distances in the bridging acetate groups with binuclear units are essentially the same in the copper(I) and in the copper(II) acetate structures[6,7] although the Cu–O bonds in the copper(II) complexes (1.96–1.98 Å) are significantly longer than the corresponding average Cu–O bond distance (1.91 Å) in copper(I) acetate.

The results of an independent structure determination of copper(I) acetate by Drew and co-workers was published almost simultaneously with our communication.[3] The mean values of the bond distances and bond angles that were reported are shown in Table II and are in essential agreement with our values.

Acknowledgment. The authors are grateful to M. G. B. Drew, D. A. Edwards, and R. Richards for permission to quote results of their structure determination.[10]

Registry No. $Cu(O_2CCH_3)$, 49830-22-0.

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 Street, 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 INORG-74-802.

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(10) M. G. B. Drew, D. A. Edwards, and R. Richards, *J. Chem. Soc., Chem. Commun.*, 124 (1973).

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Crystal and Molecular Structure of Chlorobis(triphenylphosphine)gold(I) Hemibenzenate

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The crystal and molecular structure of chlorobis(triphenylphosphine)gold(I) hemibenzenate, $[(C_6H_5)_3P]_2AuCl\cdot{}^1/_2C_6H_6$, has been solved using X-ray crystallographic data collected on a diffractometer. The colorless, bladed, triclinic crystals crystallize in the space group $P\bar{1}$ with $a = 10.187$ (1) A, $b = 12.997$ (1) A, $c = 16.596$ (1) A, $\alpha = 52.54$ (1)°, $\beta = 90.68$ (1)°, $\gamma = 75.00$ (1)°, and $Z = 2$. The structure was refined, using block diagonal least squares, to a final R factor of 0.064 on 3661 independent reflections. All of the hydrogen atoms were included in the structure determination but their parameters were not refined. The structure consists of discrete units of $[(C_6H_5)_3P]_2AuCl$. This is the first X-ray crystallographic study in which the coordination about the gold atom has been found to be essentially trigonal planar. The Au–Cl distance, 2.500 (4) A, and the average Au–P distance, 2.331 (4) A, are both longer than the corresponding distances reported for other gold(I) complexes. The P–Au–P angle, 132.1 (1)°, is larger than the P–Cu–P angle reported for the isostructural copper compound.

Introduction

Very little is known concerning the stereochemistry of Au(I) complexes. Recently the X-ray crystal structures of cyano(triphenylphosphine)gold(I)[1] and chloro(triphenylphosphine)gold(I)[2] have been reported. Both of these two-coordinated gold compounds are essentially linear. The P–Au–CN angle and the P–Au–Cl angle are 169 (2) and 179.63 (8)°, respectively. With chelating ligands, Au(I) has been found to form four-coordinated complexes which are tetrahedral.[3]

Although X-ray structure studies have demonstrated the ability of Au(I) to show linear and tetrahedral coordination, none has—until this work—shown Au(I) with trigonal-planar coordination. Chlorobis(triphenylphosphine)gold(I) seemed to be a compound which might exhibit a three-coordinate Au(I) atom. To investigate this possibility, the X-ray crystal structure of this compound was done. While the study was in progress, the structure of bromobis(triphenylphosphine)copper(I) hemibenzenate was published.[4] A comparison of the structure of chlorobis(triphenylphosphine)gold(I) hemibenzenate with the structure of bromobis(triphenylphosphine)copper(I) hemibenzenate is of interest since in both compounds the central atom is a coinage metal which is coordinated with two triphenylphosphine ligands and a halogen.

Experimental Section

Chlorobis(triphenylphosphine)gold(I) Hemibenzenate. Attempts to synthesize single crystals of chlorobis(triphenylphosphine)gold(I), in solvents other than benzene, yielded only twinned crystals. It was decided, therefore, to attempt the synthesis of chlorotris(triphenylphosphine)gold(I) which should also demonstrate a possible coordination about the Au(I) atom. The procedure for the preparation of chlorotris(triphenylphosphine)copper(I)[5] was followed. The method yielded *not* the expected tris compound but rather single crystals which analyzed as chlorobis(triphenylphosphine)gold(I) with 0.5 mol of benzene of crystallization per mole of complex.

A suspension of $[(C_6H_5)_3P]AuCl$ (1.9140 g, 0.004 mol) was refluxed with excess triphenylphosphine (8.3002 g, 0.03 mol) in 100 ml of benzene until the solution became clear. The hot solution was filtered. After 3 hr the first set of crystals was filtered, dried, and submitted for elemental analysis. *Anal.* Calcd for $[(C_6H_5)_3P]_2AuCl\cdot{}^1/_2C_6H_6$: C, 58.65; H, 4.18. Found: C, 58.56; H, 4.00. The benzene of crystallization could be removed by heating overnight in an Abderhalden. *Anal.* Calcd for $[(C_6H_5)_3P]_2AuCl$: C, 57.21; H, 3.99. Found: C, 57.18; H, 3.93.

Crystal Data. For $[(C_6H_5)_3P]_2AuCl\cdot{}^1/_2C_6H_6$, mol wt 796.1, the crystals are triclinic with $a = 10.187$ (1) A, $b = 12.997$ (1) A, $c = 16.596$ (1) A, $\alpha = 52.54$ (1)°, $\beta = 90.68$ (1)°, $\gamma = 75.00$ (1)°, $V = 1643.2$ A^3, ρ_{measd}(pycnometrically in Skellysolve at 32.6°) = 1.59 g/cm^3, $Z = 2$, $\rho_{calcd} = 1.61$ g/cm^3, $F(000) = 786$, and μ(Mo Kα) = 48.1 cm^{-1}. Cell dimensions chosen to conform with those chosen

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(1) P. L. Bellon, M. Manaserro, and M. Sonsoni, *Ric. Sci.*, 39, 173 (1969).

(2) D. M. Soboroff, Ph.D. Thesis, The University of Iowa, 1973; W. E. Bennett, D. M. Soboroff, and N. C. Baenziger to be submitted for publication.

(3) W. Cochran, F. A. Hart, and F. G. Mann, *J. Chem. Soc.*, 2816 (1957).

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

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

for the copper analog[4] would be $a' = b = 12.997$ (12.870) Å, $b' = a = 10.187$ (10.235) Å, $c' = c - b = 13.490$ (13.658) Å, $\alpha' = 105.32$ (104.97)°, $\beta' = 102.43$ (101.81)°, and $\gamma' = 75.13$ (74.37)°. The parameters for the copper compound are given in parentheses.

The crystal was mounted so that the rotation axis was approximately parallel to $[\bar{1}01]^*$ with the length of the crystal along that axis ~0.30 mm, the maximum width ~0.25 mm, and a thickness of ~0.07 mm in the b^* direction.

Since there were two molecules of $[(C_6H_5)_3P]_2AuCl\cdot{}^1/_2C_6H_6$ per unit cell, it seemed probable that the molecule of benzene would be on a center of inversion and that the space group would be $P\bar{1}$. This assumption proved to be true since the structure was successfully refined in this space group.

Data Collection and Reduction. Initial alignment of the crystal and determination of the space group were done from Weissenberg and precession films. Data were collected on a Picker four-circle automated diffractometer using Zr-filtered Mo Kα radiation (λ 0.7107 Å). Cell dimensions are a weighted average of values for the parameters determined from Weissenberg back-reflection data and the values determined for the parameters by a least-squares fit to the angular settings of 12 reflections hand-centered on the diffractometer.

Intensity measurements were made using a moving crystal–moving counter technique. Each reflection was scanned over a range of 1.5° at a rate of 1°/min with 10-sec stationary background counts at both the high and low extremes of each scan. To monitor the crystal stability, crystal alignment, and the beam stability three standard reflections (360, 032, $\bar{4}04$) were measured after each block of 58 reflections. The intensities of the standards did not vary over 5% during the entire collection period. As a result no adjustments for crystal or instrument instability were made.

The integrated intensity for each reflection was determined as $I_n = I - Bt_s/t_b$. The estimate of the standard deviation in the intensity of a reflection, S_I, was determined from the larger of the two quantities

$$S_I^2 = \sum_{i=1,N} [I_i + B_i(t_s/t_b)_i]/N$$

or

$$S_I^2 = \sum_{i=1,N} [I_n - \overline{I_n}]_i^2/(N-1) \quad \text{if } N > 2$$

B_i is the sum of the two background counts, t_s is the scan time, t_b is the sum of the sum of the background counting times, $\overline{I_n}$ is the average I_n value, and N is the number of equivalent reflections measured.[6] A reflection was considered absent if I_n was less than $3S_B$, where

$$S_B^2 = \sum_{i=1,N} B_i/N$$

The estimated standard deviation in F is $S_F = FS_I/2I$. Of the 3661 independent reflections measured, 227 were absent.

The data were corrected for Lorentz and polarization effects and for absorption,[7] with the corrections ranging from 0.363 to 0.688.

Atomic scattering factors and dispersion corrections, Δf and $\Delta f'$ were taken from ref 8. It was assumed that the gold atom was postively charged, that the chlorine atom was negatively charged, and that the phosphorus, carbon, and hydrogen atoms were neutral. The real part of the dispersion correction was applied for gold, chlorine, and phosphorus during all stages of refinement.[9] During the last three cycles of refinement, the imaginary part of the dispersion correction was applied for gold, chlorine, and phosphorus. During the initial stages of refinement unit weights were used. Any reflection below the minimum observable intensity was assigned $w = 0.0$ unless $F_o < F_c$ in which case it was assigned $w = 1$. During the final stages of refinement a scheme similar to that of Grant, Killean, and Lawrence[10] where $w = 1/(S_F^2 + c_o^2F_o^2)$ was used. The parameter c is adjusted so that the error-fit function is $[\Sigma w(\Delta F)^2/(m-n)]^{1/2} \approx 1$, where n is the number of reflections and m is the number of parameters varied.

Table I. Final Positional Parameters for all Nonhydrogen Atoms[a]

	x	y	z
Au	2208.6 (0.6)	1346.9 (0.6)	2404.9 (0.5)
Cl	435 (5)	220 (5)	3217 (4)
P(1)	2645 (5)	2767 (4)	2707 (3)
P(2)	3167 (4)	669 (4)	1459 (3)
C(1)	2463 (14)	4376 (15)	1490 (12)
C(2)	1120 (17)	5150 (17)	856 (14)
C(3)	3551 (16)	4882 (15)	1080 (12)
C(4)	885 (20)	6409 (17)	201 (13)
C(5)	3328 (19)	6101 (17)	53 (12)
C(6)	2021 (19)	6839 (17)	9416 (13)
C(7)	1529 (14)	3249 (14)	3358 (12)
C(8)	715 (17)	2500 (16)	3947 (12)
C(9)	1552 (16)	4391 (16)	3377 (12)
C(10)	133 (19)	2845 (17)	4476 (13)
C(11)	732 (19)	4769 (17)	3755 (13)
C(12)	115 (19)	4003 (19)	4360 (13)
C(13)	4410 (15)	2105 (14)	3392 (11)
C(14)	4772 (18)	2005 (17)	4251 (14)
C(15)	5430 (16)	1627 (15)	3059 (12)
C(16)	6162 (19)	1532 (21)	4708 (16)
C(17)	6846 (18)	1149 (18)	3521 (14)
C(18)	7185 (17)	1093 (17)	4337 (15)
C(19)	2950 (15)	2102 (16)	110 (12)
C(20)	2770 (19)	2016 (17)	−676 (13)
C(21)	2960 (18)	3366 (18)	−181 (13)
C(22)	2623 (22)	3151 (21)	−1724 (16)
C(23)	2815 (20)	4476 (17)	−1205 (14)
C(24)	2663 (19)	4400 (18)	−1997 (13)
C(25)	2616 (16)	−550 (16)	1438 (12)
C(26)	3539 (17)	−1419 (16)	1325 (14)
C(27)	1258 (16)	−507 (17)	1442 (14)
C(28)	3083 (20)	−2286 (19)	1230 (15)
C(29)	782 (20)	−1347 (21)	1333 (17)
C(30)	1745 (20)	−2183 (17)	1188 (14)
C(31)	5007 (15)	−128 (14)	1964 (11)
C(32)	5490 (19)	−1279 (20)	2959 (15)
C(33)	6000 (17)	409 (17)	1398 (14)
C(34)	6935 (20)	−1912 (20)	3443 (15)
C(35)	7405 (18)	−155 (19)	1847 (16)
C(36)	7836 (17)	−1328 (18)	2856 (15)
C(37)	6140 (31)	4160 (30)	5009 (27)
C(38)	4981 (31)	4977 (31)	4200 (23)
C(39)	6089 (37)	4219 (28)	5846 (22)

[a] All values in the table are multiplied by 10^4. Estimated standard deviations in the last significant digit(s) are given in parentheses.

The progress of the refinement was followed using the discrepancy factor $R_2 = [\Sigma w(\Delta F)^2/\Sigma w(F_o)^2]^{1/2}$, where $\Delta F = |F_o| - |F_c|$ (F_o is the scaled observed structure factor; F_c is the calculated structure factor). The function minimized was $\Sigma w(\Delta F)^2$.

Structure Determination and Refinement. The structure of chlorobis(triphenylphosphine)gold(I) hemibenzenate was solved using heavy-atom techniques. Analysis of a three-dimensional Patterson map gave the coordinates of all four heavy atoms. The remaining atoms were found in successive electron density maps. Although after block diagonal refinement on the positional and thermal parameters of all the nonhydrogen atoms, a difference map showed 16 peaks with electron density of 0.6 e/Å^3 and 17 peaks with electron density of 0.3 e/Å^3 in positions likely for hydrogen atoms, their positions were calculated using the assumption that each hydrogen lies in the plane of the phenyl ring at a distance of 1.08 Å from the carbon to which it is attached.[11]

During the final refinements the positional and thermal parameters of all nonhydrogen atoms were refined. Each hydrogen was assigned the isotropic thermal parameter of the carbon to which it was attached and was included in the structure determination, though not allowed to vary. New hydrogen positions and new thermal parameters, however, based upon the refined carbon parameters, were calculated after three cycles of refinement and these new

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(6) All symmetry-equivalent reflections were measured. A few reflections (standards and those arising from overlap of data collection ranges) were measured enough times to use the second error formula.

(7) A Monte Carlo method [A. Alberti and G. Gottardi, *Acta Crystallogr.*, 21, 833 (1966)] was used with the observed crystal geometry.

(8) "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1959, p 201.

(9) Programs for the IBM computer used in this analysis were developed at the University of Iowa.

(10) D. F. Grant, R. C. G. Killean, and J. L. Lawrence, *Acta Crystallogr., Sect. B*, 25, 374 (1969).

(11) It was pointed out by the referee that a more valid C–H distance as measured by X-ray crystallography is 0.95Å. The placement of hydrogen atoms 1.08 Å from carbon atom instead of 0.95 Å is not likely to change the carbon positions significantly.

Table IA. Final Anisotropic Thermal Parameters for all Nonhydrogen Atoms[a]

Atoms	β_{11}	β_{22}	β_{23}	β_{12}	β_{13}	β_{23}
Au	742 (7)	902 (7)	518 (4)	754 (11)	388 (8)	−1059 (10)
Cl	129 (6)	184 (7)	75 (4)	−225 (11)	91 (8)	−150 (8)
P(1)	104 (5)	100 (5)	69 (3)	−98 (8)	49 (7)	−138 (8)
P(2)	88 (5)	112 (5)	66 (3)	−103 (8)	62 (6)	−144 (8)
C(1)	68 (17)	115 (20)	78 (12)	−123 (31)	68 (23)	−164 (29)
C(2)	105 (22)	136 (24)	100 (15)	−109 (37)	56 (29)	−193 (35)
C(3)	110 (21)	98 (20)	61 (12)	−88 (33)	37 (25)	−112 (28)
C(4)	179 (29)	130 (24)	64 (14)	−119 (43)	20 (31)	−136 (33)
C(5)	177 (28)	126 (23)	47 (12)	−148 (41)	72 (29)	−114 (30)
C(6)	173 (28)	121 (23)	61 (13)	−116 (40)	64 (30)	−139 (31)
C(7)	88 (19)	63 (17)	57 (12)	−58 (30)	11 (23)	−79 (25)
C(8)	136 (23)	91 (20)	58 (13)	−79 (35)	40 (27)	−99 (28)
C(9)	96 (20)	107 (21)	61 (13)	−86 (34)	50 (25)	−112 (29)
C(10)	161 (27)	122 (24)	62 (14)	−111 (40)	84 (31)	−120 (32)
C(11)	180 (29)	123 (24)	66 (14)	−83 (41)	54 (31)	−147 (32)
C(12)	145 (26)	184 (29)	48 (13)	−20 (43)	31 (28)	−158 (34)
C(13)	110 (21)	79 (18)	50 (11)	−88 (21)	51 (24)	−107 (26)
C(14)	107 (23)	121 (24)	78 (15)	−1 (36)	17 (28)	−133 (33)
C(15)	114 (22)	100 (21)	59 (13)	−15 (34)	−23 (26)	−121 (29)
C(16)	118 (26)	207 (33)	105 (18)	−13 (45)	−47 (33)	−240 (43)
C(17)	106 (23)	126 (24)	87 (15)	−28 (37)	6 (30)	−152 (34)
C(18)	85 (22)	103 (23)	89 (16)	−4 (35)	−60 (29)	−92 (33)
C(19)	94 (20)	124 (22)	47 (11)	−72 (33)	46 (24)	−128 (28)
C(20)	170 (27)	105 (22)	52 (13)	−42 (38)	−8 (29)	−112 (29)
C(21)	147 (25)	133 (23)	79 (14)	−171 (40)	87 (30)	−169 (33)
C(22)	198 (33)	160 (29)	93 (18)	24 (49)	−17 (37)	−196 (40)
C(23)	181 (30)	104 (23)	85 (16)	127 (42)	114 (34)	−127 (33)
C(24)	178 (28)	126 (24)	43 (12)	−61 (41)	31 (29)	−92 (30)
C(25)	90 (20)	131 (22)	66 (13)	−133 (35)	62 (26)	−141 (30)
C(26)	126 (24)	113 (22)	79 (14)	−109 (39)	74 (29)	−143 (31)
C(27)	83 (21)	133 (24)	96 (16)	−46 (35)	−28 (28)	−173 (34)
C(28)	182 (29)	147 (26)	99 (17)	−171 (45)	126 (36)	−206 (38)
C(29)	125 (27)	190 (31)	143 (20)	−184 (47)	68 (37)	−244 (45)
C(30)	194 (30)	117 (23)	84 (15)	−184 (43)	63 (33)	−146 (34)
C(31)	105 (20)	84 (18)	43 (11)	−81 (31)	44 (23)	−91 (25)
C(32)	141 (26)	187 (29)	99 (17)	−178 (45)	108 (34)	−217 (40)
C(33)	98 (21)	138 (24)	87 (15)	−92 (37)	68 (29)	−162 (34)
C(34)	143 (28)	162 (29)	82 (17)	−47 (44)	−00 (33)	−146 (38)
C(35)	105 (23)	164 (28)	119 (16)	−92 (41)	75 (33)	−209 (40)
C(36)	95 (22)	146 (26)	100 (17)	−76 (39)	46 (31)	−168 (37)
C(37)	271 (50)	291 (50)	261 (39)	−300 (82)	349 (75)	−421 (79)
C(38)	310 (51)	342 (54)	173 (29)	−374 (87)	251 (63)	−385 (71)
C(39)	197 (39)	280 (45)	159 (27)	−275 (70)	113 (51)	−254 (60)

[a] All values in the table are multiplied by 10^4 with the exception of the Au parameters which are multiplied by 10^5. Estimated standard deviations in the last significant digit(s) are given in parentheses.

positional and thermal parameters were used in the next set of three cycles. After the inclusion of averaged experimental weights, R_2 dropped to 0.0939. Several of the low-angle reflections appeared to be suffering from extinction, so all reflections below $((\sin\theta)/\lambda)^2 = 0.02$, were omitted. After deleting these 75 reflections, the refinement coverged to final residual values $R_1 = \Sigma\Delta F/\Sigma F_o = 0.0640$ and $R_2 = [\Sigma w(\Delta F)^2/\Sigma w F_o^2]^{1/2} = 0.0809$.

During the last cycle of refinement the average parameter shift was only 0.1 of the average estimated standard deviation. The final difference map was essentially featureless with the exception of a peak of about 3 e/Å^3 near the Au atom. The peak was due to the inability of the model to describe exactly the electron density surrounding the gold. Final positional and thermal parameters derived for all nonhydrogen atoms can be found in Tables I and IA.[12] Table II gives a comparison of some of the atom parameters based on fractions of cell edges for chlorobis(triphenylphosphine)gold(I) hemibenzenate and bromobis(triphenylphosphine)copper(I) hemibenzenate. Table III gives calculated hydrogen positions.[12]

Results and Discussion

Description of Structure. Figure 1[13] presents a view of the molecular structure of chlorobis(triphenylphosphine)gold(I). Although the angles deviate somewhat from the idealized geometry of 120°, the coordination about the gold is essentially trigonal planar. The gold atom is displaced only 0.01 Å above the chlorine-phosphorus-phosphorus plane. Relevant bond distances and bond angles are given in Table IV.[14] For ease of comparison, bond distances and bond angles in related compounds are included in Table IVA. The Au-P distances of 2.323 (4) and 2.339 (4) Å are considerably longer than the Au-P distances of 2.27 (1),[1] 2.243 (4),[2] and 2.286 (3) Å[2] reported for other Au(I) complexes. Likewise, the Au-Cl distance, 2.500 (4) Å, is considerably longer than a previously reported Au-Cl distance of 2.290 (3) Å.[2]

The interatomic distances and bond angles found in the triphenylphosphine groups are consistent with those found in the isostructural copper complex.[4] The deviations of individual carbon atoms from the best least-squares planes through the phenyl rings (Table IVD) are not great enough to be considered significant. The C–C distances range from 1.330 to 1.451 Å with a mean of 1.390 Å and a calculated scatter from the mean of 0.025 Å. The C–H distances range from 1.075 to 1.090 Å with a mean of 1.08 Å.

The C–C distances in the benzene of crystallization of 1.38 (5) and 1.44 (4) Å are not significantly different from

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

(13) C. K. Johnson, "ORTEP: A Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations," Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.

(14) The best least-squares planes through the phenyl rings and the deviations of the carbon atoms from these planes appear in Table IVD and E. The average deviations of the atoms from the near planes is ±0.01 Å.

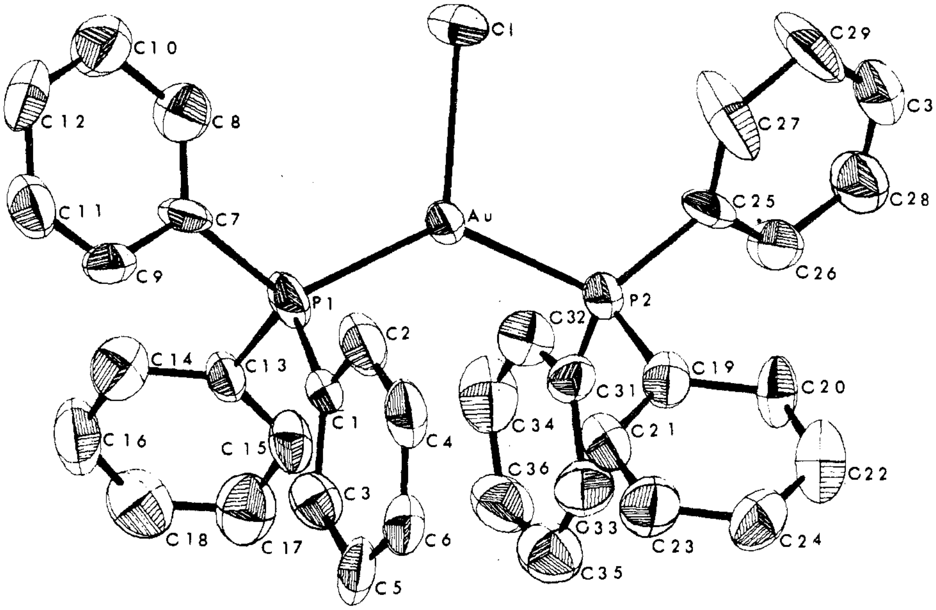

Figure 1. A perspective view of the $[(C_6H_5)_3P]_2AuCl$ unit showing the trigonal-planar coordination geometry and showing the atom-labeling scheme used. Atoms are represented by 50% probability ellipsoids.

Table II. Comparison of Atom Parameters of Chlorobis(triphenylphosphine)gold(I) Hemibenzenate with Those of Bromobis(triphenylphosphine)copper(I) Hemibenzenate[a-c]

	New coordinates of Au compd			Coordinates of Cu compd		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
M	1248.2	2791.4	2595.1	1263.5	2860.7	2590.1
X	1563	4565	1783	1603	4400	1750
P(1)[2]	−0474	2355	2291	−0408	2405	2345
P(2)[1]	2872	1833	3541	2787	1848	3554
C(1)[61]	−0866	2537	3510	−0852	2615	3579
C(7)[51]	−1607	3471	1642	−1593	3479	1709
C(13)[41]	−0497	0590	1608	−0427	0632	1689
C(19)[11]	2788	2050	4890	2728	2039	4905
C(25)[21]	4062	2384	3562	4065	2328	3584
C(31)[31]	3164	−0007	3036	3109	−0016	3046

[a] All values in the table are multiplied by 10^4. [b] The conversion of the coordinates in this paper to those of Davis, Belford, and Paul[4] go by the transformation

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} 1/2 \\ 1/2 \\ 1/2 \end{pmatrix} - \begin{pmatrix} 011 \\ 100 \\ 001 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

[c] Numbers assigned by Davis, Belford, and Paul[4] to phosphorus atoms in the copper analog are given in brackets following the numbers of the corresponding atoms of the Au compound.

Table III. Calculated Positions of the Hydrogen Atoms[a]

Atoms	*x*	*y*	*z*
H(2)	027	479	118
H(3)	460	432	157
H(4)	080	646	913
H(5)	340	613	939
H(6)	202	687	005
H(8)	076	163	400
H(9)	220	498	284
H(10)	923	225	494
H(11)	076	567	365
H(12)	925	431	474
H(14)	396	231	455
H(15)	510	163	243
H(16)	645	149	536
H(17)	768	082	324
H(18)	827	071	469
H(20)	274	106	952
H(21)	309	349	040
H(22)	248	307	768
H(23)	281	543	861
H(24)	258	528	721
H(26)	460	859	131
H(27)	057	018	154
H(28)	380	696	120
H(29)	972	866	134
H(30)	142	720	104
H(32)	472	830	337
H(33)	567	130	058
H(34)	734	718	426
H(35)	815	030	141
H(36)	894	820	319
H(37)	703	352	498
H(38)	496	494	357
H(39)	689	361	654

[a] All values in the table are multiplied by 10^3. A hydrogen atom is given the number of the carbon atom to which it is attached.

the C-C distances of the phenyl rings. The large thermal parameters, however (Table IA), indicate some degree of rotational disorder in the plane of the ring.

The packing diagram is shown in Figure 2.[13] Each unit cell of the crystal structure consists of two discrete molecules of chlorobis(triphenylphosphine)gold(I) separated by van der Waals distances with a molecule of benzene occupying interstitial sites centered about $^1/_2, {}^1/_2, {}^1/_2$.

Chlorobis(triphenylphosphine)gold(I) hemibenzenate is isostructural with bromobis(triphenylphosphine)copper(I) hemibenzenate.[4] Both crystallize in the space group $P\bar{1}$ with $Z = 2$ and with a molecule of benzene of crystallization located about the center of inversion. There is a close degree of similarity between both the unit cell parameters and the coordinates of the atoms of the two analogs (Table II). The cell axes differ by less than 0.2 Å and the cell angles by less than 0.8°. The atom coordinates differ by less than 0.02 of a cell edge. Although the Cu-P distances in the copper complex are comparable to the Cu-P distances in other Cu(I) complexes,[4] the Au-P distance in the analogous complex is longer than the Au-P distances reported for other Au(I) complexes[1,2] (Table IVA). The observed bond lengthening seemingly supports the hypothesis, originally formulated by Bent[15] for carbon bonds and more recently

(15) H. A. Bent, *Chem. Rev.*, **61**, 275 (1961).

Table IV. Summary of Important Interatomic Distances (Å) and Angles (deg)[a]

A. Coordination Geometry[b]

Compd	M–X bond	M–P(1) [M–P(2)] bond	M–P(2) [M–P(1)] bond	P(1)–M–P(2) angle	P(1)–M–X [P(2)–M–X] angle	P(2)–M–X [P(1)–M–X] angle	Ref
$((C_6H_5)P)_2AuCl$	2.500 (4)	2.323 (4)	2.339 (4)	132.1 (1)	118.7 (1)	109.2 (1)	
$((C_6H_5)P)_2CuBr$	2.346 (2)	2.263 (3)	2.282 (1)	126.0 (1)	121.0 (1)	112.8 (1)	e
$(C_6H_5)_3PAuCl$	2.290 (3)	2.243 (3)			179.63		f
$(C_6H_5)_3PAuCN$		2.27 (1)			169 (2)		g
$((C_6H_5)_3P)_2AuTCNQ$		2.286 (3)		180			f

B. Geometry of the Triphenylphosphine Group

Bond	Value	Angle	Value	Angle	Value	No. of ring atoms[c] close to Cl
P(1)–C(1)	1.772 (15)	C(1)–P(1)–C(7)	103.0 (6)	Au–P(1)–C(1)	108.4 (5)	None
P(1)–C(7)	1.826 (15)	C(1)–P(1)–C(13)	105.8 (7)	Au–P(1)–C(7)	120.1 (5)	Two H's
P(1)–C(13)	1.796 (16)	C(7)–P(1)–C(13)	106.8 (7)	Au–P(1)–C(13)	111.6 (4)	One H
P(2)–C(19)	1.797 (16)	C(19)–P(2)–C(25)	104.6 (7)	Au–P(2)–C(19)	112.7 (5)	None
P(2)–C(25)	1.830 (15)	C(19)–P(2)–C(31)	105.3 (7)	Au–P(2)–C(25)	120.1 (5)	One H and C(25)
P(2)–C(31)	1.787 (15)	C(25)–P(2)–C(31)	104.9 (7)	Au–P(2)–C(31)	108.1 (5)	None

Ring[d]	C–C bond lengths			C–C–C bond angles		
	Min	Max	Mean	Min	Max	Mean
1	1.372 (26)	1.451 (25)	1.407	117.8 (14)	122.0 (15)	120.0
2	1.360 (22)	1.419 (22)	1.396	117.0 (15)	121.9 (14)	120.0
3	1.346 (26)	1.410 (23)	1.380	119.3 (15)	121.0 (15)	120.0
4	1.375 (24)	1.408 (27)	1.395	111.6 (14)	121.7 (15)	120.0
5	1.330 (27)	1.413 (22)	1.384	117.1 (15)	123.3 (15)	120.0
6	1.342 (24)	1.425 (27)	1.378	117.1 (16)	122.7 (17)	120.0

C. Geometry of the Benzene of Crystallization

Bond	Value	Angle	Value
C(37)–C(38)	1.379 (49)	C(38)–C(37)–C(39)	117.2 (24)
C(37)–C(39)	1.438 (43)		

D. Distances of Atoms from Best Least-Squares Planes through Various Rings

Atom	Ring						
	1	2	3	4	5	6	7
C(1)	0.0161	0.0087	0.0259	−0.0072	0.0064	−0.0124	0.0053
C(2)	−0.0065	0.0012	−0.0179	0.0029	0.0067	0.0031	−0.0059
C(3)	−0.0091	−0.0122	−0.0205	0.0027	−0.0032	0.0199	−0.0056
C(4)	−0.0101	−0.0080	0.0047	0.0058	−0.0245	−0.0013	−0.0053
C(5)	−0.0080	0.0053	0.0070	0.0061	−0.0137	−0.0180	0.0059
C(6)	0.0177	0.0049	0.0080	−0.0103	0.0283	0.0087	0.0056

E. Equations of Best Planes[h]

Plane	*A*	*B*	*C*	*D*
Ring 1	−0.0016	−0.9457	−0.3252	−7.3192
Ring 2	−0.5818	0.0987	−0.8073	−4.2444
Ring 3	0.3755	0.6815	−0.6281	3.3926
Ring 4	−0.9470	0.3031	−0.1061	−2.6863
Ring 5	0.0082	0.1231	−0.9924	−1.7187
Ring 6	−0.0815	−0.9558	−0.2823	−2.9282
Ring 7	0.6785	0.5600	−0.4755	7.9318
P–P–Cl	−0.4678	0.3481	−0.8124	−2.2980

[a] See Figure 2 for atom-labeling scheme. Estimated standard deviation in the last significant digit given in parentheses. [b] Atoms of the copper analog are given in brackets after the corresponding atoms of the gold compound. [c] The number of atoms, in the related phenyl ring, that lie close to Cl. [d] For all phenyl rings the overall averages are 1.390 [25] Å and 119.9 [18]°. Calculated scatter was made using the scatter formula $S = \sqrt{\Delta^2/(n-1)}$, where Δ is the difference between the overall average and the individual value and is designated by brackets. [e] P. H. Davis, R. L. Belford, and I. C. Paul, *Inorg. Chem.*, 12, 213 (1973). [f] D. M. Soboroff, Ph.D. Thesis, The University of Iowa, 1973; W. E. Bennett, D. M. Soboroff, and N. C. Baenziger to be submitted for publication. [g] P. L. Bellon, M. Manaserro, and M. Sonsoni, *Ric. Sci.*, 39, 173 (1969). [h] The equation of the plane is in the form $AX + BY + CZ = D$, where A, B, and C are direction cosines of the plane normal with respect to cartesian axes chosen so that X is in the direction of a and Y lies in the ab plane and is perpendicular to X.

used to explain metal–phosphorus bond lengths,[16–19] that the bond length is inversely related to the per cent s-electron content in the bond (as judged by the size of the P–M–P angle). It would be interesting to see if the same trend of bond lengthening is followed in the copper series as the trend followed in going from a linear gold complex to a trigonal-planar complex.[20]

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(20) After this paper was submitted for publication, the structure of $(PPh_3CuBr)_4$ appeared: M. R. Churchill and K. L. Kalra, *J. Amer. Chem. Soc.*, 95, 5772 (1973). In this molecule a Cu_4Br_4 unit exists in a "step configuration" with Cu(I) atoms in both a tetrahedral and a trigonal-planar coordination. The tetrahedrally coordinated Cu–Br bond distance is longer than the trigonal Cu–Br distance supporting the premise, mentioned above, that as the s character decreases the length of the bond increases.

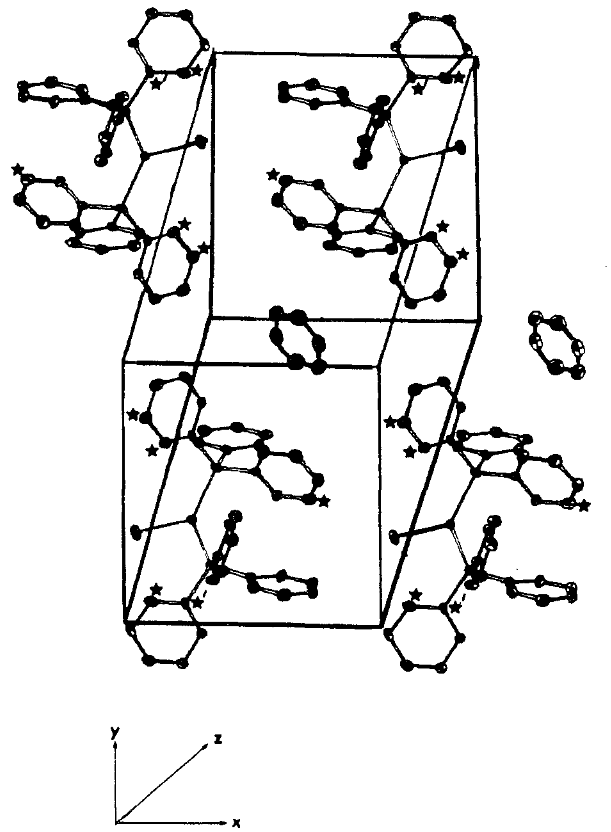

Figure 2. A view of the packing in $[(C_6H_5)_3P]_2AuCl\cdot{}^1/_2C_6H_6$ showing the arrangement of the molecules within the unit cell. Atoms are represented by 50% probability ellipsoids. Carbons which lie within the outlined unit cell have been darkened to distinguish them from those which lie outside the cell. Carbon atoms which contain hydrogen atoms which lie between 2.7 and 2.9 Å from the chlorine atom have been marked with a star. The only carbon which is bonded to a P atom and which lies less than 4.2 Å from the chlorine atom has been marked ★′.

The P-Au-P angle, 132.1 (1)°, is larger than the P-Cu-P angle of 126.0 (1)° found in the isostructural copper complex. The deviation from idealized trigonal geometry in these complexes is largely due to steric interaction. The smaller size of the chloride in the Au complex permits the P-M-P angle to open wider and thereby further to reduce interactions between the phosphine groupings. The P-Au-P angle is more nearly equal to the P-Cu-P angle of 131.2 (1)° found in $[(C_6H_5)_3P]_2Cu(NO_3)$ which can be considered a trigonal-planar configuration about the copper if the anion is considered a negatively charged entity.[4] The size of the nitrate grouping is minimized by the fact that the plane of the nitrate group is perpendicular to the P-M-P plane.

The trigonal planar configuration suggests that perhaps there is more covalent than ionic character to the Au-Cl bond. Since the d^{10} Au(I) atom is spherically symmetrical, it seems reasonable to postulate that if the Au-Cl bond is strongly ionic the $((C_6H_5)_3)_2Au^+$ unit—both for electronic and steric reasons—would be linear. In fact, the structural studies of 7,7,8,8-tetracyanoquindimethanidobis(triphenylphosphine)gold(I)[2] have shown a TCNQ radical anion associated with a bis(triphenylphosphine)gold(I) moiety which is linear. The Au-Cl bond distance of 2.500 (4) Å is closer to the sum of the covalent radii of Cl and Au (0.99 Å + 1.336 Å = 2.326 Å)[21] than it is to the sum of the ionic radii (1.81 Å + 1.37 Å = 3.18 Å).[22] Meyer and Allred[23] believed that $[(C_6H_5)_3P]_2AuCl$ in the solid state is ionic since they did not see a band in the ir spectrum at 329 cm^{-1} which had been assigned to the Au-Cl stretching mode. They did see this band in the ir spectrum of $[(C_6H_5)_3P]AuCl$[24] and thereby concluded that the bis compound is ionic and that the mono compound is covalent. Although their conductivity studies did not indicate that in solution the complex behaved as a univalent electrolyte, they believed the reason was due to the equilibrium

Table V. Close C-Cl and H-Cl Distances (Å)[a, b]

Atom	Dist from Cl	Atom	Dist from Cl
C(4)	4.021 (018)	H(4)	3.463
C(6)	3.799 (018)	H(6)	4.447
C(8)★	3.889 (016)	H(8)	2.885
C(10)★	3.569 (017)	H(10)	2.689
C(16)	3.892 (018)	H(16)	3.222
C(17)★	3.685 (018)	H(17)	2.724
C(18)	3.804 (018)	H(18)	3.044
C(25)★′	4.153	No hydrogen attached	
C(27)★	3.648 (018)	H(27)	2.813
C(35)	4.110 (019)	H(35)	3.703
C(36)	3.950 (018)	H(36)	3.378

[a] Only those distances less than 4.2 Å are listed. [b] The carbon atoms which have an attached hydrogen atom lying between 2.7 and 2.9 Å from the chlorine atom are marked ★ both in this table and in Figure 2. The only tetrahedral carbon atom which lies less than 4.2 Å from the chlorine atom is marked ★′ both in this table and in Figure 2.

$$[(C_6H_5)_3P]_2AuCl \rightarrow (C_6H_5)_3P + (C_6H_5)_3PAuCl$$

They found that if excess triphenylphosphine is added to the solution, the conductivity increased. They interpreted this to mean that the equilibrium was driven to the left giving more of the "ionic" $[(C_6H_5)_3P]_2Cl$.

More recently[25] it has been found that in solution the following equibrium exists

$$2[(C_6H_5)_3P]_2AuCl \rightarrow [(C_6H_5)_3P]_3AuCl + (C_6H_5)_3PAuCl$$

This equilibrium could account for the increase in conductivity with excess triphenylphosphine since excess triphenylphosphine would cause an increase in the amount of the tris compound which is probably more ionic than the bis compound due to the increase in the number of ligands surrounding the spherical d^{10} metal atom.

It is interesting to note that the Au-P-C bond angle is largest (most distorted from perfect tetrahedral arrangement) for those phenyl rings which contain hydrogen atoms which lie closest to the chlorine atom (Table V). There are two metal-phosphorus-carbon angles, Au-P(1)-C(7) and Au-P(2)-C(25), which are greater than 120° (Table IVB). The [C(7)-C(12)] phenyl ring contains two hydrogens which lie between ~2.7 and ~2.9 Å from the chlorine atom. The [C(13)-C(18)] phenyl ring contains only one hydrogen atom which lies between 2.7 and 2.9 Å; the carbon atom [C(25)], however, lies less than 4.2 Å from the chlorine atom. The carbon atoms to which the hydrogens lying close to the chlorine are attached and the carbon atom [C(25)] which lies closest to the chlorine are marked with a star in the packing diagram (Figure 2).

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(22) Reference 21, 514.

(23) J. M. Meyer and A. L. Allred, *J. Inorg. Nucl. Chem.*, 30, 1328 (1968).

(24) Ir spectra run in this laboratory show a band at 329 cm^{-1} for $[(C_6H_5)_3P]AuCl$ but no band at or near 329 cm^{-1} for $[(C_6H_5)_3P]_2AuCl\cdot{}^1/_2C_6H_6$.

(25) E. L. Muetterties and G. W. Alegranti, *J. Amer. Chem. Soc.*, 92, 4114 (1970).

Registry No. $[(C_6H_5)_3P]AuCl$, 14243-64-2; $(C_6H_5)_3P$, 603-35-0; $[(C_6H_5)_3P]_2AuCl\cdot{}^1/_2C_6H_6$, 49788-36-5.

Supplementary Material Available. Table VI, 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 $7.00 for photocopy or $2.00 for microfiche, referring to code number INORG-74-805.

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Crystal Structures of Tetrakis(pentafluorophenyl)tin(IV) and Tetrakis(pentafluorophenyl)germanium(IV)

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The crystal structures of tetrakis(pentafluorophenyl)tin, $(C_6F_5)_4Sn$, and tetrakis(pentafluorophenyl)germanium, $(C_6F_5)_4Ge$, have been determined from three-dimensional single-crystal X-ray data collected by the θ–2θ scan technique on a computer automated diffractometer. Both compounds crystallize in the tetragonal space group $I4_1/a$ with $a = 17.738$ (11) Å, $c = 8.094$ (5) Å, $Z = 4$ for $(C_6F_5)_4Sn$ and $a = 17.277$ (13) Å, $c = 8.122$ (7) Å, $Z = 4$ for $(C_6F_5)_4Ge$. The structures were solved by Patterson and Fourier methods and have been refined by a full-matrix least-squares procedure to a conventional R factor of 0.089 for 1011 reflections in the case of $(C_6F_5)_4Sn$ and 0.077 for 1181 reflections for $(C_6F_5)_4Ge$. In each case the structures consist of discrete $(C_6F_5)_4M$ units with exact $\bar{4}$ crystallographic symmetry. The Sn–C and Ge–C lengths and the C–Sn–C and C–Ge–C valency angles are 2.126 (8) Å, 1.956 (4) Å, 105.5 (4)°, 105.0 (2)°, respectively. The angle between the pentafluorophenyl ring plane and the C–M–C valency angle plane is 53.2° and 51.9° for the tin and germanium compounds, respectively. The rotation of the entire molecule from the a axis is 41.9° in $(C_6F_5)_4Sn$ and 42.0° in $(C_6F_5)_4Ge$. The crystal packing differs from that in the corresponding phenyl derivatives, and the structures represent examples where close packing is not required for the retention of $\bar{4}$ symmetry.

Introduction

Recently there have been a number of reports on the structures[2-8] of tetraphenyl compounds of the group IVa elements. These derivatives of the type MA_4, where M is a group IVa element and A is an organic aryl group, form molecular lattices which allow study of their crystal packing using geometrical[2] as well as nonbonded energy analysis.[9] A study of the conformations and orientations of the MA_4 molecular units in the crystalline state[10] should be very useful in providing models for the structures of more complex derivatives. The crystal structure investigations of tetrakis(pentafluorophenyl)tin and tetrakis(pentafluorophenyl)germanium[11] were undertaken to compare the structure and packing with the corresponding tetraphenyl derivatives.

Experimental Section

Clear colorless needle crystals of the title compounds[12] were kindly provided by Dr. C. Tamborski of the Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio. For each compound a crystal which gave sharp optical extinction under crossed polarizers was mounted along its needle axis. On the basis of oscillation and indexed Weissenberg photographs both crystals were found to belong to the tetragonal system and the observed absences $h + k + l = 2n + 1$, h, $(k) = 2n + 1$ for $hk0$, $l = 4n + 1$ for $00l$ uniquely determine the space group[13] as $I4_1/a$. The needle axis corresponds to the c axis. Accurate values of the unit cell parameters for each crystal were determined at ambient room temperature from a least-squares refinement of the angular settings of 12 carefully centered reflections on a Picker FACS-1 computer-controlled (PDP-8/L) diffractometer using Mo Kα radiation (λ 0.71069 Å).

Crystal Data for $(C_6F_5)_4Sn$: tetragonal; space group $I4_1/a$; $a = 17.738$ (11) Å; $c = 8.094$ (5) Å; $V = 2547$ Å^3; $Z = 4$; $d_m = 2.0$ g cm^{-3}; $d_c = 2.05$ g cm^{-3}; mol wt = 784.9; $F(000) = 1496$; μ(Mo Kα) = 11.9 cm^{-1}.

Crystal Data for $(C_6F_5)_4Ge$: tetragonal, space group $I4_1/a$; $a = 17.277$ (13) Å; $c = 8.122$ (7) Å; $V = 2424$ Å^3; $Z = 4$; $d_m = 2.0$ g cm^{-3}; $d_c = 2.03$ g cm^{-3}; mol wt = 740.8, $F(000) = 1424$, μ(Mo Kα) = 15.3 cm^{-1}. The experimental densities, d_m, were measured by flotation in an aqueous solution of potassium iodide.

Collection and Reduction of the Intensity Data. For both crystals an independent set of three-dimensional intensity data were collected on the diffractometer already mentioned; zirconium filtered Mo Kα radiation was used. The dimensions of the $(C_6F_5)_4Sn$ crystal were 0.10 × 0.14 × 0.40 mm and for $(C_6F_5)_4Ge$ 0.10 × 0.10 × 0.28 mm. All reflections out to 52.5° in 2θ for tetrakis(pentafluorophenyl)germanium and 52° for the tin derivative were collected using the θ–2θ scan mode. For each crystal a symmetrical scan range in 2θ was used from −1° to +1° of the Mo Kα peak with an allowance made for the Kα_1–Kα_2 separation. The scan rate was 1°/min. A stationary-counter, stationary-crystal background count was measured for 20 sec at each end of the scan. To minimize coincidence losses a brass attenuator was inserted automatically whenever the count rate of the diffracted beam exceeded about 10,000 counts/sec. During the data collection for each crystal the intensities of three standard reflections in different regions of reciprocal space were monitored after every 100 reflections. Their intensities showed only statistical variation which indicated little counter or crystal instability throughout the data collection.

Each net intensity, I, was corrected for Lorentz and polarization factors (Lp) but not for absorption to give the observed structure

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