I. M. Paz-Andrade, and H. A. Skinner, *J. Organomet. Chem.*, **97**, 221 (1975).
(11) R. J. Dellaca and B. R. Penfold, *Inorg. Chem.*, **11**, 1855 (1972); M. D. Brice, R. J. Dellaca, B. R. Penfold, and J. L. Spencer, *Chem. Commun.*, 72 (1971).
(12) C. H. Wei, *Inorg. Chem.*, **8**, 2384 (1969).
(13) P. H. Bird and A. R. Fraser, *J. Organomet. Chem.*, **73**, 103 (1974).
(14) R. Mason and W. R. Robinson, *Chem. Commun.*, 468 (1968).
(15) W. G. Sly, *J. Am. Chem. Soc.*, **81**, 18 (1959).
(16) O. S. Mills and B. W. Shaw, *J. Organomet. Chem.*, **11**, 595 (1968).
(17) G. G. Sumner, H. P. Klug, and L. E. Alexander, *Acta Crystallogr.*, **17**, 732 (1964).
(18) F. S. Stephens, *J. Chem. Soc., Dalton Trans.*, 1067 (1974).
(19) J. P. Nice, Ph.D. Thesis, University of Manchester, 1966.
(20) O. S. Mills, private communication.
(21) A. A. Hock and O. S. Mills, *Acta Crystallogr.*, **14**, 139 (1961).
(22) In this context see the discussion of covalent radii by M. R. Churchill, *Perspect. Struct. Chem.*, **3**, 91 (1970).
(23) K. Hedberg, Oregon State University, private communication. There is an older structure by L. O. Brockaway and J. S. Anderson, *Trans. Faraday Soc.*, **33**, 1233 (1937).
(24) (a) A. P. Cox and A. H. Brittain, *Trans. Faraday Soc.*, **66**, 557 (1970); (b) I. A. Ronova, N. V. Alekseeva, N. N. Veniaminov, and M. A. Kravers, *Zh. Strukt. Khim.*, **16**, 476 (1975).
(25) (a) N. A. Bailey and R. Mason, *Acta Crystallogr.*, **21**, 652 (1966); (b) M. Gerloch and R. Mason, *Proc. R. Soc. London, Ser. A*, **279**, 170 (1964).
(26) C. H. Wei and L. F. Dahl, *Inorg. Chem.*, **4**, 493 (1965).
(27) L. F. Dahl and P. W. Sutton, *Inorg. Chem.*, **2**, 1067 (1963).
(28) (a) S. Otsuka, A. Nakamura, and T. Yoshida, *Inorg. Chem.*, **7**, 261 (1968); (b) M. Sorai, A. Kosaki, H. Suga, S. Seki, T. Yoshida, and S. Otsuka, *Bull. Chem. Soc. Jpn.*, **44**, 2364 (1971).
(29) P. D. Frisch and L. F. Dahl, *J. Am. Chem. Soc.*, **94**, 5082 (1972).
(30) Our extended Hückel calculations on $(CO)_9M_3S_2$ and $Cp_3M_3S_2$ concur in this assignment.
(31) B. Rees and P. Coppens, *Acta Crystallogr., Sect. B*, **29**, 2515 (1973).
(32) A. Haaland, *Acta Chem. Scand.*, **19**, 41 (1965).
(33) E. Keulen and F. Jellinek, *J. Organomet. Chem.*, **5**, 490 (1966).
(34) M. F. Bailey and L. F. Dahl, *Inorg. Chem.*, **4**, 1298 (1965).
(35) G. Huttner and S. Lange, *Acta Crystallogr., Sect. B*, **28**, 2049 (1972).
(36) This is accomplished by σ–π mixing of what were e_{1g} and e_{1u} orbitals in benzene. For illustrations of these orbitals see W. L. Jorgensen and L. Salem, "The Organic Chemist's Book of Orbitals", Academic Press, New York, N.Y., 1973, pp 257–259.
(37) S. F. A. Kettle, *Inorg. Chim. Acta*, **1**, 303 (1967).
(38) K. O. Hodgson and K. N. Raymond, *Inorg. Chem.*, **12**, 458 (1973).
(39) H. R. van der Wal, F. Overzet, H. O. van Oven, J. L. de Boer, H. J. de Liefde Meijer, and F. Jellinek, *J. Organomet. Chem.*, **92**, 329 (1975).
(40) R. K. Bohn and A. Haaland, *J. Organomet. Chem.*, **5**, 470 (1966).
(41) J. A. Ibers, *J. Organomet. Chem.*, **73**, 389 (1974).
(42) M. R. Churchill and J. Wormald, *Inorg. Chem.*, **10**, 572 (1971).
(43) See references surveyed in ref 38.
(44) R. P. Dodge and V. Schomaker, *Acta Crystallogr.*, **18**, 614 (1965).
(45) J. D. Dunitz, H. C. Mez, O. S. Mills, and H. M. M. Shearer, *Helv. Chim. Acta*, **45**, 647 (1962).
(46) S. Murahashi, T. Mizoguchi, T. Hosokawa, I. Moritani, Y. Kai, M. Kohara, N. Yasuoka, and N. Kasai, *J. Chem. Soc., Chem. Commun.*, 563 (1974).
(47) M. D. Rausch, R. M. Tuggle, and D. L. Weaver, *J. Am. Chem. Soc.*, **92**, 4981 (1970); R. M. Tuggle and D. L. Weaver, *Inorg. Chem.*, **10**, 1504 (1971).
(48) R. M. Tuggle and D. L. Weaver, *Inorg. Chem.*, **10**, 2599 (1971).
(49) See the discussion on p 1069 of ref 4.
(50) A. F. Berndt and R. E. Marsh, *Acta Crystallogr.*, **16**, 118 (1963).
(51) O. L. Carter, A. T. McPhail, and G. A. Sim, *J. Chem. Soc. A*, 822 (1966).
(52) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963); R. Hoffmann and W. N. Lipscomb, *ibid.*, **36**, 2179, 3489 (1962); **37**, 2872 (1962).
(53) J. W. Richardson, W. C. Nieuwpoort, R. R. Powell, and W. F. Edgell, *J. Chem. Phys.*, **36**, 1057 (1962).

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Structural Determinations of Four Mono- and Binuclear Tertiary Phosphine and Arsine Complexes of Copper(I) Chloride

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The structure of $[(C_6H_5)_3P]_3CuCl$ has been determined by x-ray diffraction. The compound crystallizes in the trigonal space group $P3$, with unit cell dimensions $a = 19.2775$ (14) Å and $c = 10.4720$ (9) Å, and $Z = 3$. A crystallographic threefold rotation axis passes through the Cu–Cl bond. Some important bond distances and angles are Cu–Cl(av) = 2.34 (2) Å, Cu–P(av) = 2.351 (4) Å, Cl–Cu–P(av) = 109.1 (7)°, and P–Cu–P(av) = 109.8 (7)°. The compound $[(C_6H_5)_2(CH_3)P]_3CuCl$ crystallizes in the orthorhombic space group $Pn2_1a$, with $Z = 4$ and cell constants $a = 20.229$ (14) Å, $b = 17.180$ (10) Å, and $c = 10.309$ (5) Å. The molecular geometry is approximately tetrahedral. The rotational conformation about the three Cu–P bonds creates a sterically favorable pocket for the chlorine atom. Some distances and angles are Cu–Cl = 2.366 (4) Å, Cu–P(av) = 2.289 (6) Å, Cl–Cu–P(av) = 103 (2)°, and P–Cu–P = 108.3 (1), 117.7 (1), 118.1 (1)°. The compound $\{[(C_6H_5)(CH_3)_2As]_2CuCl\}_2$ crystallizes in the monoclinic space group $P2_1/n$, with unit cell parameters $a = 9.888$ (3) Å, $b = 17.082$ (5) Å, $c = 11.277$ (6) Å, and $\beta = 94.11$ (2)°, and $Z = 2$ (dimers). The molecule is a dichloride-bridged dimer having two pseudotetrahedral copper atoms related by an inversion center. Selected distances and angles are Cu–Cl(av) = 2.380 (6) Å, Cu–As(av) = 2.36 (1) Å, As–Cu–As = 118.00 (9)°, Cl–Cu–Cl = 100.9 (1)°, and Cl–Cu–As = 100.7 (1), 105.3 (1), 115.1 (1), 115.8 (1)°. Finally, $[(C_6H_5)_3P]_3Cu_2Cl_2 \cdot C_6H_6$ is triclinic, space group $P\bar{1}$, with cell constants $a = 12.307$ (5) Å, $b = 18.722$ (9) Å, $c = 13.574$ (5) Å, $\alpha = 117.174$ (13)°, $\beta = 73.794$ (6)°, and $\gamma = 107.554$ (12)°, and $Z = 2$. Each molecule contains the di-μ-chloro-dicopper(I) core with two triphenylphosphine ligands bonded to one copper atom and one triphenylphosphine ligand bonded to the other copper atom. The result is a binuclear compound containing both three- and pseudotetrahedral four-coordinate copper. The mean copper–chlorine distance of 2.46 (2) Å and copper–phosphorus distance of 2.260 (5) Å in the latter are significantly longer than the respective values of 2.28 (2) and 2.183 (3) Å in the former. Selected interbond angles are Cl–Cu–P(trig) = 123.63 (9), 134.74 (8)°, Cl–Cu–Cl(trig) = 101.63 (9)°, P–Cu–P(tet) = 130.40 (8)°, Cl–Cu–Cl(tet) = 91.57 (8)°, and Cu–Cl–Cu(av) = 82.9 (2)°. Geometries of the four compounds are discussed in detail and compared to those of other $L_m(CuX)_n$ complexes, where L = tertiary phosphine or arsine and X = coordinating anion.

Introduction

Until 1967, only two x-ray structural studies of tertiary monodentate group 5 ligand–copper(I) complexes had been reported. These were Wells' investigation of $[(C_2H_5)_3AsCuI]_4$[1] and the study of $[(CH_3)_3P(C_6H_5C\equiv C)Cu]_4$ by Corfield and Shearer.[2] The x-ray structure determination of $[(C_6H_5)_3P]_2CuBH_4$[3] in that year, however, presaged a strong new interest in these compounds, not only in our laboratory but in several others as well. Numerous stoichiometries and structures are now known for $L_m(CuX)_n$ complexes, where L

Table I. Structurally Characterized Monodentate Tertiary Phosphine or Arsine Complexes of Copper(I), Together with Some Copper(I) Halide Species

	L_3CuX
1	$[(C_6H_5)_3P]_3CuBF_4$[a]
2	$[(C_6H_5)_3P]_3CuCl$[b]
3	$[(C_6H_5)_2(CH_3)P]_3CuCl$[b]
4	$[(C_6H_5)_2(CH_3)P]_3CuNO_3$[c]
	L_2CuX
5	$[(C_6H_5)_3P]_2CuBr\cdot{}^1/_2C_6H_6$[d]
6	$\{[(C_6H_5)_3P]_2CuNCBH_3\}_2$[e]
7	$\{[(C_6H_5)_3P]_2CuN_3\}_2$[f]
8	$\{[(C_6H_5)_2(CH_3)P]_2CuNCS\}_2$[g]
9	$\{[(C_6H_5)(CH_3)_2As]_2CuCl\}_2$[b]
9a	$[(C_6H_{11})_3P]_2CuClO_4$[ll]
	$L_2Cu(XX)$[nn]
10	$[(C_6H_5)_3P]_2CuHFA$[h]
11	$[(C_6H_5)_3P]_2CuTFA$[h,i]
12	$[(C_6H_5)_3P]_2CuTTA$[h]
13	$[(C_6H_5)_3P]_2CuBH_4$[j]
14	$[(C_6H_5)_3P]_2CuB_3H_8$[k]
15	$\{[(C_6H_5)_3P]_2Cu(B_{10}H_{10})_{1/2}\}_2\cdot CHCl_3$[l]
16	$[(C_6H_5)_3P]_2CuNO_3$[m]
17	$[(C_6H_5)_3P]_2CuS_2CSC_2H_5$[n]
18	$[(C_6H_5)_2(CH_3)P]_2CuB_3H_8$[o]
19	$[(C_6H_{11})_3P]_2CuNO_3$[i]
	$L_{1.5}CuX$
20	$[(C_6H_5)_3P]_3Cu_2Cl_2$[p]
21	$[(C_6H_5)_3P]_3Cu_2Cl_2\cdot C_6H_6$[b]
22	$[(C_6H_5)_3P]_3Cu_2I_2$[q]
	$LCuX$
23	$[(C_6H_5)_3P]Cu(\pi\text{-}C_5H_5)$[r]
24	$[(C_6H_5)_3P]Cu\{(C_2C_6F_5)_2(CO)_3[(C_6H_5)_3P]Re\}$[s]
25	$\{[(C_6H_5)_3P]CuCl\}_4$[t]
26	$\{[(C_6H_5)_3P]CuBr\}_4\cdot 1.5CHCl_3$[u]
27	$\{[(C_6H_5)_3P]CuI\}_4$[v]
28	$\{[(CH_3)_3P]Cu(C_2C_6H_5)\}_4$[w]
29	$\{[(C_2H_5)_3P]CuI\}_4$[x]
29a	$\{[(C_2H_5)_3P]CuCl\}_4$[mm]
29b	$\{[(C_2H_5)_3P]CuBr\}_4$[mm]
30	$\{[(C_2H_5)_3As]CuI\}_4$[x,y]
31	$\{[(C_6H_5)_3P]CuH\}_6\cdot HCON(CH_3)_2$[z]
	$(Cu_pX_q)^{r-}$
32	$CuCl$[aa]
33	Cu_3Cl_3[bb]
34	$\{(C_6H_5)_2P(O)(CH)_2NH(C_2H_5)_2\}^+(CuCl_2)^-$[cc]
35	$\{N_6P_6[N(CH_3)_2]_{12}Cu^{II}Cl\}^+(Cu^ICl_2)^-$[dd]
36	$[(bpy)_2Cu^{II}(Cu^ICl_2)]^+(Cu^ICl_2)^-$[ee]
37	$K_2(CuCl_3)^{2-}$[ff]
38	$(NH_4)_2(CuCl_3)^{2-}$[gg]
39	$[Cu^{II}(NH_3)_4]^{2+}[(Cu^ICl_2)_2]^{2-}\cdot H_2O$[hh]
40	$[Cu^{II}(NH_3)_4]^{2+}[(Cu^IBr_2)_2]^{2-}$[hh]
41	$[Cu^{II}(NH_3)_4]^{2+}[(Cu^II_2)_2]^{2-}$[ii]
42	$(paraquat)^{2+}[(CuCl_2)_2]^{2-}$[jj]
43	$\{[Co(NH_3)_6]^{3+}\}_4Cl^-(Cu_5Cl_{16})^{11-}$[kk]

[a] Reference 26. [b] This work. [c] Reference 28. [d] Reference 47. [e] Reference 3b. [f] R. F. Ziolo, A. P. Gaughan, Z. Dori, C. G. Pierpont, and R. Eisenberg, *Inorg. Chem.*, **10**, 1289 (1971). [g] Reference 29. [h] Reference 36. [i] Reference 37. [j] Reference 3. [k] Reference 38. [l] Reference 3c. [m] Reference 41. [n] Reference 35. [o] Reference 40. [p] Reference 9. [q] Reference 48. [r] F. A. Cotton and J. Takats, *J. Am. Chem. Soc.*, **92**, 2353 (1970). [s] O. M. Abu Salah, M. I. Bruce, and A. D. Redhouse, *J. Chem. Soc., Chem. Commun.*, 855 (1974). [t] References 10b, g, and h. [u] Reference 10c. [v] Reference 10e. [w] Reference 2. [x] Reference 10d. [y] Reference 1. [z] Reference 10a. [aa] Reference 43. [bb] C. Wong and V. Schomaker, *J. Phys. Chem.*, **61**, 358 (1957). [cc] G. Newton, H. D. Caughman, and R. C. Taylor, *J. Chem. Soc. A*, 258 (1974). [dd] W. C. Marsh and J. Trotter, *ibid.*, 1482 (1971). [ee] J. Kaiser, G. Brauer, F. A. Schroder, I. F. Taylor, and S. E. Rasmussen, *ibid.*, 1490 (1974). [ff] C. Brink and C. H. MacGillavry, *Acta Crystallogr.*, **2**, 158 (1949). [gg] C. Brink and A. E. van Arkel, *ibid.*, **5**, 506 (1952). [hh] J. A. Baglio and P. A. Vaughan, *J. Inorg. Nucl. Chem.*, **32**, 803 (1970). [ii] J. A. Baglio, H. A. Weakliem, F. Demelio, and P. A. Vaughan, *ibid.*, **32**, 795 (1970). [jj] C. K. Prout and P. Murray-Rust, *J. Chem. Soc. A*, 1520 (1969). [kk] Reference 44. [ll] R. J. Restivo, A. Costin, G. Ferguson, and A. J. Carty, *Can. J. Chem.*, **53**, 1949 (1975); this compound has the largest P-Cu-P angle (144.46 (6)°) to date. [mm] Reference 10f. [nn] **Note Added in Proof.** A recent addition to this class is $[(C_6H_5)_3P]_2CuO_2CCH_3$: M. G. B. Drew, A. H. Othman, D. A. Edwards, and R. Richards, *Acta Crystallogr., Sect. B*, **31**, 2695 (1975).

is a monodentate phosphine or arsine ligand and X is a coordinating anion, from more than 30 x-ray crystal structure determinations.

The known geometries for various $L_m(CuX)_n$ classes are shown in Figure 1; Table I lists complexes for which x-ray structural results are available, although accidental omissions are possible. The table also includes selected related copper(I) halide structures. The only class without an example of known structure is L_4Cu^+,[4] which is expected to be tetrahedral (Figure 1). Table I, Figure 1, and the discussion in this paper do not consider the various bidentate (tertiary phosphine)-copper(I) complexes which have been the subjects of several recent investigations.[5]

A specific interest has been to characterize the solid-state[6,7] and solution[8] structures of prototype members of several $L_m(CuX)_n$ stoichiometries, where X = halide, since these are the common starting materials in the syntheses of complexes with other coordinating anions. Here are reported two structures in the class L_3CuX, $[(C_6H_5)_3P]_3CuCl$ and $[(C_6H_5)_2(CH_3)P]_3CuCl$,[7,8] which reveal the effect of the hydrocarbon groups of the phosphine ligand on the P_3CuCl coordination geometry. The diffraction study of an arsine complex of empirical formula L_2CuX, the dimeric $\{[(C_6H_5)(CH_3)_2As]_2CuCl\}_2$,[8] is also included here. This is the first reported structure of a strictly dimeric copper(I) halide complex having monodentate group 5 ligands. Following the previous communication of the structure of $[(C_6H_5)_3P]_3Cu_2Cl_2\cdot C_6H_6$,[6] the first known example in the class $L_{1.5}CuX$, the structure of an unsolvated form of the same complex was reported.[9] Differences between the two geometries are related to packing interactions,[9] which are further discussed here.

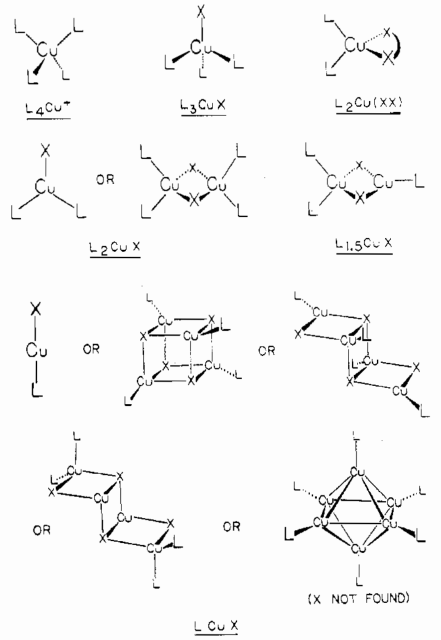

Figure 1. Known and (for L_4Cu^+) postulated structures of the various $L_m(CuX)_n$ stoichiometries, where L = tertiary monodentate phosphine or arsine ligand and X = coordinating anion.

Table II. Experimental Details of the X-Ray Diffraction Study of $[(C_6H_5)_3P]_3CuCl$

(A) Crystal Parameters[a] at 23 °C

$a = 19.2775\ (14)$ Å $\quad c = 10.4720\ (9)$ Å
$V = 3370.2\ (7)$ Å^3 $\quad$ Mol wt 885.9
Space group $P3$ $\quad Z = 3$
$\rho(\text{calcd}) = 1.309$ g/cm^3 $\quad \rho(\text{obsd})^b = 1.316\ (4)$ g/cm^3

(B) Measurement of Intensity Data

Instrument: Picker FACS-I-DOS diffractometer
Radiation: Mo Kα (λ_{α_1} 0.70926 Å), graphite monochromatized
Takeoff angle: 1.9°
Detector aperture: 4 mm × 4 mm
Crystal–detector distance: 33 cm
Scan technique: coupled θ(crystal)–2θ(counter)
Scan range: 1.50° (symmetric, plus Kα_1–Kα_2 dispersion)
Scan rate: 1.0°/min
Maximum 2θ: 50°
Background measurements: stationary crystal, stationary counter; 10-s counts at each end of 2θ scan range
Standards: three reflections [$(\bar{5}14)$, $(\bar{8}\bar{2}0)$, $(5\bar{1}0)$] measured every 100 data; correction later made for ca. 3% crystal decomposition
No. of reflections collected: 10 211 ($\pm h, \pm k, +l$)

(C) Treatment of Intensity Data[c]

Reduction to preliminary F_o^2 and $\sigma(F_o^2)$: correction for background, attenuators, and Lorentz–polarization of monochromatized x radiation in the usual manner;[d,e] $\epsilon^f = 0.04$
Absorption correction: because $\mu = 7.09$ cm^{-1} and because of uniform crystal shape, not applied
Averaging: three equivalent forms; agreement factor $R_{av}{}^g = 0.081$
Scaling: Wilson's method;[h] $\bar{B} = 2.92$ Å^2
Observed data: 2850 unique reflections for which $F_o^2 > 3\sigma(F_o^2)$

[a] From a least-squares fit to the setting angles of 33 reflections. [b] By suspension in aqueous K_2CO_3. [c] Programs for an IBM 360/91 computer used in this work include NUMODE, the local version of the Brookhaven diffractometer setting, cell constant, and orientation refinement program; AVERAGE, a program for weighted averaging of equivalent reflections, by Gill; XDATA, the Brookhaven Wilson plot and scaling program; FORDAP, the Zalkin Fourier program; CULS, a local version of the Busing–Martin–Levy structure factor calculation and least-squares refinement program (ORFLS); CUGLS, a local version of ORFLS, modified by Ibers and Doedens for rigid-body refinement; ORFFE, the Busing–Martin–Levy molecular geometry and error function program; TRACER II, the Lawton lattice transformation–cell reduction program; ORTEP II, the Johnson thermal ellipsoid plotting program; and various local data processing programs. [d] B. G. Segal and S. J. Lippard, *Inorg. Chem.*, 13, 822 (1974). [e] See reference 3c. [f] P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, 6, 197 (1967). [g] $R_{av} = \sum_{i=1}^{N}\sum_{j=1}^{n} |\overline{F_i^2} - F_{ij}^2| / \sum_{i=1}^{N}\overline{F_i^2}$, where N is the number of reflections measured more than once and n is the number of observations of the Nth reflection. [h] A. J. C. Wilson, *Nature* (*London*), 150, 151 (1942).

Recent work in other laboratories on complexes of empirical formula LCuX has provided additional, badly needed, structural information.[10]

Experimental Section

Collection and Reduction of X-Ray Data. Chlorotris(triphenylphosphine)copper(I) was prepared as previously described[11] and recrystallized from chloroform–methanol solution yielding large, colorless, rhombohedral crystals with 12 faces of the forms {100}, {010}, {101}, and {01$\bar{1}$}. A crystal of approximate dimensions 0.25 mm × 0.3 mm × 0.4 mm was mounted with nail polish on the end of a glass fiber, along [010]. Preliminary precession photographs using Cu K$\bar{\alpha}$ radiation showed a threefold rotation symmetry about the c^* axis, but no other symmetries or systematic absences. The space group was taken to be either $P3$ or $P\bar{3}$.[12] The former choice was later confirmed by successful refinement of the structure (vide infra). Details of the data collection and reduction are given in Table II.

Table III. Experimental Details of the X-Ray Diffraction Study of $[(C_6H_5)_2(CH_3)P]_3CuCl$

(A) Crystal Parameters[a] at 23 °C

$a = 20.229\ (14)$ Å $\quad$ Space group $Pn2_1a$
$b = 17.180\ (10)$ Å $\quad Z = 4$
$c = 10.309\ (5)$ Å $\quad \rho(\text{calcd}) = 1.30$ g/cm^3
$V = 3582\ (6)$ Å^3 $\quad \rho(\text{obsd})^b = 1.29\ (4)$ g/cm^3
Mol wt 699.7

(B) Measurement of Intensity Data

Instrument: Picker four-angle programmed diffractometer
Radiation: Cu K$\bar{\alpha}$ ($\bar{\lambda}$ 1.5418 Å), Ni filtered
Takeoff angle: 2.0°
Detector aperture: 3 mm × 3 mm
Crystal–detector distance: 25 cm
Scan technique: coupled θ(crystal)–2θ(counter)
Scan range: 1.25° (symmetric, plus Kα_1–Kα_2 dispersion)
Scan rate: 1.0°/min
Maximum 2θ: 107°
Background measurements: stationary crystal, stationary counter; 10-s counts at each end of 2θ scan range
Standard: one reflection, $(13\bar{5})$, measured every 76 data
No. of reflections collected: 4312 ($\pm h, +k, +l$)

(C) Treatment of Intensity Data[c]

Reduction to preliminary F_o^2 and $\sigma(F_o^2)$: correction for background, attenuators, Lorentz–polarization, and ±5% intensity fluctuations of standard reflection in the usual manner;[d] $\epsilon^e = 0.04$
Absorption correction: $\mu = 27.8$ cm^{-1}; transmission factors varied between 0.40 and 0.61
Averaging: done over two equivalent forms; direct mean of F_o^2's taken
Scaling: Wilson's method;[f] $\bar{B} = 3.87$ Å^2; nine reflections for which $((\sin\theta)/\lambda)^2 < 0.006$ were mistakenly deleted here
Observed data: 1973 unique reflections for which $I_{obsd} > 3\sigma(I_{obsd})$

[a] From a least-squares fit to the setting angles of 15 reflections. [b] By suspension in aqueous KI solution. [c] See footnote *c* of Table II; additional programs employed were GSET, the Prewitt diffractometer setting routine, and ACAC-3, a revised version of the Prewitt absorption correction and data reduction program. [d] See footnote *d* of Table II. [e] See footnote *f* of Table II. [f] See footnote *h* of Table II.

Chlorotris(diphenylmethylphosphine)copper(I) was prepared as previously described.[8] A triangular prism, of face dimensions 0.4 mm × 0.5 mm × 0.35 mm and of 0.2-mm thickness, was mounted on a glass fiber with clear nail enamel. The mounting axis, which passed through one of the apices of the triangular face, was collinear with b^*. Precession photographs taken with Mo K$\bar{\alpha}$ radiation showed the crystal to have *mmm* Laue symmetry. Systematic extinctions $hk0$, $h = 2n + 1$, and $0kl$, $k + l = 2n + 1$, limited the space group choices to $Pnma$ or $Pn2_1a$.[13] Subsequent work (vide infra) indicated the latter to be correct. Details of the data collection and reduction are given in Table III.

Di-μ-chloro-tetrakis(dimethylphenylarsine)dicopper(I) was prepared as previously described.[8] Several crystals of the colorless complex were sealed in glass capillaries. Preliminary precession photographs taken with Cu K$\bar{\alpha}$ radiation showed the lattice to have the Laue symmetry $2/m$ with systematic absences of $h0l$, $l = 2n + 1$, and $0k0$, $k = 2n + 1$, properties of the monoclinic space group $P2_1/c$.[14] The crystal used for data collection was mounted along the c^* axis and was of approximately octahedral shape with maximum dimensions 0.1 mm × 0.1 mm × 0.1 mm. Details of the data collection and reduction are given in Table IV.

Di-μ-chloro-tris(triphenylphosphine)dicopper(I)–benzene, prepared as described in the literature,[15] was recrystallized from benzene solution. A colorless, nearly rectangular prism of approximate dimensions 0.28 mm × 0.10 mm × 0.40 mm was selected and mounted with nail polish on the end of a glass fiber. The mounting axis was the largest of the three crystal dimensions and was coincident with b^*. Preliminary precession photographs taken with Cu K$\bar{\alpha}$ radiation revealed no symmetry higher than $\bar{1}$ and no systematic absences. The choice of space group $P\bar{1}$[16] was subsequently confirmed by successful refinement of the structure. Details of the data collection and reduction are given in Table V.

Determination and Refinement of the Structures. Chlorotris(triphenylphosphine)copper(I). The structure was solved by conventional Patterson, Fourier, and least-squares refinement techniques. Several cycles of unit-weight, individual isotropic refinement for 3 Cu, 3 Cl, 3 P, and 54 C atoms resulted in discrepancy values $R_1 = 0.136$ and $R_2 = 0.150$.[17] This successful refinement was carried out in space

Table IV. Experimental Details of the X-Ray Diffraction Study of $\{[(C_6H_5)(CH_3)_2As]_2CuCl\}_2$

(A) Crystal Parameters at 20°

Standard Unit Cell[a]

$a = 9.888$ (3) Å $\beta = 133.56$ (2)°
$b = 17.082$ (5) Å Space group $P2_1/c$
$c = 15.522$ (8) Å

Derived Cell Used in Refinement

$a = 9.888$ Å $\beta = 94.11°$
$b = 17.082$ Å Space group $P2_1/n$
$c = 11.277$ Å

Data for Both Cells

$V = 1900$ (3) Å^3 ρ(calcd) = 1.62 g/cm^3
$Z = 2$ (dimers) ρ(obsd)[b] = 1.61 (2) g/cm^3
Mol wt 926.4

(B) Measurement of Intensity Data

Instrument: Picker four-angle programmed diffractometer
Radiation: Mo K$\bar{\alpha}$ (λ 0.7107 Å); balanced Y-Zr filters
Takeoff angle: 1.5°
Detector aperture: 3 mm × 3 mm
Crystal-detector distance: 25 cm
Scan technique: coupled θ(crystal)-2θ(counter); one full scan for each balanced filter
Scan range: 1.5° (symmetric, plus Kα_1-Kα_2 dispersion)
Scan rate: 2°/min
Maximum 2θ: 40°
Background measurements: stationary crystal, stationary counter; 4-s counts at either end of each 2θ scan range
Standards: four measured every 100 reflections; intensities varied randomly, ±4%
No. of reflections collected: 1899; $h0l$, $h = 2n + 1$, reflections (in $P2_1/c$ system) accidentally omitted

(C) Treatment of Intensity Data[c]

Reduction of balanced filter data to preliminary F_o^2 and $\sigma(F_o^2)$: $I_{obsd} = I_{Zr} - I_Y$; each of the latter corrected separately for background; $\sigma(I_{obsd}) = [C_{Zr} + C_Y + (T_s/2T_b)^2(B_1 + B_2 + B_3 + B_4) + (\epsilon I_{obsd})^2]^{1/2}$, where C is the intensity uncorrected for background and attenuation, T_s is the scan time for each 2θ scan, T_b is the time of each background count, B is the background count, and $\epsilon^d = 0.05$; correction for background, attenuators, and Lorentz-polarization in usual manner[e]
Absorption correction: $\mu = 49.7$ cm^{-1}; because of small symmetric crystal shape, not applied; calcd transmission factors vary ±8%
Scaling: Wilson's method;[f] $\bar{B} = 3.42$ Å^2
Observed data: 1345 unique reflections for which $I_{obsd} > 3\sigma(I_{obsd})$

[a] From a least-squares fit to the setting angles of 13 reflections. [b] By pycnometry with water. [c] See footnote *c* of Table III. [d] See footnote *f* of Table II. [e] See footnote *d* of Table II. [f] See footnote *h* of Table II.

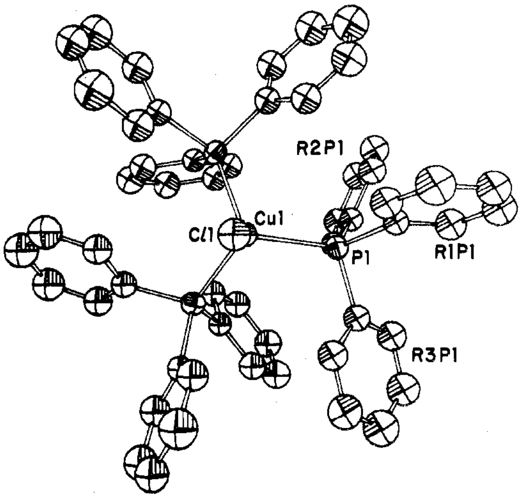

Figure 2. View of chlorotris(triphenylphosphine)copper(I), molecule no. 1, where all hydrogen atoms have been omitted for clarity. The shapes of all atoms represent 50% probability contours of thermal motion.

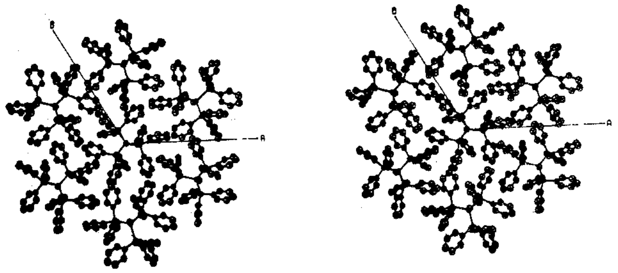

Figure 3. Stereoscopic view of the crystal packing of chlorotris(triphenylphosphine)copper(I). Atom shapes represent 50% probability contours, and hydrogen atoms have been omitted. Axes shown extend one unit cell from the origin.

group $P3$, but assignment of absolute configuration was deferred. Phenyl rings were then constrained to be 11-atom rigid groups,[18] in which the isotropic temperature factor of each hydrogen atom was fixed to be 1.0 greater than the refined temperature factor of the attached phenyl carbon atom. In addition, the 9 heaviest atoms were assigned anisotropic temperature factors.[19] Scattering factors for neutral Cu, Cl, P, C, and H atoms[20] with corrections for anomalous dispersion[21] of Cu, Cl, and P were employed. A few cycles of full-matrix refinement converged at $R_1 = 0.049$ and $R_2 = 0.057$ for transformed data and atom coordinate sets $\bar{k}\bar{h}\bar{l}$ and y, x, z, respectively, and $R_1 = 0.050$ and $R_2 = 0.058$ for the data and coordinates as originally designated. The standard deviation of an observation of unit weight was 1.64 in the former case and 1.67 in the latter. In addition, bond distances between Cu, Cl, and P atoms were more reasonable when derived from the transformed data set, and the accompanying least-squares refinement, based upon 153 variable parameters, was deemed final. The transformed coordinates determine the absolute configuration in a right-handed system. The specific transformation used permits comparison with parameters published for similar structures (vide infra). Inspection of the function $w\Delta^2$, for data sectioned with respect to $|F_o|$ and (sin θ)/λ, showed satisfactory consistency, and the weighting scheme was considered adequate.[22] No systematic secondary extinction effects were apparent in the data set. A final difference Fourier map showed peaks ≤0.76 e/Å^3 in the vicinity of the heavy atoms and the group-refined phenyl carbon atoms.

Table VI contains the final nonhydrogen atom positional and thermal parameters, the standard deviations of which are derived from the inverse matrix of the final least-squares cycle. A listing of important interatomic distances and angles appears in Table VII. Tables S1–S3, listing the final positional and thermal parameters for all hydrogens, the root-mean-square amplitudes of thermal motion for anisotropically refined atoms, and the final observed and calculated structure factor amplitudes, are available.[23] Figure 2 illustrates the nongroup atom and group labeling scheme for molecule no. 1. There are of course three unique molecules per unit cell, all labeled similarly. A stereoscopic view down the c axis, displaying lateral packing interactions in the a and b directions among $2^1/_3$ unit cells is presented in Figure 3.

Chlorotris(diphenylmethylphosphine)copper(I). The structure was solved by the usual Patterson, Fourier, and least-squares techniques. The solution of the structure required the acentric space group $Pn2_1a$. Individual isotropic refinement of all nonhydrogen atoms resulted in convergence at $R_1 = 0.089$ and $R_2 = 0.123$.[17] Form factors for neutral Cu, Cl, P, and C atoms and corrections for anomalous dispersion were obtained from ref 24. All phenyl carbons were then converted to six-atom rigid groups,[18] in which each carbon atom was allowed an individual isotropic temperature factor. Refinement of six rigid groups and eight anisotropic[19] individual atoms led to $R_1 = 0.070$ and $R_2 = 0.097$. Since transforming the y coordinates of all atoms to $-y$ at this stage produced a slightly less satisfactory refinement ($R_1 = 0.071$ and $R_2 = 0.098$), the polarity as originally chosen was assumed to be correct. Upon inspection of the function $w\Delta^2$ for data sectioned according to $|F_o|$, it was decided that an empirical weighting function would be useful.[22] The standard deviation of an observation of unit weight decreased from 3.43 to 1.00 upon application of the weighting formula $w = (1.823 + 0.031F)^{-2}$. Systematic secondary extinction effects were not apparent within the data. Final refinement of 144 variable parameters, omitting all hydrogen atoms, converged at R_1

Table V. Experimental Details of the X-Ray Diffraction Study of $[(C_6H_5)_3P]_3Cu_2Cl_2 \cdot C_6H_6$

(A) Crystal Parameters at 21 °C

Unit Cell[a] Used in All Calculations

$a = 12.307$ (5) Å	$\alpha = 117.174$ (13)°
$b = 18.722$ (9) Å	$\beta = 73.794$ (6)°
$c = 13.574$ (5) Å	$\gamma = 107.554$ (12)°

Normal Reduced[b] Type II[c] Unit Cell

$a = 13.574$ Å	$\alpha = 96.133°$
$b = 17.395$ Å	$\beta = 106.200°$
$c = 12.307$ Å	$\gamma = 106.780°$

General Parameters

Transformation matrix to reduced cell: $(00\bar{1}; 011; 100)$	Mol wt 1063.0
	$V = 2616$ (4) Å^3
Space group $P\bar{1}$	ρ(calcd) = 1.35 g/cm^3
$Z = 2$	ρ(obsd)[d] = 1.34 (7) g/cm^3

(B) Measurement of Intensity Data

Instrument: Picker four-angle programmed diffractometer
Radiation: Cu $K\bar{\alpha}$ ($\bar{\lambda}$ 1.5418 Å), Ni filtered
Takeoff angle: 2.5°
Detector aperture: 2 mm × 2 mm
Crystal-detector distance: 25 cm
Scan technique: coupled θ(crystal)–2θ(detector)
Scan range: 1.25° (symmetric, plus $K\alpha_1$-$K\alpha_2$ dispersion) for $2\theta \leq 90°$; 1.50° for $2\theta > 90°$
Scan rate: 1.0°/min
Maximum 2θ: 92°
Background measurements: stationary crystal, stationary counter; 10-s counts at each end of 2θ scan range
Standards: four [(003), (306), $(\bar{4}70)$, (222)] measured every 100 reflections; intensities varied randomly, ±4%
No. of reflections collected: 4844

(C) Treatment of Intensity Data[e]

Reduction to preliminary F_o^2 and $\sigma(F_o^2)$: correction for background and Lorentz–polarization in usual manner;[f] ϵ[g] = 0.04; no attenuators were used because of equipment failure
Absorption correction: $\mu = 34.9$ cm^{-1}; transmission factors varied from 0.38 to 0.70
Averaging: 192 equivalent pairs, 1 equivalent triplet; agreement factor R_{av}[h] = 0.028
Scaling: Wilson's method;[i] $\bar{B} = 3.90$ Å^2
Observed data: 4014 unique reflections for which $I_{obsd} > 3$ $3\sigma(I_{obsd})$

[a] From a least-squares fit to the setting angles of 19 reflections. [b] See footnote *c* of Table II. [c] M. J. Buerger, "Elementary Crystallography", Wiley, New York, N.Y., 1956, pp 107–111. [d] By pycnometry with bromoform. [e] See footnote *c* of Table III. [f] See footnote *d* of Table II. [g] See footnote *f* of Table II. [h] See footnote *g* of Table II. [i] See footnote *h* of Table II.

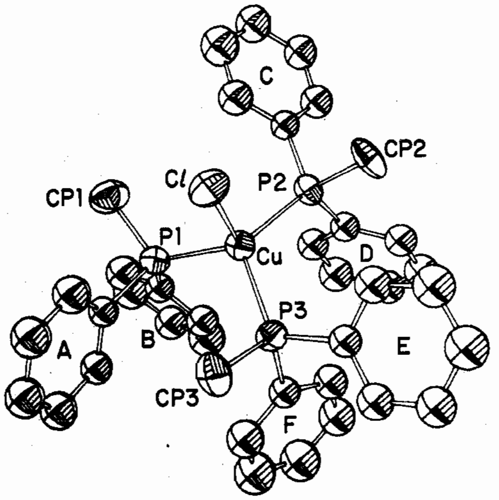

Figure 4. Diagram of the molecule chlorotris(diphenylmethylphosphine)copper(I), where atom shapes represent 50% probability contours.

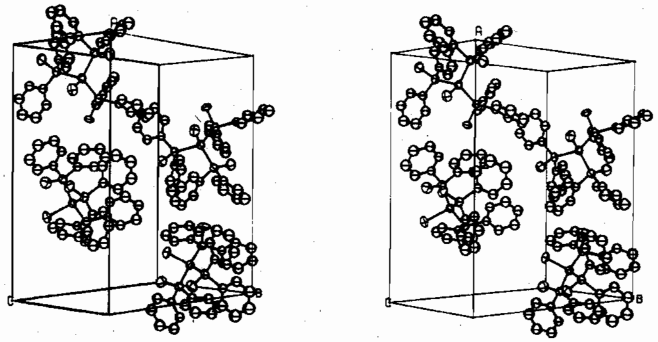

Figure 5. Stereoscopic view of the contents of one unit cell of chlorotris(diphenylmethylphosphine)copper(I). For the cell outlined, *a* extends from $-1/2$ to $1/2$, *b* from $-1/4$ to $3/4$, and *c* from $-1/2$ to $1/2$, in fractional coordinates. Atoms are contoured at 50% probability.

= 0.068 and $R_2 = 0.089$. A final difference Fourier map showed only residual electron density, ≤0.54 e/Å^3, in the vicinity of the group-refined phenyl carbon atoms.

Final atomic positional and thermal parameters, along with their standard deviations as derived from the inverse matrix of the final cycle of least-squares refinement, are given in Table VIII. Table IX contains a summary of important interatomic distances and angles. Tables S4 and S5, containing the amplitudes of the major, median, and minor axes of thermal vibration and listing final observed and calculated structure factor amplitudes, are available.[23] The geometry of chlorotris(diphenylmethylphosphine)copper(I), as well as the nongroup atom and group labeling scheme and relative orientations of the thermal ellipsoids, is shown in Figure 4. Figure 5 displays the contents of one unit cell.

Di-μ-chloro-tetrakis(dimethylphenylarsine)dicopper(I). The structure was solved by conventional Patterson, Fourier, and least-squares refinement techniques. Least-squares refinement of the positional parameters and individual isotropic temperature factors of As, Cu, Cl, and C atoms led to values of R_1 and R_2 of 0.139 and 0.150, respectively.[17] Neutral atom form factors and corrections for anomalous dispersion were obtained as previously described.[20a,21] After a few cycles of refinement with each atom given an anisotropic temperature factor,[19] the values of R_1 and R_2 fell to 0.060 and 0.078, respectively. A difference Fourier map at this stage showed residual electron density (0.5–1.2 e/Å^3) about the chlorine, copper, and arsenic atoms and in probable hydrogen atom positions (~0.45 e/Å^3). Attempts to refine the hydrogen atom positional and isotropic thermal parameters, however, met with only limited success. No hydrogen atoms were, therefore, included in the final structure.

The data set was then inspected for incongruities. Three reflections, (110), (210), and $(\bar{2}\bar{8}2)$, which suffered errors during data reduction, were removed. No systematic secondary extinction effects were apparent. Inspection of the function $w\Delta^2$ for data sectioned according to $|F_o|$, however, led to the introduction of an empirical function $w = (14.51 - 0.4134F + 0.006504F^2)^{-1}$ for a more even weighting of the data set.[22] Upon application of the new weight function, the standard deviation of an observation of unit weight fell from 1.72 to 1.03, while the variation in $w\Delta^2$ was reduced. The final least squares, refining all nonhydrogen atoms in 181 variable parameters, converged at values of $R_1 = 0.059$ and $R_2 = 0.074$. The final difference Fourier map differed little from that described above.

Final atomic positional and thermal parameters, along with their standard deviations as derived from the inverse matrix of the final cycle of least-squares refinement, are listed in Table X. Table XI contains a summary of important interatomic distances and angles, dihedral angles, and best planes. Tables S6 and S7, containing the amplitudes of the major, median, and minor axes of thermal vibration and listing final observed and calculated structure factor amplitudes, are available.[23] The full di-μ-chloro-tetrakis(dimethylphenylarsine)dicopper(I) molecule, along with the atom labeling scheme and relative orientation of the thermal ellipsoids, is shown in Figure 6. Figure 7 depicts the contents of one $P2_1/n$ unit cell, as well as dimers in neighboring unit cells along the [100] and $[\bar{1}00]$ directions.

Di-μ-chloro-tris(triphenylphosphine)dicopper(I)–Benzene. The structure was solved by conventional Patterson, Fourier, and least-squares refinement techniques. Several cycles of least-squares refinement of the positional parameters and individual isotropic

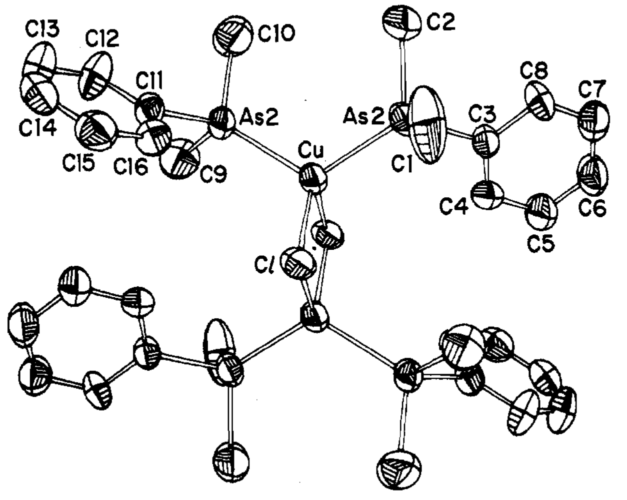

Figure 6. View of di-μ-chloro-tetrakis(dimethylphenylarsine)dicopper(I), where the crystallographic inversion center has been indicated. Atom shapes are contoured at 50% probability.

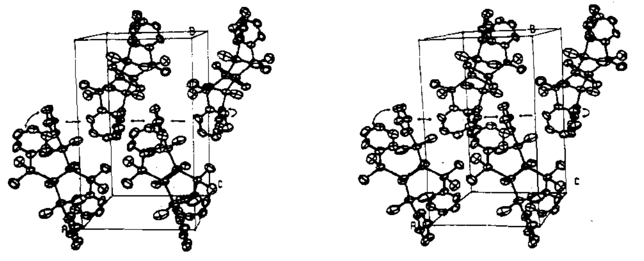

Figure 7. Packing diagram of di-μ-chloro-tetrakis(dimethylphenylarsine)dicopper(I), showing the contents of one unit cell and neighboring dimers along the [100] and [$\bar{1}$00] directions. The cell drawn extends along *a* and *b* from $-^1/_4$ to $^3/_4$ and along *c* from $^1/_4$ to $^5/_4$, in fractional coordinates. Atom shapes represent 50% probability contours. The arrows showing nonbonded contacts are discussed in the text.

temperature factors of all Cu, P, Cl, and C atoms led to values of 0.107 and 0.151 for the indexes R_1 and R_2, respectively.[17] Form factors for neutral Cu, Cl, P, C, and H atoms were employed,[20] with the effects of anomalous dispersion[21] being included in the contributions of Cu, Cl, and P to the calculated structure factors. Subsequent refinement was carried out with each heavy atom being given anisotropic temperature factors[19] and with each phenyl ring being refined as an 11-atom (6 C and 5 H) rigid body.[18] The benzene of solvation was similarly treated as a 12-atom (6 C and 6 H) rigid body. The ring carbon atoms were allowed individual isotropic temperature factors, and the thermal parameter of each H atom was set equal to 1.0 plus that of the attached carbon. A few cycles of full-matrix refinement resulted in values of R_1 and R_2 of 0.067 and 0.098, respectively.

The data were then inspected for improper reduction and effects of secondary extinction. It was found that 15 reflections suffered from significantly disparate backgrounds ($B_i/B_j > 2$) and that 56 intense reflections with $F > 105$ were affected by extinction or coincidence losses. The former were therefore rejected, and the latter were given zero weight in the refinement, leaving a working data set of 3999 observed reflections. When the function $w\Delta^2$ was then inspected for data sectioned by $|F_o|$, it was found that an empirical function $w = (4.076 - 0.0909F + 0.00323F^2)^{-1}$ would more equally weight the reflections.[22] Upon further refinement the standard deviation of an observation of unit weight decreased from 4.04 to 1.02, with $w\Delta^2$ showing less variation. A final least squares, accounting for all atoms of the unit cell in 184 variable parameters, converged at $R_1 = 0.068$ (or $R_1 = 0.064$, excluding the data with $F > 105$) and $R_2 = 0.079$. A final difference Fourier map showed only peaks ≤ 0.83 e/Å^3 in the vicinity of group-refined phenyl carbon atoms.

The atomic positional and thermal parameters, along with their standard deviations as derived from the inverse matrix of the final least-squares refinement cycle, are given in Table XII. A summary of important bond distances and angles, dihedral angles, and distances from planes appears in Table XIII. Final positional and thermal parameters for all hydrogens, the root-mean-square amplitudes of thermal vibration for all anisotropically refined atoms, and the final observed and calculated structure factor amplitudes are available as Tables S8–S10, respectively.[23] Figure 8 illustrates the di-μ-chloro-tris(triphenylphosphine)dicopper(I)–benzene unit, as well as the nongroup atom and group labeling scheme and the orientation of the thermal ellipsoids. Figure 9 depicts the contents of one unit cell, plus two additional molecules of solvation.

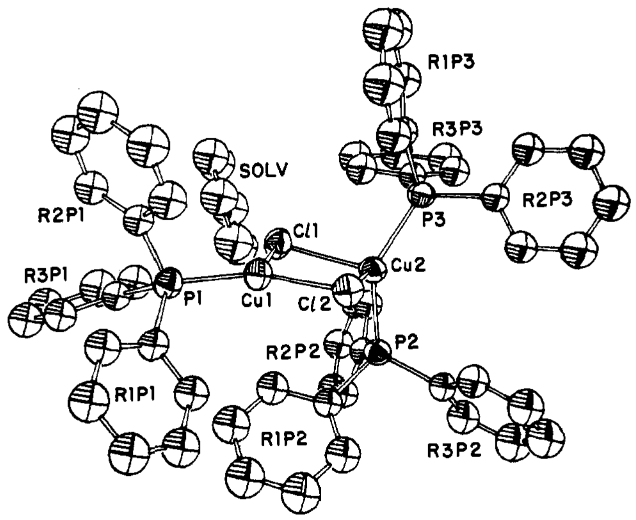

Figure 8. View of the di-μ-chloro-tris(triphenylphosphine)dicopper(I), showing a benzene of solvation at $x + 1.0, y, z$. Hydrogen atoms have been omitted for clarity. Atom shapes depict 50% probability contours of thermal motion.

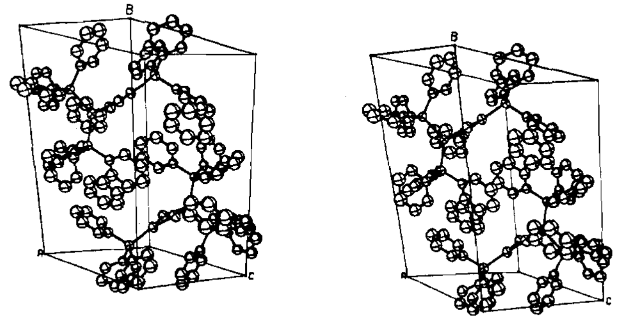

Figure 9. Contents of one unit cell of di-μ-chloro-tris(triphenylphosphine)dicopper(I)–benzene, plus solvent molecules of the positions $x + 1.0, y, z$ and $\bar{x} - 1.0, \bar{y}, \bar{z}$. The cell shown spans *a*, *b*, and *c* from $-^1/_2$ to $^1/_2$, in fractional coordinates. Atom contours represent 50% thermal probability, and all hydrogens have been omitted.

Descriptions of the Structures

The structure of **chlorotris(triphenylphosphine)copper(I)** is closely related to those of several other tris(triphenylphosphine)metal complexes that crystallize in the acentric space group *P*3.[25,26] The unit cell, previously reported in ref 25b, contains three independent molecules. The copper–chlorine bond of each molecule lies along a crystallographic threefold symmetry axis. Two of the three molecules have nearly superimposable phenyl rings, while the third is an enantiomorph. Chirality is defined by the "steering wheel" convention.[25a] The crystal chosen for data collection here happened to be of chirality (*S,R,R*) (Figure 3), similar to that found for $[(C_6H_5)_3P]_3PtCO$[25a] and enantiomorphic to the (*R,S,S*) structures found for $[(C_6H_5)_3P]_3IrNO$[25b] and -$CuBF_4$.[26] The structural parameters reported in Table VI for the chloro compound were chosen to facilitate comparison with those reported previously.[25b,26]

The angles at the copper atoms are nearly tetrahedral. This result is a consequence of the approximately equal steric

Table VI

Final Positional Parameters for the Nongroup Atoms of $[(C_6H_5)_3P]_3CuCl$[a,b]

Atom	x	y	z	Atom	x	y	z
Cu1	0	0	0	Cl3	$-{}^1/_3$	${}^1/_3$	0.3047 (4)
Cu2	${}^1/_3$	$-{}^1/_3$	0.2937 (2)	P1	−0.1234 (1)	−0.1044 (1)	−0.0734 (2)
Cu3	$-{}^1/_3$	${}^1/_3$	0.5292 (2)	P2	0.2380 (1)	−0.3014 (1)	0.2176 (3)
Cl1	0	0	0.2230 (4)	P3	−0.4256 (1)	0.3712 (1)	0.6002 (3)
Cl2	${}^1/_3$	$-{}^1/_3$	0.5153 (4)				

Final Derived Positional and Isotropic Thermal Parameters for Ring Carbon Atoms of $[(C_6H_5)_3P]_3CuCl$[c,d]

Atom	x	y	z	B, Å^2	Atom	x	y	z	B, Å^2
C111	−0.1788 (5)	−0.1967 (3)	0.0206 (5)	3.0 (1)	C422	0.3083 (4)	−0.1938 (4)	−0.1877 (5)	5.6 (2)
C211	−0.1543 (4)	−0.1982 (4)	0.1451 (6)	4.3 (2)	C522	0.3266 (4)	−0.1438 (3)	−0.0822 (6)	5.5 (2)
C311	−0.1987 (4)	−0.2652 (4)	0.2216 (4)	6.5 (3)	C622	0.3022 (3)	−0.1765 (3)	0.0392 (5)	4.6 (2)
C411	−0.2676 (5)	−0.3308 (4)	0.1736 (6)	5.0 (2)	C132	0.1373 (4)	−0.3896 (5)	0.2115 (6)	3.6 (2)
C511	−0.2921 (4)	−0.3294 (4)	0.0491 (6)	5.2 (2)	C232	0.1163 (3)	−0.4434 (5)	0.3123 (5)	4.8 (2)
C611	−0.2477 (4)	−0.2623 (3)	−0.0274 (4)	4.5 (2)	C332	0.0394 (5)	−0.5095 (3)	0.3190 (6)	6.1 (2)
C121	−0.1180 (4)	−0.1415 (3)	−0.2331 (4)	2.7 (1)	C432	−0.0165 (4)	−0.5218 (5)	0.2248 (7)	6.0 (3)
C221	−0.1071 (3)	−0.2073 (3)	−0.2442 (4)	3.9 (2)	C532	0.0045 (3)	−0.4679 (5)	0.1240 (6)	6.0 (2)
C321	−0.0906 (4)	−0.2282 (3)	−0.3629 (5)	4.5 (2)	C632	0.0814 (4)	−0.4019 (3)	0.1173 (5)	5.1 (2)
C421	−0.0849 (4)	−0.1833 (4)	−0.4705 (4)	4.4 (2)	C113	−0.5167 (3)	0.3465 (6)	0.5091 (5)	3.3 (2)
C521	−0.0959 (3)	−0.1175 (3)	−0.4593 (4)	3.9 (2)	C213	−0.5756 (3)	0.3600 (3)	0.5600 (4)	4.5 (2)
C621	−0.1124 (4)	−0.0965 (3)	−0.3406 (5)	3.5 (2)	C313	−0.6427 (4)	0.3435 (5)	0.4875 (6)	5.5 (2)
C131	−0.2015 (5)	−0.0764 (6)	−0.0858 (5)	3.3 (2)	C413	−0.6508 (4)	0.3135 (6)	0.3642 (6)	5.7 (2)
C231	−0.1985 (3)	−0.0224 (4)	0.0053 (5)	4.2 (2)	C513	−0.5919 (3)	0.3000 (3)	0.3133 (4)	5.2 (2)
C331	−0.2542 (5)	0.0034 (4)	0.0020 (6)	5.5 (2)	C613	−0.5249 (4)	0.3165 (5)	0.3858 (5)	3.7 (2)
C431	−0.3129 (5)	−0.0247 (6)	−0.0923 (6)	6.2 (3)	C123	−0.4631 (3)	0.3369 (3)	0.7618 (4)	3.5 (2)
C531	−0.3159 (3)	−0.0788 (5)	−0.1833 (5)	5.5 (2)	C223	−0.4129 (3)	0.3752 (3)	0.8651 (5)	3.8 (2)
C631	−0.2602 (4)	−0.1046 (4)	−0.1801 (5)	4.3 (2)	C323	−0.4357 (3)	0.3437 (4)	0.9874 (5)	4.9 (2)
C112	0.2151 (6)	−0.2324 (6)	0.3040 (5)	3.6 (2)	C423	−0.5086 (4)	0.2738 (4)	1.0065 (4)	5.3 (2)
C212	0.1733 (4)	−0.1992 (3)	0.2466 (4)	4.2 (2)	C523	−0.5587 (3)	0.2355 (3)	0.9032 (6)	5.3 (2)
C312	0.1523 (5)	−0.1515 (5)	0.3177 (6)	5.0 (2)	C623	−0.5360 (3)	0.2670 (3)	0.7808 (5)	4.1 (2)
C412	0.1731 (7)	−0.1370 (6)	0.4462 (6)	5.5 (2)	C133	−0.3799 (5)	0.4804 (2)	0.6057 (5)	2.9 (2)
C512	0.2149 (4)	−0.1702 (3)	0.5036 (4)	5.3 (2)	C233	−0.3999 (3)	0.5221 (3)	0.6929 (5)	4.4 (2)
C612	0.2359 (5)	−0.2179 (5)	0.4324 (5)	4.0 (2)	C333	−0.3610 (5)	0.6054 (3)	0.6885 (5)	5.4 (2)
C122	0.2595 (4)	−0.2592 (3)	0.0550 (4)	3.6 (2)	C433	−0.3023 (5)	0.6469 (2)	0.5970 (6)	5.4 (2)
C222	0.2412 (4)	−0.3093 (3)	−0.0505 (6)	4.2 (2)	C533	−0.2823 (3)	0.6052 (3)	0.5098 (5)	4.8 (2)
C322	0.2656 (4)	−0.2766 (4)	−0.1719 (5)	5.2 (2)	C633	−0.3212 (4)	0.5220 (3)	0.5142 (5)	3.8 (2)

Final Rigid-Group Parameters of $[(C_6H_5)_3P]_3CuCl$[e]

Group	X_0	Y_0	Z_0	ϕ	θ	ρ
R1P1	−0.2232 (2)	−0.2638 (3)	0.0971 (4)	−1.358 (6)	−2.294 (3)	−2.088 (6)
R2P1	−0.1015 (2)	−0.1624 (2)	−0.3518 (4)	−3.101 (4)	−2.709 (3)	1.388 (4)
R3P1	−0.2572 (2)	−0.0506 (2)	−0.0890 (4)	−0.806 (5)	−2.205 (4)	0.041 (6)
R1P2	0.1941 (2)	−0.1847 (2)	0.3751 (4)	0.825 (6)	2.202 (3)	−2.006 (6)
R2P2	0.2839 (2)	−0.2265 (3)	−0.0663 (4)	2.665 (4)	2.741 (3)	1.440 (4)
R3P2	0.0604 (3)	−0.4557 (3)	0.2182 (4)	−2.668 (6)	−2.130 (4)	−3.047 (6)
R1P3	−0.5838 (2)	0.3300 (2)	0.4367 (4)	0.568 (5)	−2.283 (3)	0.987 (6)
R2P3	−0.4858 (2)	0.3054 (2)	0.8841 (4)	−1.158 (4)	−2.767 (3)	−1.718 (4)
R3P3	−0.3411 (2)	0.5637 (2)	0.6013 (4)	1.046 (5)	−2.253 (4)	3.089 (5)

Final Anisotropic Thermal Parameters for the Nongroup Atoms of $[(C_6H_5)_3P]_3CuCl$[f]

Atom	β_{11}	β_{22} $(=\beta_{11})$	β_{33}	β_{12} $(=\beta_{11}/2)$	β_{13}	β_{23}	Atom	β_{11}	β_{22} $(=\beta_{11})$	β_{33}	β_{12} $(=\beta_{11}/2)$	β_{13}	β_{23}
Cu1	2.55 (7)	2.55	5.2 (2)	1.28	0	0	Cl3	4.4 (2)	4.4	5.2 (4)	2.2	0	0
Cu2	2.69 (7)	2.69	7.0 (2)	1.35	0	0	P1	2.44 (9)	2.25 (9)	5.6 (2)	1.08 (8)	−0.3 (1)	0.1 (1)
Cu3	2.49 (7)	2.49	5.8 (2)	1.24	0	0	P2	2.75 (9)	2.63 (9)	7.3 (2)	1.59 (8)	−0.0 (1)	−0.0 (1)
Cl1	4.0 (2)	4.0	5.2 (4)	2.0	0	0	P3	2.18 (9)	2.60 (9)	6.4 (2)	1.20 (8)	0.1 (1)	−0.1 (1)
Cl2	4.1 (2)	4.1	6.3 (4)	2.0	0	0							

[a] Nongroup atoms and groups of molecule 1 are labeled as indicated in Figure 2. [b] Standard deviations, in parentheses beside each entry, occur in the last significant figure(s) for each parameter. [c] Carbon atom labeling proceeds in order around each ring, C1*xy* being that carbon of ring *x* bonded directly to phosphorus *y*. [d] For each of the three independent molecules of $[(C_6H_5)_3P]_3CuCl$, ring 1 lies closest to its chlorine, ring 2 farthest away, and ring 3 nearest the plane of its phosphorus atoms. [e] X_0, Y_0, and Z_0 are the fractional coordinates of the center of gravity of the rigid-body-constrained phenyl rings, and ϕ, θ, and ρ are the orientational angles given in radians. These parameters are defined in ref 18c. [f] The form of the anisotropic temperature factor is given in ref 19 and the values reported are ×10^3.

factors, near the copper coordination sphere, of the chlorine and phosphine ligands. The Cl–Cu–P angles are 109.11 (6), 109.83 (6), and 108.41 (7)°, while the P–Cu–P' angles are 109.83 (6), 109.12 (6), and 110.51 (6). These values reflect slight environmental differences for each of the independent molecules. For example, it can be seen from Figure 3 that molecules 2 and 3 form a six-membered packing ring. Molecules 1 lie above and below the center of this ring. The six-membered packing ring is sterically and energetically stabilized by quasi-graphitic stacking of phenyl groups[9] R3P2 and R1P3. The dihedral angle between these groups is 13.1° and their centers are 3.99 Å apart.

The three independent Cu–P bond distances are rather invariant to packing interactions, the average being 2.351 (4) Å. This distance is the longest found in a copper(I)–phosphine system to date. The Cu–Cl bond distances range from 2.320

Table VII. Interatomic Distances (Å) and Angles (deg) in $[(C_6H_5)_3P]_3CuCl$[a]

	Distances		
Cu1–Cl1	2.336 (4)	P1–C131	1.84 (1)
Cu2–Cl2	2.320 (4)	P2–C112	1.83 (1)
Cu3–Cl3	2.350 (4)	P2–C122	1.84 (1)
Cu1–P1	2.348 (2)	P2–C132	1.83 (1)
Cu2–P2	2.351 (2)	P3–C113	1.84 (1)
Cu3–P3	2.355 (2)	P3–C123	1.83 (1)
P1–C111	1.84 (1)	P3–C133	1.83 (1)
P1–C121	1.84 (1)		
	Angles		
Cl1–Cu1–P1	109.11 (6)	Cu3–P3–C113	121.8 (3)
Cl2–Cu2–P2	109.83 (6)	Cu3–P3–C123	113.8 (2)
Cl3–Cu3–P3	108.41 (7)	Cu3–P3–C133	111.3 (2)
P1–Cu1–P1′	109.83 (6)	C111–P1–C121	103.2 (3)
P2–Cu2–P2′	109.12 (6)	C111–P1–C131	99.1 (4)
P3–Cu3–P3′	110.51 (6)	C121–P1–C131	105.3 (3)
Cu1–P1–C111	120.2 (2)	C112–P2–C122	102.6 (4)
Cu1–P1–C121	113.6 (2)	C112–P2–C132	99.4 (4)
Cu1–P1–C131	113.5 (3)	C122–P2–C132	106.1 (3)
Cu2–P2–C112	121.7 (3)	C113–P3–C123	103.4 (3)
Cu2–P2–C122	113.3 (2)	C113–P3–C133	99.3 (3)
Cu2–P2–C132	111.9 (2)	C123–P3–C133	105.2 (3)

[a] See footnotes *a–d* of Table VI.

(4) to 2.350 (4) Å with an average value of 2.335 (15) Å. Because of short intramolecular Cl···H nonbonded contacts, the Cl–Cu–P angle affects the Cu–Cl distance. Table VII reveals that the smallest Cl–Cu–P angle correlates with the longest Cu–Cl bond (molecule 3), while the largest Cl–Cu–P angle (molecule 2) allows closest approach of the chlorine atom. Short Cl···H nonbonded distances are 2.66, 2.74, and 2.74 Å (molecules 1, 2, and 3, respectively).

Geometries within the phosphine ligands are standard.[27] The phosphorus–carbon bond lengths are 1.83–1.84 Å. The Cu–P–C angles are greater than tetrahedral, and the C–P–C angles, smaller. Angles Cu–P–C11, average 121.2 (9)°, have values higher than others of the class, average 113 (1)°. This is perhaps a further result of the steric interaction between phenyl rings no. 1 and the chlorine atom.

The structure of **chlorotris(diphenylmethylphosphine)copper(I)** (Figures 4 and 5) consists of discrete monomers of approximate C_{3v} symmetry. The Cl–Cu–P angles are 101.7 (1), 103.8 (1), and 104.8 (1)°, while the P1–Cu–P2 and P2–Cu–P3 angles are 118.1 (1) and 117.7 (1)°, respectively. The small 108.3 (1)° P1–Cu–P3 angle seems a consequence of intramolecular packing interactions which prevent threefold symmetry. Phenyl ring B is rotated by approximately 60° about the P1–CB1 bond from its ideal C_{3v} position. Smaller-than-tetrahedral Cl–Cu–P angles reflect the stereochemical pocket generated by the three phosphine ligands. These are rotated such that the chlorine atom and methyl groups are in a gauche conformation. The resulting methyl or phenyl carbon to chlorine closest contacts vary from 3.87 to 4.01 Å.

The copper–chlorine distance of 2.366 (4) Å is similar to that found in $[(C_6H_5)_3P]_3CuCl$. The copper–phosphorus distances of 2.282 (3), 2.292 (4), and 2.294 (4) Å are in the range of those found for $[(C_6H_5)_2(CH_3)P]_3CuNO_3$ but show less variation.[28]

Geometries within the phosphine ligands are standard.[27] The average phosphorus–carbon distance is 1.84 (1) Å. Anticipated differences in P–C(sp^3) and P–C(sp^2) bond lengths are not observed. The difference is barely recognizable in the structure of $\{[(C_6H_5)_2(CH_3)P]_2CuNCS\}_2$.[29] There is no evidence for quasi-graphitic stacking of phenyl rings[9] in this structure.

The molecule **di-μ-chloro-tetrakis(dimethylphenylarsine)dicopper(I),** Figures 6 and 7, has a crystallographic center of symmetry that requires the Cu_2Cl_2 moiety to be strictly planar. The copper atom has a distorted tetrahedral geometry. The As1–Cu–As2 angle of 118.00 (9)°, compared to 100.9 (1)° for the Cl–Cu–Cl′ angle, reflects the greater steric bulk of the arsine compared to the chlorine ligands. The dihedral angle between planes defined by atoms As1, Cu, As2 and Cl, Cu, Cl′ is 81.0 (1)°, compared to the value of 90° for a regular tetrahedron. The direction of the twist minimizes nonbonded intramolecular chlorine–phenyl ring contacts. The resultant As–Cu–Cl angles fall into two sets, one greater than tetrahedral and one smaller (Table XI).

Copper–chlorine distances of 2.374 (4) and 2.385 (4) Å are similar to those of the two L_3CuX complexes described above. The copper–arsenic distances of 2.350 (2) and 2.367 (2) Å resemble those of 2.334 Å reported for the complex di-μ-iodo-bis[(*o*-dimethylaminophenyl)dimethylarsine-*As*,*N*]dicopper(I)[30] and 2.361 Å for tetrakis(iodotriethylarsinecopper(I)).[10d]

Deviations from tetrahedral symmetry about the arsenic atoms (Table XI) are standard for tertiary phosphine[27] and arsine[31] ligands. The mean As–C(methyl) bond length of 1.97 (2) Å here is close to that of 1.95 (2) Å in $[(CH_3)_3AsPtCl_2]_2$[31a] and to 1.98 (6) Å in $[Mo(diars)_2(CO)_2I]I$.[31b] The average As–C(phenyl) distance of 1.94 (1) Å agrees with the 1.93 (2) Å value determined for $[(C_6H_5)_3AsCo(CO)_2NO]$[31c] and is, as expected, slightly shorter than the As–C(methyl) distance.

The packing of phenyl rings in the lattice (Figure 7) is similar to that of the molecule (Figure 6). The two arsine ligands bound to each copper atom direct their phenyl rings away from each other; each ring lies almost perpendicular to its nearest neighbor in the other half of the dimer (curved arrows, Figure 7). An analogous orthogonal arrangement of phenyl groups occurs between adjacent dimers (straight arrows, Figure 7) and is the outstanding feature of the lattice packing. This interaction of nearly orthogonal phenyl rings within and between neighboring molecules propagates in both the *a* and *c* directions, forming corrugated "sheets" perpendicular to *b*. Within the "sheets" there are no close quasi-graphitic stackings of phenyl groups.[9]

The structure of **di-μ-chloro-tris(triphenylphosphine)dicopper(I)–benzene** (I), shown in Figure 8, consists of molecules containing both three- and four-coordinate copper atoms. The geometry about Cu1 is approximately trigonal planar (no longer considered a rare or anomalous result[32]), while that about Cu2 is a distorted tetrahedron. From Figure 9 it can be seen that a centrosymmetric pair forms the basic repeating unit of the crystal.

Two triphenylphosphine ligands bind copper 2. The P2–Cu2–Cl1, P2–Cu2–Cl2, and P3–Cu2–Cl1 angles have values of 103.93 (9), 102.96 (8), and 103.30 (9)°, respectively, while the P3–Cu2–Cl2 angle is 116.87 (9)°. The dihedral angle between planes formed by atoms P2, Cu2, P3 and Cl1, Cu2, Cl2 is 85.69 (7)°. This angle is quite similar to, and of the same sense as, that of the monoclinic, unsolvated form of $[(C_6H_5)_3P]_3Cu_2Cl_2$ (II) (NB: the numberings of Cl1 and Cl2 and of P2 and P3 in Figure 8 are the reverse of those in ref 9). In fact, if one compares Figure 9 with Figure 2 of ref 9 (*a* axis down), it is apparent that the dispositions of phenyl rings in the Cu2 coordination spheres are nearly superimposable. The P2–Cu2–P3 angle here is 130.40 (8)°. Large P–Cu–P angles are common in this type of complex and have been discussed elsewhere.[7] The size of this angle, as compared to the 91.57 (8)° Cl1–Cu2–Cl2 angle, is a consequence of the great steric bulk of the triphenylphosphine ligand and of constraints of the four-membered Cu_2Cl_2 ring.

Copper 1 lies only 0.006 Å above the plane defined by its phosphine and chloride ligands (cf. 0.23 Å in compound II), yet the bond angles about the metal differ considerably. Thus,

Table VIII

Final Positional Parameters for the Nongroup Atoms of $[(C_6H_5)_2(CH_3)P]_3CuCl$[a]

Atom	x	y	z	Atom	x	y	z
Cu	0.3783 (1)	0.0	0.2013 (2)	P3	0.4059 (2)	−0.0428 (2)	0.4048 (3)
Cl	0.3240 (2)	−0.1102 (2)	0.1144 (3)	CP1	0.4596 (8)	−0.0021 (12)	−0.0948 (14)
P1	0.4733 (1)	0.0091 (2)	0.0807 (3)	CP2	0.2190 (6)	0.0724 (8)	0.2424 (17)
P2	0.3029 (2)	0.0984 (2)	0.1859 (3)	CP3	0.4476 (7)	−0.1367 (7)	0.4036 (15)

Final Derived Positional and Isotropic Thermal Parameters for Ring Carbon Atoms of $[(C_6H_5)_2(CH_3)P]_3CuCl$[b]

Atom	x	y	z	B, Å^2	Atom	x	y	z	B, Å^2
CA1	0.5298 (4)	−0.0721 (5)	0.1150 (8)	3.6 (2)	CD1	0.3240 (6)	0.1856 (6)	0.2784 (8)	4.0 (3)
CA2	0.5115 (4)	−0.1462 (5)	0.0742 (9)	5.5 (3)	CD2	0.2893 (4)	0.2079 (7)	0.3888 (9)	4.8 (3)
CA3	0.5507 (5)	−0.2101 (4)	0.1056 (10)	5.9 (3)	CD3	0.3117 (5)	0.2699 (6)	0.4638 (7)	5.8 (3)
CA4	0.6082 (5)	−0.1998 (5)	0.1778 (10)	5.8 (3)	CD4	0.3689 (6)	0.3096 (6)	0.4284 (10)	5.7 (3)
CA5	0.6264 (3)	−0.1257 (6)	0.2186 (8)	5.4 (3)	CD5	0.4036 (5)	0.2873 (7)	0.3180 (10)	6.4 (4)
CA6	0.5872 (4)	−0.0618 (4)	0.1872 (8)	4.3 (3)	CD6	0.3812 (5)	0.2253 (5)	0.2430 (8)	4.9 (3)
CB1	0.5266 (15)	0.0947 (12)	0.0967 (9)	4.1 (3)	CE1	0.3401 (4)	−0.0619 (10)	0.5224 (7)	3.7 (2)
CB2	0.5631 (9)	0.1231 (6)	−0.0075 (7)	6.2 (4)	CE2	0.2751 (4)	−0.0653 (5)	0.4787 (6)	4.8 (3)
CB3	0.6010 (8)	0.1902 (10)	−0.0068 (9)	6.9 (4)	CE3	0.2242 (3)	−0.0817 (9)	0.5654 (9)	6.0 (4)
CB4	0.6023 (15)	0.2290 (13)	0.1253 (11)	6.3 (4)	CE4	0.2383 (4)	−0.0947 (10)	0.6957 (8)	6.1 (4)
CB5	0.5658 (9)	0.2006 (6)	0.2295 (8)	7.1 (4)	CE5	0.3033 (5)	−0.0913 (5)	0.7394 (6)	5.2 (3)
CB6	0.5280 (8)	0.1335 (10)	0.2152 (8)	5.0 (3)	CE6	0.3542 (3)	−0.0749 (8)	0.6527 (8)	4.6 (3)
CC1	0.2812 (5)	0.1362 (5)	0.0233 (7)	3.6 (2)	CF1	0.4628 (4)	0.0219 (5)	0.4961 (9)	3.9 (3)
CC2	0.2503 (4)	0.2079 (5)	0.0069 (8)	5.1 (3)	CF2	0.4384 (4)	0.0935 (6)	0.5373 (10)	5.1 (3)
CC3	0.2286 (5)	0.2306 (5)	−0.1156 (9)	5.2 (3)	CF3	0.4804 (5)	0.1469 (5)	0.5966 (11)	6.5 (4)
CC4	0.2378 (6)	0.1816 (6)	−0.2215 (7)	5.9 (3)	CF4	0.5468 (5)	0.1287 (6)	0.6147 (12)	7.3 (4)
CC5	0.2687 (5)	0.1099 (6)	−0.2051 (8)	6.5 (4)	CF5	0.5712 (3)	0.0571 (7)	0.5735 (12)	7.4 (4)
CC6	0.2904 (5)	0.0872 (5)	−0.0826 (9)	5.2 (3)	CF6	0.5292 (4)	0.0037 (5)	0.5142 (11)	5.7 (3)

Final Rigid-Group Parameters for $[(C_6H_5)_2(CH_3)P]_3CuCl$[c]

Group	X_0	Y_0	Z_0	ϕ	θ	ρ
A	0.5690 (3)	−0.1360 (4)	0.1464 (5)	−0.813 (5)	−2.637 (6)	−2.873 (6)
B	0.5645 (3)	0.1618 (4)	0.1110 (7)	1.33 (2)	−1.880 (7)	−2.79 (2)
C	0.2595 (3)	0.1589 (4)	−0.0991 (6)	−2.769 (6)	2.749 (5)	1.764 (7)
D	0.3464 (3)	0.2476 (4)	0.3534 (6)	−1.411 (7)	2.468 (6)	−0.791 (8)
E	0.2892 (3)	−0.0783 (4)	0.6090 (6)	−1.674 (9)	−2.302 (4)	−1.851 (9)
F	0.5048 (3)	0.0753 (4)	0.5554 (6)	−2.269 (6)	3.043 (7)	−0.457 (7)

Final Anisotropic Thermal Parameters for the Nongroup Atoms of $[(C_6H_5)_2(CH_3)P]_3CuCl$[d]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	2.20 (4)	2.36 (6)	8.8 (2)	0.0 (1)	−0.2 (1)	0.0 (1)	P3	2.7 (1)	2.4 (1)	8.0 (3)	0.2 (1)	−0.1 (1)	0.3 (2)
Cl	3.8 (1)	3.1 (1)	11.0 (4)	−0.9 (1)	−0.5 (2)	−1.0 (2)	CP1	4.0 (5)	6.4 (8)	10 (2)	−0.3 (6)	−0.5 (7)	1 (1)
P1	2.2 (1)	3.1 (1)	8.8 (4)	−0.0 (1)	−0.3 (1)	0.2 (2)	CP2	1.4 (3)	4.2 (6)	20 (2)	−0.1 (4)	1.3 (7)	2 (1)
P2	2.1 (1)	2.3 (1)	10.5 (4)	0.1 (1)	0.2 (1)	0.3 (2)	CP3	3.5 (4)	2.2 (5)	16 (2)	0.7 (4)	0.9 (7)	0.1 (8)

[a] Nongroup atoms and groups are labeled as indicated in Figure 4; see also footnote *b* of Table VI. [b] Carbon atom labeling proceeds in order around each ring, C(A→F)1 being the carbon directly bonded to phosphorus. [c] See footnote *e* of Table VI. [d] See footnote *f* of Table VI.

the Cl1–Cu1–P1 angle is 123.63 (9)° while the Cl2–Cu1–P1 angle is 134.74 (8)°. A similar distortion is found in II, but in the opposite direction (again compare Figure 9 with Figure 2 of ref 9). The smaller 101.63 (9)° Cl1–Cu1–Cl2 angle reflects phosphine steric and Cu_2Cl_2 ring constraints.

A major distortion of the molecule is a bending of the Cu_2Cl_2 core by 11.9 (1)° about the Cl1···Cl2 axis, compared to a value of 21.3° in II. For both crystals this distortion is a result of close-packed intermolecular contacts and quasi-graphitic stacking of phenyl rings across the centers of symmetry. With the molecules in close contact, phosphine ligand no. 3 of I (or no. 2 of II) is forced away from the crystallographic center of symmetry to minimize nonbonded intermolecular phenyl repulsions (Figure 9). This distortion bends the Cu_2Cl_2 group about the Cl1···Cl2 vector, which, in light of the nonbonding nature of the Cu1···Cu2 contact, is not unfavorable. The greater distortions of the Cu_2Cl_2 moiety and Cu1 coordination sphere of II are a result of more extensive quasi-graphitic phenyl interactions involving phosphines 1, 1', and 2'.[9] Phosphine 1 stacks with ligand 2' in the adjacent molecule, creating the observed angular distortions about Cu1 and forcing the metal out of the plane of its ligands. The result is a larger dihedral angle in the Cu_2Cl_2 group of II than in that of I. Addition of benzene of solvation to the lattice of I reduces the number of intermolecular quasi-graphitic stacking interactions and allows Cu1 to lie nearly in the plane of its ligands. The only phenyl stackings present in I are between groups R1P3 and R1P3' (as mentioned above), the interplanar distance of these rings being 3.64 Å, and between R2P3 and R2P3' of the neighboring cell (*x*, *y*, *z* − 1), this distance being 3.79 Å. Geometries within the phosphine ligands of I are standard.[27]

The distances from the two chlorines to a copper atom within the Cu_2Cl_2 ring of I are inequivalent, but in a sense opposite to that of II, taking the coordination sphere of Cu2 as a frame of reference. This result derives from differences in chlorine–phenyl hydrogen nonbonded contacts for I and II. Each copper atom has a long and a short distance to chlorine within the Cu_2Cl_2 moiety. The Cu1–Cl1 distance is 2.292 (2) Å and Cu1–Cl2 is 2.260 (2) Å, while Cu2–Cl1 is 2.441 (2) Å and Cu2–Cl2 is 2.482 (2) Å. The disparities in the Cu1–Cl and Cu2–Cl distances and the Cl1–Cu1–Cl2 and Cl1–Cu2–Cl2 angles reflect the different coordination numbers of the metal centers, as do the more invariant copper–phosphorus bond lengths, Cu1–P1 (2.183 (3) Å) being shorter than the Cu2–P2 (2.265 (2) Å) and Cu2–P3 (2.256 (3) Å) distances.

The Cu1···Cu2 distance, 3.138 (3) Å, is 0.23 Å longer than that of compound II because of a more nearly planar Cu_2Cl_2

Table IX. Interatomic Distances (Å) and Angles (deg) in $[(C_6H_5)_2(CH_3)P]_3CuCl^a$

Distances

Cu–Cl	2.366 (4)	P2–CD1	1.83 (1)
Cu–P1	2.294 (4)	P2–CP2	1.85 (1)
Cu–P2	2.282 (3)	P3–CE1	1.83 (1)
Cu–P3	2.292 (4)	P3–CF1	1.86 (1)
P1–CA1	1.84 (1)	P3–CP3	1.82 (1)
P1–CB1	1.83 (2)	Cl···CP1	3.95 (2)
P1–CP1	1.84 (1)	Cl···CP2	4.01 (1)
P2–CC1	1.85 (1)	Cl···CP3	3.92 (2)

Angles

Cl–Cu–P1	103.8 (1)	Cu–P3–CE1	119.1 (3)
Cl–Cu–P2	104.8 (1)	Cu–P3–CF1	115.0 (3)
Cl–Cu–P3	101.7 (1)	Cu–P3–CP3	113.0 (5)
P1–Cu–P2	118.1 (1)	CA1–P1–CB1	103.0 (7)
P1–Cu–P3	108.3 (1)	CA1–P1–CP1	101.7 (6)
P2–Cu–P3	117.7 (1)	CB1–P1–CP1	105.1 (8)
Cu–P1–CA1	111.4 (3)	CC1–P2–CD1	103.9 (5)
Cu–P1–CB1	120.0 (6)	CC1–P2–CP2	98.8 (6)
Cu–P1–CP1	113.6 (5)	CD1–P2–CP2	104.4 (6)
Cu–P2–CC1	118.8 (3)	CE1–P3–CF1	102.9 (5)
Cu–P2–CD1	114.5 (3)	CE1–P3–CP3	100.5 (6)
Cu–P2–CP2	114.4 (5)	CF1–P3–CP3	104.3 (6)

[a] See footnotes *a* and *b* of Table VIII.

core. The Cl1···Cl2 distance of 3.528 (3) Å (0.07 Å less than the sum of the van der Waals radii[33]) is shorter by 0.13 Å than the comparable distance found in II. Greater chlorine–phenyl hydrogen contacts on both ends of the Cl1···Cl2 axis in the benzene-solvated crystal (Figure 9) contribute to this result.

Discussion

As shown in Figure 1, a compound of stoichiometry $L_m(CuX)_n$ can have more than one geometry in the solid state. The molecular structure is not always predictable, being the result of complicated electronic, steric, and perhaps crystal packing factors. For example, the molecule $[(C_6H_5)_3PCuBr]_4$ exists in a step structure,[10c] while the stoichiometrically identical compound $[(C_6H_5)_3PCuCl]_4$ has nearly T_d core geometry.[10b] The structures corresponding to potential energy minima for $L_m(CuX)_n$ compounds are difficult to compute, and reliable geometrical predictions are beyond our present capabilities. It does seem possible, however, to understand trends in bond distances and angles in these compounds by focusing attention on isolated geometric parameters.

The coordination to copper(I) of phosphines, arsines, halides, and most of the anionic ligands listed in Table I involves little or no metal→ligand π back-bonding.[7,34] The metal ion may therefore be viewed as a "fat proton", usually accepting four electron pairs from σ-donor ligands in a geometry (approximately tetrahedral) that minimizes nonbonded interligand repulsions. The metal–ligand bond energies are determined by the relative coordinating abilities and steric sizes of the various ligands and are revealed by the bond lengths. Interbond angles are primarily the result of interligand steric repulsions, which depend on the ligand bulk and, to a lesser extent, bond distances.

Copper(I)–Group 5 Atom Distances. For the $L_m(CuX)_n$ complexes of Table I, the phosphine or arsine ligands are the largest and most basic, forming the strongest bonds to copper(I). Remaining coordination sites are occupied by the smaller, weaker halide, oxygen, nitrogen, or terminal boron–hydrogen σ donors or the comparatively weak acetylenic and cyclopentadienyl π donors. Even the sulfur atoms in $[(C_6H_5)_3P]_2Cu(S_2CSC_2H_5)$[35] are probably weaker donors than the phosphines.

Judging from the Cu–L bond distances, the degree of electronic donation by, and/or steric crowding of, a single group 5 ligand depends upon the number of similar ligands in the molecule. This result does not appear to be greatly affected by coordination number or the presence of additional smaller, weaker donor ligands. As shown in Figure 10, a rough correlation exists between the copper–phosphorus bond lengths and the number of phosphine ligands bound to the same metal center in $L_m(CuX)_n$ compounds, where L is always triphenylphosphine. The structures described in this paper nicely illustrate this point. The copper–phosphorus distance at the three-coordinate copper (one phosphine) of $[(C_6H_5)_3P]_3Cu_2Cl_2 \cdot C_6H_6$ is 2.183 (3) Å, those at the four-coordinate center (two phosphines) are 2.256 (3) and 2.265 (2) Å, and those in $[(C_6H_5)_3P]_3CuCl$ (three phosphines) are 2.348 (2), 2.351 (2), and 2.355 (2) Å. Structural studies of bidentate phosphine–copper(I) halide compounds[5] reveal similar trends.

The vertical spread in the distance data of Figure 10 for monophosphine complexes exceeds that of bis- or trisphosphine compounds. The Cu–P distances in the former appear to be more susceptible to the presence of other ligands. Assuming the relative steric requirements and donor abilities toward Cu(I) to vary as π-acetylide < π-$C_5H_5^-$ < Cl^- < Br^- < I^-, it is possible to rationalize the trend in copper–monophosphorus bond lengths. These effects are less easily identified in bis(triphenylphosphine)copper(I) complexes, in which the variation in Cu–P distances is smaller. These distances in several compounds, however, vary in the order L_2CuHFA[7,36] <

Table X. Final Atomic Positional and Anisotropic Thermal Parameters for $\{[(C_6H_5)(CH_3)_2As]_2CuCl\}_2{}^{a,b}$

Atom	*x*	*y*	*z*	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
As1	−0.0715 (2)	−0.1105 (1)	0.2498 (1)	17.1 (2)	2.3 (1)	6.5 (1)	−1.1 (1)	0.3 (1)	−0.4 (1)
As2	0.2088 (2)	0.0612 (1)	0.2961 (1)	12.7 (2)	2.3 (1)	7.1 (2)	−0.6 (1)	0.8 (1)	0.4 (1)
Cu	0.0340 (2)	−0.0140 (1)	0.3729 (1)	15.9 (3)	2.3 (1)	6.4 (2)	−0.9 (1)	1.4 (2)	−0.2 (1)
Cl	−0.1460 (4)	0.0597 (2)	0.4459 (3)	15.2 (5)	2.8 (1)	6.3 (3)	0.8 (2)	0.7 (3)	−0.1 (2)
C1	−0.256 (2)	−0.082 (1)	0.187 (2)	26 (4)	3.4 (7)	28 (4)	−2 (1)	−12 (3)	3 (1)
C2	0.013 (2)	−0.139 (1)	0.102 (2)	37 (4)	5.2 (9)	7 (2)	−5 (2)	5 (2)	−1 (1)
C3	−0.104 (1)	−0.212 (1)	0.319 (1)	10 (2)	2.4 (6)	7 (1)	−1 (1)	0 (1)	0 (1)
C4	−0.087 (2)	−0.220 (1)	0.438 (1)	15 (2)	3.4 (6)	7 (2)	−1 (1)	3 (1)	0 (1)
C5	−0.108 (2)	−0.293 (1)	0.494 (1)	20 (3)	3.3 (7)	10 (2)	−1 (1)	2 (2)	0 (1)
C6	−0.146 (2)	−0.358 (1)	0.425 (2)	18 (3)	3.0 (7)	13 (2)	−2 (1)	1 (2)	0 (1)
C7	−0.165 (2)	−0.350 (1)	0.303 (2)	13 (2)	3.6 (7)	12 (2)	−1 (1)	1 (2)	0 (1)
C8	−0.145 (1)	−0.277 (1)	0.246 (1)	14 (2)	2.4 (6)	10 (2)	0 (1)	−1 (1)	−1 (1)
C9	0.357 (2)	0.091 (1)	0.414 (2)	17 (3)	6.4 (9)	10 (2)	−1 (1)	−2 (2)	1 (1)
C10	0.313 (2)	0.012 (1)	0.174 (2)	23 (3)	4.3 (8)	16 (2)	2 (1)	9 (2)	0 (1)
C11	0.167 (2)	0.162 (1)	0.222 (1)	15 (2)	2.6 (6)	6 (1)	−1 (1)	−1 (1)	1 (1)
C12	0.268 (2)	0.207 (1)	0.175 (2)	12 (2)	4.9 (8)	14 (2)	−2 (1)	1 (2)	3 (1)
C13	0.230 (2)	0.281 (1)	0.124 (2)	14 (2)	4.0 (8)	15 (2)	−2 (1)	1 (2)	3 (1)
C14	0.098 (2)	0.305 (1)	0.121 (1)	15 (2)	3.1 (6)	10 (2)	1 (1)	−1 (2)	−1 (1)
C15	−0.001 (2)	0.260 (1)	0.169 (1)	19 (3)	4.2 (8)	9 (2)	1 (1)	0 (2)	0 (1)
C16	0.033 (2)	0.187 (1)	0.219 (1)	13 (2)	3.5 (6)	6 (1)	0 (1)	−2 (1)	1 (1)

[a] Atoms are labeled as in Figure 6; see also footnote *b* of Table VI. [b] See footnote *f* of Table VI.

Table XI. Interatomic Distances (Å) and Angles (deg), Dihedral Angles (deg), and Distances (Å) of Atoms from Best Planes in $\{[(C_6H_5)(CH_3)_2As]_2CuCl\}_2$[a]

	Distances		
Cu–As1	2.350 (2)	As2–C9	1.97 (2)
Cu–As2	2.367 (2)	As2–C10	1.97 (2)
Cu–Cl	2.374 (4)	As2–C11	1.94 (1)
Cu–Cl′	2.385 (4)	Cu· · ·Cu′	3.029 (4)
As1–C1	1.97 (2)	Cl· · ·Cl′	3.671 (7)
As1–C2	1.97 (2)	C–C(Ph, av)	1.39 (2)
As1–C3	1.94 (1)		
	Angles		
As1–Cu–As2	118.00 (9)	Cu–As1–C3	118.2 (4)
As1–Cu–Cl	105.3 (1)	Cu–As2–C9	114.8 (5)
As1–Cu–Cl′	115.8 (1)	Cu–As2–C10	117.0 (6)
As1–Cu–Cu′	123.4 (1)	Cu–As2–C11	120.0 (5)
As2–Cu–Cl	115.1 (1)	C1–As1–C2	101 (1)
As2–Cu–Cl′	100.7 (1)	C1–As1–C3	100.7 (7)
As2–Cu–Cu′	118.6 (1)	C2–As1–C3	102.2 (7)
Cl–Cu–Cl′	100.9 (1)	C9–As2–C10	100.5 (8)
Cu–Cl–Cu′	79.1 (1)	C9–As2–C11	100.9 (7)
Cu–As1–C1	113.7 (6)	C10–As2–C11	100.6 (7)
Cu–As1–C2	118.2 (6)		

Plane 1	Plane 2	Dihedral angle
As1–Cu–As2	Cl–Cu–Cl′	81.0 (1)
As1–Cu–Cl	As2–Cu–Cl′	95.8 (1)
As1–Cu–Cl′	As2–Cu–Cl	87.2 (1)

Atoms defining Best plane and eq of plane[b]	Distances of atoms from best plane					
C3–C4–C5–C6–C7–C8	C3	0.01 (1)	C5	−0.01 (2)	C7	0.00 (2)
	C4	0.00 (2)	C6	0.01 (2)	C8	0.00 (1)
$9.581x - 3.993y - 1.694z + 0.696 = 0$						
C11–C12–C13–C14–C15–C16	C11	0.00 (1)	C13	0.01 (2)	C15	0.01 (2)
	C12	0.00 (2)	C14	−0.01 (1)	C16	0.00 (1)
$1.243x + 7.500y + 9.905z - 3.619 = 0$						

[a] See footnote *a*, Table X. [b] Insertion of fractional coordinates x, y, z of any atom in the cell into the plane expression $Ax + By + Cz - D$ yields the perpendicular distance, in Å, of that atom from the plane. In general triclinic space, if **m** is a 1-Å vector normal to the plane, $A = m_1a^2 + m_2ab \cos\gamma + m_3ac \cos\beta$, $B = m_1ab \cos\gamma + m_2b^2 + m_3bc \cos\alpha$, and $C = m_1ac \cos\beta + m_2bc \cos\alpha + m_3c^2$: V. Shomaker, J. Waser, R. E. Marsh, and G. Bergman, *Acta Crystallogr.*, **12**, 600 (1959); W. C. Hamilton, *ibid.*, **14**, 185 (1961).

$L_2CuTTA^{7,36} < L_2CuTFA^{7,36,37} < L_2CuB_3H_8^{38} \sim L_2CuBH_4^{3}$ and appear to reflect increasing anion basicity[7] and steric size.

Copper(I)–phosphorus bond distances also depend upon the alkyl substituents of the phosphine, although data are scarce. Diphenylmethylphosphine, having smaller steric size and being a stronger base than triphenylphosphine,[39] has a 0.06 Å shorter attachment to copper in the L_3CuCl structures. A smaller but significant difference is noted for the Cu–P distances in $[(C_6H_5)_3P]_2CuB_3H_8$,[38] about 0.02 Å longer than those of $[(C_6H_5)_2(CH_3)P]_2CuB_3H_8$.[40] This shortening of bond lengths upon substitution of a phosphine phenyl by a methyl group contributes to the greater chloroform solution stability of $[(C_6H_5)_2(CH_3)P]_3CuCl$ vs. $[(C_6H_5)_3P]_3CuCl$.[8] Since the results of the solution study indicate the stability of the L_3CuCl complexes to be about equivalent for L = diphenylmethylphosphine and phenyldimethylphosphine, an x-ray structural investigation of the latter would be of interest. It may be noted that the Cu–P distance in $[(C_6H_{11})_3P]_2CuNO_3$[37] is 0.03 Å longer than in $[(C_6H_5)_3P]_2CuNO_3$,[41] owing to the great steric bulk of tricyclohexylphosphine.

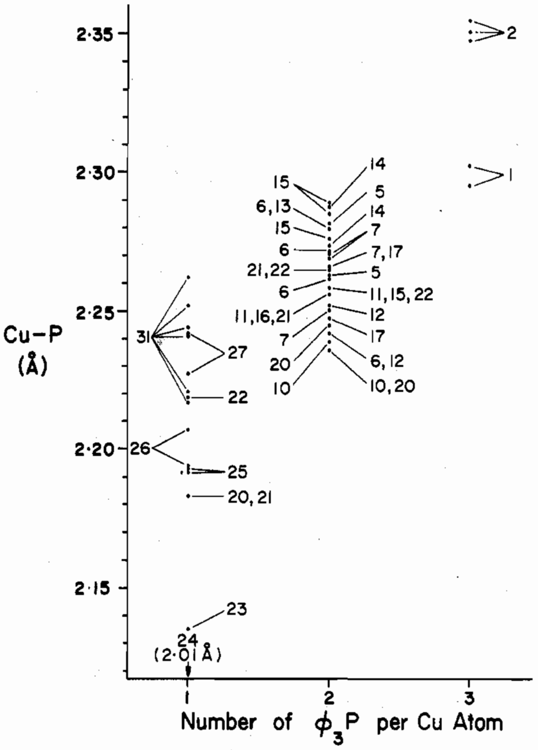

Figure 10. Graph of copper–phosphorus distances, for all copper(I) triphenylphosphine complexes noted in Table I, vs. the number of phosphine ligands bound to the metal center. The numbers by the points refer to the compounds listed in Table I.

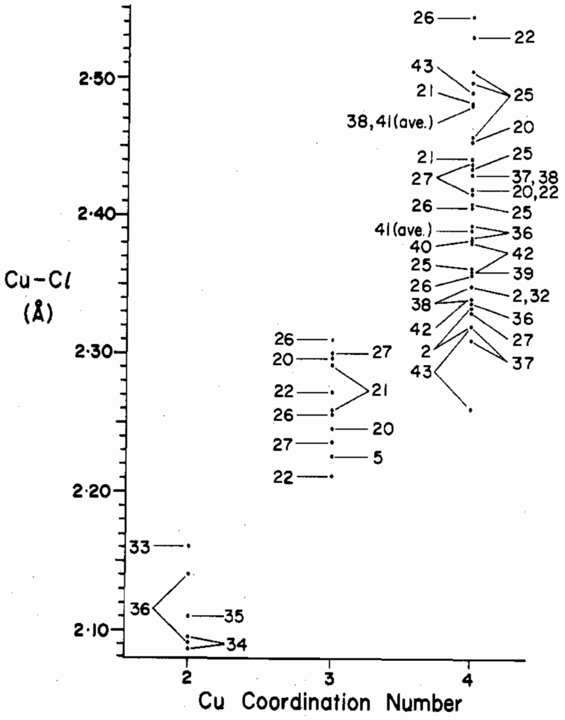

Figure 11. Plot of copper–halide distances (normalized to copper–chloride lengths[42]) vs. the coordination number of the metal center. Data point numbers refer to copper(I) halide compounds of Table I containing zero, one, or more triphenylphosphine ligands. Each entry for compound **41** represents an average of values, for chemically equivalent bond lengths, which would have fallen outside the limits of this graph.

Copper(I)–Halide Distances. Inspection of a number of copper(I)–halide bond distances in $[(C_6H_5)_3P]_m(CuX)_n$ compounds (in the case of $m = 0$, various $(Cu_pX_q)^{r-}$ species have been examined) reveals a correlation between the coordination number of the copper(I) species and the Cu–X bond length (Figure 11). In this figure, all Cu–X distances are normalized to Cu–Cl bond lengths by subtracting the ap-

Table XII

Final Positional Parameters for the Nongroup Atoms of $[(C_6H_5)_3P]_3Cu_2Cl_2\cdot C_6H_6$[a]

Atom	x	y	z	Atom	x	y	z
Cu1	0.1241 (1)	0.2942 (1)	0.0304 (1)	P1	0.0798 (2)	0.3800 (1)	0.2036 (1)
Cu2	0.2264 (1)	0.1841 (1)	−0.2143 (1)	P2	0.3571 (1)	0.2747 (1)	−0.2781 (1)
Cl1	0.2702 (2)	0.2241 (1)	−0.0293 (1)	P3	0.1938 (1)	0.0459 (1)	−0.2878 (1)
Cl2	0.0540 (1)	0.2479 (1)	−0.1300 (1)				

Final Derived Positional and Isotropic Thermal Parameters for Ring Carbon Atoms of $[(C_6H_5)_3P]_3Cu_2Cl_2\cdot C_6H_6$[b]

Atom	x	y	z	B, Å^2	Atom	x	y	z	B, Å^2
C111	0.0234 (4)	0.4649 (2)	0.2197 (4)	3.8 (1)	C132	0.3487 (4)	0.2640 (3)	−0.4165 (3)	3.7 (1)
C211	0.0598 (4)	0.4910 (3)	0.1326 (3)	4.7 (2)	C232	0.2381 (3)	0.2407 (3)	−0.4426 (4)	4.8 (2)
C311	0.0262 (4)	0.5591 (3)	0.1432 (4)	5.6 (2)	C332	0.2234 (4)	0.2308 (3)	−0.5464 (4)	6.2 (2)
C411	−0.0436 (5)	0.6013 (3)	0.2409 (4)	6.1 (2)	C432	0.3192 (5)	0.2443 (4)	−0.6241 (3)	7.0 (2)
C511	−0.0799 (4)	0.5753 (3)	0.3280 (3)	5.9 (2)	C532	0.4298 (4)	0.2677 (3)	−0.5980 (4)	7.0 (2)
C611	−0.0464 (4)	0.5071 (3)	0.3175 (3)	4.9 (2)	C632	0.4445 (3)	0.2776 (3)	−0.4942 (4)	5.5 (2)
C121	−0.0319 (4)	0.3328 (3)	0.2899 (4)	3.8 (1)	C113	0.0788 (3)	−0.0032 (3)	−0.2073 (4)	3.9 (1)
C221	−0.0124 (3)	0.3305 (4)	0.3845 (4)	4.6 (2)	C213	0.0846 (4)	−0.0726 (3)	−0.1971 (4)	5.7 (2)
C321	−0.1003 (4)	0.2920 (3)	0.4449 (3)	5.8 (2)	C313	−0.0111 (5)	−0.1118 (3)	−0.1438 (5)	6.8 (2)
C421	−0.2078 (4)	0.2558 (4)	0.4107 (4)	6.4 (2)	C413	−0.1126 (4)	−0.0816 (3)	−0.1008 (5)	7.0 (2)
C521	−0.2273 (3)	0.2582 (5)	0.3161 (5)	6.5 (2)	C513	−0.1184 (3)	−0.0123 (3)	−0.1110 (5)	7.2 (2)
C621	−0.1394 (4)	0.2966 (3)	0.2557 (3)	5.6 (2)	C613	−0.0227 (4)	0.0270 (3)	−0.1643 (4)	5.3 (2)
C131	0.1993 (3)	0.4293 (3)	0.2834 (3)	3.7 (1)	C123	0.1559 (4)	−0.0095 (3)	−0.4277 (3)	3.8 (1)
C231	0.2958 (4)	0.3935 (3)	0.2413 (3)	5.6 (2)	C223	0.1891 (4)	0.0312 (2)	−0.4987 (4)	5.0 (2)
C331	0.3877 (4)	0.4267 (3)	0.3004 (4)	6.9 (2)	C323	0.1640 (4)	−0.0097 (3)	−0.6074 (4)	6.4 (2)
C431	0.3831 (4)	0.4956 (3)	0.4016 (4)	6.4 (2)	C423	0.1058 (5)	−0.0913 (3)	−0.6451 (3)	6.1 (2)
C531	0.2867 (4)	0.5314 (3)	0.4437 (3)	5.6 (2)	C523	0.0726 (4)	−0.1319 (2)	−0.5741 (4)	5.6 (2)
C631	0.1948 (4)	0.4983 (3)	0.3846 (4)	4.7 (2)	C623	0.0977 (4)	−0.0910 (3)	−0.4654 (4)	4.8 (2)
C112	0.3501 (4)	0.3816 (2)	−0.1874 (3)	3.9 (1)	C133	0.3203 (4)	0.0081 (3)	−0.3003 (4)	3.7 (1)
C212	0.3632 (5)	0.4092 (3)	−0.0765 (4)	5.0 (2)	C233	0.3714 (4)	−0.0448 (3)	−0.4026 (3)	5.0 (2)
C312	0.3549 (5)	0.4893 (3)	−0.0012 (3)	6.4 (2)	C333	0.4697 (4)	−0.0696 (3)	−0.4086 (3)	6.4 (2)
C412	0.3334 (5)	0.5418 (2)	−0.0370 (4)	6.9 (2)	C433	0.5169 (4)	−0.0416 (4)	−0.3123 (4)	6.1 (2)
C512	0.3203 (5)	0.5142 (3)	−0.1479 (5)	7.1 (2)	C533	0.4659 (4)	0.0113 (3)	−0.2099 (3)	5.8 (2)
C612	0.3286 (5)	0.4342 (3)	−0.2232 (3)	5.6 (2)	C633	0.3676 (4)	0.0361 (2)	−0.2039 (3)	5.1 (2)
C122	0.5072 (3)	0.2741 (2)	−0.2844 (4)	3.5 (1)	CB1	−0.4686 (5)	0.1365 (4)	0.0925 (5)	7.5 (2)
C222	0.5299 (3)	0.2034 (2)	−0.2910 (4)	4.5 (2)	CB2	−0.3540 (6)	0.1279 (4)	0.0609 (6)	8.4 (3)
C322	0.6419 (4)	0.2006 (2)	−0.2917 (4)	5.3 (2)	CB3	−0.2739 (4)	0.1720 (4)	0.0031 (6)	8.5 (3)
C422	0.7310 (3)	0.2683 (3)	−0.2858 (4)	5.2 (2)	CB4	−0.3084 (5)	0.2247 (4)	−0.0231 (5)	8.9 (3)
C522	0.7083 (3)	0.3390 (2)	−0.2792 (4)	4.7 (2)	CB5	−0.4230 (6)	0.2333 (4)	0.0085 (6)	8.7 (3)
C622	0.5963 (4)	0.3418 (2)	−0.2785 (4)	4.1 (1)	CB6	−0.5031 (4)	0.1892 (4)	0.0663 (6)	7.8 (2)

Final Rigid-Group Parameters for $[(C_6H_5)_3P]_3Cu_2Cl_2\cdot C_6H_6$[c]

Group	X_0	Y_0	Z_0	ϕ	θ	ρ
R1P1	−0.0101 (3)	0.5331 (2)	0.2303 (3)	−0.015 (3)	2.750 (3)	−0.946 (3)
R2P1	−0.1198 (3)	0.2943 (2)	0.3503 (3)	2.648 (4)	−2.336 (3)	2.440 (4)
R3P1	0.2912 (3)	0.4625 (2)	0.3425 (3)	−1.945 (3)	−2.901 (3)	−1.114 (3)
R1P2	0.3417 (3)	0.4617 (2)	−0.1122 (3)	−2.996 (3)	2.967 (3)	−1.486 (3)
R2P2	0.6191 (3)	0.2712 (2)	−0.2851 (2)	2.815 (2)	3.025 (3)	−0.153 (3)
R3P2	0.3339 (3)	0.2542 (2)	−0.5203 (3)	1.673 (3)	−3.050 (3)	1.960 (3)
R1P3	−0.0169 (3)	−0.0424 (2)	−0.1540 (3)	−2.599 (3)	3.064 (3)	−2.807 (3)
R2P3	0.1309 (3)	−0.0504 (2)	−0.5364 (3)	−0.457 (3)	3.049 (2)	1.382 (3)
R3P3	0.4186 (3)	−0.0168 (2)	−0.3063 (3)	−2.229 (3)	2.706 (2)	−1.471 (3)
SOLV	−0.3885 (4)	0.1806 (3)	0.0347 (3)	−2.339 (4)	−3.048 (4)	0.401 (4)

Final Anisotropic Thermal Parameters for the Nongroup Atoms of $[(C_6H_5)_3P]_3Cu_2Cl_2\cdot C_6H_6$[d]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu1	9.0 (1)	4.1 (1)	6.0 (1)	1.6 (1)	−0.3 (1)	1.6 (1)	P1	7.3 (2)	4.0 (1)	5.7 (2)	1.8 (1)	−0.7 (1)	1.7 (1)
Cu2	7.4 (1)	3.1 (1)	6.2 (1)	0.8 (1)	−0.3 (1)	1.9 (1)	P2	6.1 (2)	3.1 (1)	6.2 (2)	0.7 (1)	−0.2 (1)	2.0 (1)
Cl1	11.4 (2)	4.3 (1)	6.1 (1)	3.2 (1)	−1.3 (1)	1.7 (1)	P3	7.1 (2)	2.9 (1)	6.2 (2)	0.9 (1)	−0.3 (1)	1.8 (1)
Cl2	7.5 (2)	4.2 (1)	7.3 (2)	1.5 (1)	−1.4 (1)	1.9 (1)							

[a] Nongroup atoms and groups are labeled as indicated in Figure 8; see also footnote *b* of Table VI. [b] See footnote *c* of Table VI. [c] See footnote *e* of Table VI. [d] See footnote *f* of Table VI.

propriate difference in Pauling's tetrahedral covalent radii.[42] The copper–halide bond, being weaker than the Cu–L bond in these compounds, is influenced mainly by the grossest of steric and electronic perturbations: change in coordination number. While the number and kind of group 5 ligands bonded to the copper atom have some influence on Cu–X distances, these factors are not of primary importance.

The distances for each coordination number of Figure 11 vary to different extents. Four-coordinate complexes show the largest vertical spread. Distances in this class are perturbed by a greater number of ligands, a secondary effect that influences the degree of covalent binding of halide to copper. For a given compound, the Cu–X distances to triply bridging halides are usually longer than to doubly bridging halides which, in turn, are longer than to terminal halides. This generalization is less valid among different compounds. Exceptions also occur for compounds having no group 5 donor ligand. Thus the bond to the quadruply bridging chloride of CuCl[43] is not enlongated, since this compound has no group 5 ligands to supply electron density. Again we see that the pnicogen-containing ligand is a more effective donor than the halide ion. Another exception is the linear chlorine bridge to

Table XIII. Interatomic Distances (Å) and Angles (deg), Dihedral Angles (deg), and Distances (Å) of Atoms from Planes Defined by Three Atoms in $[(C_6H_5)_3P]_3Cu_2Cl_2 \cdot C_6H_6$[a]

Distances

Cu1–Cl1	2.292 (2)	P1–C131	1.828 (5)
Cu1–Cl2	2.260 (2)	P2–C112	1.823 (5)
Cu1–P1	2.183 (3)	P2–C122	1.829 (4)
Cu2–Cl1	2.441 (2)	P2–C132	1.825 (5)
Cu2–Cl2	2.482 (2)	P3–C113	1.819 (5)
Cu2–P2	2.265 (2)	P3–C123	1.817 (5)
Cu2–P3	2.256 (3)	P3–C133	1.834 (5)
P1–C111	1.823 (5)	Cu1· · ·Cu2	3.138 (3)
P1–C121	1.832 (6)	Cl1· · ·Cl2	3.528 (3)

Angles

Cl1–Cu1–P1	123.63 (9)	C111–P1–C131	104.3 (2)
Cl2–Cu1–P1	134.74 (8)	C121–P1–C131	103.6 (3)
Cl1–Cu1–Cl2	101.63 (9)	Cu2–P2–C112	113.9 (2)
Cl1–Cu2–Cl2	91.57 (8)	Cu2–P2–C122	113.7 (1)
Cu1–Cl1–Cu2	83.01 (8)	Cu2–P2–C132	116.3 (2)
Cu1–Cl2–Cu2	82.71 (8)	C112–P2–C122	101.8 (2)
Cl1–Cu2–P2	103.93 (9)	C112–P2–C132	104.0 (2)
Cl1–Cu2–P3	103.30 (9)	C122–P2–C132	105.7 (2)
Cl2–Cu2–P2	102.96 (8)	Cu2–P3–C113	115.8 (2)
Cl2–Cu2–P3	116.87 (9)	Cu2–P3–C123	117.6 (2)
P2–Cu2–P3	130.40 (8)	Cu2–P3–C133	112.3 (2)
Cu1–P1–C111	115.1 (2)	C113–P3–C123	102.3 (2)
Cu1–P1–C121	113.8 (2)	C113–P3–C133	103.6 (3)
Cu1–P1–C131	114.9 (2)	C123–P3–C133	103.5 (2)
C111–P1–C121	103.8 (3)		

Plane 1	Plane 2	Dihedral angle
Cu1–Cl1–Cl2	Cu2–Cl1–Cl2	168.1 (1)
Cu1–Cl1–P1	Cu1–Cl1–Cl2	179.6 (1)
Cu1–P1–Cl1	Cu1–P1–Cl2	179.4 (2)
Cu1–Cl2–Cl1	Cu1–Cl2–P1	179.5 (1)
Cu2–Cl1–Cl2	Cu2–P2–P3	85.69 (7)
Cu2–Cl1–P2	Cu2–Cl2–P3	92.24 (7)
Cu2–Cl1–P3	Cu2–Cl2–P2	95.51 (8)

Atoms defining plane and eq of plane[b]	Distances of atoms from plane			
Cl1–Cl2–P1	Cu1	0.006	P2	2.590
	Cu2	0.346	P3	−1.329
$4.361x + 14.269y - 5.986z - 4.551 = 0$				
Cu2–Cl1–Cl2	Cu1	0.296	P2	2.136
	P1	0.729	P3	−1.937
$3.643x + 15.376y - 4.183z - 4.553 = 0$				
P1–P2–P3	Cu1	−0.225	Cl1	1.533
	Cu2	−0.184	Cl2	−1.980
$11.395x - 8.488y + 8.412z + 0.602 = 0$				

[a] See footnotes *a–c* of Table VI. [b] See footnote *b* of Table XI.

the central copper of $[Cu_5Cl_{16}]^{11-}$,[44] which is shorter than the terminal Cu–Cl distance in the same compound, perhaps reflecting differences in the chlorine atom hybridizations.

Angular Distortions. Interbond and dihedral angles in copper–phosphine and copper–arsine complexes are also influenced primarily by coordination number and, for a given geometry, the number of group 5 ligands. The steric bulk of the pnicogen ligand, relative to most other ligands, is a major factor. The dominant role of steric interactions in phosphine complexes of Ni(0)[45] and Co(II)[46] has already been demonstrated. Angular distortions in the Cu(I) systems arise from the distribution of bulk about the metal which minimizes nonbonded contacts.

In three of the four complexes described here, interbond angles follow the order Cl–Cu–Cl < Cl–Cu–L < L–Cu–L, since the group 5 ligand is bulkier than chlorine. In the structure of $[(C_6H_5)_3P]_3CuCl$, however, close chlorine–phenyl hydrogen nonbonded contacts produce nearly equivalent Cl–Cu–P and P–Cu–P angles. The diphenylmethylphosphine ligand in the L_3CuCl complex is oriented to minimize chlorine–methyl and –phenyl contacts which are less severe than the chlorine–phenyl interactions in $[(C_6H_5)_3P]_3CuCl$. The average Cl–Cu–P angle of the former compound is thus smaller and the P–Cu–P angle is larger than those of the latter complex. A similar effect occurs for $[(C_6H_5)_2(CH_3)P]_2CuB_3H_8$,[40] in which the P–Cu–P angle is significantly wider than that of the triphenylphosphine analogue.[38] The effective bulk of $[(C_6H_5)(CH_3)_2As]$ is less than that of $[(C_6H_5)_3P]$, as revealed by comparing the L–Cu–L and Cl–Cu–Cl angles of $\{[(C_6H_5)(CH_3)_2As]_2CuCl\}_2$ (118.00 (9) and 100.9 (1)°, respectively) with those at the four-coordinate copper in $[(C_6H_5)_3P]_3Cu_2Cl_2 \cdot C_6H_6$ (130.48 (8) and 91.57 (8)°, respectively).

Steric effects on bond angles in other $L_m(CuX)_n$ compounds are too numerous to describe fully. Many have been discussed previously.[7] One prime influence on the P–Cu–P bond angle is the size and, more importantly, the out-of-plane thickness of the anion(s) in $[(C_6H_5)_3P]_2Cu(X)$, -(XX), and -XX compounds. The steric bulk of anions in these complexes increases in the following order, judging by the P–Cu–P angle (in parentheses): NO_3^- (131°)[41] < 2 Cl^- (130°)[9] < "acac⁻" (127°)[36,37] < Br^- (126°)[47] < BH_4^- (123°)[3] ~ 2 I^- (123°)[48] < $B_3H_8^-$ (120°).[38] Since fluorine has a smaller van der Waals radius than chlorine,[33] the average P–Cu–P angle of $[(C_6H_5)_3P]_3CuBF_4$[26] is about 6° wider than that of the chloride analogue.

These steric arguments may be extended to other compounds, for example, to explain the differences in the geometries observed for $[(C_2H_5)_3PCuI]_4$ and $[(C_2H_5)_3AsCuI]_4$.[10d] The hydrocarbon bulk of the $[(C_2H_5)_3As]$ ligand is somewhat farther away from the metal than that of $[(C_2H_5)_3P]$, since the Cu–As and As–C distances are longer than the Cu–P and P–C bonds. The iodide ligands are thus able to spread farther apart on the copper coordination sphere of the arsine compound and achieve a less repulsive steric balance. The resultant angles vary as As–Cu–I < P–Cu–I and Cu–I–Cu(As) < Cu–I–Cu(P), and the intracluster Cu···Cu and Cu···I distances are smaller in the arsine than in the phosphine compound.

Summary. The dependence of copper(I)–phosphorus bond lengths upon the number of triphenylphosphine ligands bound to the metal has been demonstrated for the compounds $L_m(CuX)_n$. The coordination number of these compounds has been shown to affect copper–halide distances. Discussion of these trends and other factors perturbing Cu–P and Cu–X distances has been presented. The relative steric sizes of ligands have been used to explain variations in interbond angles for $L_m(CuX)_n$ complexes.

Steric arguments, along with Figures 10 and 11, should enable the prediction of structural results for $L_m(CuX)_n$ complexes of unknown geometry. Thus, the Cu–P distance in the tetrakis(triphenylphosphine)copper(I) cation[4] is expected to be ≥2.40 Å. A structural study of this species would be of value.

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Registry No. $[(C_6H_5)_3P]_3CuCl$, 15709-76-9; $[(C_6H_5)_2(CH_3)P]_3CuCl$, 36386-10-4; $\{[(C_6H_5)(CH_3)_2As]_2CuCl\}_2$, 36393-04-1; $[(C_6H_5)_3P]_3Cu_2Cl_2 \cdot C_6H_6$, 29938-60-1.

Supplementary Material Available: Tables S1–S10 listing structure factor amplitudes, positional and isotropic thermal parameters, and rms amplitudes of vibration (66 pages). Ordering information is given on any current masthead page.

References and Notes

(1) F. G. Mann, D. Purdie, and A. F. Wells, *J. Chem. Soc.*, 1503 (1936).
(2) P. W. R. Corfield and H. M. M. Shearer, *Acta Crystallogr.*, **21**, 957 (1966).

(3) (a) S. J. Lippard and K. M. Melmed, *Inorg. Chem.*, **6**, 2223 (1967); (b) K. M. Melmed, T. Li, J. J. Mayerle, and S. J. Lippard, *J. Am. Chem. Soc.*, **96**, 69 (1974); (c) J. T. Gill and S. J. Lippard, *Inorg. Chem.*, **14**, 751 (1975).

(4) (a) F. A. Cotton and D. M. L. Goodgame, *J. Chem. Soc.*, 5267 (1960); (b) J. W. Collier, A. R. Fox, I. G. Hinton, and F. G. Mann, *ibid.*, 1819 (1964); (c) F. Cariati and L. Naldini, *Gazz. Chim. Ital.*, **95**, 3 (1965).

(5) (a) A. Camus, N. Marsich, G. Nardin, and L. Randaccio, *J. Organomet. Chem.*, **60**, C39 (1973); (b) G. Nardin and L. Randaccio, *Cryst. Struct. Commun.*, **3**, 607 (1974); (c) A. Camus, G. Nardin, and L. Randaccio, *Inorg. Chim. Acta*, **12**, 23 (1975), and references cited therein.

(6) D. F. Lewis, S. J. Lippard, and P. S. Welcker, *J. Am. Chem. Soc.*, **92**, 3805 (1970).

(7) S. J. Lippard and G. J. Palenik, *Inorg. Chem.*, **10**, 1322 (1971).

(8) S. J. Lippard and J. J. Mayerle, *Inorg. Chem.*, **11**, 753 (1972).

(9) V. G. Albano, P. L. Bellon, G. Ciani, and M. Manassero, *J. Chem. Soc., Dalton Trans.*, 171 (1972).

(10) (a) M. R. Churchill, S. A. Bezman, J. A. Osborn, and J. Wormald, *Inorg. Chem.*, **11**, 1818 (1972); (b) M. R. Churchill and K. L. Kalra, *ibid.*, **13**, 1065 (1974); (c) M. R. Churchill and K. L. Kalra, *ibid.*, **13**, 1427 (1974); (d) M. R. Churchill and K. L. Kalra, *ibid.*, **13**, 1899 (1974); (e) M. R. Churchill, B. G. DeBoer, and D. J. Donovan, *ibid.*, **14**, 617 (1975); (f) M. R. Churchill, B. G. DeBoer, and S. J. Mendak, *ibid.*, **14**, 2041 (1975); (g) W. R. Clayton and S. G. Shore, *Cryst. Struct. Commun.*, **2**, 605 (1973); (h) M. R. Truter, private communication; (i) structural results of analogous silver(I) compounds given by B.-K. Teo and J. C. Calabrese, *J. Am. Chem. Soc.*, **97**, 1256 (1975); M. R. Churchill and B. G. DeBoer, *Inorg. Chem.*, **14**, 2502 (1975).

(11) S. J. Lippard and D. A. Ucko, *Inorg. Chem.*, **7**, 1051 (1968).

(12) "International Tables for X-Ray Crystallography", Vol. I, 2d ed, Kynoch Press, Birmingham, England, 1965, pp 249, 252.

(13) Reference 12, pp 119, 151.

(14) Reference 12, p 99.

(15) G. Costa, E. Reisenhofer, and L. Stefani, *J. Inorg. Nucl. Chem.*, **27**, 2581 (1965).

(16) Reference 12, p 75.

(17) In all the work in this paper $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, where $w = 4F_o^2/\sigma^2(F_o^2)$. In least-squares refinement, the function $\sum w(|F_o| - |F_c|)^2$ was minimized.

(18) (a) S. J. La Placa and J. A. Ibers, *Acta Crystallogr.*, **18**, 511 (1965); (b) R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, **4**, 773 (1965); (c) R. J. Doedens in "Crystallographic Computing", F. R. Ahmed, S. R. Hall and C. P. Huber, Ed., Munskgaard, Copenhagen, 1970, pp 198–200. Rigid-group phenyl ring C–C distances were 1.392 Å and C–H distances were 0.96 Å in all cases.

(19) All anisotropic thermal parameters given in this paper are of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

(20) (a) Nonhydrogen atom scattering factors: H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Crystallogr.*, **17**, 1040 (1964). (b) Hydrogen atom scattering factors: R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

(21) D. T. Cromer and D. Liberman, *J. Chem. Phys.*, **53**, 1891 (1970).

(22) D. W. J. Cruickshank in "Computing Methods of Crystallography", J. S. Rollett, Ed., Pergamon Press, New York, N.Y., 1965, pp 112–115.

(23) Supplementary material.

(24) "International Tables for X-Ray Crystallography", Vol. III, 3d ed, Kynoch Press, Birmingham, England, 1969, pp 202–207, 214.

(25) (a) V. G. Albano, P. Bellon, and M. Sansoni, *Chem. Commun.*, 899 (1969); see also *errata corrige*, *ibid.*, 188 (1970); (b) V. G. Albano, P. Bellon, and M. Sansoni, *J. Chem. Soc. A*, 2420 (1971).

(26) A. P. Gaughan, Z. Dori, and J. A. Ibers, *Inorg. Chem.*, **13**, 1657 (1974).

(27) (a) J. J. Daly, *J. Chem. Soc.*, 3799 (1964); (b) M. K. Wang, *Acta Chem. Scand.*, **19**, 879 (1965); (c) M. R. Churchill and T. A. O'Brien, *J. Chem. Soc. A*, 2970 (1968); (d) C. P. Brock and J. A. Ibers, *Acta Crystallogr., Sect. B*, **29**, 2426 (1973).

(28) M. Mathew, G. J. Palenik, and A. J. Carty, *Can. J. Chem.*, **49**, 4119 (1971).

(29) A. P. Gaughan, R. F. Ziolo, and Z. Dori, *Inorg. Chim. Acta*, **4**, 640 (1970).

(30) R. Graziani, G. Bombieri, and E. Forsellini, *J. Chem. Soc. A*, 2331 (1971).

(31) (a) S. F. Watkins, *J. Chem. Soc. A*, 168 (1970); (b) M. G. B. Drew and J. D. Wilkins, *J. Chem. Soc., Dalton Trans.*, 2664 (1973); (c) G. Gilli, M. Sacerdoti, and G. Reichenbach, *Acta Crystallogr., Sect. B*, **29**, 2306 (1973).

(32) (a) R. C. Cass, G. E. Coates, and R. G. Hayter, *Chem. Ind. (London)*, 1485 (1954); (b) S. Ahrland and J. Chatt, *ibid.*, 96 (1955); (c) W. T. Reichle, *Inorg. Nucl. Chem. Lett.*, **5**, 981 (1969); (d) S. S. Sandhu and H. Singh, *J. Inorg. Nucl. Chem.*, **33**, 1457 (1971); (e) F. H. Jardine, *Adv. Inorg. Chem. Radiochem.*, **17**, 115 (1975).

(33) L. Pauling, "The Nature of the Chemical Bond", 3d ed, Cornell University Press, Ithaca, N.Y., 1960, p 260.

(34) Back-bonding to the isoelectronic Zn(II) ion has been discussed by F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 3d ed, Interscience, New York, N.Y., 1972, p 504.

(35) A. Avdeef and J. P. Fackler, Jr., *J. Coord. Chem.*, **4**, 211 (1975).

(36) (a) TFA = trifluoroacetylacetonate, TTA = 2-thenoyltrifluoroacetylacetonate, HFA = hexafluoroacetylacetonate. (b) M. W. Bartlett, Ph.D. Thesis, University of Waterloo, 1970. (c) W. A. Anderson, A. J. Carty, G. J. Palenik, and G. Schreiber, *Can. J. Chem.*, **49**, 761 (1970).

(37) M. Bartlett and G. J. Palenik, *Acta Crystallogr., Sect. A*, **25**, S173 (1969).

(38) S. J. Lippard and K. M. Melmed, *Inorg. Chem.*, **8**, 2755 (1969).

(39) W. A. Henderson and C. A. Streuli, *J. Am. Chem. Soc.*, **82**, 5791 (1960).

(40) J. T. Gill, T. Li, K. M. Melmed, D. A. Ucko, and S. J. Lippard, unpublished results. Selected distances and angles for this compound are Cu–P1 = 2.252 (4) Å, Cu–P2 = 2.262 (4) Å, Cu–B2 = 2.29 (2) Å, Cu–B3 = 2.25 (3) Å, Cu–H5 = 1.7 (2) Å, Cu–H6 = 1.8 (2) Å, P1–Cu–P2 = 128.2 (1)°, P1–Cu–B2 = 111.1 (6)°, P1–Cu–B3 = 112.1 (7)°, P2–Cu–B2 = 116.6 (6)°, and P2–Cu–B3 = 115.3 (7)°. For the atom labeling scheme, see ref 38. The terminal boron atom, B1, in this molecule has very large thermal motion, precluding final refinement and accurate determination of the geometry of the octahydrotriborate ion.

(41) (a) G. G. Messmer and G. J. Palenik, *Can. J. Chem.*, **47**, 1440 (1969); (b) G. G. Messmer and G. J. Palenik, *Inorg. Chem.*, **8**, 2750 (1969).

(42) Reference 33, p 246. The correction factors used were −0.12 and −0.29 Å for Cu–Br and Cu–I distances, respectively.

(43) L. Vegard and G. Skofteland, *Arch. Math. Naturvidensk.*, **45**, 163 (1942).

(44) P. Murray-Rust, P. Day, and C. K. Prout, *Chem. Commun.*, 277 (1966).

(45) C. A. Tolman, *J. Am. Chem. Soc.*, **92**, 2956 (1970).

(46) M. Bressan and P. Rigo, *Inorg. Chem.*, **14**, 38 (1975).

(47) P. H. Davis, R. L. Belford, and I. C. Paul, *Inorg. Chem.*, **12**, 213 (1973).

(48) P. G. Eller, private communication.