the simple potassium salt, and no further work was done using them.

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Registry No. $K_5[(CN)_5CoO_2Co(CN)_5]\cdot H_2O$, 12145-87-8.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.00 for photocopy or $2.00 for microfiche, referring to code number AIC40655N.

References and Notes

(1) D. Fremy, *Ann. Chim. Phys.*, **35**, 271 (1852).
(2) A. Werner, *Justus Liebigs Ann. Chem.*, **375**, 1 (1910).
(3) A. Werner, *Justus Liebigs Ann. Chem.*, **375**, 1 (1910). Translated by G. G. Christoph, University Microfilms, Inc., Ann Arbor, Mich., 1969, Order Number 70-12, 256.
(4) M. F. Perutz, *Nature (London)*, **228**, 726 (1970), and references therein.
(5) D. L. Duffy, D. A. House, and J. A. Weil, *J. Inorg. Nucl. Chem.*, **31**, 2053 (1969).
(6) M. Mori, J. A. Weil, and J. K. Kinnaird, *J. Phys. Chem.*, **71**, 103 (1967).
(7) W. P. Schaefer and R. E. Marsh, *Acta Crystallogr.*, **21**, 735 (1966).
(8) R. E. Marsh and W. P. Schaefer, *Acta Crystallogr., Sect. B*, **24**, 246 (1968).
(9) F. R. Fronczek and W. P. Schaefer, *Inorg. Chim. Acta*, **9**, 143 (1974).
(10) A. Haim and W. K. Wilmarth, *J. Amer. Chem. Soc.*, **83**, 509 (1961).
(11) A. A. Vlcek, *Trans. Faraday Soc.*, **56**, 1137 (1960).
(12) N.-G. Vannerberg and C. Brosset, *Acta Crystallogr.*, **16**, 247 (1963).
(13) These complexes have been discussed in several recent reviews, for example: (a) R. G. Wilkins, *Advan. Chem. Ser.*, No. **100**, 111 (1971); (b) J. S. Valentine, *Chem. Rev.*, **73**, 235 (1973).
(14) E. R. Howells, D. C. Phillips, and D. Rogers, *Acta Crystallogr.*, **3**, 20 (1950).
(15) D. Rogers and A. J. C. Wilson, *Acta Crystallogr.*, **6**, 439 (1953).
(16) B. Delaunay, *Z. Kristallogr. Kristallgeometrie, Kristallphys., Kristallchem.*, **84**, 109 (1933).
(17) W. R. Busing and H. A. Levy, *Acta Crystallogr.*, **10**, 180 (1957).
(18) “International Tables for X-Ray Crystallography,” Vol. III, Kynoch Press, Birmingham, England, 1962, p 202.
(19) See paragraph at end of paper regarding supplementary material.
(20) C. J. Ballhausen and H. B. Gray, “Molecular Orbital Theory,” W. A. Benjamin, New York, N. Y., 1964, p 81.
(21) F. R. Fronczek, W. P. Schaefer, and R. E. Marsh, *Acta Crystallogr., Sect. B*, **30**, 117 (1974).
(22) W. P. Schaefer, *Inorg. Chem.*, **7**, 725 (1968).
(23) S. Abrahams, *Acta Crystallogr.*, **8**, 503 (1955).
(24) J. R. Fritch, G. G. Christoph, and W. P. Schaefer, *Inorg. Chem.*, **12**, 2170 (1973).
(25) J. A. Stanko, private communication.
(26) W. Ozbirn and R. A. Jacobson, *Inorg. Chim. Acta*, **4**, 377 (1970).
(27) B. C. Wang, W. P. Schaefer, and R. E. Marsh, *Inorg. Chem.*, **10**, 1492 (1971).
(28) F. R. Fronczek and W. P. Schaefer, *Inorg. Chem.*, **13**, 727 (1974).
(29) C. K. Johnson, “ORTEP, a Fortran Thermal Ellipsoid Plot Program (ORNL-3794),” Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.

Contribution from the Department of Chemistry,
University of Illinois at Chicago Circle, Chicago, Illinois 60680

Molecules with an M_4X_4 Core. IV.[1-3] Crystallographic Detection of a “Step” Configuration for the Cu_4I_4 Core in Tetrameric Triphenylphosphinecopper(I) Iodide, $[PPh_3CuI]_4$

MELVYN ROWEN CHURCHILL,* BARRY G. DeBOER, and DANIEL J. DONOVAN[4]

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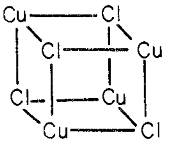
Tetrameric triphenylphosphinecopper(I) iodide crystallizes in the centrosymmetric monoclinic space group $C2/c$ [C_{2h}^6; No. 15] with $a = 25.845$ (6) Å, $b = 16.137$ (4) Å, $c = 18.264$ (5) Å, $\beta = 110.75$ (2°), $V = 7123$ (3) Å^3, and $Z = 4$. Single-crystal X-ray diffraction data, complete to $2\theta = 35°$ (Mo Kα radiation), were collected with a Picker FACS-1 automated diffractometer and the structure was solved by conventional Patterson, Fourier, and least-squares refinement techniques. The final discrepancy indices are $R_F = 6.74\%$ and $R_{wF} = 5.05\%$ for 2255 independent reflections. The molecule has crystallographically dictated C_i ($\bar{1}$) symmetry, with the Cu_4I_4 core defining a “step” structure. Most surprisingly, nonsolvated $[Ph_3PCuI]_4$ is both isomorphous and isostructural with the *solvated* bromo analog, of idealized composition $[Ph_3PCuBr]_4\cdot 2CHCl_3$. Within the $[Ph_3PCuI]_4$ molecule, the symmetry-related copper atoms Cu(2) and Cu(2′) are in tetrahedral coordination, with Cu(2)–P(2) = 2.242 (4) Å, Cu(2)–I(1) = 2.620 (2) Å, Cu(2)–I(2) = 2.728 (2) Å, and Cu(2)–I(2′) = 2.707 (2) Å; the other two symmetry-related copper atoms [Cu(1) and Cu(1′)] are in trigonal coordination with Cu(1)–P(1) = 2.228 (5) Å, Cu(1)–I(1) = 2.527 (2) Å, and Cu(1)–I(2) = 2.591 (2) Å. Intramolecular copper···copper distances are (in order) Cu(1)···Cu(2) = Cu(1′)···Cu(2′) = 2.835 (3) Å, Cu(2)···Cu(2′) = 3.404 (4) Å, and Cu(1)···Cu(2′) = Cu(1′)···Cu(2) = 4.295 (3) Å. Iodine···iodine contacts show considerably less variation, individual values (in order) being I(1)···I(2′) = I(1′)···I(2) = 4.204 (2) Å, I(2)···I(2′) = 4.238 (2) Å, and I(1)···I(2) = I(1′)···I(2′) = 4.384 (2) Å.

Introduction

We have shown previously that the Cu_4Cl_4 core of $[PPh_3CuCl]_4$ has the “cubane-like” structure I,[1,5] whereas the Cu_4Br_4 core of the analogous bromo compound, $[PPh_3CuBr]_4$, has the “step” structure II.[2,5] The overall geometry of Cu_4X_4 (X = halogen) cores is not, however, a function only of the identity or size of the halogen atoms; iodo derivatives are known both with a cubane-like core {$[AsEt_3CuI]_4$[3,6] and $[PEt_3CuI]_4$[3,7]} and with a step structure {$(Ph_2PCH_2PPh_2)_2Cu_4I_4$[8]}.



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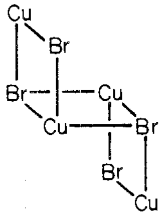

II

As a continuation of our studies on species with a Cu_4X_4 core, we decided that a determination of the crystal structure of $[PPh_3CuI]_4$ was necessary. Our results, which show the $[PPh_3CuI]_4$ molecule to be another member of the growing family of compounds known to have a step structure, are given below.

Collection of the X-Ray Diffraction Data

A sample of $[PPh_3CuI]_4$ was prepared following the procedure of Costa, Reisenhofer, and Stefani.[9] Small diamond-shaped crystals (mp 265–268°) were present in the initial reaction product. Subsequent exhaustive attempts at recrystallization failed to produce better crystals of the desired product (but did give a variety of other complexes, including $(Ph_3P)_3Cu_2I_2$!).

The best available crystal from the initial preparation was used for the X-ray structural analysis; it was, however, far from ideal, showing essentially no detectable diffraction pattern beyond $2\theta = 35°$ (Mo Kα radiation). The crystal approximated to a diamond-shaped plate between {100} faces, 0.06 mm apart; the maximum dimension was 0.29 mm along [010]. Other major faces were ($\bar{1}12$), ($\bar{1}\bar{1}2$), ($1\bar{1}2$), and ($11\bar{2}$) (defining the diamond, with parallel pairs being 0.15 mm apart). There were also very small, but distinct, {001} faces, separated by 0.14 mm.

The crystal was mounted along its extended *b* direction; a *b*-axis rotation photograph, *h*(0–1)*l* Weissenberg photographs, (0–1)*kl* and *hk*(0–1) precession photographs, and cone-axis photographs about *a* and *c* yielded approximate unit cell parameters, indicated C_{2h} (2/*m*) Laue symmetry, and exhibited the systematic absences *hkl* for $h + k = 2n + 1$ and *h*0*l* for $l = 2n + 1$, consistent with the noncentrosymmetric space group *Cc* [C_s^4; No. 9][10a] or the centrosymmetric space group *C*2/*c* [C_{2h}^6; No. 15].[10b]

The crystal was transferred to a Picker FACS-1 computer-controlled diffractometer, was accurately centered, and was aligned along [010]. As a check on possible variations in transmission factor, the strong 020 reflection was measured (by a θ–2θ scan) at $\chi = 90°$ and at 10° intervals from $\phi = 0°$ to $\phi = 350°$. The maximum variation from the mean was ~4%, suggesting that absorption was not a serious problem.

The crystal was now deliberately offset from a precise *b*-axis mounting by ~3° to minimize the effects of multiple reflection. The data collection was carried out as described in ref 11; details specific to the present study are given in Table I. [Note that the data were so weak that about 7–8 min was spent in measuring each reflection in the shell $30° < 2\theta \leq 35°$. The intensity of the standard reflections dropped by *ca.* 10% during the course of data collection; this was taken into account by the use of an anisotropic linear decay correction.]

Solution and Refinement of the Structure

Cromer and Mann's[12] analytical scattering factors for neutral copper, iodine, phosphorus, and carbon were used; for neutral hydrogen, the "best floated spherical H atom" values of Stewart, *et al.*,[13] were converted into analytical form.[14] Both the real and the imaginary components of anomalous dispersion were included for all nonhydrogen atoms, using the values of Cromer and Liberman.[15]

The function minimized during the least-squares refinement process was $\sum w(|F_o| - |F_c|)^2$, where $w(hkl) = \sigma^{-2}[F(hkl)]$. Discrepancy indices used below are defined as

$$R_F = \frac{\Sigma ||F_o| - |F_c||}{\Sigma |F_o|} \times 100\ (\%)$$

$$R_{wF} = \left[\frac{\Sigma w(|F_o| - |F_c|)^2}{\Sigma w |F_o|^2}\right]^{1/2} \times 100\ (\%)$$

All computer calculations were performed on an IBM 370/158 computer at the Computer Center of the University of Illinois at Chicago Circle. Programs used were FORDAP (Fourier synthesis, by A. Zalkin), LSHF (structure factor calculation and least-squares refinement, by B. G. DeBoer), STAN1 (calculation of distances and angles, and their esd's, by B. G. DeBoer), HAITCH (calculation of idealized H atom positions, by B. G. DeBoer), PLOD (least-squares planes, by B. G. DeBoer), and ORTEP (thermal ellipsoid drawings, by C. K. Johnson).

The analysis was begun using only the 1445 reflections with $2\theta < 30°$. A three-dimensional Patterson map led to the location of the copper, iodine, and phosphorus atoms and suggested that the true space group was the centrosymmetric *C*2/*c* with the molecule lying on a crystallographic center of symmetry. The initial structure factor calculation phased by these atoms had $R_F = 48.5\%$ and $R_{wF} = 48.2\%$. Refinement of the scale factor, along with positional and isotropic thermal parameters for atoms in the $P_2Cu_2I_2$ asymmetric unit (25 parameters), led to convergence in four cycles with $R_F = 24.7\%$ and $R_{wF} = 26.7\%$. A difference-Fourier synthesis now led to the location of all carbon atoms; three cycles of full-matrix least-squares refinement of all positional and isotropic thermal parameters, along with the scale factor (169 parameters), led to convergence with $R_F = 8.86\%$ and $R_{wF} = 7.62\%$.

Table I. Experimental Data for the X-Ray Diffraction Study of $[PPh_3CuI]_4$

(A) Crystal Parameters (at 22.5°)[a]

$a = 25.8447\ (61)$ Å	Space group *C*2/*c*
$b = 16.1371\ (38)$ Å	$Z = 4$ (tetramers)
$c = 18.2638\ (46)$ Å	Mol wt 1810.95
$\cos\beta = -0.35422\ (25)$	ρ(calcd) = 1.688 g cm^{-3}
$\beta = 110.75\ (2)°$	ρ(obsd) = 1.74 g cm^{-3} [b]
$V = 7123.4\ (3.1)$ Å^3	

(B) Measurement of Intensity Data

Radiation: Mo Kα ($\bar{\lambda}$ 0.710730 Å)[c]
Filter(s): Nb foil at counter aperture (~47% transmission of Mo Kα)
Attenuators: not used ($I_{max} \approx 5000$ counts sec^{-1})
Takeoff angle: 3.5°
Detector aperture: 6.3 × 6.3 mm
Crystal–detector distance: 330 mm
Crystal orientation: ϕ axis ~3° from [010]
Reflections measured: $\pm h, +k, +l$
Maximum 2θ: 35°
Scan type: Coupled θ(crystal)–2θ(counter)
Scan speed: 1.0°/min for $2\theta \leq 30°$; 0.5°/min for $30° < 2\theta \leq 35°$
Scan length: $\Delta(2\theta) = (1.60 + 0.692 \tan\theta)°$; starting 0.80° below the Mo Kα peak
Background measurement: stationary-crystal, stationary-counter; 40 sec each at beginning and end of 2θ scan for $2\theta \leq 30°$; 100 sec each for $30° < 2\theta \leq 35°$
Standard reflections: three remeasured after every 48 reflections; rms deviations (after application of an anisotropic linear decay correction)[d] were 0.72% for 600, 2.13% for $\bar{2}02$, and 1.62% for 020.
Reflections collected: 2257 independent measurements, 136 duplicate or equivalent measurements (averaged into primary data set), and 1065 systematic absences

(C) Treatment of Intensity Data[d]

Conversion to $|F_o|$ and $\sigma(|F_o|)$: as in ref 11, using "ignorance factor" of $p = 0.03$
Absorption coefficient: $\mu = 31.06$ cm^{-1}; no absorption corrections applied

[a] Unit cell parameters are from a least-squares fit to the setting angles of the Mo K$\bar{\alpha}$ peaks ($\bar{\lambda}$ 0.710730 Å)[c] of 12 reflections (2θ = 30–39°). Maximum and root-mean-square disagreements were 0.040 and 0.019°, respectively. [b] Neutral buoyancy in CCl_4–*sym*-$C_2H_2Br_4$. [c] J. A. Bearden, *Rev. Mod. Phys.*, 39, 78 (1967). [d] Data reduction was performed using the FORTRAN IV program RDUS2, by B. G. DeBoer.

All 2257 reflections ($2\theta_{max} = 35°$) were now included; the use of anisotropic thermal parameters for copper, iodine, and phosphorus atoms and continued refinement of all positional parameters, isotropic thermal parameters for the carbon atoms, and the scale factor (199 parameters) converged with $R_F = 7.15\%$ and $R_{wF} = 5.71\%$.

Hydrogen atoms were now introduced in calculated positions, 0.95 Å[16] outward along the (centroid of ring)–(carbon atom) vectors, with $B(H) = [B(C) + 1.0]$ Å^2. Four cycles of full-matrix least-squares refinement, with shifts of hydrogen atom parameters set equal to those of the corresponding carbon atoms, led to convergence with $R_F = 6.80\%$ and $R_{wF} = 5.68\%$. Finally, two reflections with very poor agreement between F_o and F_c [110, $\Delta F/\sigma(F) = 33.6$; 020, $\Delta F/\sigma(F) = 13.2$] were given zero weight in the refinement.[17] Hydrogen atoms were repositioned by the above criteria and two additional cycles of refinement produced convergence at $R_F = 6.74\%$ and $R_{wF} = 5.05\%$. Maximum shifts during the final cycle of refinement were $(\Delta/\sigma)_{max} = 0.017$ for a "heavy-atom" (*i.e.*, Cu, I, or P) parameter, $(\Delta/\sigma)_{max} = 0.127$ for a [C–H] group's positional parameter, and $(\Delta/\sigma)_{max} = 0.028$ for a [C–H] group's thermal parameter. [Note that, since each [C–H] moiety was refined as a rigid nonrotating group, with a constant difference between *B*(H) and *B*(C), the inclusion of hydrogen atoms involves *no* extra adjustable parameters.]

The average deviation in an observation of unit weight, defined by $[\sum w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$, was 1.53. The number of reflections (*m*) was 2255 and the number of refined parameters (*n*) was 199, yielding an *m*:*n* ratio of 11.33:1. The function $\sum w(|F_o| - |F_c|)^2$ was not significantly dependent either upon $|F_o|$ or upon $(\sin\theta)/\lambda$, thereby indicating a correctly chosen weighting scheme.

The validity of the structure was confirmed by means of a final

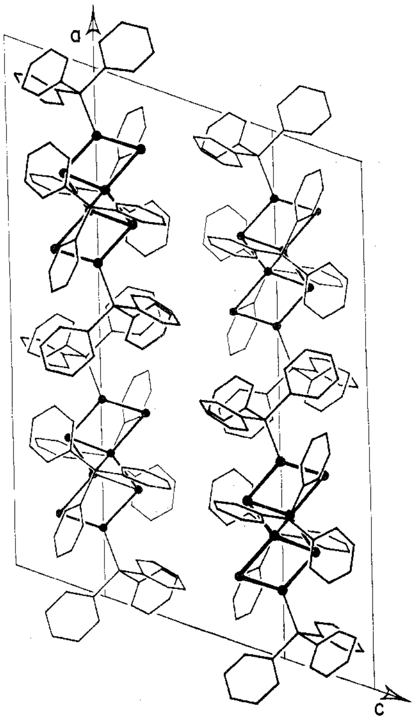

Figure 1. Packing of $[PPh_3CuI]_4$ molecules within the unit cell, as viewed along "*b*."

difference-Fourier synthesis; the greatest peaks (in order) were of height 0.96 e Å^{-3} (at 0.18, 0.24, 0.045—near I(2) and Cu(1)), 0.88 e Å^{-3} (at 0.17, 0.16, −0.075—near I(1) and Cu(2)), 0.78 e Å^{-3} (at 0.07, 0.20, −0.045—close to Cu(1)), and 0.77 e Å^{-3} (at 0.06, 0.12, −0.135—close to I(1)). All other peaks were below 0.7 e Å^{-3} in height.

A table of observed and calculated structure factor amplitudes is available.[18] Final positional and isotropic thermal parameters with their estimated standard deviations (esd's) are collected in Table II. Anisotropic thermal parameters (with esd's) for the heavy atoms are given in Table III.

The Crystal Structure

The crystal consists of discrete tetrameric molecular units of stoichiometry $[PPh_3CuI]_4$, which are mutually separated by normal van der Waals distances. There are no abnormally short intermolecular contacts. Most surprisingly, ***unsolvated*** $[PPh_3CuI]_4$ is both isomorphous and isostructural with crystals of the solvated bromo analog, which have the idealized stoichiometry $[PPh_3CuBr]_4 \cdot 2CHCl_3$.[2]

The packing of $[PPh_3CuI]_4$ molecules within the unit cell is shown in Figure 1. It is interesting to consider the relationship between the species $[PPh_3CuI]_4$ and $[PPh_3CuBr]_4 \cdot 2CHCl_3$. The macroscopic effect of the "addition" of $CHCl_3$ (accompanied by the substitution of Br for I) is an expansion of the cell edge *a* by *ca.* 9.2% along with contractions of *ca.* 1% in *b*, *c*, and *β*, such that the net volume increase is only about 6%. One remarkable feature of these two structures is that the P(1)···P(1') distances are almost identical—10.82 Å in $[PPh_3CuI]_4$ as opposed to 10.79 Å in $[PPh_3CuBr]_4 \cdot 2CHCl_3$.

Referred to Figure 1, the location of the $CHCl_3$ molecule in the bromo compound corresponds to a position approximately above (in *y*) atom I(1') of the molecule centered at ($^1/_4$, $^1/_4$, 0) and interacting with two of the phenyl rings on P(2'). It is also roughly on the extension of the vector Cu(1)→P(1) of the molecule centered at ($^3/_4$, $^3/_4$, 0) and is in contact with two of the phenyl rings on that P(1), as well as with one ring on P(1) of the molecule at ($^1/_4$, $^3/_4$, $^1/_2$).

Comparison of the phenyl group orientations in the two crystals shows only a small rotation of the Ph_3P group about

Table II. Final Positional and Isotropic Thermal Parameters for $[PPh_3CuI]_4$[a]

Atom	*x*	*y*	*z*	*B*, Å^2
Cu(1)	0.12807 (9)	0.20725 (11)	−0.00157 (12)	4.36[b]
Cu(2)	0.22590 (8)	0.15161 (11)	−0.02259 (11)	4.23[b]
I(1)	0.12548 (5)	0.13189 (7)	−0.12412 (6)	4.62[b]
I(2)	0.22384 (4)	0.25032 (7)	0.09761 (6)	3.63[b]
P(1)	0.05805 (18)	0.22833 (24)	0.04045 (24)	3.87[b]
P(2)	0.26835 (17)	0.03010 (22)	0.01830 (23)	3.24[b]
C(11)	−0.0083 (6)	0.2487 (10)	−0.0332 (8)	3.9 (3)
C(12)	−0.0509 (8)	0.2865 (12)	−0.0179 (13)	7.7 (5)
C(13)	−0.1030 (9)	0.3011 (13)	−0.0798 (13)	8.4 (6)
C(14)	−0.1088 (8)	0.2819 (11)	−0.1526 (11)	6.2 (5)
C(15)	−0.0685 (8)	0.2432 (12)	−0.1693 (12)	7.4 (5)
C(16)	−0.0183 (7)	0.2270 (10)	−0.1105 (10)	5.8 (4)
C(21)	0.0483 (7)	0.1393 (10)	0.0948 (10)	4.9 (4)
C(22)	0.0006 (9)	0.0962 (14)	0.0722 (13)	8.6 (6)
C(23)	−0.0053 (13)	0.0257 (17)	0.1187 (17)	12.3 (8)
C(24)	0.0376 (10)	0.0047 (15)	0.1791 (14)	9.5 (6)
C(25)	0.0869 (9)	0.0457 (14)	0.2041 (14)	8.7 (6)
C(26)	0.0899 (9)	0.1148 (13)	0.1586 (12)	7.6 (5)
C(31)	0.0681 (6)	0.3146 (9)	0.1076 (9)	3.8 (3)
C(32)	0.0575 (7)	0.3126 (11)	0.1757 (10)	5.7 (4)
C(33)	0.0652 (7)	0.3842 (11)	0.2248 (11)	6.2 (5)
C(34)	0.0843 (7)	0.4517 (12)	0.2040 (11)	5.8 (4)
C(35)	0.0972 (7)	0.4582 (12)	0.1393 (11)	6.2 (5)
C(36)	0.0898 (7)	0.3874 (11)	0.0887 (10)	5.8 (4)
C(41)	0.2466 (6)	−0.0256 (9)	0.0898 (9)	3.8 (3)
C(42)	0.2839 (7)	−0.0659 (9)	0.1539 (9)	4.2 (4)
C(43)	0.2640 (7)	−0.1083 (10)	0.2032 (10)	5.2 (4)
C(44)	0.2107 (7)	−0.1095 (10)	0.1920 (10)	5.1 (4)
C(45)	0.1730 (8)	−0.0707 (11)	0.1313 (11)	6.4 (5)
C(46)	0.1901 (7)	−0.0269 (10)	0.0780 (10)	4.8 (4)
C(51)	0.3421 (6)	0.0387 (9)	0.0637 (8)	3.2 (3)
C(52)	0.3802 (6)	−0.0187 (10)	0.0578 (9)	4.4 (4)
C(53)	0.4346 (7)	−0.0061 (10)	0.0912 (9)	4.8 (4)
C(54)	0.4575 (7)	0.0645 (10)	0.1333 (9)	5.3 (4)
C(55)	0.4207 (7)	0.1214 (11)	0.1404 (9)	5.0 (4)
C(56)	0.3648 (6)	0.1095 (9)	0.1068 (8)	3.3 (3)
C(61)	0.2583 (6)	−0.0447 (9)	−0.0577 (8)	3.4 (3)
C(62)	0.2623 (6)	−0.0241 (10)	−0.1269 (9)	4.3 (4)
C(63)	0.2529 (7)	−0.0751 (11)	−0.1898 (11)	5.6 (4)
C(64)	0.2406 (7)	−0.1573 (11)	−0.1810 (11)	6.2 (5)
C(65)	0.2358 (9)	−0.1815 (14)	−0.1140 (13)	8.7 (6)
C(66)	0.2450 (7)	−0.1269 (12)	−0.0512 (12)	6.9 (5)
H(12)[c]	−0.0448	0.3014	0.0348	8.7
H(13)	−0.1332	0.3261	−0.0700	9.4
H(14)	−0.1428	0.2937	−0.1934	7.2
H(15)	−0.0746	0.2283	−0.2221	8.4
H(16)	0.0107	0.2006	−0.1222	6.8
H(22)	−0.0289	0.1139	0.0267	9.6
H(23)	−0.0385	−0.0055	0.1055	13.3
H(24)	0.0339	−0.0423	0.2081	10.5
H(25)	0.1168	0.0284	0.2492	9.7
H(26)	0.1232	0.1459	0.1733	8.6
H(32)	0.0439	0.2623	0.1889	6.7
H(33)	0.0572	0.3836	0.2717	7.2
H(34)	0.0894	0.4986	0.2372	6.8
H(35)	0.1111	0.5089	0.1273	7.2
H(36)	0.0984	0.3892	0.0424	6.8
H(42)	0.3224	−0.0647	0.1625	5.2
H(43)	0.2892	−0.1369	0.2467	6.2
H(44)	0.1984	−0.1390	0.2278	6.1
H(45)	0.1348	−0.0729	0.1244	7.4
H(46)	0.1642	0.0012	0.0348	5.8
H(52)	0.3664	−0.0681	0.0291	5.4
H(53)	0.4592	−0.0472	0.0857	5.8
H(54)	0.4963	0.0733	0.1566	6.3
H(55)	0.4352	0.1703	0.1693	6.0
H(56)	0.3400	0.1505	0.1124	4.3
H(62)	0.2718	0.0320	−0.1318	5.3
H(63)	0.2555	−0.0569	−0.2379	6.6
H(64)	0.2347	−0.1956	−0.2227	7.2
H(65)	0.2264	−0.2378	−0.1096	9.7
H(66)	0.2422	−0.1446	−0.0032	7.9

[a] Esd's, shown in parentheses, are right-adjusted to the least significant digit of the preceding number. [b] "Equivalent isotropic thermal parameter," corresponding to the average mean-square displacement along the three principal axes of the vibration ellipsoid. [c] Hydrogen atoms are in restrained positions (see text).

Table III. Anisotropic Thermal Parameters[a] for the Heavy Atoms in $[PPh_3CuI]_4$

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	$\langle U\rangle^b$
Cu(1)	5.59 (12)	3.61 (10)	4.30 (11)	−0.27 (9)	2.26 (10)	−0.26 (9)	0.211, 0.222, 0.268
Cu(2)	5.13 (12)	2.79 (10)	4.58 (12)	0.44 (8)	1.47 (10)	0.36 (8)	0.184, 0.242, 0.261
I(1)	5.31 (7)	4.21 (6)	4.12 (7)	−0.41 (5)	1.39 (5)	−0.97 (5)	0.201, 0.255, 0.265
I(2)	4.95 (6)	3.07 (5)	3.25 (5)	−0.52 (5)	1.91 (4)	−0.45 (5)	0.183, 0.199, 0.254
P(1)	4.95 (24)	3.20 (22)	3.57 (22)	−0.58 (18)	1.67 (19)	−0.24 (17)	0.196, 0.209, 0.255
P(2)	4.58 (25)	2.11 (19)	2.95 (22)	0.11 (16)	1.25 (19)	0.09 (16)	0.163, 0.193, 0.244

[a] These anisotropic thermal parameters have units of Å^2 and are analogous to the normal isotropic thermal parameters, entering the expression for the structure factor in the form $\exp[-0.25(B_{11}a^{*2}h^2 + B_{22}b^{*2}k^2 + B_{33}c^{*2}l^2 + 2B_{12}a^*b^*hk + 2B_{13}a^*c^*hl + 2B_{23}b^*c^*kl)]$. [b] These values correspond to the root-mean-square amplitudes of vibration (in Å) of the atom along the three principal axes of its vibration ellipsoid.

Table IV. Interatomic Distances (Å) with Esd's for $[PPh_3CuI]_4$[a-c]

Atoms	Distance	Atoms	Distance
(A) Copper···Copper Distances			
Cu(1)···Cu(2)	2.8345 (29)	Cu(2)···Cu(2′)	3.4040 (36)
Cu(1)···Cu(2′)	4.2949 (29)		
(B) Iodine···Iodine Distances			
I(1)···I(2)	4.3842 (17)	I(2)···I(2′)	4.2375 (22)
I(1)···I(2′)	4.2044 (18)		
(C) Copper–Iodine Bond Lengths			
Cu(1)–I(1)	2.5273 (22)	Cu(2)–I(1)	2.6203 (23)
Cu(1)–I(2)	2.5913 (24)	Cu(2)–I(2)	2.7281 (23)
		Cu(2)–I(2′)	2.7073 (22)
(D) Copper–Phosphorus Bond Lengths			
Cu(1)–P(1)	2.2277 (47)	Cu(2)–P(2)	2.2418 (39)
(E) Phosphorus–Carbon Bond Lengths			
P(1)–C(11)	1.795 (15)	P(2)–C(41)	1.830 (16)
P(1)–C(21)	1.813 (17)	P(2)–C(51)	1.794 (14)
P(1)–C(31)	1.812 (15)	P(2)–C(61)	1.787 (15)
(F) Carbon–Carbon Bond Lengths			
C(11)–C(12)	1.370 (22)	C(41)–C(42)	1.388 (19)
C(12)–C(13)	1.438 (25)	C(42)–C(43)	1.370 (20)
C(13)–C(14)	1.322 (24)	C(43)–C(44)	1.320 (20)
C(14)–C(15)	1.338 (23)	C(44)–C(45)	1.342 (21)
C(15)–C(16)	1.385 (22)	C(45)–C(46)	1.397 (21)
C(16)–C(11)	1.387 (20)	C(46)–C(41)	1.398 (19)
C(21)–C(22)	1.348 (24)	C(51)–C(52)	1.384 (19)
C(22)–C(23)	1.460 (29)	C(52)–C(53)	1.334 (19)
C(23)–C(24)	1.301 (30)	C(53)–C(54)	1.385 (20)
C(24)–C(25)	1.363 (27)	C(54)–C(55)	1.360 (20)
C(25)–C(26)	1.408 (26)	C(55)–C(56)	1.370 (19)
C(26)–C(21)	1.335 (22)	C(56)–C(51)	1.395 (18)
C(31)–C(32)	1.364 (21)	C(61)–C(62)	1.346 (19)
C(32)–C(33)	1.432 (22)	C(62)–C(63)	1.363 (20)
C(33)–C(34)	1.307 (22)	C(63)–C(64)	1.387 (22)
C(34)–C(35)	1.341 (22)	C(64)–C(65)	1.331 (24)
C(35)–C(36)	1.437 (22)	C(65)–C(66)	1.398 (25)
C(36)–C(31)	1.397 (20)	C(66)–C(61)	1.385 (21)

[a] The $[PPh_3CuI]_4$ molecule lies on a center of symmetry at ($^1/_4$, $^1/_4$, 0). Atoms in the basic asymmetric unit are labeled normally; atoms in the "other half" of the molecule are labeled with a prime and are related to those in the basic asymmetric unit by the transformation $x' = {}^1/_2 - x$, $y' = {}^1/_2 - y$, $z' = -z$. [b] Esd's were calculated from the full positional correlation matrix using the FORTRAN IV program STAN1 by B. G. DeBoer. Contributions from errors in the unit cell parameters were included. [c] Bond lengths are not corrected for any possible effects of thermal motion.

the P(1)–Cu(1) bond, plus a small rotation of the C(61)–C(66) phenyl ring about the C(61)–P(2) bond.

We have carried out some calculations to determine whether $CHCl_3$ molecules can fit into the $[PPh_3CuI]_4$ structure. We note first that, within the $[PPh_3CuBr]_4\cdot 2CHCl_3$ crystal, the three (poorly defined) chlorine atoms are involved in no contacts shorter than the sum of the appropriate van der Waals radii. If three hypothetical chlorine atoms are introduced into the present $[PPh_3CuI]_4$ structure at the same fractional coordinates that they occupy in the solvated bromo complex, there arise "Cl"···C(phenyl) contacts of 2.47, 2.49, 3.11, 3.16, 3.24, and 3.35 Å—all of which are shorter than the minimum van der Waals distance of *ca.* 3.50 Å. In addition, one "Cl"···I contact of 3.68 Å is found (*cf.* the accepted Cl···I van der Waals distance of *ca.* 3.95 Å). The corresponding Cl···Br distance in $[PPh_3CuBr]_4\cdot 2CHCl_3$ is 3.90 Å, *i.e.*, greater than the accepted van der Waals distance of *ca.* 3.75 Å.

To summarize, then, there *is* a substantial cavity within the present $[PPh_3CuI]_4$ crystal; however, its radius is about 1 Å too small to accommodate a chloroform molecule.

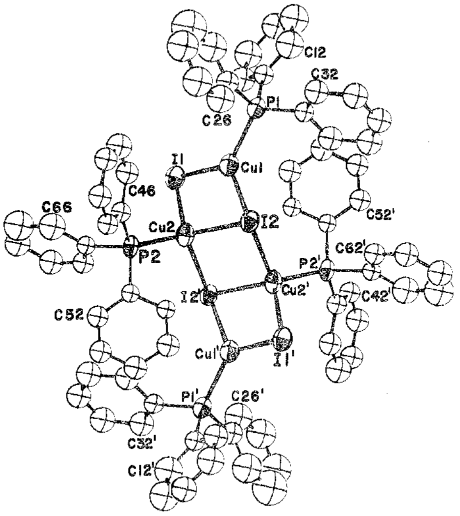

Figure 2. $[PPh_3CuI]_4$ molecule projected onto the plane defined by the four copper atoms [ORTEP diagram, showing 50% probability envelopes of the atomic vibration ellipsoids].

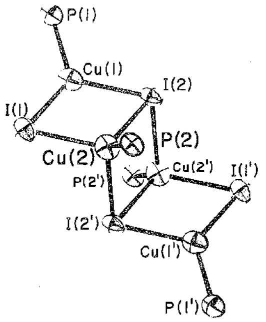

Figure 3. $P_4Cu_4I_4$ portion of the $[PPh_3CuI]_4$ molecule, oriented so as to demonstrate the "step structure" of the Cu_4I_4 molecular core [ORTEP diagram, 50% probability envelopes].

The Molecular Structure

Interatomic distances (with esd's) are shown in Table IV; bond angles and their associated esd's are collected in Table V. The overall molecular geometry of $[PPh_3CuI]_4$ is depicted in Figure 2. The molecule has crystallographically imposed C_i ($\bar{1}$) symmetry and is centered on the special position ($^1/_4$, $^1/_4$, 0) of space group $C2/c$. The $P_4Cu_4I_4$ portion of the

Table V. Bond Angles (deg) for $[PPh_3CuI]_4$

Atoms	Angle	Atoms	Angle
(A) Angles within the Cu_4I_4 Core			
I(1)–Cu(1)–I(2)	117.85 (9)	Cu(2')–I(2)–Cu(1)	108.29 (7)
Cu(1)–I(2)–Cu(2)	64.34 (7)	Cu(2')–I(2)–Cu(2)	77.55 (7)
I(2)–Cu(2)–I(1)	110.10 (8)	I(2')–Cu(2)–I(1)	104.20 (7)
Cu(2)–I(1)–Cu(1)	66.80 (7)	I(2')–Cu(2)–I(2)	102.45 (7)
(B) Phosphorus–Copper–Iodine Angles			
P(1)–Cu(1)–I(1)	127.49 (14)	P(2)–Cu(2)–I(1)	112.00 (12)
P(1)–Cu(1)–I(2)	114.18 (13)	P(2)–Cu(2)–I(2)	112.92 (13)
		P(2)–Cu(2)–I(2')	114.45 (13)
(C) Copper· · ·Copper–Phosphorus Angles			
Cu(2)· · ·Cu(1)–P(1)	165.34 (14)	Cu(1)· · ·Cu(2)–P(2)	125.92 (14)
(D) Copper–Phosphorus–Carbon Angles			
Cu(1)–P(1)–C(11)	116.55 (51)	Cu(2)–P(2)–C(41)	115.42 (51)
Cu(1)–P(1)–C(21)	110.77 (57)	Cu(2)–P(2)–C(51)	113.64 (37)
Cu(1)–P(1)–C(31)	114.31 (52)	Cu(2)–P(2)–C(61)	114.36 (49)
(E) Carbon–Phosphorus–Carbon Angles			
C(11)–P(1)–C(21)	105.90 (77)	C(41)–P(2)–C(51)	104.62 (69)
C(11)–P(1)–C(31)	103.66 (71)	C(41)–P(2)–C(61)	103.02 (69)
C(21)–P(1)–C(31)	104.60 (74)	C(51)–P(2)–C(61)	104.48 (68)
(F) Phosphorus–Carbon–Carbon Angles			
P(1)–C(11)–C(12)	123.5 (14)	P(2)–C(41)–C(42)	122.3 (12)
P(1)–C(11)–C(16)	120.0 (12)	P(2)–C(41)–C(46)	117.8 (12)
P(1)–C(21)–C(22)	122.1 (15)	P(2)–C(51)–C(52)	125.6 (12)
P(1)–C(21)–C(26)	119.3 (15)	P(2)–C(51)–C(56)	119.3 (11)
P(1)–C(31)–C(32)	124.9 (13)	P(2)–C(61)–C(62)	121.6 (13)
P(1)–C(31)–C(36)	116.9 (13)	P(2)–C(61)–C(66)	123.6 (13)
(G) Carbon–Carbon–Carbon Angles			
C(16)–C(11)–C(12)	116.5 (16)	C(46)–C(41)–C(42)	119.9 (15)
C(11)–C(12)–C(13)	120.6 (20)	C(41)–C(42)–C(43)	118.6 (15)
C(12)–C(13)–C(14)	119.6 (22)	C(42)–C(43)–C(44)	121.4 (18)
C(13)–C(14)–C(15)	121.3 (21)	C(43)–C(44)–C(45)	122.2 (18)
C(14)–C(15)–C(16)	120.1 (20)	C(44)–C(45)–C(46)	119.8 (18)
C(15)–C(16)–C(11)	121.9 (18)	C(45)–C(46)–C(41)	118.1 (16)
C(26)–C(21)–C(22)	118.7 (19)	C(56)–C(51)–C(52)	115.1 (13)
C(21)–C(22)–C(23)	119.8 (23)	C(51)–C(52)–C(53)	121.7 (16)
C(22)–C(23)–C(24)	117.7 (29)	C(52)–C(53)–C(54)	123.7 (17)
C(23)–C(24)–C(25)	124.8 (29)	C(53)–C(54)–C(55)	115.6 (16)
C(24)–C(25)–C(26)	115.3 (23)	C(54)–C(55)–C(56)	121.7 (16)
C(25)–C(26)–C(21)	123.7 (21)	C(55)–C(56)–C(51)	122.2 (15)
C(36)–C(31)–C(32)	118.1 (16)	C(66)–C(61)–C(62)	114.8 (16)
C(31)–C(32)–C(33)	121.6 (17)	C(61)–C(62)–C(63)	126.3 (16)
C(32)–C(33)–C(34)	118.2 (19)	C(62)–C(63)–C(64)	117.3 (18)
C(33)–C(34)–C(35)	123.9 (20)	C(63)–C(64)–C(65)	119.2 (20)
C(34)–C(35)–C(36)	119.1 (19)	C(64)–C(65)–C(66)	121.6 (22)
C(35)–C(36)–C(31)	118.9 (17)	C(65)–C(66)–C(61)	120.7 (19)

molecule is shown in Figure 3. As can clearly be seen, the Cu_4I_4 core of the molecule has a step structure, rather than a cubane-like configuration.

The “step structure” of $[PPh_3CuI]_4$ is defined by three four-membered systems: Cu(1)–I(1)–Cu(2)–I(2) [plane I of Table VI], Cu(2)–I(2)–Cu(2')–I(2') [plane II of Table VI], and Cu(1')–I(1')–Cu(2')–I(2') [related to “plane I” by an inversion center at $^1/_4$, $^1/_4$, 0]. The dihedral angle between planes I and II is 115.06° as opposed to a value of 107.8° in $[PPh_3CuBr]_4$.[2] The increased value for the iodo species would appear to result from steric factors (*vide infra*).

Atoms Cu(2), I(2), Cu(2'), and I(2') are required crystallographically to be precisely coplanar. Atoms Cu(1) and I(1) lie −2.071 and −2.307 Å from the plane, while atoms Cu(1') and I(1') are displaced in the opposite sense by +2.071 and +2.307 Å, respectively.

Atoms Cu(1), I(1), Cu(2), and I(2) are *not* precisely coplanar, individual deviations from the least-squares plane being −0.0843 Å for Cu(1), −0.0725 Å for Cu(2), +0.0803 Å for I(1), and +0.0766 Å for I(2). The nonplanarity of this four-membered system is conveniently described in terms of the dihedral angles of 167.26° [between I(1)–Cu(1)–I(2) and I(1)–Cu(2)–I(2)] and 171.78° [between Cu(1)–I(1)–Cu(2) and Cu(1)–I(2)–Cu(2)].

Atoms in the step-like Cu_4I_4 core of the $[PPh_3CuI]_4$ molecule have variable coordination numbers (CN's). Thus, Cu(1) and Cu(1') are in trigonal coordination (CN = 3), while Cu(2) and Cu(2') each have an essentially tetrahedral coordination environment (CN = 4). Atoms I(1) and I(1') have an angular geometry (CN = 2), while I(2) and I(2') are in pyramidal sites (CN = 3).

As was previously noted for the Cu_4Br_4 core of $[PPh_3CuBr]_4$,[2] the copper–halogen distances show significant differences and increase systematically as the CN's of the component atoms increase. Thus, Cu(1)–I(1) = Cu(1')–I(1') = 2.5273 (22) Å [CN = 3 and 2], Cu(1)–I(2) = Cu(1')–I(2') = 2.5913 (24) Å [CN = 3 and 3], Cu(2)–I(1) = Cu(2')–I(1') = 2.6203 (23) Å [CN = 4 and 2], Cu(2)–I(2') = Cu(2')–I(2) = 2.7073 (22) Å [CN = 4 and 3], and Cu(2)–I(2) = Cu(2')–I(2') = 2.7281 (23) Å [CN = 4 and 3].

The four copper atoms are *precisely* coplanar (see plane III of Table VI) and define a parallelogram in which Cu(1)···Cu(2) = Cu(1')···Cu(2') = 2.8345 (29) Å and Cu(1)···Cu(2') = Cu(1')···Cu(2) = 4.2949 (29) Å; the short diagonal of the parallelogram, Cu(2)···Cu(2'), is 3.4040 (36) Å in length.

For the sake of comparison we note that the four copper atoms in $[PPh_3CuBr]_4$[2] define a parallelogram with edges of 2.9905 (22) and 3.9873 (23) Å and a short diagonal of 3.4481 (29) Å; in $(Ph_2PCH_2PPh_2)_2Cu_4I_4$,[8] the “$Cu_4$ parallelogram” has edges of 2.682 and 3.108 Å; and in $Cu_4[SC(NH_2)_2]_9(NO_3)_4$ there are rectangles of copper atoms with edges of 2.707 (5) and >4 Å.[19] Within the “cubane-like” tetrameric pnicogen–copper halide derivatives, copper···copper distances again show large variations—3.1179 (13) to 3.4298 (18) Å in $[PPh_3CuCl]_4$,[1] 2.9272 (20) Å in $[PEt_3CuI]_4$,[3] and 2.7826 (24) Å in $[AsEt_3CuI]_4$.[3]

The four iodine atoms of $[PPh_3CuI]_4$ are precisely coplanar [see plane IV of Table VI]. Individual iodine···iodine distances show considerably less variation than do the copper···copper distances; in order, we have I(1)···I(2') = I(1')···I(2) = 4.2044 (18) Å, I(2)···I(2') = 4.2375 (22) Å, and I(1)···I(2) = I(1')···I(2') = 4.3842 (17) Å. [*Cf.* iodine···iodine contacts of 4.3800 (11) and 4.4237 (15) Å in the cubane-like species $[PEt_3CuI]_4$ and $[AsEt_3CuI]_4$, respectively.[3]]

Angles within the four-membered ring defined by Cu(1)–I(1)–Cu(2)–I(2) (and, of course, the symmetry-related system Cu(1')–I(1')–Cu(2')–I(2')) vary grossly from 90°. Angles at the copper atoms are close to the ideal trigonal or tetrahedral values [I(1)–Cu(1)–I(2) = 117.85 (9)° and I(2)–Cu(2)–I(1) = 110.10 (8)°, respectively] while angles at the iodine atoms are quite acute [Cu(2)–I(1)–Cu(1) = 66.80 (7)° and Cu(1)–I(2)–Cu(2) = 64.34 (7)°].

A similar, but less pronounced, pattern occurs within the strictly planar central ring Cu(2)–I(2)–Cu(2')–I(2'). Individual angles are I(2')–Cu(2)–I(2) = I(2)–Cu(2')–I(2') = 102.45 (7)° and Cu(2')–I(2)–Cu(2) = Cu(2)–I(2')–Cu(2') = 77.55 (7)°; the lower spread of angles here is presumably due to a complex set of interrelated factors including the higher connectivity of the atoms concerned, the greater length of the Cu(2)–I(2) and Cu(2)–I(2') bonds (relative to other such bonds within the molecule), and a greater and more restrictive set of steric restraints.

Angles between atoms in different planes of the step are not similarly dependent upon the nature of the central atom; thus Cu(1)–I(2)–Cu(2') = Cu(1')–I(2')–Cu(2) = 108.29 (7)° and I(1)–Cu(2)–I(2') = I(1')–Cu(2')–I(2) = 104.20 (7)°.

Small angles at the iodine atoms are general to species with a Cu_4I_4 core, irrespective of the gross geometry of the molecule. Cu–I–Cu angles are 58.9, 68.7, and 83.6° in $(Ph_2PCH_2PPh_2)_2Cu_4I_4$,[8] which has a step structure; corre-

Table VI. Least-Squares Planes, Deviations Therefrom, and Dihedral Angles for $[PPh_3CuI]_4$[a-c]

Atom	Dev, Å	Atom	Dev, Å
Plane I: $0.22208X + 0.84236Y - 0.49103Z = 3.6520$			
Cu(1)*	−0.0843	P(1)	−0.612
I(1)*	0.0803	P(2)	−1.882
Cu(2)*	−0.0725	Cu(2′)	2.435
I(2)*	0.0766	I(2′)	2.286
Plane Ia: $0.10451X + 0.87523Y - 0.47228Z = 3.2867$			
I(1)*	0.000	I(2)*	0.000
Cu(1)*	0.000	Cu(2)	−0.338
Plane Ib: $0.31410X + 0.80745Y - 0.49937Z = 4.0479$			
I(1)*	0.000	I(2)*	0.000
Cu(2)*	0.000	Cu(1)	−0.291
Plane Ic: $0.23700X + 0.87347Y - 0.42530Z = 3.7194$			
Cu(1)*	0.000	Cu(2)*	0.000
I(1)*	0.000	I(2)	0.321
Plane Id: $0.19949X + 0.81165Y - 0.54902Z = 3.3915$			
Cu(1)*	0.000	Cu(2)*	0.000
I(2)*	0.000	I(1)	0.307
Plane II: $0.73347X - 0.36029Y + 0.57639Z = 3.2856$			
Cu(2)*	0.000	I(1)	−2.307
I(2)*	0.000	Cu(1′)	2.071
Cu(2′)*	0.000	I(1′)	2.307
I(2′)*	0.000	P(2)	1.720
Cu(1)	−2.071	P(2′)	−1.720
Plane III: $0.04646X - 0.24904Y + 0.96738Z = -0.7045$			
Cu(1)*	0.000	P(2)	1.203
Cu(2)*	0.000	P(2′)	−1.203
Cu(1′)*	0.000	I(1)	−1.688
Cu(2)*	0.000	I(1′)	1.688
P(1)	0.513	I(2)	1.551
P(1′)	−0.513	I(2′)	−1.551
Plane IV: $-0.40048X + 0.85980Y - 0.31679Z = 0.8811$			
I(1)*	0.000	Cu(1)	0.673
I(2)*	0.000	Cu(1′)	−0.673
I(1′)*	0.000	Cu(2)	−1.052
I(2′)*	0.000	Cu(2′)	1.052
Plane V: $0.42167X + 0.89427Y - 0.14993Z = 3.6669$			
C(11)*	0.007	C(15)*	−0.008
C(12)*	0.007	C(16)*	−0.007
C(13)*	−0.022	P(1)	0.047
C(14)*	0.023		
Plane VI: $0.56835X - 0.59577Y - 0.56748Z = -1.8956$			
C(21)*	−0.001	C(25)*	0.005
C(22)*	0.013	C(26)*	−0.008
C(23)*	−0.016	P(1)	0.012
C(24)*	0.008		
Plane VII: $0.80444X - 0.30133Y + 0.51193Z = 0.2847$			
C(31)*	−0.018	C(35)*	0.006
C(32)*	0.013	C(36)*	0.000
C(33)*	−0.001	P(1)	−0.045
C(34)*	−0.006		
Plane VIII: $-0.09914X + 0.82596Y + 0.55494Z = -0.0577$			
C(41)*	−0.006	C(45)*	0.001
C(42)*	0.009	C(46)*	0.002
C(43)*	−0.006	P(2)	−0.044
C(44)*	0.002		
Plane IX: $-0.31949X - 0.44726Y + 0.83540Z = -2.0596$			
C(51)*	−0.003	C(55)*	0.002
C(52)*	−0.000	C(56)*	0.002
C(53)*	0.005	P(2)	−0.075
C(54)*	−0.006		
Plane X: $0.90803X - 0.23801Y + 0.34472Z = 6.2356$			
C(61)*	−0.004	C(65)*	−0.006
C(62)*	0.011	C(66)*	0.001
C(63)*	−0.015	P(2)	−0.054
C(64)*	0.012		

Dihedral Angles

Planes	Angle, deg	Planes	Angle, deg
I–II	115.06	Ib–II	110.39
Ia–Ib	167.26	Id–II	117.55
Ic–Id	171.78	III–IV	122.63

[a] All calculations were performed using the FORTRAN IV program PLOD, by B. G. DeBoer. [b] Equations to planes are presented in cartesian coordinates, such that $[X, Y, Z] = [xa + zc \cos \beta, yb, zc \sin \beta]$. [c] Atoms identified by an asterisk were assigned unit weights; all others were given zero weight.

sponding angles in the cubane-like species $[PEt_3CuI]_4$ and $[AsEt_3CuI]_4$ are 66.10 (4) and 62.63 (5)°, respectively.[3]

These small angles could be the result of any of (or any combination of) the following: (i) restrictions imposed by the coordination geometry of the metal atom, (ii) metal–metal bonding, and (iii) van der Waals repulsions between the halogen atoms. The available data are consistent with item (iii) being the dominant consideration. Thus, Cu–I–Cu angles as low as ~60° are required to give reasonable I···I separations [*i.e.*, separations corresponding to about two van der Waals radii or about 4.3 Å[20]] in the iodo complexes. In contrast, Cu–Br–Cu angles within the four-membered rings of the bromo species $[PPh_3CuBr]_4$ are 71.74 (6), 76.04 (6), and 83.24 (6)° (twice);[2] these increased angles are associated with Br···Br contacts of 3.8801 (25)–3.9565 (20) Å [*cf.* a value of ~3.9 Å based upon two van der Waals radii for bromine[20]].

Atoms Cu(1) and Cu(1′) are each in approximately trigonal-planar coordination, individual angles being P(1)–Cu(1)–I(1) = 127.49 (14)°, P(1)–Cu(1)–I(2) = 114.18 (13)°, and I(1)–Cu(1)–I(2) = 117.85 (9)°. Cu(2) and Cu(2′) each have a distorted tetrahedral environment. P(2)–Cu(2)–I angles are each greater than the ideal tetrahedral angle of 109.47° and range from 112.00 (12) to 114.45 (13)°; I–Cu(2)–I angles are 102.45 (7), 104.20 (7), and 110.10 (8)°. The Cu(trigonal)–P distance of 2.2277 (47) Å is slightly shorter than the Cu(tetrahedral)–P distance of 2.2418 (39) Å.

The Triphenylphosphine Ligand

Phosphorus–carbon distances range from 1.787 (15) to 1.830 (16) Å, averaging 1.805 ± 0.016 Å.[21] Cu–P–C angles range from 110.77 (57) to 116.55 (51)° [average 114.18°], while C–P–C angles range from 103.02 (69) to 105.90 (77)° [average 104.38°]. This form of angular distortion from T_d toward C_{3v} symmetry is general for metal–phosphine complexes.[22]

Carbon–carbon distances within the triphenylphosphine ligands range from 1.301 (30) to 1.460 (29) Å, the average of the 36 independent values being 1.372 ± 0.037 Å.[21] The rather large range of these distances is similar to that observed in $[PPh_3CuBr]_4$ (1.302 (17)–1.426 (15) Å)[2] and is clearly the net result of two factors—(i) large esd's on individual bond lengths and (ii) a systematic error due to rigid-body motion of the phenyl rings; in this latter context we note the C(meta)–C(para) bonds, which are the most distant from the molecular center of gravity and thus the most affected by phenyl groups "waving" about their P–C bonds, are sys-

Table VII. Comparison of $[PPh_3CuX]_4$ Species

	X = Cl[a]	X = Br[b]	X = I
Geometry of Cu_4X_4 core	Cubane	Step	Step
Cu–X, Å	2.3632 (19)–2.5050 (20)	2.3765 (20)–2.6637 (19)	2.5273 (22)–2.7281 (23)
Cu· · ·Cu, Å	3.1179 (13)–3.4298 (18)	2.9905 (22)–3.9873 (23)	2.8345 (29)–4.2949 (29)
X· · ·X, Å	3.3925 (33)–3.7223 (26)[c]	3.8801 (25)–3.9565 (20)	4.2044 (18)–4.3842 (17)
Av X· · ·X, Å	3.5762[c]	3.9173	4.2829
van der Waals X· · ·X, Å[d]	3.6	3.9	4.3

[a] See ref 1. [b] See ref 2. [c] In Table III of ref 1, the Cl(1)· · ·Cl(1′) distance is given erroneously as 3.0596 (34) Å; its true value is 3.5096 (34) Å. Unfortunately, the value with transposed digits was also used in calculating the average chlorine· · ·chlorine distance, which is erroneously given in the text of ref 1 as 3.5012 Å; the true value is 3.5762 Å, as given above. [d] See ref 20.

tematically low, ranging from 1.301 (30) to 1.387 (22) Å and averaging only 1.341 ± 0.028 Å.[21] Average isotropic thermal parameters are 3.83 $Å^2$ for C(P-bonded), 5.78 $Å^2$ for C(ortho), 7.08 $Å^2$ for C(meta), and 6.35 $Å^2$ for C(para).

The 36 independent C–C–C angles vary from 114.8 (16) to 126.3 (16)°, the average value being 120.0 ± 3.3°.[21] As has been noted in recent structural studies of $[PPh_3CuCl]_4$,[1] $[PPh_3CuBr]_4$,[2] $(PPh_2Me)_2Ni(\sigma\text{-}C_6F_5)Br$,[23] and $(PPh_2Me)_2Ni(\sigma\text{-}C_6F_5)_2$,[24] the C–C–C angles at the P-bonded carbon atoms are all systematically reduced from the ideal trigonal value of 120°. Individual angles range from C(66)–C(61)–C(62) = 114.8 (16)° to C(46)–C(41)–C(42) = 119.9 (15)°, with an average of 117.2 ± 2.0°.[21]

The six phenyl groups are each planar within the limits of experimental error, *maximum* deviations of atoms from their least-squares planes being 0.023 Å for the phenyl group defined by C(11) through C(16), 0.016 Å for C(21)–C(26), 0.018 Å for C(31)–C(36), 0.009 Å for C(41)–C(46), 0.006 Å for C(51)–C(56), and 0.015 Å for C(61)–C(66) [see Table VI].

Conclusion

The molecule $[PPh_3CuI]_4$ has been shown to have a central Cu_4I_4 core with a step structure (as does $[PPh_3CuBr]_4$[2]) rather than the cubane-like configuration of $[PPh_3CuCl]_4$.[1] The presently available structural data suggest that the step structure is favored over the cubane-like arrangement in $[PR_3CuX]_4$ tetramers only when both bulky phosphine ligands *and* large halogen atoms are present.

Selected data on the $[PPh_3CuX]_4$ molecules (X = Cl,[1] Br,[2] and I) are collected in Table VII. As can easily be seen, the nonbonding copper···copper distances and even the *bonding* copper–halogen distances vary appreciably within each of these three species. While the nonbonding halogen···halogen distances between second nearest neighbors also show quite wide variations within a given molecule, the average halogen···halogen distance is not statistically distinguishable from the value expected from considerations of the appropriate van der Waals radii.

Current work (to be reported at a later date) is aimed toward determining the conditions influencing the occurrence of the step *vis à vis* the cubane structure in tetrameric complexes of the type $[AsR_3CuX]_4$, $[PR_3AgX]_4$, and $[AsR_3AgX]_4$.

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Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number AIC40484M.

References and Notes

(1) Part I: M. R. Churchill and K. L. Kalra, *Inorg. Chem.*, **13**, 1065 (1974).
(2) Part II: M. R. Churchill and K. L. Kalra, *Inorg. Chem.*, **13**, 1427 (1974).
(3) Part III: M. R. Churchill and K. L. Kalra, *Inorg. Chem.*, **13**, 1899 (1974).
(4) Undergraduate student participant.
(5) M. R. Churchill and K. L. Kalra, *J. Amer. Chem. Soc.*, **95**, 5772 (1973).
(6) A. F. Wells, *Z. Kristallogr., Kristallgeometrie, Kristallphys., Kristallchem.*, **94**, 447 (1936).
(7) F. G. Mann, D. Purdie, and A. F. Wells, *J. Chem. Soc.*, 1503 (1936).
(8) M. Marsich, G. Nardin, and L. Randaccio, *J. Amer. Chem. Soc.*, **95**, 4053 (1973).
(9) G. Costa, E. Reisenhofer, and L. Stefani, *J. Inorg. Nucl. Chem.*, **27**, 2581 (1965).
(10) “International Tables for X-Ray Crystallography,” Vol. I, 2nd ed, Kynoch Press, Birmingham, England, 1965: (a) p 89; (b) p 101.
(11) M. R. Churchill and B. G. DeBoer, *Inorg. Chem.*, **12**, 525 (1973).
(12) D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, **24**, 321 (1968).
(13) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965); see, especially, Table II on p 3178.
(14) The Cromer and Mann analytical scattering factors take the form of a constant plus four exponentials; *viz.*

$$f((\sin\theta)/\lambda) = c + \sum_{i=1}^{i=4} a_i \exp[-b_i(\sin^2\theta)/\lambda^2]$$

We have converted the Stewart scattering factors for hydrogen into the analytical form. The constants are as follows: $c = 0.00175$, $a_1 = 0.39679$, $b_1 = 8.81473$, $a_2 = 0.37788$, $b_2 = 19.8553$, $a_3 = 0.11593$, $b_3 = 43.9069$, $a_4 = 0.10755$, $b_4 = 2.68878$. The maximum absolute error is 2×10^{-4} electron for $0 \leq (\sin\theta)/\lambda \leq 1.50$.
(15) D. T. Cromer and D. Liberman, *J. Chem. Phys.*, **53**, 1891 (1970).
(16) M. R. Churchill, *Inorg. Chem.*, **12**, 1213 (1973).
(17) We refer the reader to the comment of C. J. Fritchie in Proceedings of the Symposium on Accuracy in X-Ray Intensity Measurement, Suffern, N.Y., Feb 1965 (*Trans. Amer. Crystallogr. Assoc.*, **1**, 30 (1965)): “I think that one should be extremely generous in throwing out reflections that seem the least bit suspicious.”
(18) See paragraph at end of paper regarding supplementary material.
(19) R. G. Vranka and E. L. Amma, *J. Amer. Chem. Soc.*, **88**, 4270 (1966).
(20) L. Pauling, “The Nature of the Chemical Bond,” 3rd ed, Cornell University Press, Ithaca, N.Y., 1960, p 260. Appropriate van der Waals radii are 1.95 Å for Br and 2.15 Å for I.
(21) Estimated standard deviations on average bond distances and angles are preceded, in the text, by “±.” They are calculated *via* the scatter formula, *viz.*, $\sigma(\text{mean}) = [\sum(X_i - \bar{X})^2/(N-1)]^{1/2}$, where X_i is the *ith* measurement and $\bar{X}$ is the mean of N “equivalent” measurements.
(22) M. R. Churchill and T. A. O’Brien, *J. Chem. Soc. A*, 2970 (1968)—see particularly Table VII.
(23) M. R. Churchill, K. L. Kalra, and M. V. Veidis, *Inorg. Chem.*, **12**, 1656 (1973).
(24) M. R. Churchill and M. V. Veidis, *J. Chem. Soc., Dalton Trans.*, 670 (1972).