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

Molecules with an M_4X_4 Core. I. Crystal and Molecular Structure of Tetrameric Triphenylphosphinecopper(I) Chloride, a "Cubane-Like" Molecule, Including the Location and Refinement of All Hydrogen Atoms

MELVYN ROWEN CHURCHILL* and KRISHAN L. KALRA

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Tetrameric triphenylphosphinecopper(I) chloride, $[PPh_3CuCl]_4$, crystallizes in the centrosymmetric orthorhombic space group *Pbcn* $[D_{2h}^{14}$; No. 60] with $a = 17.468$ (2) Å, $b = 20.519$ (3) Å, and $c = 18.215$ (2) Å. The observed density of 1.45 (2) g cm^{-3} is consistent with the value of 1.471 g cm^{-3} calculated for $Z = 4$ and mol wt 1445. X-Ray diffraction data were collected with a Picker FACS-1 diffractometer and the structure was solved by means of Patterson, Fourier, and least-squares refinement techniques. All atoms, including hydrogens, have been located. The final discrepancy indices are $R_F = 8.7\%$ and $R_{wF} = 4.8\%$ for the 3067 independent reflections representing data complete to $2\theta = 40°$ [Mo Kα radiation] or $R_F = 3.8\%$ and $R_{wF} = 4.0\%$ for the 1818 reflections for which $I > 3\sigma(I)$. The molecule has precise (*i.e.*, crystallographically required) C_2 symmetry. The four copper and four chlorine atoms, taken alternately, define the eight corners of a slightly distorted cube within which the copper–chlorine bond lengths range from 2.363 (2) to 2.505 (2) Å. Intramolecular copper–copper distances are 3.118 (1), 3.118 (1), 3.337 (2), 3.417 (1), 3.417 (1), and 3.430 (1) Å, suggesting that there are no significant copper· · ·copper interactions. This result is at variance with the copper· · ·copper distance of 2.60 Å reported by Wells in 1936 for the analogous "cubane-like" molecule $[AsEt_3CuI]_4$ and suggests that this latter structural determination is of limited accuracy. Copper–phosphorus bond lengths in $[PPh_3CuCl]_4$ are 2.192 (2) and 2.193 (2) Å, other distances being P–C = 1.805 (7)–1.835 (7) Å (average 1.821 Å), C–C(phenyl) = 1.334 (12)–1.400 (15) Å (average 1.373 Å), and C–H = 0.79 (7)–1.04 (6) Å (average 0.90 Å).

Introduction

The copper(I) halides (CuX) form a diversity of products with monodentate tertiary phosphines and arsines (L), including stable isolable species of composition $[L_4Cu^+][X^-]$, L_3CuX, $[L_2CuX]_2$, $L_3Cu_2X_2$, and $[LCuX]_4$.[1] Perhaps surprisingly, an X-ray structural analysis has been performed on only one of the tetrameric species; Wells, in 1936, showed that triethylarsinecopper(I) iodide is tetrameric and that the Cu_4I_4 core of the molecule consists of "a tetrahedron of copper atoms, of side 2.60 Å, and an iodine atom rests on each face of the tetrahedron."[2] An equivalent (and more fashionable) description of the Cu_4I_4 core is "a cubane-like arrangement with alternating copper and iodine atoms."

Wells also showed that the species tri-*n*-butylcopper(I) iodide and triethylarsinesilver(I) iodide were tetrameric, but the crystallographic information on these species is qualitative only.[2]

Recent structural studies on copper cluster species have revealed copper–copper distances of 2.494 (6)–2.674 (5) Å in $[PPh_3CuH]_6$,[3] 2.663 (6)–2.829 (6) Å in $(PPh_3Ir)_2Cu_4(C{\equiv}CPh)_8$,[4] 2.69 Å in $[Cu(S_2CNEt_2)]_4$,[5] 2.701–3.057 Å in $[Cu(SOCNPr_2)]_6$,[6] 2.783–2.871 Å in $[Cu_8(S_2CC(CN)_2)_6{}^{4-}]$,[7] 2.48–2.70 Å in $[Cu(2\text{-}Me_2NC_6H_4)]_4(CuBr)_2$,[8] and 2.377 (3)–2.389 (3) Å in tetrameric (4-methyl-2-cupriobenzyl)dimethylamine.[9] While the partition of these copper–copper distances into "bonding" and "nonbonding" situations is a matter of some controversy, it is clear that the copper–copper distance of ~2.60 Å reported[2] for $[AsEt_3CuI]_4$ may well be incompatible with the view that the copper atoms in this species do not interact directly. The reported distance may thus be erroneous (or of lower accuracy than claimed) or, alternatively, the model for the bonding within $[LCuX]_4$ clusters may need to be carefully reexamined.

We have now completed a single-crystal X-ray diffraction study of the species $[PPh_3CuCl]_4$. As outlined below, the copper· · ·copper distances within this molecule range from 3.118 (1) to 3.430 (1) Å, suggesting that there is no significant direct metal· · ·metal interaction in these tetrameric species. A preliminary account of this work has appeared previously.[10]

Collection and Reduction of the X-Ray Diffraction Data

Crystals were obtained from CH_2Cl_2 solution as colorless needles, extended along the 001 direction. The crystal chosen for the analysis was essentially cylindrical in shape, with a length of 0.3 mm and a radius of 0.04 mm.

A preliminary photographic study [*hk*(0–2) Weissenberg photo-

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(1) The literature for these species is covered excellently by the references given in the paper by S. J. Lippard and J. J. Mayerle, *Inorg. Chem.*, **11**, 753 (1972).

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graphs, a *c*-axis rotation photograph, $h(0\text{-}3)l$ and $(0\text{-}3)kl$ precession photographs, and *a* and *b* cone-axis photographs, all taken with Mo Kα radiation] provided approximate unit cell dimensions, demonstrated the D_{2h} (*mmm*) Laue symmetry of the diffraction pattern and indicated the systematic absences $0kl$ for $k = 2n + 1$, $h0l$ for $l = 2n + 1$, and $hk0$ for $h + k = 2n + 1$. This pattern of extinctions is compatible only with the centrosymmetric orthorhombic space group *Pbcn* [$D_{2h}{}^{14}$; No. 60].[11]

The crystal was centered on a Picker FACS-1 diffractometer with the crystal's c^* axis coincident with the instrumental ϕ axis. Using "high-resolution" conditions (*i.e.*, takeoff angle of 1.0° and detector aperture ~2 mm × 2 mm, 330 mm from crystal) the 2θ, ω, and χ settings of the resolved Mo Kα_1 components (λ 0.70926 Å) of 12 high-angle ($2\theta = 35\text{-}45°$) reflections, which were well dispersed in reciprocal space, were determined. These values were used in a least-squares refinement of the cell and orientation parameters, yielding the unit cell parameters (at 25 ± 1°) $a = 17.4675$ (22) Å, $b = 20.5193$ (29) Å, and $c = 18.2148$ (21) Å. The unit cell volume is 6528.7 Å^3. The observed density (1.45 (2) g cm^{-3}, by flotation) is consistent with the value of 1.471 g cm^{-3} calculated for mol wt 1445.1 and $Z = 4$. Thus, in the absence of disorder, the tetrameric molecule is required to possess a crystallographic twofold axis (C_2) or a crystallographic center of symmetry (C_i).

Intensity data were measured as described previously.[12] Details specific to the present study are as follows. (1) Data were collected *via* a θ(crystal)-2θ(counter) coupled scan, using Mo Kα radiation (*i.e.*, Mo radiation filtered through an Nb filter such that ~47% of the incident Mo Kα radiation is transmitted). (2) Scan speed was 2.0°/min. (3) Scan width was $(1.20 + \delta)°$, where δ is the angular separation (in 2θ) of the Mo Kα_1 and Mo Kα_2 components of the characteristic radiation. The scan thus commences 0.60° below the Mo Kα_1 peak and terminates 0.60° above the Mo Kα_2 peak. (4) Background counting time was 20 sec each for low-angle and high-angle background. (5) The takeoff angle was 3.0°. (6) The detector aperture was 6 mm × 6 mm, 330 mm from crystal.

All reflections in the range $0 < 2\theta \leqslant 40°$ having positive *h*, *k*, and *l* indices were measured. These consisted of 3067 independent reflections (excluding systematic absences). Three standard reflections (080, 602, 004) were measured after each batch of 48 reflections. The root-mean-square deviations of their intensities from the mean were 1.10, 1.02, and 0.99% (respectively). These values were reduced slightly to values of 0.77, 0.68, and 0.97% upon applying a "linear-decay" correction to the entire data set.[13] The raw intensity data were assigned estimated standard deviations (assuming an "ignorance factor" of 0.04) and reduced to values of $|F_o|$ and $\sigma(F_o)$ precisely as has been described before.[12,13] A "β-filter" correction [12] was included. Note that *no reflections were rejected on the basis of being not significantly above background; all were retained.*

Finally, a strong axial reflection (008) was measured, by a θ-2θ scan, at $\chi = 90°$ and at 10° intervals from $\phi = 0°$ to $\phi = 350°$. The variation of intensity with ϕ was less than 2%, indicating that no absorption corrections were necessary ($\mu = 16.38$ cm^{-1} for Mo Kα radiation and $\mu R = 0.066$).

Solution and Refinement of the Structure

Scattering factors for neutral copper, chlorine, phosphorus, and carbon were taken from the compilation of Cromer and Waber.[14] For hydrogen, the scattering curve of Mason and Robertson[15] was used. Both the real and the imaginary components of dispersion[16] for copper, chlorine, phosphorus, and carbon were included specifically in the calculation of structure factor amplitudes. The function minimized during least-squares refinement was $\Sigma w(|F_o| - |F_c|)^2$. Discrepancy indices referred to below are defined as

$$R_F = \Sigma||F_o| - |F_c||/\Sigma|F_o| \times 100\ (\%)$$

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

The positions of the copper and chlorine atoms were quickly and unambiguously determined from a three-dimensional Patterson synthesis,[17] which also showed the molecule to lie on a crystallographic twofold axis. The remaining nonhydrogen atoms were located *via* a series of three-dimensional difference-Fourier maps,[17] each successive map being phased by an increasing number of atoms. Least-squares refinement[18,19] of positional and anisotropic parameters of the 42 independent nonhydrogen atoms which define the asymmetric unit led to convergence at $R_F = 9.9\%$ and $R_{wF} = 6.0\%$. A difference-Fourier synthesis now led to the location of all 30 independent hydrogen atoms, individual peak heights ranging from 0.49 to 0.80 e Å^{-3}. Continued refinement,[19] now including positional and isotropic thermal parameters for all hydrogen atoms, led to final convergence [$(\Delta/\sigma)_{\max} < 0.2$] with $R_F = 8.7\%$ and $R_{wF} = 4.8\%$ for the complete data set of 3067 independent reflections or $R_F = 3.8\%$ and $R_{wF} = 4.0\%$ for the 1818 reflections for which $I > 3\sigma(I)$.

A final difference-Fourier synthesis (based on all data) had, as its greatest feature, a peak of height 0.70 e Å^{-3}. The correctness and completeness of the least-squares refinement process is thus confirmed.

The standard deviation of an observation of unit weight, defined by $[\Sigma w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$, was 1.04, where the number of reflections (m) was 3067 and the number of parameters (n) was 499, yielding an $m{:}n$ ratio of 6.1:1. The function $\Sigma w(|F_o| - |F_c|)^2$ was not significantly dependent either upon $(\sin\theta)/\lambda$ or upon $|F_o|$, thereby indicating a correctly chosen weighting scheme. Data were inspected for evidence of extinction; none was found.

A table of observed and calculated structure factor amplitudes is available.[20] Final positional and isotropic thermal parameters are collected in Table I. Anisotropic thermal parameters are listed in Table II.

Description of the Molecular Structure

Interatomic distances and their estimated standard deviations[21] (esd's) are shown in Table III. Bond angles and their esd's[21] are collected in Table IV. The molecule possesses precise (*i.e.*, crystallographically required) C_2 symmetry. The numbering scheme and thermal ellipsoids for all nonhydrogen atoms are shown in Figure 1. [Hydrogen atoms, omitted from this figure for the sake of clarity, are numbered similarly to their attached carbon atoms.] The individual tetrameric molecules are mutually separated by normal van der Waals distances and there are no abnormally short intermolecular contacts.

The stereochemistry of the heavy-atom (*i.e.*, $P_4Cu_4Cl_4$) portion of the molecule is illustrated in Figure 2. The Cu_4Cl_4 core of the molecule defines a rather irregular "cubane-like" framework, with the phosphorus atoms being approximately apical, thereby completing a distorted tetrahedral arrangement of ligands about each copper(I) atom.

The copper-chlorine bond lengths vary appreciably, ranging from Cu(2)-Cl(1) = 2.3632 (19) to Cu(2)-Cl(1′) = 2.5050 (20) Å. The mean of the six independent measurements is 2.4441 Å, with the average for the bonds involving Cu(1) (*i.e.*, Cu(1)-Cl(1), Cu(1)-Cl(2), and Cu(1)-Cl(2′)) being 2.4466 Å and the average for bonds involving Cu(2)

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(18) Structure factor calculations and least-squares refinement were carried out using the program SFIX, which is a much modified version of SFLS5, by C. T. Prewitt.

(19) Due to the large number of variables, each "cycle of refinement" was carried out in two steps: first, the parameters for one triphenylphosphine ligand were refined; then the parameters for the other triphenylphosphine ligand were refined. The scale factor and parameters for the copper and chlorine atoms were refined during each step.

(20) See paragraph at end of paper regarding supplementary material.

(21) Estimated standard deviations were calculated using the FORTRAN IV program STAN1, by B. G. DeBoer. See footnote *a* to Table III.

Table I. Final Positional and Isotropic Thermal Parameters[a] for Atoms in the $[PPh_3CuCl]_4$ Molecule, with Esd's

Atom	*x*	*y*	*z*	*B*,[a] (Å^2)
Cu(1)	0.092693 (51)	0.436028 (46)	0.218974 (52)	3.89
Cu(2)	0.046430 (56)	0.327325 (45)	0.330049 (50)	4.01
Cl(1)	0.090521 (96)	0.314716 (81)	0.208215 (94)	3.98
Cl(2)	0.032954 (93)	0.446301 (79)	0.337600 (92)	4.00
P(1)	0.20369 (10)	0.47812 (9)	0.18873 (10)	2.87
P(2)	0.08037 (11)	0.27422 (9)	0.42927 (10)	2.86
C(1)	0.28644 (38)	0.43403 (36)	0.22592 (37)	3.60
C(2)	0.34618 (46)	0.46436 (40)	0.26201 (44)	4.43
C(3)	0.40602 (51)	0.42780 (60)	0.29001 (52)	6.78
C(4)	0.40643 (58)	0.36209 (68)	0.28259 (72)	6.98
C(5)	0.34935 (53)	0.33206 (45)	0.24669 (62)	6.92
C(6)	0.28786 (47)	0.36775 (42)	0.21868 (56)	5.96
C(7)	0.22347 (37)	0.56205 (33)	0.21602 (38)	3.15
C(8)	0.19345 (45)	0.58504 (37)	0.28056 (40)	3.78
C(9)	0.21336 (53)	0.64630 (42)	0.30735 (44)	5.04
C(10)	0.26183 (53)	0.68545 (42)	0.26787 (48)	5.36
C(11)	0.29031 (51)	0.66443 (39)	0.20182 (48)	5.20
C(12)	0.27114 (47)	0.60312 (40)	0.17578 (44)	4.68
C(13)	0.22218 (38)	0.48161 (32)	0.09104 (38)	3.20
C(14)	0.16623 (45)	0.50763 (37)	0.04751 (44)	4.20
C(15)	0.17797 (54)	0.51862 (42)	−0.02581 (51)	5.69
C(16)	0.24822 (60)	0.50136 (44)	−0.05733 (45)	5.65
C(17)	0.30321 (52)	0.47417 (39)	−0.01562 (45)	4.92
C(18)	0.29029 (44)	0.46354 (38)	0.05847 (41)	3.85
C(19)	0.18112 (37)	0.26180 (31)	0.44951 (33)	2.49
C(20)	0.22969 (48)	0.31121 (41)	0.43263 (53)	5.25
C(21)	0.30484 (54)	0.30998 (47)	0.45630 (65)	6.93
C(22)	0.33301 (50)	0.25646 (54)	0.49308 (61)	6.67
C(23)	0.28434 (47)	0.20504 (46)	0.50737 (49)	5.48
C(24)	0.20908 (46)	0.20777 (33)	0.48526 (47)	3.90
C(25)	0.03947 (37)	0.19345 (32)	0.43179 (38)	3.02
C(26)	0.03001 (53)	0.16167 (41)	0.36706 (50)	5.63
C(27)	−0.00280 (61)	0.09970 (44)	0.36337 (61)	7.06
C(28)	−0.02410 (52)	0.06964 (42)	0.42599 (76)	7.15
C(29)	−0.01715 (54)	0.09993 (44)	0.49046 (60)	6.23
C(30)	0.01525 (48)	0.16103 (38)	0.49463 (47)	4.77
C(31)	0.04927 (39)	0.31306 (32)	0.51493 (37)	3.35
C(32)	0.08311 (49)	0.30228 (43)	0.58252 (44)	5.22
C(33)	0.05800 (51)	0.33436 (46)	0.64367 (43)	5.29
C(34)	−0.00072 (52)	0.37631 (38)	0.63960 (45)	4.95
C(35)	−0.03447 (47)	0.38898 (38)	0.57369 (49)	4.87
C(36)	−0.01072 (41)	0.35732 (35)	0.51085 (41)	3.63
H(2)	0.3489 (32)	0.5117 (30)	0.2685 (31)	4.1 (15)
H(3)	0.4426 (39)	0.4481 (34)	0.3080 (37)	5.9 (18)
H(4)	0.4431 (43)	0.3435 (44)	0.2991 (46)	8.1 (29)
H(5)	0.3420 (35)	0.2859 (32)	0.2312 (34)	5.1 (17)
H(6)	0.2527 (33)	0.3513 (28)	0.1939 (31)	3.9 (14)
H(8)	0.1640 (32)	0.5632 (28)	0.3086 (31)	4.0 (14)
H(9)	0.1932 (38)	0.6571 (32)	0.3528 (37)	5.7 (16)
H(10)	0.2795 (36)	0.7241 (34)	0.2849 (37)	5.7 (16)
H(11)	0.3190 (42)	0.6844 (37)	0.1732 (39)	7.2 (20)
H(12)	0.2865 (34)	0.5942 (30)	0.1323 (34)	4.5 (14)
H(14)	0.1194 (31)	0.5165 (26)	0.0724 (30)	3.2 (12)
H(15)	0.1382 (38)	0.5453 (33)	−0.0552 (37)	5.9 (20)
H(16)	0.2586 (35)	0.5100 (29)	−0.1061 (36)	4.7 (14)
H(17)	0.3562 (34)	0.4607 (28)	−0.0367 (32)	4.2 (14)
H(18)	0.3251 (34)	0.4493 (29)	0.0892 (32)	4.2 (15)
H(20)	0.2142 (45)	0.3460 (37)	0.4125 (41)	7.3 (25)
H(21)	0.3380 (48)	0.3388 (42)	0.4475 (47)	8.9 (27)
H(22)	0.3803 (47)	0.2511 (41)	0.5094 (46)	8.6 (25)
H(23)	0.3011 (38)	0.1714 (33)	0.5268 (36)	5.7 (23)
H(24)	0.1882 (41)	0.1736 (34)	0.4877 (41)	6.5 (22)
H(26)	0.0456 (42)	0.1801 (36)	0.3292 (38)	6.7 (18)
H(27)	−0.0012 (38)	0.0778 (35)	0.3155 (37)	6.5 (18)
H(28)	−0.0469 (39)	0.0345 (34)	0.4229 (37)	6.1 (17)
H(29)	−0.0256 (35)	0.0804 (31)	0.5364 (35)	5.1 (16)
H(30)	0.0183 (32)	0.1867 (29)	0.5397 (32)	3.9 (13)
H(32)	0.1234 (40)	0.2741 (34)	0.5862 (37)	6.1 (17)
H(33)	0.0819 (40)	0.3255 (35)	0.6819 (38)	6.4 (18)
H(34)	−0.0187 (35)	0.3980 (29)	0.6794 (34)	4.8 (16)
H(35)	−0.0706 (36)	0.4185 (31)	0.5722 (34)	5.0 (15)
H(36)	−0.0358 (34)	0.3676 (28)	0.4646 (33)	4.5 (14)

[a] "Equivalent isotropic thermal parameters" provided for non-hydrogen atoms correspond to the average mean-square displacement along the three principal axes of the vibration ellipsoid.

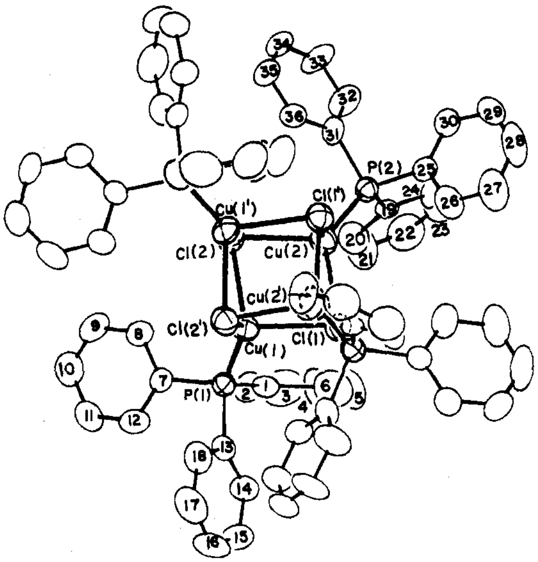

Figure 1. Stereochemistry of the $[PPh_3CuCl]_4$ molecule, showing labeling of atoms (ORTEP diagram, 50% atomic vibration ellipsoids).

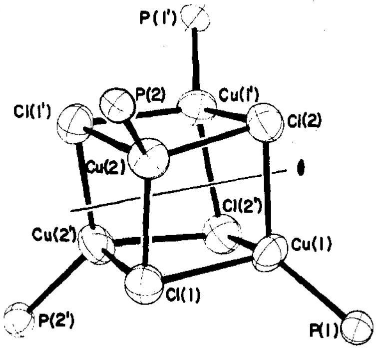

Figure 2. The $P_4Cu_4Cl_4$ portion of the $[PPh_3CuCl]_4$ molecule, showing the molecular C_2 axis (ORTEP diagram, 50% atomic vibration ellipsoids).

(*i.e.*, Cu(2)-Cl(1), Cu(2)-Cl(1′), and Cu(2)-Cl(2)) being essentially the same, at 2.4416 Å.

The six copper-copper distances, in order of increasing length, are Cu(1)· · ·Cu(2) = Cu(1′)· · ·Cu(2′) = 3.1179 (13) Å, Cu(2)· · ·Cu(2′) = 3.3369 (19) Å, Cu(1)· · ·Cu(2′) = Cu(1′)· · ·Cu(2) = 3.4173 (13) Å, and Cu(1)· · ·Cu(1′) = 3.4298 (18) Å. The average value is 3.3062 Å. All these distances are sufficiently great to preclude the possibility of any significant direct copper-copper interaction. [We note here that the average Cu-Cu distance of 2.739 Å in $(PPh_3Ir)_2Cu_4(C{\equiv}CPh)_8$ has been interpreted in terms of a bonding situation with a copper-copper bond order of $^3/_4$ (see ref 4b) while the mean Cu-Cu distance of 2.83 Å in $[Cu_8(S_2CC(CN)_2)_6{}^{4-}]$ represents a bond order only $^2/_3$ (see ref 7)].

The present data thus strongly suggest that the copper-copper distance of 2.60 Å reported for $[AsEt_3CuI]_4{}^2$ is of low accuracy, the true value being considerably greater than 2.6 Å. It is not surprising that the reported distance *is* in error, for the structural analysis was performed in 1936, a very limited data set was used, atomic parameters were not subjected to least-squares refinement, and the copper atoms in the $[AsEt_3CuI]_4$ molecule are not even the major contributors to the intensities of scattered X-rays (*Z*(Cu) = 29, whereas *Z*(I) = 53 and *Z*(As) = 33). A re-examination of the crystal structure of $[AsEt_3CuI]_4$ and

Table II. Anisotropic Thermal Parameters[a] for $[PPh_3CuCl]_4$

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	$\langle U \rangle^b$
Cu(1)	2.85 (5)	3.92 (5)	4.90 (6)	−0.69 (5)	0.79 (5)	0.21 (5)	0.26, 0.23, 0.17
Cu(2)	4.78 (6)	3.93 (5)	3.33 (5)	0.50 (5)	−0.66 (5)	0.69 (5)	0.25, 0.24, 0.18
Cl(1)	3.56 (9)	3.73 (9)	4.66 (10)	0.34 (8)	0.11 (8)	−0.15 (8)	0.24, 0.22, 0.20
Cl(2)	4.29 (10)	3.75 (9)	3.96 (10)	−0.14 (8)	−0.15 (8)	−0.33 (8)	0.23, 0.23, 0.21
P(1)	2.77 (11)	2.60 (10)	3.23 (11)	−0.12 (9)	0.30 (9)	−0.06 (9)	0.21, 0.18, 0.18
P(2)	3.14 (12)	2.74 (10)	2.70 (10)	0.39 (9)	−0.25 (9)	0.06 (9)	0.21, 0.19, 0.17
C(1)	3.59 (46)	3.98 (56)	3.22 (46)	−0.44 (43)	0.74 (39)	0.39 (44)	0.23, 0.23, 0.17
C(2)	3.47 (47)	4.57 (57)	5.26 (53)	−0.09 (47)	−0.19 (41)	−0.90 (46)	0.27, 0.23, 0.21
C(3)	3.59 (63)	10.66 (83)	6.10 (62)	−0.56 (66)	−2.14 (55)	−1.22 (66)	0.37, 0.30, 0.17
C(4)	4.22 (64)	8.08 (88)	8.66 (74)	−0.98 (66)	−0.05 (59)	1.09 (70)	0.35, 0.31, 0.22
C(5)	4.33 (59)	4.72 (66)	11.71 (83)	0.15 (58)	0.79 (57)	2.41 (63)	0.40, 0.23, 0.22
C(6)	3.19 (56)	4.42 (57)	10.28 (76)	−0.35 (47)	0.00 (52)	1.48 (54)	0.37, 0.23, 0.20
C(7)	3.24 (42)	2.83 (41)	3.38 (48)	0.37 (38)	0.27 (40)	−0.19 (41)	0.21, 0.21, 0.18
C(8)	4.21 (50)	4.08 (53)	3.05 (45)	0.64 (43)	0.07 (43)	−0.09 (40)	0.25, 0.21, 0.20
C(9)	6.69 (60)	5.03 (55)	3.38 (56)	0.73 (47)	−0.17 (47)	−1.70 (47)	0.30, 0.27, 0.17
C(10)	6.51 (64)	3.86 (53)	5.70 (67)	−1.37 (49)	−0.80 (53)	−1.16 (53)	0.30, 0.28, 0.18
C(11)	6.48 (62)	3.50 (51)	5.63 (60)	−2.67 (45)	0.73 (49)	−0.24 (44)	0.32, 0.26, 0.16
C(12)	5.51 (53)	4.73 (54)	3.82 (50)	−1.31 (44)	1.33 (45)	−0.83 (48)	0.30, 0.22, 0.20
C(13)	2.72 (48)	2.76 (43)	4.13 (47)	−0.52 (37)	0.48 (42)	0.21 (37)	0.23, 0.20, 0.16
C(14)	4.53 (56)	3.95 (48)	4.14 (61)	−0.48 (42)	−1.51 (50)	−0.10 (42)	0.27, 0.23, 0.18
C(15)	6.12 (69)	5.57 (59)	5.39 (67)	−1.43 (52)	−2.50 (56)	1.22 (51)	0.34, 0.24, 0.20
C(16)	8.04 (74)	6.52 (69)	2.39 (61)	−3.20 (60)	0.26 (60)	−0.02 (50)	0.37, 0.23, 0.17
C(17)	5.95 (68)	5.15 (52)	3.66 (58)	−1.10 (51)	1.07 (53)	−0.83 (45)	0.30, 0.24, 0.20
C(18)	3.91 (57)	4.27 (49)	3.37 (55)	−0.59 (42)	0.06 (44)	0.00 (40)	0.24, 0.21, 0.21
C(19)	2.43 (37)	2.76 (39)	2.27 (39)	−0.36 (35)	0.71 (31)	−0.14 (32)	0.20, 0.18, 0.14
C(20)	3.32 (48)	4.89 (42)	7.55 (59)	−0.66 (46)	0.82 (42)	0.37 (48)	0.31, 0.25, 0.19
C(21)	4.44 (69)	4.94 (58)	11.40 (72)	−1.48 (52)	0.13 (55)	0.37 (52)	0.38, 0.28, 0.20
C(22)	3.31 (58)	7.60 (69)	9.12 (69)	−0.24 (55)	0.38 (52)	−0.90 (57)	0.35, 0.30, 0.20
C(23)	3.50 (55)	6.61 (60)	6.33 (57)	2.02 (48)	−0.91 (46)	0.62 (47)	0.31, 0.29, 0.17
C(24)	4.05 (48)	2.68 (48)	4.96 (47)	1.73 (37)	0.05 (38)	0.10 (39)	0.26, 0.25, 0.14
C(25)	2.58 (40)	3.24 (42)	3.24 (48)	0.21 (33)	−0.04 (39)	−0.30 (41)	0.21, 0.19, 0.18
C(26)	6.66 (62)	4.08 (53)	6.14 (61)	−1.22 (46)	−0.26 (48)	0.23 (46)	0.30, 0.28, 0.21
C(27)	9.25 (74)	4.31 (61)	7.63 (75)	−1.31 (46)	−2.39 (60)	−0.77 (56)	0.37, 0.29, 0.21
C(28)	5.17 (58)	3.10 (58)	13.18 (97)	−0.85 (47)	−0.31 (67)	1.22 (71)	0.41, 0.26, 0.18
C(29)	6.73 (61)	4.31 (59)	7.65 (76)	0.70 (46)	3.37 (56)	1.80 (53)	0.37, 0.24, 0.20
C(30)	5.63 (50)	3.61 (51)	5.07 (60)	0.94 (41)	0.10 (43)	0.17 (45)	0.29, 0.24, 0.20
C(31)	3.06 (42)	2.70 (43)	4.28 (48)	0.73 (37)	−0.43 (40)	−0.11 (37)	0.24, 0.21, 0.16
C(32)	5.50 (54)	6.52 (35)	3.65 (46)	3.39 (46)	−1.43 (44)	−0.30 (44)	0.35, 0.22, 0.16
C(33)	5.73 (54)	6.71 (55)	3.44 (50)	2.34 (46)	−0.07 (42)	−1.93 (44)	0.34, 0.24, 0.17
C(34)	7.28 (62)	4.31 (50)	3.27 (50)	1.62 (47)	1.30 (46)	−0.67 (42)	0.32, 0.24, 0.17
C(35)	4.85 (55)	4.21 (47)	5.57 (56)	2.17 (41)	1.91 (50)	0.35 (46)	0.32, 0.24, 0.16
C(36)	3.33 (42)	3.95 (41)	3.62 (48)	0.41 (35)	0.52 (37)	0.34 (38)	0.24, 0.21, 0.19

[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.

of the related species, $[PEt_3CuI]_4$, is currently in progress in our laboratories.[22]

Chlorine· · ·chlorine distances within the $[PPh_3CuCl]_4$ molecule spread over a slightly larger range than the copper· · ·copper distances. The shortest is Cl(1)· · ·Cl(1′) = 3.0596 (34), while the longest are Cl(1)· · ·Cl(2) and Cl(1′)· · · Cl(2′) with values of 3.7223 (26) Å. The average of the six chlorine· · ·chlorine distances is 3.5012 Å—*i.e.*, about 0.2 Å greater than the average copper· · ·copper distance.

Angles within the Cu_4Cl_4 "cube" vary significantly from the idealized value of 90°. Angles about Cu(1) [Cl(1)-Cu(1)-Cl(2) = 98.69 (6)°, Cl(1)-Cu(1)-Cl(2′) = 92.26 (6)°, and Cl(2)-Cu(1)-Cl(2′) = 88.94 (6)°] average 93.30°, while angles about Cu(2) [Cl(1)-Cu(2)-Cl(2) = 101.11 (7)°, Cl(1)-Cu(2)-Cl(1′) = 92.21 (6)°, and Cl(2)-Cu(2)-Cl(1′) = 91.53 (6)°] average 94.95°. Angles about the chlorine atoms are, on average, smaller. Thus, angles centered on Cl(1) range from 79.75 (6) to 86.49 (6)° (average 84.14°), and angles centered on Cl(2) range from 79.71 (6) to 90.19 (6)° (average 86.19°). There is no unambiguous explanation as to why such large variations in bond angle are observed. We assume that these cage angles are "soft" and are easily affected by their different environments within the crystal (*i.e.*, by intermolecular forces).

The two independent copper-phosphorus distances are Cu(1)-P(1) = 2.1928 (21) Å and Cu(2)-P(2) = 2.1921 (21) Å. These bond lengths are shorter than in most other four-coordinate copper(I)-triphenylphosphine complexes. [Typical values range from 2.23 to 2.27 Å,[23] one exception being the pseudo four-coordinate complex $PPh_3Cu(\pi\text{-}C_5H_5)$ in which Cu-P = 2.135 (1) Å.[24]]

As with other angles involving atoms of the cubane cage, the phosphorus-copper-chlorine angles are irregular. Individual angles around Cu(1) vary from P(1)-Cu(1)-Cl(1) = 112.73 (7)° to P(1)-Cu(1)-Cl(2′) = 131.06 (8)°, while angles around Cu(2) range from P(2)-Cu(2)-Cl(1′) = 115.87 (7)° to P(2)-Cu(2)-Cl(1) = 129.17 (8)°.

The Triphenylphosphine Ligands. The six independent phosphorus-carbon bond lengths range from 1.805 (7) to 1.835 (7) Å, averaging 1.821 Å. As has been noted for other phosphine-metal complexes,[25] angles about the phosphorus atoms deviate significantly and systematically

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[22] M. R. Churchill and K. L. Kalra, to be submitted for publication.

[23] A table of Cu-P distances is available. See S. J. Lippard and G. J. Palenik, *Inorg. Chem.*, 10, 1322 (1971).

[24] F. A. Cotton and J. Takats, *J. Amer. Chem. Soc.*, 92, 2353 (1970).

[25] M. R. Churchill and T. A. O'Brien, *J. Chem. Soc. A*, 2970 (1968); see, especially, Table 7, p 2976.

Table III. Interatomic Distances (Å) with Esd's for $[PPh_3CuCl]_4$[a,b]

A. Copper-Copper Distances			
Cu(1)···Cu(1′)	3.4298 (18)	Cu(2)···Cu(2′)	3.3369 (19)
Cu(1)···Cu(2)	3.1179 (13)	Cu(1′)···Cu(2)	3.4173 (13)
Cu(1)···Cu(2′)	3.4173 (13)	Cu(1′)···Cu(2′)	3.1179 (13)
B. Copper-Chlorine Distances			
Cu(1)-Cl(1)	2.4972 (19)	Cu(2)-Cl(1)	2.3632 (19)
Cu(1)-Cl(2)	2.4088 (19)	Cu(2)-Cl(1′)	2.5050 (20)
Cu(1)-Cl(2′)	2.4338 (19)	Cu(2)-Cl(2)	2.4565 (19)
C. Copper-Phosphorus Distances			
Cu(1)-P(1)	2.1928 (21)	Cu(2)-P(2)	2.1921 (21)
D. Chlorine-Chlorine Distances			
Cl(1)···Cl(1′)	3.0596 (34)	Cl(2)···Cl(1′)	3.5551 (24)
Cl(1)···Cl(2)	3.7223 (26)	Cl(2)···Cl(2′)	3.3925 (33)
Cl(1)···Cl(2′)	3.5551 (24)	Cl(1′)···Cl(2′)	3.7223 (26)
E. Phosphorus-Carbon Distances			
P(1)-C(1)	1.835 (7)	P(2)-C(19)	1.816 (7)
P(1)-C(7)	1.825 (7)	P(2)-C(25)	1.805 (7)
P(1)-C(13)	1.810 (7)	P(2)-C(31)	1.834 (7)
F. Carbon-Carbon Distances			
C(1)-C(2)	1.381 (10)	C(19)-C(20)	1.357 (10)
C(2)-C(3)	1.384 (11)	C(20)-C(21)	1.382 (11)
C(3)-C(4)	1.355 (16)	C(21)-C(22)	1.377 (12)
C(4)-C(5)	1.342 (13)	C(22)-C(23)	1.380 (12)
C(5)-C(6)	1.397 (13)	C(23)-C(24)	1.376 (10)
C(6)-C(1)	1.367 (11)	C(24)-C(19)	1.375 (9)
C(7)-C(8)	1.371 (10)	C(25)-C(26)	1.358 (10)
C(8)-C(9)	1.393 (11)	C(26)-C(27)	1.396 (12)
C(9)-C(10)	1.371 (11)	C(27)-C(28)	1.349 (13)
C(10)-C(11)	1.372 (11)	C(28)-C(29)	1.334 (12)
C(11)-C(12)	1.386 (11)	C(29)-C(30)	1.378 (11)
C(12)-C(7)	1.393 (10)	C(30)-C(25)	1.390 (10)
C(13)-C(14)	1.367 (9)	C(31)-C(32)	1.384 (9)
C(14)-C(15)	1.370(10)	C(32)-C(33)	1.366 (10)
C(15)-C(16)	1.400 (15)	C(33)-C(34)	1.341 (12)
C(16)-C(17)	1.346 (10)	C(34)-C(35)	1.362 (11)
C(17)-C(18)	1.386 (10)	C(35)-C(36)	1.380 (10)
C(18)-C(13)	1.380 (9)	C(36)-C(31)	1.389 (9)
G. Carbon-Hydrogen Distances			
C(2)-H(2)	0.98 (6)	C(20)-H(20)	0.85 (8)
C(3)-H(3)	0.83 (7)	C(21)-H(21)	0.84 (8)
C(4)-H(4)	0.80 (7)	C(22)-H(22)	0.88 (8)
C(5)-H(5)	1.00 (6)	C(23)-H(23)	0.83 (7)
C(6)-H(6)	0.83 (6)	C(24)-H(24)	0.79 (7)
C(8)-H(8)	0.85 (5)	C(26)-H(26)	0.83 (7)
C(9)-H(9)	0.93 (7)	C(27)-H(27)	0.98 (7)
C(10)-H(10)	0.91 (6)	C(28)-H(28)	0.83 (6)
C(11)-H(11)	0.83 (7)	C(29)-H(29)	0.94 (6)
C(12)-H(12)	0.86 (6)	C(30)-H(30)	0.98 (6)
C(14)-H(14)	0.95 (5)	C(32)-H(32)	0.91 (7)
C(15)-H(15)	1.03 (6)	C(33)-H(33)	0.83 (7)
C(16)-H(16)	0.92 (6)	C(34)-H(34)	0.91 (6)
C(17)-H(17)	1.04 (6)	C(35)-H(35)	0.88 (6)
C(18)-H(18)	0.88 (6)	C(36)-H(36)	0.97 (6)

[a] Esd's were calculated by considering those elements of the full positional correlation matrix (see text) whose magnitudes were greater than 0.05. The calculation was performed using the FORTRAN IV program STAN1 by B. G. DeBoer. Contributions from errors in the unit cell dimensions are included.
[b] Bond lengths are not corrected for the effects of thermal motion.

from the ideal tetrahedral value of 109° 28′. While the distortion is not completely regular, it *approximates* to a lowering of the angular symmetry about phosphorus from T_d toward C_{3v} symmetry, with the Cu-P bonds defining the pseudo-threefold axes. Thus, Cu-P-C angles are all greater than the ideal tetrahedral angle and range from 111.74 (24) to 119.95 (22)°, while C-P-C angles are all less than the ideal tetrahedral angle, with individual values ranging from 100.09 (30) to 105.07 (31)°.

The 36 independent carbon-carbon bond distances within the six phenyl rings range from C(28)-C(29) = 1.334 (12) Å up to C(15)-C(16) = 1.400 (15) Å. The average value

Table IV. Bond Angles (deg) for $[PPh_3CuCl]_4$

A. Angles within Cu_4Cl_4 "Cube"			
Cl(1)-Cu(1)-Cl(2)	98.69 (6)	Cu(1)-Cl(1)-Cu(2)	79.75 (6)
Cl(1)-Cu(1)-Cl(2′)	92.26 (6)	Cu(1)-Cl(1)-Cu(2′)	86.18 (6)
Cl(2)-Cu(1)-Cl(2′)	88.94 (6)	Cu(2)-Cl(1)-Cu(2′)	86.49 (6)
Cl(1)-Cu(2)-Cl(2)	101.11 (7)	Cu(1)-Cl(2)-Cu(2)	79.71 (6)
Cl(1)-Cu(2)-Cl(1′)	92.21 (6)	Cu(1)-Cl(2)-Cu(1′)	90.19 (6)
Cl(2)-Cu(2)-Cl(1′)	91.53 (6)	Cu(2)-Cl(2)-Cu(1′)	88.66 (6)
B. Phosphorus-Copper-Chlorine Angles			
P(1)-Cu(1)-Cl(1)	112.73 (7)	P(2)-Cu(2)-Cl(1)	129.17 (8)
P(1)-Cu(1)-Cl(2)	125.02 (8)	P(2)-Cu(2)-Cl(2)	118.28 (7)
P(1)-Cu(1)-Cl(2′)	131.06 (8)	P(2)-Cu(2)-Cl(1′)	115.87 (7)
C. Copper-Phosphorus-Carbon Angles			
Cu(1)-P(1)-C(1)	114.18 (24)	Cu(2)-P(2)-C(19)	119.95 (22)
Cu(1)-P(1)-C(7)	118.07 (22)	Cu(2)-P(2)-C(25)	111.74 (24)
Cu(1)-P(1)-C(13)	114.86 (23)	Cu(2)-P(2)-C(31)	113.90 (23)
D. Carbon-Phosphorus-Carbon Angles			
C(1)-P(1)-C(7)	102.44 (32)	C(19)-P(2)-C(25)	104.45 (30)
C(1)-P(1)-C(13)	104.00 (31)	C(19)-P(2)-C(31)	100.09 (30)
C(7)-P(1)-C(13)	101.34 (31)	C(25)-P(2)-C(31)	105.07 (31)
E. Internal Angles of the Phenyl Rings			
C(6)-C(1)-C(2)	118.7 (7)	C(24)-C(19)-C(20)	119.2 (7)
C(1)-C(2)-C(3)	120.1 (8)	C(19)-C(20)-C(21)	120.6 (8)
C(2)-C(3)-C(4)	120.4 (9)	C(20)-C(21)-C(22)	120.4 (8)
C(3)-C(4)-C(5)	120.1 (11)	C(21)-C(22)-C(23)	118.8 (9)
C(4)-C(5)-C(6)	120.6 (10)	C(22)-C(23)-C(24)	120.1 (9)
C(5)-C(6)-C(1)	120.0 (8)	C(23)-C(24)-C(19)	120.7 (7)
C(12)-C(7)-C(8)	118.1 (7)	C(30)-C(25)-C(26)	116.6 (7)
C(7)-C(8)-C(9)	121.0 (7)	C(25)-C(26)-C(27)	122.0 (9)
C(8)-C(9)-C(10)	120.0 (8)	C(26)-C(27)-C(28)	119.3 (9)
C(9)-C(10)-C(11)	120.0 (7)	C(27)-C(28)-C(29)	120.4 (9)
C(10)-C(11)-C(12)	119.9 (7)	C(28)-C(29)-C(30)	120.7 (9)
C(11)-C(12)-C(7)	120.9 (8)	C(29)-C(30)-C(25)	121.0 (8)
C(18)-C(13)-C(14)	118.2 (7)	C(36)-C(31)-C(32)	118.3 (7)
C(13)-C(14)-C(15)	121.5 (8)	C(31)-C(32)-C(33)	120.8 (8)
C(14)-C(15)-C(16)	119.3 (9)	C(32)-C(33)-C(34)	120.6 (8)
C(15)-C(16)-C(17)	119.9 (8)	C(33)-C(34)-C(35)	120.1 (8)
C(16)-C(17)-C(18)	119.9 (9)	C(34)-C(35)-C(36)	120.7 (8)
C(17)-C(18)-C(13)	121.1 (8)	C(35)-C(36)-C(31)	119.4 (7)
F. External Angles of the Phenyl Rings			
P(1)-C(1)-C(2)	123.3 (6)	P(2)-C(19)-C(20)	117.1 (6)
P(1)-C(1)-C(6)	118.0 (6)	P(2)-C(19)-C(24)	123.6 (5)
H(2)-C(2)-C(1)	123 (3)	H(20)-C(20)-C(19)	122 (6)
H(2)-C(2)-C(3)	117 (3)	H(20)-C(20)-C(21)	117 (6)
H(3)-C(3)-C(2)	117 (5)	H(21)-C(21)-C(20)	125 (7)
H(3)-C(3)-C(4)	122 (5)	H(21)-C(21)-C(22)	114 (6)
H(4)-C(4)-C(3)	116 (6)	H(22)-C(22)-C(21)	127 (6)
H(4)-C(4)-C(5)	124 (6)	H(22)-C(22)-C(23)	115 (6)
H(5)-C(5)-C(4)	132 (5)	H(23)-C(23)-C(22)	120 (5)
H(5)-C(5)-C(6)	107 (5)	H(23)-C(23)-C(24)	120 (5)
H(6)-C(6)-C(5)	124 (5)	H(24)-C(24)-C(23)	113 (6)
H(6)-C(6)-C(1)	116 (4)	H(24)-C(24)-C(19)	125 (6)
P(1)-C(7)-C(8)	119.1 (5)	P(2)-C(25)-C(26)	117.8 (6)
P(1)-C(7)-C(12)	122.7 (6)	P(2)-C(25)-C(30)	125.5 (6)
H(8)-C(8)-C(7)	124 (4)	H(26)-C(26)-C(25)	117 (5)
H(8)-C(8)-C(9)	115 (4)	H(26)-C(26)-C(27)	121 (6)
H(9)-C(9)-C(8)	116 (4)	H(27)-C(27)-C(26)	117 (4)
H(9)-C(9)-C(10)	124 (4)	H(27)-C(27)-C(28)	123 (4)
H(10)-C(10)-C(9)	123 (5)	H(28)-C(28)-C(27)	118 (6)
H(10)-C(10)-C(11)	117 (5)	H(28)-C(28)-C(29)	121 (5)
H(11)-C(11)-C(10)	128 (6)	H(29)-C(29)-C(28)	125 (4)
H(11)-C(11)-C(12)	112 (6)	H(29)-C(29)-C(30)	114 (4)
H(12)-C(12)-C(11)	116 (4)	H(30)-C(30)-C(29)	124 (3)
H(12)-C(12)-C(7)	123 (5)	H(30)-C(30)-C(25)	115 (4)
P(1)-C(13)-C(14)	117.3 (6)	P(2)-C(31)-C(32)	124.1 (6)
P(1)-C(13)-C(18)	124.5 (5)	P(2)-C(31)-C(36)	117.5 (5)
H(14)-C(14)-C(13)	114 (4)	H(32)-C(32)-C(31)	120 (4)
H(14)-C(14)-C(15)	124 (4)	H(32)-C(32)-C(33)	119 (4)
H(15)-C(15)-C(14)	119 (4)	H(33)-C(33)-C(32)	115 (5)
H(15)-C(15)-C(16)	121 (4)	H(33)-C(33)-C(34)	125 (5)
H(16)-C(16)-C(15)	121 (4)	H(34)-C(34)-C(33)	122 (4)
H(16)-C(16)-C(17)	119 (4)	H(34)-C(34)-C(35)	117 (4)
H(17)-C(17)-C(16)	122 (3)	H(35)-C(35)-C(34)	118 (4)
H(17)-C(17)-C(18)	118 (4)	H(35)-C(35)-C(36)	121 (4)
H(18)-C(18)-C(17)	124 (4)	H(36)-C(36)-C(35)	119 (3)
H(18)-C(18)-C(13)	114 (4)	H(36)-C(36)-C(31)	122 (3)

of 1.373 Å is significantly lower than the accepted C-C (aromatic) distance of 1.394 ± 0.005 Å.[26] We believe this contraction to be the result of rigid-body thermal motion of the phenyl groups. There are indications (at the borderline of statistical significance, *vide infra*) of systematic variations in carbon-carbon distance around the phenyl rings.

For the purpose of subsequent arguments we define the root-mean-square scatter (which is an external estimate of the standard deviations on individual bond lengths) by eq 1 and the σ(of mean) (which is the estimated standard

$$\text{rms scatter} = \left[\sum_{i=1}^{i=N} (\chi_i - \bar{\chi})^2/(N-1)\right]^{1/2} \qquad (1)$$

deviation of the average value) by eq 2. Here, χ_i is the

$$\sigma(\text{of mean}) = \left[\sum_{i=1}^{i=N} (\chi_i - \bar{\chi})^2/N(N-1)\right]^{1/2} \qquad (2)$$

*i*th bond length and $\bar{\chi}$ is the mean of the *N* equivalent bond lengths.

The C(P bonded)-C(ortho) distances range from 1.357 (10) to 1.393 (10) Å with an average value of 1.376 Å [rms scatter = 0.0123 Å; σ(of mean) = 0.0035 Å], C(ortho)-C(meta) distances range from 1.366 (10) to 1.397 (13) Å with an average value of 1.383 Å [rms scatter = 0.0098 Å; σ(of mean) = 0.0028 Å], and C(meta)-C(para) distances range from 1.334 (12) to 1.400 (15) Å, the average being 1.361 Å [rms scatter = 0.0197 Å; σ(of mean) = 0.0057 Å]. The bond lengths thus vary in the order C(ortho)-C(meta) > C(P bonded)-C(ortho) > C(meta)-C(para) by successive increments of 0.007 Å (1.5σ) and 0.015 Å (2.2σ).[27] the mean C(ortho)-C(meta) distance is 0.022 Å (or 3.5σ) greater than the C(meta)-C(para) distance. A similar pattern of variations has been noted previously in the structural analysis of *trans*-$(PPh_2Me)_2Ni(\sigma\text{-}C_6F_5)Br$.[28] All, of course, are believed to be artifacts of thermal motion.

Carbon-carbon-carbon angles within the six independent phenyl groups range from C(30)-C(25)-C(26) = 116.6 (7)° to C(25)-C(26)-C(27) = 122.0 (9)°, averaging 120.0° (as expected for the internal angles of a planar hexagon). Internal angles at the P-bonded carbon atoms are all less than the ideal trigonal value, with C(6)-C(1)-C(2) = 118.7 (7), C(12)-C(7)-C(8) = 118.1 (7), C(18)-C(13)-C(14) = 118.2 (7), C(24)-C(19)-C(20) = 119.2 (7), C(30)-C(25)-C(26) = 116.6 (7), and C(36)-C(31)-C(32) = 118.3 (7)°; the average value is 118.2° [rms scatter = 0.80°; σ(of mean) = 0.33°]. Other internal angles are as follows: 119.4 (7)-122.0 (9)° (average 120.7°) at the ortho carbons, 119.3 (9)-120.7 (8)° (average 120.1°) at the meta carbons, and 118.8 (9)-120.4 (9)° (average 119.7°) at the para carbons.

The pattern of small angles at the P-bonded carbons and large angles at the ortho carbons has been noted previously for phenyl groups bonded to phosphorus in reports of the structures of *trans*-$(PPh_2Me)_2Ni(\sigma\text{-}C_6F_5)Br$[28] and *trans*-$(PPh_2Me)_2Ni(\sigma\text{-}C_6F_5)_2$.[29]

The six carbocyclic phenyl rings are planar within the limits of experimental error. Root-mean-square deviations of carbon atoms from their appropriate least-squares plane (see Table V) are 0.006 Å for C(1)-C(6), 0.012 Å for C(7)-C(12), 0.010 Å for C(13)-C(18), 0.016 Å for C(19)-C(24), 0.010 Å for C(25)-C(30), and 0.007 Å for C(31)-C(36).

Table V. Least-Squares Planes within the $[PPh_3CuCl]_4$ Molecules[a-c]

Atom	Dev, Å	Atom	Dev, Å
Plane I: $-0.4909X - 0.0964Y + 0.8659Z = 0.2480$			
C(1)*	0.001	P(1)	0.036
C(2)*	−0.003	H(2)	−0.02
C(3)*	−0.002	H(3)	−0.07
C(4)*	0.008	H(4)	−0.01
C(5)*	−0.010	H(5)	−0.10
C(6)*	0.005	H(6)	−0.05
Plane II: $0.7865X - 0.3900Y + 0.4789Z = 0.4389$			
C(7)*	0.018	P(1)	0.180
C(8)*	−0.016	H(8)	−0.00
C(9)*	0.002	H(9)	0.03
C(10)*	0.010	H(10)	0.09
C(11)*	−0.007	H(11)	−0.02
C(12)*	−0.007	H(12)	−0.10
Plane III: $0.3620X + 0.9103Y + 0.2010Z = 10.7176$			
C(13)*	0.016	P(1)	0.192
C(14)*	−0.011	H(14)	−0.05
C(15)*	−0.000	H(15)	0.14
C(16)*	0.006	H(16)	0.05
C(17)*	−0.001	H(17)	0.00
C(18)*	−0.010	H(18)	0.06
Plane IV: $-0.2493X + 0.4260Y + 0.8697Z = 8.5988$			
C(19)*	0.022	P(2)	0.249
C(20)*	−0.025	H(20)	0.03
C(21)*	0.012	H(21)	−0.02
C(22)*	0.004	H(22)	0.00
C(23)*	−0.007	H(23)	−0.07
C(24)*	−0.006	H(24)	−0.18
Plane V: $0.9085X - 0.4060Y + 0.0988Z = -0.2110$			
C(25)*	0.003	P(2)	−0.025
C(26)*	0.001	H(26)	0.03
C(27)*	−0.010	H(27)	0.11
C(28)*	0.015	H(28)	−0.06
C(29)*	−0.011	H(29)	0.10
C(30)*	0.002	H(30)	−0.08
Plane VI: $0.6503X + 0.7391Y - 0.1757Z = 3.6633$			
C(31)*	−0.004	P(2)	0.035
C(32)*	0.001	H(32)	0.02
C(33)*	0.007	H(33)	0.02
C(34)*	−0.011	H(34)	−0.01
C(35)*	0.008	H(35)	0.05
C(36)*	−0.001	H(36)	0.02

[a] All calculations were performed using the FORTRAN IV program PLOD, by B. G. DeBoer. [b] Cartesian coordinates, *i.e.*, $[X, Y, Z] = [xa, yb, zc]$. [c] Atoms marked with an asterisk were given unit weight; all other atoms were assigned zero weight.

The phosphorus atoms are not coplanar with their appropriate three phenyl groups. As shown in Table V, atom P(1) lies 0.036 Å from plane I (defined by C(1)-C(6)), 0.180 Å from plane II (defined by C(7)-C(12)), and 0.192 Å from plane III (defined by C(13)-C(18)). In a similar fashion, atom P(2) is 0.249 Å from plane IV, 0.025 Å from plane V, and 0.035 Å from plane VI.

The Hydrogen Atoms. The 30 independent hydrogen atoms were all located and refined in the study. The validity of this procedure may be checked by considering the final properties and the geometry of these atoms.

(1) The thermal parameters of hydrogen atoms are all reasonable and range from $B = 3.2\ (12)$ Å^2 for H(14) through $B = 8.1\ (29)$ Å^2 for H(4). [For comparison we may note that the "equivalent isotropic thermal parameters" for carbon atoms (see Table I) range from 2.49 Å^2 for C(19) through 6.98 Å^2 for C(4).]

(2) The 30 independent carbon-hydrogen bond lengths

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(26) *Chem. Soc., Spec. Publ.*, No. 18, S16s (1965).

(27) σ(diff) is calculated as $[\sigma(\text{of mean})_A{}^2 + \sigma(\text{of mean})_B{}^2]^{1/2}$.

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range from C(24)-H(24) = 0.79 (7) Å through C(17)-H(17) = 1.04 (6) Å. The average value is 0.90 Å (rms scatter = 0.070 Å; σ(of mean) = 0.013 Å). This value is contracted from the accepted internuclear C-H distance of ~1.08 Å[30] due to the asphericity of the electron density about the bonded hydrogen atom[31] and is lower than the value of ~0.95 Å normally found from X-ray diffraction studies,[32] probably as a result of librational shortening due to the rigid-body motion of the phenyl groups (*vide supra*).

(3) The external hydrogen-carbon-carbon angles of the phenyl groups are each expected to be ~120°. The most asymmetrically situated hydrogen atom is H(5), which is involved in the angles H(5)-C(5)-C(4) = 132 (5)° and H(5)-C(5)-C(6) = 107 (5)°. However each of these angles varies by only ~2.5σ from its expected value. All other H-C-C angles lie in the range 112 (6)-128 (6)° and no other angle varies from the idealized value of ~120° by more than 1.4σ.

(4) The coplanarity of hydrogen atoms with carbon atoms of the phenyl groups may be examined in Table V. The largest deviations from planarity are (in order) 0.18 Å (or ~2.6σ) for H(24), 0.14 Å (or ~2.3σ) for H(15), and 0.11 Å (or ~1.6σ) for H(27). All other hydrogen atoms are within 0.10 Å (or ~1.5σ) of the appropriate carbocyclic plane.

Finally, it should be emphasized that the above summary demonstrates that the positions of the refined hydrogen atoms are (within the limits of experimental error) entirely consistent with chemical expectations. Observed deviations of individual hydrogen atoms from the locations predicted by assuming idealized pseudo-D_{6h} geometry of the phenyl rings are of no statistical significance.

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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 \$4.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-74-1065.

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Contribution from Bell Laboratories,
Murray Hill, New Jersey 07974

Crystal Structure of Iodine Pentafluoride at −80°

R. D. BURBANK* and G. R. JONES

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Iodine pentafluoride, IF$_5$, is monoclinic: a = 15.07 (2) Å, b = 6.836 (10) Å, c = 18.24 (2) Å, β = 92.96 (14)°, most probable space group $C2/c$, 20 molecules per unit cell, and 2.5 molecules in the asymmetric unit. The intensities were measured by the stationary-crystal technique using a scintillation counter. The structure was refined by least squares to R = 0.064, R_w = 0.049. Although there are individual variations among the three crystallographically distinct molecules, they appear to be chemically equivalent with the distorted tetragonal-pyramidal shape to be expected from the Gillespie–Nyholm valence shell electron pair repulsion theory. The molecular dimensions (weighted average over all molecules) are I-F$_{\text{apical}}$ = 1.75 (3) Å, I-F$_{\text{basal}}$ = 1.87 (3) Å, and F$_{\text{apical}}$-I-F$_{\text{basal}}$ = 81.9 (4)°. The pattern of polar contacts between molecules forms an extended three-dimensional array which fills space. The structure is of interest because the IF$_5$ molecule is isoelectronic with the XeF$_5{}^+$ ion.

Introduction

IF$_5$ in the crystalline state was studied more than 20 years ago by photographic techniques.[1] The unit cell is monoclinic with most probable space group symmetry of Cc or $C2/c$. Assuming 20 molecules per unit cell and a calculated density of ~3.9 g cm^{-3} implies that the asymmetric unit contains either 5 or 2.5 molecules depending on the space group. In either event the structure appeared complex for the techniques available at the time and the analysis was not completed.

The recent analysis of the cubic XeF$_6$ structure[2,3] has created renewed interest in the IF$_5$ structure because the IF$_5$ molecule is isoelectronic with the XeF$_5{}^+$ ion. In the known crystalline phases of XeF$_6$ the molecules are always dissociated into XeF$_5{}^+$ and F$^-$ ions.[2,4] The valence electron lone pair is sterically active and the XeF$_5{}^+$ ion has the shape of a distorted tetragonal pyramid as expected by the Gillespie–Nyholm theory.[5,6] The XeF$_5{}^+$ ions are bridged by F$^-$ ions to form tetrameric or hexameric rings of nearly spherical overall shape. The bridging F$^-$ ions make angles of about 35° with the Xe-lone pair axis.

One would expect the IF$_5$ molecule to have the same shape as the XeF$_5{}^+$ ion. Then the question arises as to whether it is possible for the molecules to be oriented in

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