)	1.373 (24)	C(1)—C(2)	1.390 (16)
C(5)—C(6)	1.323 (22)	C(2)—C(3)	1.387 (17)
C(7)—C(12)	1.379 (17)	C(4)—C(5)	1.402 (25)
C(9)—C(10)	1.351 (23)	C(13)—C(40)	1.516 (15)
C(11)—C(12)	1.415 (21)	P(2)—C(20)	1.807 (11)
P(2)—C(14)	1.829 (12)	C(26)—C(40)	1.557 (15)
P(2)—C(26)	1.863 (12)	P(3)—C(33)	1.823 (12)
P(3)—C(27)	1.822 (12)	C(39)—C(40)	1.568 (16)

Cl(1)—Cu(1)—P(1)	126.1 (1)	C(13)—C(40)—C(41)	107.6 (8)
P(1)—Cu(1)—P(2)	95.8 (1)	C(39)—C(40)—C(41)	105.5 (9)
P(1)—Cu(1)—P(3)	91.9 (1)	Cl(1)—Cu(1)—P(2)	120.5 (1)
Cu(1)—P(1)—C(1)	117.8 (4)	Cl(1)—Cu(1)—P(3)	120.4 (2)
C(1)—P(1)—C(7)	101.3 (5)	P(2)—Cu(1)—P(3)	94.2 (1)
C(1)—P(1)—C(13)	104.8 (5)	Cu(1)—P(1)—C(7)	124.5 (4)
P(1)—C(1)—C(2)	117.1 (9)	Cu(1)—P(1)—C(13)	103.2 (3)
C(2)—C(1)—C(6)	118.5 (11)	C(7)—P(1)—C(13)	102.9 (5)
C(2)—C(3)—C(4)	121.5 (14)	P(1)—C(1)—C(6)	124.3 (9)
C(4)—C(5)—C(6)	122.9 (16)	C(1)—C(2)—C(3)	119.7 (12)
P(1)—C(7)—C(8)	124.2 (9)	C(3)—C(4)—C(5)	117.2 (13)
C(8)—C(7)—C(12)	118.1 (11)	C(1)—C(6)—C(5)	120.2 (13)
C(8)—C(9)—C(10)	120.2 (15)	P(1)—C(7)—C(12)	117.8 (9)
C(10)—C(11)—C(12)	120.1 (15)	Cu(1)—P(2)—C(14)	121.6 (4)
P(1)—C(13)—C(40)	119.4 (7)	C(14)—P(2)—C(20)	100.5 (5)
Cu(1)—P(2)—C(20)	119.8 (4)	C(14)—P(2)—C(26)	102.9 (5)
Cu(1)—P(2)—C(26)	105.3 (4)	P(2)—C(14)—C(15)	119.7 (9)
C(20)—P(2)—C(26)	104.4 (5)	P(2)—C(20)—C(21)	125.4 (9)
P(2)—C(14)—C(19)	122.5 (9)	P(2)—C(26)—C(40)	115.6 (7)
P(2)—C(20)—C(25)	117.3 (8)	Cu(1)—P(3)—C(33)	120.9 (4)
Cu(1)—P(3)—C(27)	118.2 (5)	Cu(1)—P(3)—C(39)	106.8 (4)
C(27)—P(3)—C(33)	101.4 (6)	C(33)—P(3)—C(39)	103.4 (5)
C(27)—P(3)—C(39)	104.2 (5)	P(3)—C(27)—C(32)	124.0 (10)
P(3)—C(27)—C(28)	119.4 (10)	P(3)—C(33)—C(38)	116.2 (9)
P(3)—C(33)—C(34)	126.8 (9)	C(13)—C(40)—C(26)	114.1 (9)
P(3)—C(39)—C(40)	116.0 (8)	C(26)—C(40)—C(39)	110.1 (9)
C(13)—C(40)—C(39)	112.6 (9)	C(26)—C(40)—C(41)	106.3 (9)

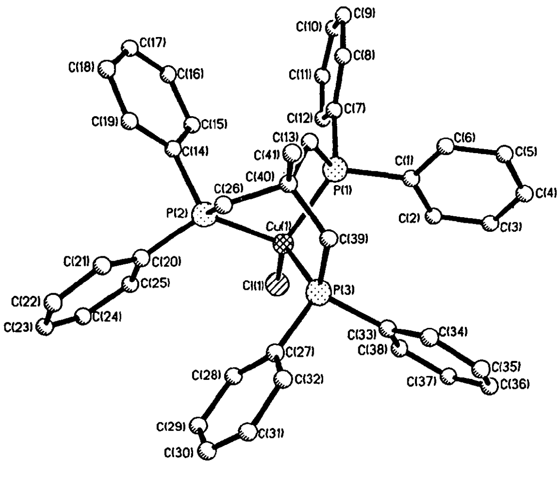

Fig. 1. Diagram of the [({$(C_6H_5)_2PCH_2$}$_3CCH_3$)CuCl] molecule showing the atom-labeling scheme.

extinction coefficient was 0.00003, S = 1.30, and the maximum and minimum excursions on the final difference map were 0.32 and −0.33 e Å^{-3}, respectively. The largest shift/e.s.d. for the final refinement cycle was 0.571 with a mean Δ/σ of 0.049.

Coordinates for the non-H atoms are listed in Table 1.* Selected bond lengths and bond angles are listed in Table 2. The labeling for the atoms is shown in Fig. 1 and a unit-cell packing diagram is shown in Fig. 2.

Discussion. The crystal structure of the monodentate analog compound, [{$(C_6H_5)_2(CH_3)P$}$_3$CuCl], exhibits the same space group *Pna*2$_1$ with *Z* = 4; however, the bond angles about the Cu atom are almost perfectly tetrahedral, with Cl—Cu—P(av.) = 109.1 and P—Cu—P(av.) = 109.8° (Gill *et al.*, 1976). In [({$(C_6H_5)_2PCH_2$}$_3CCH_3$)CuCl] the P—Cu—P angles have considerable strain due to the bridgehead atom,

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, full geometry and data-collection parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71240 (17 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HH1044]

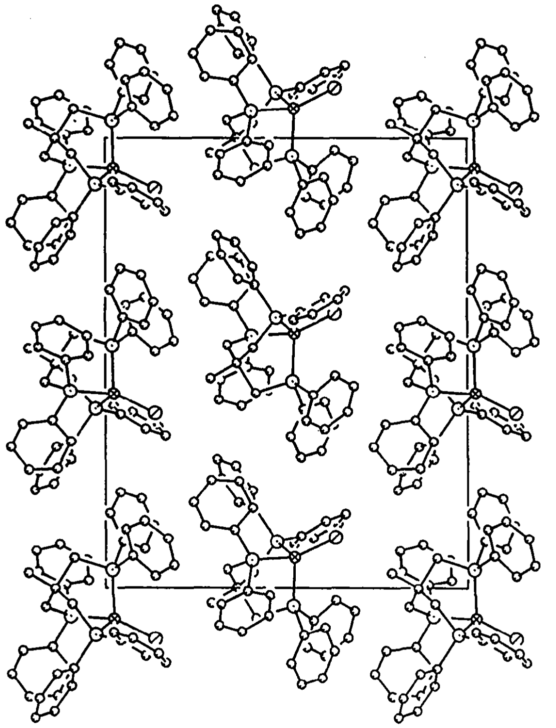

Fig. 2. Unit-cell packing diagram for $[(\{(C_6H_5)_2PCH_2\}_3CCH_3)CuCl]$ projected along the *b* axis.

with Cl—Cu—P(av.) = 122.4 and P—Cu—P(av.) = 93.4°. This strain almost certainly affects the orbital overlap of the P—Cu bond. The electronic transition in the arylphosphines has been described in terms of a $\sigma,d \rightarrow a_\pi$ transition (Fife, Moore & Morse, 1984*a*). The σ,d indicates that a synergistic bonding is involved in the transition. Preliminary experiments show considerable difference in the triplet sensitization of norbornadiene by the two compounds. Photochemical constants are being experimentally determined to better compare the electronic properties of these analogous compounds.

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Structure of $[3,5-(C_6H_5)_2C_3H_2N_2]_4$. A 3,5-Diphenylpyrazole Tetramer Linked by Hydrogen Bonds

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Abstract. 3,5-Diphenylpyrazole, $C_{15}H_{12}N_2$, M_r = 220.1, monoclinic, $C2/c$ (No. 15), a = 16.948 (4) Å, b = 17.163 (4) Å, c = 17.677 (6) Å, β = 109.59 (2)°, V = 4844 (2) Å^3, Z = 32, D_x = 1.21 Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, μ = 0.07 mm^{-1}, $F(000)$ = 1861.6, T = 298 K, final R = 0.056 and wR = 0.058 for 259 variable parameters and 2073 reflections with $F_o^2 > 3\sigma(F_o^2)$. The asymmetric unit consists of a hydrogen-bonded dimer of 3,5-diphenylpyrazole which is further hydrogen bonded to form four discrete tetrameric aggregates per unit cell. Each tetrameric unit forms a twelve-membered $(N—N—H)_4$ heterocycle.

Introduction. Pyrazolato anions of the type 3,5-R_2pz (R = alkyl group, pz = C_3HN_2) are extensively used in the synthesis of transition-metal complexes (Trofimenko, 1972, 1986) where they can act as mono- or bidentate ligands. We have been particularly interested in the homoleptic complexes $[M(\mu$-3,5-$Ph_2pz)]_3$, M is a Group 11 metal, which contain a triangular arrangement of the metal core (Raptis

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