The Structure of Triphenylphosphine(*pentahapto*cyclopentadienyl)copper(I)[1]

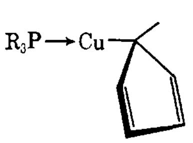
F. A. Cotton and J. Takats

Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139. *Received November 3, 1969*

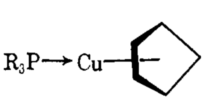
Abstract: The crystal and molecular structures of triphenylphosphine(*pentahapto*cyclopentadienyl)copper(I), $(h^5\text{-}C_5H_5)P(C_6H_5)_3Cu$, have been determined from 2295 independent, nonzero reflections collected with a counter diffractometer. The compound crystallizes in the triclinic space group $P\bar{1}$ with two molecules per unit cell of dimensions $a = 9.583(3)$ Å, $b = 9.414(3)$ Å, $c = 11.494(4)$ Å, $\alpha = 100.28(2)°$, $\beta = 97.63(2)°$, and $\gamma = 108.02(2)°$ ($\rho_{obsd} = 1.36$ g cm^{-3}; $\rho_{calcd} = 1.370$ g cm^{-3}). The structure, including hydrogen atoms, was solved using the Karle–Hauptman sigma-2 relationship and refined by least squares to a conventional unweighted R factor of 2.8%. All H atoms were refined with independent isotropic temperature factors, while all other atoms were refined with anisotropic temperature factors. The salient feature of the structure is the *pentahapto*cyclopentadienyl ring. The distance from the ring center to the copper atom is 1.864 Å; individual Cu–C distances (in Å) are 2.200(3) 2.229(3), 2.232(2), 2.205(2), and 2.190(3). The cyclopentadienyl group is a virtually perfect regular pentagon, with C–C distances (in Å) of 1.398(4), 1.409(3), 1.393(3), 1.402(3), and 1.393(4). The copper to phosphorus distance, 2.135 Å, is shorter than previously found distances in phosphine–Cu(I) complexes. The 20 apparent C–H distances have a mean value of 0.94 Å, a range of 0.90–1.02 Å, and individual esd's of 0.03–0.04 Å. When empirical correction is made for the difference between the centroid of electron density and the nuclear position for the H atoms, the mean C–H internuclear distance is found to be 1.06 Å.

The present study was undertaken to provide unequivocal, detailed structural information about a representative molecule of the type $C_5H_5CuPR_3$.

The first description, outside the patent literature, of such a compound was given in the reports by Wilkinson and Piper[2] of the preparation and characterization of $C_5H_5CuP(C_2H_5)_3$. The physical and chemical evidence was considered to favor a σ- or *monohapto*cyclopentadienyl[3] structure, I. In at least two subsequent papers[4,5] this structure was regarded as consistent with certain physical data, and at no time does it appear to have been challenged until early in 1969. At that time, a careful reexamination of the infrared spectra of $C_5H_5CuP(C_2H_5)_3$ and $C_5H_5CuP(C_4H_9)_3$ by Cotton and Marks[6] led them to conclude that in both the crystalline and dissolved states these molecules contain *pentahapto*cyclopentadienyl rings, as represented in structure II. Although the conclusion drawn from the infrared investigation was quite secure in a qualitative sense, an X-ray diffraction study was considered to be highly desirable in order to provide a detailed and absolutely unequivocal description of the structure.



I



II

Preliminary crystallographic examination of the three compounds $C_5H_5CuP(C_2H_5)_3$, $C_5H_5CuP(C_4H_9)_3$, and $C_5H_5CuP(C_6H_5)_3$ showed that the triphenylphosphine compound was distinctly the best prospect for a structural determination of high precision. It therefore became the subject of the investigation reported here.

Experimental Section

The compound $C_5H_5CuP(C_6H_5)_3$ was prepared and recrystallized from ether solution by Mr. T. J. Marks. The white crystals so obtained are triclinic parallelipipeds elongated along the a axis. The compound in the solid state is slightly air sensitive. Hence the crystal chosen for X-ray work was mounted on the end of a glass fiber and coated with shellac. Preliminary Weissenberg ($0kl$, $1kl$) and precession photographs ($h0l$, $h1l$, $hk0$, $hk1$) indicated one of the triclinic space groups P1 or $P\bar{1}$, having the following equipoints, respectively: x, y, z and x, y, z; $\bar{x}, \bar{y}, \bar{z}$. A Delaunay reduction[7] did not reveal any higher symmetry. The following unit cell dimensions were obtained at 22°, from a least-squares refinement of the setting angles of 39 reflections that had been carefully centered on a General Electric XRD-5 automated diffractometer using Mo Kα radiation (Mo $K\bar{\alpha} = 0.7107$ Å): $a = 9.583(3)$ Å, $b = 9.414(3)$ Å, $c = 11.494(4)$ Å, $\cos\alpha = 0.1785(1)$, $\cos\beta = -0.1329(2)$, and $\cos\gamma = -0.3093(2)$. The observed density of 1.36 ± 0.01 g cm^{-3}, obtained by flotation in aqueous potassium iodide solution, agrees well with the calculated value of 1.370 g cm^{-3} for a formula weight of 390.90, $Z = 2$, and a unit cell volume of 947 Å^3.

Intensity data were collected on a General Electric XRD-5 manual diffractometer, equipped with scintillation counter and pulse-height discriminator, which was set to accept 95% of the Cu Kα peak. The crystal was so aligned that its a^* axis coincided with the φ axis of the instrument. The distances from the crystal to the source and from the crystal to the circular screening aperture (2°) were 5.73 and 7.05 in., respectively. The integrated intensities of 2561 independent reflections within the sphere $\theta \leq 57°$ were measured using nickel-filtered Cu Kα radiation. The data were collected using a $\theta/2\theta$ scan technique at a 2θ scan rate of 4°/min. The peak counts, P, were obtained from a 2θ scan of 2.66° from $2\theta_{calcd} - 1.33°$ to $2\theta_{calcd} + 1.33°$. Stationary background counts, B_1 and B_2, of 20 sec were taken at each of the limits of the scan. From these readings the intensity, I, assuming a linear change in background (or its equivalent), between the two limits of the scan,

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[1] Research supported in part by the Petroleum Research Fund, administered by the American Chemical Society, to whom grateful acknowledgment is made.

[2] (a) G. Wilkinson and T. S. Piper, *J. Inorg. Nucl. Chem.*, **2**, 32 (1956); (b) T. S. Piper and G. Wilkinson, *ibid.*, **3**, 104 (1956).

[3] This form of notation is explained by F. A. Cotton, *J. Amer. Chem. Soc.*, **90**, 6230 (1968).

[4] H. P. Fritz, *Advan. Organometal. Chem.*, **1**, 239 (1964).

[5] G. M. Whitesides and J. S. Fleming, *J. Amer. Chem. Soc.*, **89**, 2855 (1967).

[6] F. A. Cotton and T. J. Marks, *ibid.*, **91**, 7281 (1969).

[7] B. Delaunay, *Z. Kristallogr.*, **84**, 109 (1933).

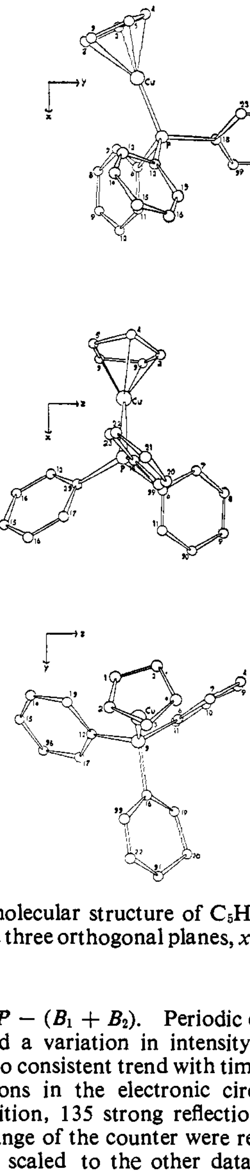

Figure 1. The molecular structure of $C_5H_5CuP(C_6H_5)_3$ as seen in projections on the three orthogonal planes, *xy*, *xz*, and *yz*.

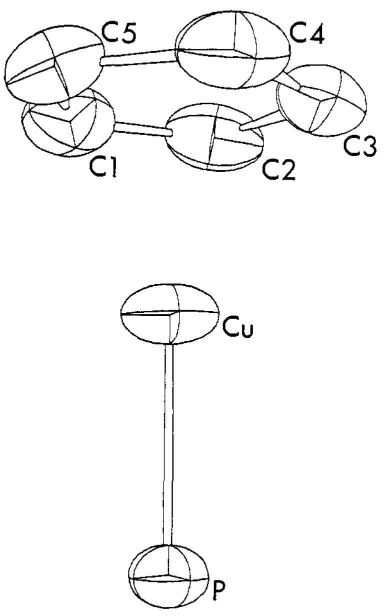

Figure 2. The C_5–Cu–P part of the molecule showing ellipsoids of thermal vibration.

is given by: $I = P - (B_1 + B_2)$. Periodic checks of four standard reflections showed a variation in intensity ($\pm 2\%$) having no 2θ dependence and no consistent trend with time, which is indicative of random fluctuations in the electronic circuits rather than with crystal decomposition, 135 strong reflections which exceeded the linear response range of the counter were remeasured with a lower current and were scaled to the other data by using medium intensity reflections measured with both current settings.

Statistically insignificant reflections (266) were rejected using the criteria: (1) $I < 0$ and (2) $I < 3(P + B_1 + B_2)^{1/2}$. The remaining 2295 reflections were corrected for Lorentz and polarization effects and a set of $|F_o|^2$ and $|F_o|$ values (on a relative scale) was thus obtained.

Appreciable variations in the intensities of the $h00$ reflections were observed as a function of crystal orientation; φ scans of several of these reflections indicated variations of 20%. Consequently, absorption corrections (μ = 24.0 cm^{-1}), based on the equations of the crystal faces, were applied to the data for the final stages of refinement. The transmission factors were in the range 0.62–0.75. The crystal faces were identified as 310, $\bar{3}\bar{1}0$, 010, $0\bar{1}0$, 001, and $00\bar{1}$; the distances between opposite pairs of faces were 0.437 × 0.137 × 0.175 mm, respectively.

Solution and Refinement of the Structure

The reduced data (F_o's) were converted by the program FAME to normalized structure factors (E's), by the relationship $E^2 = F_o^2 \exp(T \sin^2 \theta/\lambda)/\epsilon K^2 S$, where F_o is the observed structure factor, T is an overall temperature factor, ϵ is an integer to correct for extinct reflections in special zones, K is the scale factor necessary to place the observed structure factor amplitudes on an absolute scale, and S is the sum of the scattering factors of all atoms in the unit cell for the particular value of (h, k, l). The overall temperature factor T and scale factor K may be evaluated from a Wilson plot, which the program calculates. Solution of the structure was accomplished using the symbolic addition procedure[8] for application of the Karle–Hauptman sigma-2 relationship[9] to determine the phases of 997 of the largest structure factors. An E-map for the second most probable sign combination (the most consistent combination was the all-plus one, but in the triclinic case this is occasionally meaningless and hence was not considered) revealed the locations of all atoms other than hydrogen atoms. Refinement of the structure was accomplished by the conventional, full-matrix least-squares method. For atoms other than hydrogen, the scattering factors used during this analysis were those of Cromer and Waber,[10] while the form factors used for hydrogen were those experimentally determined for H atoms in diphenyl by Mason and Robertson.[11] Anomalous dispersion corrections to the scattering factors for Cu ($\Delta f' = -2.10$ e, $\Delta f'' = 0.70$ e) and for P ($\Delta f' = 0.20$ e, $\Delta f'' = 0.50$ e) were included in the calculation of structure factors.[12,13] The function minimized in the least-squares refinement was $\Sigma w(|F_o| - |F_c|)^2$, where $|F_o|$ is the observed structure amplitude, $|F_c|$ is the calculated structure amplitude, and the weighting factor $w = [\sigma(F)]^{-2}$.

Three cycles of full-matrix least-squares refinement of scale factor and positional and isotropic thermal parameters for all heavy atoms, that is one Cu, one P, and 23 C atoms, but neglecting hydrogen, led to a discrepancy index $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ of 0.111. The weighted residual $R_2 = \{\Sigma w[|F_o| - |F_c|]^2/\Sigma w|F_o|^2\}^{1/2}$ was 0.156, using a weighting scheme similar to that of Doedens and Ibers[14] with $p = 0.045$. Refinement was changed

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(8) J. Karle and I. L. Karle, *Acta Crystallogr.*, **21**, 849 (1966).

(9) H. Hauptman and J. Karle, "Solution of the Phase Problem, T. The Centrosymmetric Crystals," ACA Monograph No. 3, Polycrystal Book Service, Pittsburgh, Pa.

(10) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).

(11) R. Mason and G. B. Robertson in "Advances in Structure Research by Diffraction Methods," Vol. 2, R. Brill and R. Mason, Ed., Interscience–Wiley, New York, N. Y., 1966, p 57.

(12) C. T. Prewitt, Ph.D. Thesis, MIT, 1962, p 163.

(13) "International Tables for X-ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1965, p 215.

(14) R. J. Doedens and J. A. Ibers, *Inorg. Chem.*, **6**, 204 (1967).

Table I. Atomic Positional and Thermal Parameters[a]

Atom	x	y	z	B, Å^{2} [b]
Cu	0.07254(3)	0.37517(3)	0.22132(3)	4.110
P	−0.14495(5)	0.39113(5)	0.22188(4)	2.899
C_1	0.2017(3)	0.2337(3)	0.1524(2)	4.72
C_2	0.2186(3)	0.2451(3)	0.2768(2)	4.80
C_3	0.2911(2)	0.4015(3)	0.3345(2)	4.66
C_4	0.3171(2)	0.4844(3)	0.2458(2)	4.50
C_5	0.2623(2)	0.3803(3)	0.1330(2)	4.64
C_6	−0.2326(2)	0.3100(2)	0.3382(2)	3.04
C_7	−0.1403(3)	0.2873(3)	0.4235(2)	3.90
C_8	−0.1991(3)	0.2234(3)	0.5217(2)	4.65
C_9	−0.3514(3)	0.1818(3)	0.5190(2)	4.38
C_{10}	−9.4436(3)	0.2036(3)	0.4268(2)	4.35
C_{11}	−0.3854(2)	0.2672(3)	0.3365(2)	3.77
C_{12}	−0.2815(2)	0.2918(2)	0.0811(2)	3.00
C_{13}	−0.2593(3)	0.1702(3)	0.0067(2)	4.35
C_{14}	−0.3608(3)	0.0894(3)	−0.0995(2)	5.03
C_{15}	−0.4843(3)	0.1276(3)	−0.1334(2)	4.40
C_{16}	−0.5080(3)	0.2492(3)	−0.0606(2)	3.98
C_{17}	−0.4064(2)	0.3300(3)	0.0462(2)	3.53
C_{18}	−0.1470(2)	0.5878(2)	0.2473(2)	3.02
C_{19}	−0.2184(3)	0.6485(3)	0.3305(2)	4.29
C_{20}	−0.2074(3)	0.8015(3)	0.3483(3)	5.22
C_{21}	−0.1269(3)	0.8938(3)	0.2837(3)	5.19
C_{22}	−0.0581(3)	0.8349(3)	0.1995(3)	4.97
C_{23}	−0.0669(3)	0.6829(3)	0.1823(2)	4.04
H_1	0.159(3)	0.145(3)	0.096(3)	7.3(7)
H_2	0.180(3)	0.169(3)	0.316(2)	6.3(5)
H_3	0.309(3)	0.437(3)	0.420(2)	6.8(6)
H_4	0.358(3)	0.588(3)	0.264(2)	7.4(6)
H_5	0.267(3)	0.410(3)	0.057(2)	5.9(5)
H_7	−0.043(3)	0.307(3)	0.429(3)	4.9(5)
H_8	−0.138(4)	0.200(4)	0.582(3)	7.6(7)
H_9	−0.399(3)	0.137(3)	0.580(2)	6.5(6)
H_{10}	−0.546(3)	0.174(3)	0.420(2)	6.0(6)
H_{11}	−0.452(3)	0.282(3)	0.271(2)	5.6(5)
H_{13}	−0.179(3)	0.144(3)	0.029(2)	5.7(5)
H_{14}	−0.342(3)	0.008(3)	−0.145(3)	6.9(6)
H_{15}	−0.561(3)	0.070(3)	−0.209(2)	5.2(5)
H_{16}	−0.589(3)	0.281(3)	−0.082(2)	5.3(5)
H_{17}	−0.418(3)	0.414(3)	0.092(2)	4.0(4)
H_{19}	−0.272(3)	0.585(3)	0.373(2)	6.1(6)
H_{20}	−0.261(3)	0.844(3)	0.404(3)	7.0(6)
H_{21}	−0.127(4)	0.996(4)	0.295(3)	8.9(8)
H_{22}	−0.005(3)	0.907(3)	0.150(2)	6.8(6)
H_{23}	−0.019(3)	0.643(3)	0.127(2)	4.7(5)

[a] Numbers in parentheses are the estimated standard deviations occurring in the last digit listed. [b] The equivalent isotropic thermal parameters given for atoms other than hydrogen atoms were calculated by SFLS5 from the anisotropic temperature factors listed in Table II.

Table II. Anisotropic Temperature Parameters (×10^{4})[a]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	83.7(4)	164.1(5)	107.5(3)	60.8(4)	28.4(3)	31.6(3)
P	71.1(6)	104.4(7)	70.2(4)	37.5(5)	15.8(4)	18.2(4)
C_1	118(3)	152(4)	122(3)	71(3)	27(2)	1(3)
C_2	108(3)	162(4)	141(3)	64(3)	22(2)	64(3)
C_3	94(3)	205(4)	94(2)	52(3)	9(2)	27(2)
C_4	89(3)	142(4)	125(3)	29(3)	33(2)	23(2)
C_5	117(3)	199(4)	101(2)	69(3)	52(2)	38(3)
C_6	95(3)	89(3)	68(2)	33(2)	12(2)	13(2)
C_7	97(3)	138(3)	84(2)	36(3)	2(2)	23(2)
C_8	154(4)	159(4)	78(2)	43(3)	−8(2)	35(2)
C_9	149(4)	127(3)	84(2)	23(3)	22(2)	33(2)
C_{10}	102(4)	153(4)	101(2)	23(3)	26(2)	41(2)
C_{11}	90(3)	139(3)	88(2)	37(3)	14(2)	37(2)
C_{12}	89(3)	103(3)	67(2)	37(2)	24(2)	20(2)
C_{13}	131(4)	158(4)	91(2)	85(3)	13(2)	4(2)
C_{14}	166(4)	164(4)	94(2)	85(3)	14(3)	−18(3)
C_{15}	139(4)	152(4)	74(2)	49(3)	4(2)	1(2)
C_{16}	108(3)	147(4)	82(2)	57(3)	4(2)	17(2)
C_{17}	110(3)	117(3)	75(2)	53(3)	19(2)	11(2)
C_{18}	79(3)	104(3)	65(2)	30(2)	4(2)	16(2)
C_{19}	148(4)	133(4)	98(2)	64(3)	47(2)	31(2)
C_{20}	188(4)	145(4)	119(3)	87(4)	39(3)	14(3)
C_{21}	182(4)	104(4)	123(3)	49(4)	−9(3)	16(3)
C_{22}	166(4)	125(4)	107(2)	23(3)	11(3)	38(2)
C_{23}	131(3)	122(3)	78(2)	28(3)	21(2)	18(2)

[a] Numbers in parentheses are the estimated standard deviation occurring in the last digits listed.

Table III. Intramolecular Distances[a]

Atoms	Distance, Å	Atoms	Distance, Å
Cu–C_1	2.200(3)	Cu–P	2.135(1)
Cu–C_2	2.229(3)	P–C_6	1.828(2)
Cu–C_3	2.232(2)	P–C_{12}	1.829(2)
Cu–C_4	2.205(2)	P–C_{18}	1.829(2)
Cu–C_5	2.190(3)		
C_1–C_2	1.398(4)	C_{12}–C_{13}	1.392(3)
C_2–C_3	1.409(3)	C_{13}–C_{14}	1.382(3)
C_3–C_4	1.393(3)	C_{14}–C_{15}	1.368(4)
C_4–C_5	1.402(3)	C_{15}–C_{16}	1.390(4)
C_5–C_1	1.393(4)	C_{16}–C_{17}	1.387(3)
		C_{17}–C_{12}	1.383(3)
C_6–C_7	1.396(3)	C_{18}–C_{19}	1.389(4)
C_7–C_8	1.376(4)	C_{19}–C_{20}	1.387(3)
C_8–C_9	1.384(4)	C_{20}–C_{21}	1.367(4)
C_9–C_{10}	1.374(4)	C_{21}–C_{22}	1.372(4)
C_{10}–C_{11}	1.384(4)	C_{22}–C_{23}	1.383(4)
C_{11}–C_6	1.390(3)	C_{23}–C_{18}	1.384(3)
C_1–H_1	0.90(3)	C_{13}–H_{13}	0.90(3)
C_2–H_2	0.92(3)	C_{14}–H_{14}	0.92(3)
C_3–H_3	0.95(3)	C_{15}–H_{15}	1.00(2)
C_4–H_4	0.91(3)	C_{16}–H_{16}	0.93(3)
C_5–H_5	0.97(3)	C_{17}–H_{17}	0.91(3)
C_7–H_7	0.90(3)	C_{19}–H_{19}	0.92(3)
C_8–H_8	0.94(3)	C_{20}–H_{20}	0.98(3)
C_9–H_9	0.97(3)	C_{21}–H_{21}	0.95(4)
C_{10}–H_{10}	0.92(3)	C_{22}–H_{22}	1.02(3)
C_{11}–H_{11}	0.97(3)	C_{23}–H_{23}	0.92(3)

[a] Numbers in parentheses are the estimated standard deviations occurring in the last digits listed.

to anisotropic using thermal parameters of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ for all 25 atoms. Three further cycles of refinement resulted in $R_1 = 0.054$ and $R_2 = 0.079$. At this point absorption corrections were included; this lowered R_1 and R_2 to 0.052 and 0.074, respectively. A difference Fourier map revealed all 20 hydrogen atoms. Four final cycles, where positional and isotropic temperature factors of hydrogen atoms were refined, while refinement of the other atoms was continued anisotropically, resulted in convergence with $R_1 = 0.028$ and $R_2 = 0.038$. The refinement in these last four cycles was accomplished in two parts: first Cu, P, and the three phenyl rings were allowed to refine while all the parameters of the C_5H_5 ring were held constant; in the second part of the cycle Cu, P, and the atoms of the C_5H_5 ring were refined while the three phenyl rings were held constant. This kind of "block" refinement was necessary since the number of parameters to be varied for the entire molecule exceeded the capacity of our least-squares program. A Hamilton R factor test[15] validated both the anisotropic model and the model including the hydrogen atoms at the 99.5% confidence level.

The last cycle of refinement showed no parameter shift greater than one-fifth of its estimated standard deviation, except for a few hydrogen atoms where shifts of one-third of an esd were observed. The highest

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(15) W. C. Hamilton, *Acta Crystallogr.*, **18**, 502 (1965).

Table IV. Bond Angles[a]

Atoms	Angle, deg	Atoms	Angle, deg
C_1–Cu–P	146.1(1)	C_6–P–Cu	113.1(1)
C_2–Cu–P	142.8(1)	C_{12}–P–Cu	114.7(1)
C_3–Cu–P	145.6(1)	C_{18}–P–Cu	114.0(1)
C_4–Cu–P	150.7(1)	C_6–P–C_{12}	104.7(1)
C_5–Cu–P	151.2(1)	C_{12}–P–C_{18}	103.9(1)
		C_{18}–P–C_6	105.5(1)
C_1–C_2–C_3	107.4(2)	C_{12}–C_{13}–C_{14}	120.3(3)
C_2–C_3–C_4	108.2(2)	C_{13}–C_{14}–C_{15}	120.7(3)
C_3–C_4–C_5	108.0(2)	C_{14}–C_{15}–C_{16}	119.8(2)
C_4–C_5–C_1	108.0(2)	C_{15}–C_{16}–C_{17}	119.5(3)
C_5–C_1–C_2	108.5(2)	C_{16}–C_{17}–C_{12}	121.0(2)
		C_{17}–C_{12}–C_{13}	118.6(2)
C_6–C_7–C_8	120.8(2)	C_{18}–C_{19}–C_{20}	120.3(2)
C_7–C_8–C_9	120.0(2)	C_{19}–C_{20}–C_{21}	120.3(3)
C_8–C_9–C_{10}	119.8(2)	C_{20}–C_{21}–C_{22}	120.1(3)
C_9–C_{10}–C_{11}	120.5(2)	C_{21}–C_{22}–C_{23}	119.9(3)
C_{10}–C_{11}–C_6	120.3(2)	C_{22}–C_{23}–C_{18}	120.9(2)
C_{11}–C_6–C_7	118.5(2)	C_{23}–C_{18}–C_{19}	118.5(2)
P–C_6–C_9	176.7(2) P–C_{12}–C_{15}	177.0(2) P–C_{18}–C_{21}	175.5(2)
H_1–C_1–C_2	124(2)	H_{13}–C_{13}–C_{14}	120(2)
H_1–C_1–C_5	127(2)	H_{13}–C_{13}–C_{12}	119(2)
H_2–C_2–C_3	124(2)	H_{14}–C_{14}–C_{15}	122(1)
H_2–C_2–C_1	128(2)	H_{14}–C_{14}–C_{13}	117(1)
H_3–C_3–C_4	130(2)	H_{15}–C_{15}–C_{16}	118(2)
H_3–C_3–C_2	122(2)	H_{15}–C_{15}–C_{14}	122(2)
H_4–C_4–C_5	130(2)	H_{16}–C_{16}–C_{17}	118(1)
H_3–C_4–C_3	122(2)	H_{16}–C_{16}–C_{15}	122(1)
H_5–C_5–C_1	128(2)	H_{17}–C_{17}–C_{12}	119(1)
H_5–C_5–C_4	124(2)	H_{17}–C_{17}–C_{16}	120(1)
H_7–C_7–C_8	121(2)	H_{19}–C_{19}–C_{20}	121(2)
H_7–C_7–C_6	118(2)	H_{19}–C_{19}–C_{18}	118(2)
H_8–C_8–C_9	119(2)	H_{20}–C_{20}–C_{21}	119(2)
H_8–C_8–C_7	121(2)	H_{20}–C_{20}–C_{19}	121(2)
H_9–C_9–C_{10}	117(2)	H_{21}–C_{21}–C_{22}	122(2)
H_9–C_9–C_8	124(2)	H_{21}–C_{21}–C_{20}	118(2)
H_{10}–C_{10}–C_{11}	117(2)	H_{22}–C_{22}–C_{23}	123(2)
H_{10}–C_{10}–C_9	122(2)	H_{22}–C_{22}–C_{21}	117(2)
H_{11}–C_{11}–C_6	120(2)	H_{23}–C_{23}–C_{18}	119(2)
H_{11}–C_{11}–C_{10}	120(1)	H_{23}–C_{23}–C_{22}	120(2)

[a] Numbers in parentheses are the estimated standard deviations occurring in the last digits listed.

Table V. Selected Intermolecular Contacts

Atom I	Atom J	Vector from molecule containing I to molecule containing J	Distance, Å
C_2	H_{11}	$(x + 1, y, z)$	3.08
C_2	H_{10}	$(x + 1, y, z)$	2.94
C_5	H_{17}	$(x + 1, y, z)$	3.09
C_1	H_{22}	$(x, y + 1, z)$	3.09
C_7	H_{21}	$(x, y + 1, z)$	2.96
C_1	H_{14}	$(\bar{x}, \bar{y}, \bar{z})$	2.98
C_{17}	H_5	$(\bar{x}, -y + 1, \bar{z})$	2.93
C_{23}	H_5	$(\bar{x}, -y + 1, \bar{z})$	2.95
C_{11}	H_{15}	$(-x - 1, \bar{y}, \bar{z})$	3.10
C_{18}	H_8	$(\bar{x}, -y + 1, -z + 1)$	3.02
C_9	H_4	$(\bar{x}, -y + 1, -z + 1)$	3.02
C_{22}	H_8	$(\bar{x}, -y + 1, -z + 1)$	3.06
H_2	H_{10}	$(x + 1, y, z)$	2.72
H_5	H_{16}	$(x + 1, y, z)$	2.62
H_1	H_{22}	$(x, y + 1, z)$	2.53
H_2	H_{22}	$(x, y + 1, z)$	2.76
H_1	H_{14}	$(\bar{x}, \bar{y}, \bar{z})$	2.66
H_{19}	H_3	$(\bar{x}, -y + 1, -z + 1)$	2.48
H_4	H_9	$(\bar{x}, -y + 1, -z + 1)$	2.76

noise peak in the difference Fourier map computed at this point contained 0.17 e/Å^3. A comparison of the observed and final calculated structure amplitudes indicated that 12 very strong, low angle reflections ($\sin \theta/\lambda \leq 0.13$) apparently suffer from extinction, but these had been rejected during final refinement. Calculation of the structure factors for the reflections which had been rejected as being too weak to have satisfactory counting statistics gave no $|F_c|$ greater than twice the minimum observable. The weighting scheme used satisfies Cruickshank's criterion[16] as $\Sigma w[|F_o| - |F_c|]^2$ was substantially the same in different ranges of both $|F_o|$ and $\sin \theta/\lambda$. The final standard deviation of an observation of unit weight was 1.19, indicating a slight underestimation in the standard deviation of the intensity data.

The following programs for the IBM 360 computer were used in this structural analysis and interpretation: (1) D. P. Shoemaker, MIT X-Ray Goniometer Package MIXG-2, 1962; (2) R. C. Elder, Convenient Listing of Diffractometer Settings PDATA-2; (3) M. J. Bennett, General Data Reduction Program PMMO (modified by M. D. LaPrade); (4) A Modified Version of Programs FAME, MAGIC, LINK, and SYMPL (Dewar and Stone, University of Chicago, 1966) by P. F. Stokely, 1968; (5) A Modified Version of A. Zalkin, Fourier Analysis Program FORDAP by B. M. Foxman and L. N. Becka; (6) A Modified Version of C. T. Prewitt, Full-Matrix Least-Squares Program SFLS5, 1966; (7) W. C. Hamilton, Absorption Correction Program GONO9; (8) J. S. Wood, Molecular Geometry with Estimated Standard Deviations MGEOM, 1964; (9) F. A. Kundell, J. M. Stewart, and R. V. Chastain, Bond Length and Angle and Contact Distance Program BONDLA, 1967; (10) C. K. Johnson, Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations ORTEP, 1965; (11) J. A. Ibers, Cell Parameters Refinement Program PICK 2, 1966; (12) R. C. Elder, Data Presentation Program PUBTAB.

A table of the final observed and calculated structure factors has been deposited with the American Documentation Institute.[17] Three projections of the molecular structure are shown in Figure 1, where the numbering system of atoms can also be found. Final atomic positional and thermal parameters are given in Table I, with the listed estimated standard deviations being derived from the inverse matrix of the final cycle of least-squares refinement. The hydrogen atoms are labeled according to the carbon atoms to which they are bonded. Anisotropic temperature parameters are listed in Table II. Figure 2 shows the thermal vibration ellipsoids for the C_5–Cu–P portion of the molecule. Intramolecular distances and bond angles are given in Tables III and IV. Table V gives some selected intermolecular contacts, while Table VI gives the equations for the planes through the cyclopentadienyl and phenyl rings and the distances of pertinent atoms from these mean planes.

Discussion

The points of greatest interest in this structure determination are (1) that it proves incontrovertibly that

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(16) D. W. J. Cruickshank in "Computing Methods in Crystallography," J. S. Rollett, Ed., Pergamon Press, New York, N. Y., 1965, p 113.

(17) This table has been deposited as Document No. NAPS-00895 with the ASIS National Auxiliary Publication Service, c/o CCM Information Corp., 909 3rd Ave., New York, N. Y. 10022. A copy may be secured by citing the document number and by remitting $2.00 for microfiche or $5.00 for photocopies. Advance payment is required. Make checks or money orders payable to: CCMI–NAPS.

Table VI

Atoms	Plane	Best Weighted Least-Squares Planes[a] L	M	N	D
C_1–C_5	1	0.9032	−0.4287	0.0223	0.8324
C_6–C_{11}	2	0.0258	0.8438	0.5361	4.3926
C_{12}–C_{17}	3	−0.6326	−0.6005	0.4890	0.1276
C_{18}–C_{23}	4	0.6946	−0.1274	0.7080	−0.0802

Atoms	Distances of Atoms from Planes, Å Plane 1	Atoms	Plane 2	Atoms	Plane 3	Atoms	Plane 4
C_1	0.000	C_6	0.000	C_{12}	0.001	C_{18}	0.003
C_2	−0.001	C_7	0.001	C_{13}	−0.002	C_{19}	−0.006
C_3	0.003	C_8	−0.003	C_{14}	0.000	C_{20}	0.001
C_4	−0.003	C_9	0.002	C_{15}	0.002	C_{21}	0.009
C_5	0.002	C_{10}	0.000	C_{16}	−0.002	C_{22}	−0.009
Cu	−1.862	C_{11}	0.000	C_{17}	0.000	C_{23}	0.002
P	−3.993	P	−0.037	P	0.033	P	−0.011
H_1	0.00	H_7	−0.07	H_{13}	0.00	H_{19}	−0.01
H_2	−0.09	H_8	−0.07	H_{14}	0.02	H_{20}	−0.04
H_3	−0.05	H_9	0.00	H_{15}	0.02	H_{21}	−0.05
H_4	−0.05	H_{10}	−0.03	H_{16}	−0.03	H_{22}	−0.06
H_5	0.00	H_{11}	0.00	H_{17}	−0.06	H_{23}	0.01

[a] The equations of the planes are $LX + MY + NZ = D$, where L, M, and N are the direction cosines referred to an orthogonal axis system. The matrix to transform triclinic to orthogonal coordinates is

$$\begin{array}{rrr} 9.113 & -2.964 & 0.0 \\ 0.0 & 9.414 & 0.0 \\ 2.273 & -2.051 & 11.098 \end{array}$$

$C_5H_5CuP(C_6H_5)_3$ contains a *pentahapto-* (or "sandwich bonded") cyclopentadienyl ring and (2) that it provides detailed dimensions for the $(h^5\text{-}C_5H_5)Cu$ grouping. The crystal structure is an array of closely packed $(h^5\text{-}C_5H_5)CuP(C_6H_5)_3$ molecular units, with normal van der Waals contacts between the units (see Table V). No major feature of the molecule appears to be attributable to intermolecular forces.

The C_5H_5Cu group has nearly perfect C_{5v} symmetry. The cyclopentadienyl group itself is rigorously planar, with the largest deviation of any carbon atom from the plane being 0.003 Å. It is also a virtually perfect regular pentagon, with C–C distances lying between 1.393 and 1.409 Å (each with an esd of 0.004 Å) and C–C–C angles lying in the range 107.4–108.5° (each with an individual esd of 0.2°). Distances from the copper atom to the carbon atoms fall in the narrow range from 2.190 to 2.232 Å. The copper atom lies 1.862 Å from the mean plane of the cyclopentadienyl carbon atoms. This distance is somewhat larger than the ones found in $(h^5\text{-}C_5H_5)NiC_5H_5C_2(CO_2CH_3)_2$, 1.75 Å,[18] and in $(h^5\text{-}C_5H_5)Ni[(CH_3)_4C_4C_5H_5]$, 1.76 Å,[19a] which indicates a definite weakening of the *pentahapto* interaction. The mean C–C distance, 1.399 Å, compares well with corresponding average distances in other molecules obtained by X-ray diffraction, which vary from 1.39 to 1.43 Å.[18]

The C_5H_5Cu geometry observed here, with its essentially perfect C_{5v} symmetry and low standard deviations, provides perhaps the strongest structural proof yet reported for the existence of the fully delocalized and hence fully symmetrical cyclopentadienyl metal interaction. Although the concept has long been recognized and the occurrence of such bonding taken for granted in many molecules, rigorous structural proof has actually been lacking to an extent perhaps not generally recognized. In many cases where perfectly symmetrical bonding is believed to occur, rotational disorder of the rings has denied us direct proof of this.[20] Ferrocene itself is a case in point.[21] In many instances where a symmetrical structure has been reported, the precision is low enough to reveal appreciable variations in distances presumed to be equivalent. There are of course also many cases where deviations from C_{5v} symmetry have been definitely observed[18,22] and interpreted in terms of appreciable localization of the bonding. This has been especially true when the arrangement of other ligands has deviated markedly from axial symmetry about an axis colinear with the potential C_5 axis.[22] The most perfectly symmetrical and well-ordered C_5H_5M groupings previously characterized with high precision are found in $(h^5\text{-}C_5H_5)Ni[(CH_3)_4C_4C_5H_5]$[19a] and $(h^5\text{-}C_5H_5)H(SiCl_3)_2(CO)Fe$.[19b]

Because the $(h^5\text{-}C_5H_5)$ ring here is so exceptionally well ordered and lacking in excessive librational motion, it has been possible to locate and refine the hydrogen atoms of the C_5H_5 ring (as well as those of the C_6H_5 rings). This does not appear to have been done with comparable precision for any other cyclopentadienyl-metal compound. We shall comment later on the C–H distances. We note here that slight deviations of the H atoms from the mean C_5 plane are found, such that the H atoms apparently tend to lie toward the metal. While this seems somewhat surprising, and the indications of it are at the threshold of significance, it may be noted that a small displacement of the hydrogen

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(18) L. F. Dahl and C. H. Wei, *Inorg. Chem.*, **2**, 713 (1963).

(19) (a) W. Oberhansli and L. F. Dahl, *ibid.*, **4**, 150 (1965), and references contained therein; (b) L. Manojlovic-Muir, K. W. Muir, and J. A. Ibers, private communication.

(20) R. A. Schunn, C. J. Fritchie, Jr., and C. T. Prewitt, *Inorg. Chem.*, **5**, 892 (1966).

(21) J. D. Dunitz, L. E. Orgel, and A. Rich, *Acta Crystallogr.*, **9**, 373 (1956).

(22) M. J. Bennett, M. R. Churchill, M. Gerloch, and R. Mason, *Nature*, **201**, 1318 (1964).

atoms in the same sense has been reported for dibenzenechromium.[23]

The Cu–P distance, 2.135 Å, is shorter than the corresponding ones reported for $[(C_6H_5)_3P]_2CuBH_4$, 2.276 Å,[24] and for $[(C_6H_5)_3P]_2CuNO_3$, 2.222 Å.[25] Messmer and Palenik[25] argued in the latter case that there was a shortening due to $d\pi$–$d\pi$ overlap between the copper and phosphorus atoms. We believe that the additional shortening in $(h^5\text{-}C_5H_5)CuP(C_6H_5)_3$ is due to least in part to the simple steric effect of there being less crowding with only one triphenylphosphine group present.

The greatest distortions in the molecule are connected with a slight bending of the P to Cu to ring center axis. The angle at Cu is 175°, and there are also variations in the P–Cu–C angles, which run from 142.8 to 151.2°. The overall pattern of these distortions suggests that there is a small bending stress applied to the molecule by a combination of intermolecular forces in the crystal and by nonbonded intramolecular contact interactions.

The triphenylphosphine geometry is in good agreement with the results of previous determinations.[24–26] All C–C bond lengths are within 3σ of the mean value of 1.383 Å, and the average value of the internal angles of the phenyl rings is 120° within a range of 118.5–121.0° with individual esd's of 0.2°. The three phenyl rings are planar as expected. The maximum deviation of a ring carbon atom from this mean plane is 0.009 Å. It may be seen that the largest deviation of a C–C–C angle from 120° occurs consistently at the carbon atom bound to the phosphorus atom. The three such angles are 118.5°. Phosphorus–carbon distances of 1.828, 1.829, and 1.829 Å are to be compared with the mean P–C bond length of 1.820 Å found in other $P(C_6H_5)_3$ complexes.[24–27] As observed before[24–27] the angles C–P–C are a bit smaller and the C–P–Cu angles a bit larger than the expected tetrahedral values, having average values of 104.7° and 113.9°, respectively.

A final point of interest is the location of all 20 hydrogen atoms and the refinement of the positional parameters and an isotropic thermal parameter for each. The mean C–H distance and its mean deviation for the cyclopentadienyl ring is 0.93 ± 0.03 Å, for the phenyl rings we have the value of 0.94 ± 0.03 Å, and the respective H–C–C angles are 126 ± 2° and 120 ± 2°. These distances are distinctly shorter than the accepted C–H bond length of 1.08 Å, by highly significant amounts ($\Delta/\sigma \approx 3.5$). It is of considerable interest, however, that Coppens[28] has shown in his study of S-triazine that X-ray data and conventional isotropic least-squares refinement of the hydrogen position using a spherically symmetric form factor resulted in a C–H distance 0.12 Å shorter than the value obtained from a neutron diffraction study where the actual location of the nucleus was ascertained for the same molecule. If we adopt 0.12 Å as the proper correction factor in the present case we obtain a mean C–H bond length of 1.06 ± 0.03 Å, which is satisfactorily close to 1.08 Å. In fact, a slightly low value (by perhaps 0.02–0.03 Å) would be expected since we have made no allowance for the apparent bond shortening effect of thermal vibration.[29]

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[23] E. Keulen and F. Jellinek, *J. Organometal. Chem.*, **5**, 490 (1966).

[24] S. J. Lippard and K. M. Melmed, *Inorg. Chem.*, **6**, 2223 (1967).

[25] G. G. Messmer and G. J. Palenik, *Can. J. Chem.*, 47, 1440 (1969).

[26] *Cf.* S. J. LaPlaca and J. A. Ibers, *Inorg. Chem.*, 4, 778 (1965), and references contained therein.

[27] R. P. Taylor, D. H. Templeton, A. Zalkin, and W. D. Horrocks, Jr., *ibid.*, 7, 2629 (1968).

[28] P. Coppens, *Science*, **158**, 1577 (1967).

[29] NOTE ADDED IN PROOF. We have been informed by L. T. J. Delbaere, D. W. McBride, and R. B. Ferguson, Department of Chemistry, University of Manitoba, Winnipeg, Canada, that they have determined the structure of $(h^5\text{-}C_5H_5)CuP(C_2H_5)_3$, obtaining results in excellent accord with those reported here. A paper describing their work has been submitted to *Acta Crystallographica.*