Acta Cryst. (1985). C**41**, 1036–1038

Structure of (η-Methylcyclopentadienyl)(triphenylphosphine)copper(I), $[Cu(CH_3C_5H_4)\{P(C_6H_5)_3\}]$

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(*Received* 26 *November* 1984; *accepted* 14 *March* 1985)

Abstract. $M_r = 404\cdot96$, monoclinic, $I2/a$, $a = 18\cdot687\,(6)$, $b = 8\cdot871\,(5)$, $c = 25\cdot016\,(19)$ Å, $\beta = 103\cdot80\,(5)°$, $V = 4028\,(4)$ Å^3, $Z = 8$, $D_x = 1\cdot336$ Mg m^{-3}, λ(Mo $K\alpha$) = $0\cdot71073$ Å, $\mu = 1\cdot167$ mm^{-1}, $F(000) = 2832$, $T = 297$ K, $R = 0\cdot051$ for 2105 unique observed data. The cyclopentadienyl ring is bonded in a pentahapto manner to the Cu, with Cu—C = 2·214 (6) Å (ave.). The ring-centroid—Cu—P grouping forms a nearly linear array (173·1°) for which Cu—centroid = 1·865 (9) Å and Cu—P = 2·131 Å. Around P, the geometry is roughly tetrahedral.

Introduction. The pentahapto cyclopentadienyl ligand, although ubiquitous in most areas of organometallic chemistry, is rare among complexes of the Cu triad. For Cu itself, few structural studies are available which present information on the metal—cyclopentadienyl interaction. Only two early studies provide details pertaining to the Cu—C_5H_5 unit: (η-C_5H_5)$CuPPh_3$ (Cotton & Takats, 1970) and (η-C_5H_5)$CuPEt_3$ (Delbaere, McBride & Ferguson, 1970). Recently, a communication on the structures of two metal clusters, (η-C_5Me_5)$_3Rh_2Cu(CO)_2$ and (η-C_5Me_5)(η-C_5H_5)(μ-CC_6H_4Me-4)$PtWCu(CO)_2(PMe_3)_2$, containing the (η-C_5Me_5)Cu fragment has appeared (Carriedo, Howard & Stone, 1983), but the focal point of the investigation was not the detailed structure of the cyclopentadienylcopper unit. This X-ray diffraction study of the title compound provides structural information on a substituted cyclopentadienyl—copper system and permits comparison with the known (η-C_5H_5)CuPR_3 structures.

Experimental. Complex prepared from reaction of $Na(CH_3C_5H_4)$ with Ph_3PCuCl in THF (Cotton & Marks, 1970). Colorless crystals grown from hexane solution at room temperature. Crystal $0\cdot15 \times 0\cdot35 \times 0\cdot42$ mm sealed in glass capillary under N_2. Syntex $P2_1$ diffractometer, graphite-monochromated Mo $K\alpha$. Lattice parameters from setting angles of 15 reflections with $13° < 2\theta < 23°$. Systematic absences hkl, $h + k + l \neq 2n$; $h0l$, $h \neq 2n$. I-centered setting allowed use of smaller β angle than that required by an A-centered cell ($a = 18\cdot69$, $b = 8\cdot87$, $c = 27\cdot42$ Å, $\beta = 117\cdot6°$). Intensities of 3881 unique reflections with $0° \leq 2\theta \leq 50°$ measured in θ–2θ mode with scan rate 2–12° min^{-1}, scan range $-1\cdot2°$ in 2θ from $K\alpha_1$ to $+1\cdot2°$ from $K\alpha_2$. Three check reflections ($80\bar{6}$, $81\bar{3}$, $12\bar{7}$) monitored every 100 data indicated 7% net decay; decay correction applied. Backgrounds evaluated from 96-step peak profile. Analytical absorption correction by Gaussian integration applied (min.–max. transmission factors: 0·796–0·921) to total of 2105 unique observed reflections [$I > 3\sigma(I)$]. Structure solved by Patterson and difference Fourier techniques. Full-matrix refinement based on F; weights given by Corfield, Doedens & Ibers (1967) with $p = 0\cdot05$. Anisotropic temperature factors for all non-hydrogen atoms; 18 H atoms located from difference maps, the rest included in fixed positions (C—H = 0·95 Å); none were refined. With 235 variable parameters, refinement converged to $R = 0\cdot051$, $wR = 0\cdot061$, $S = 1\cdot737$; max. Δ/σ during final cycle = 0·02. Largest peak on final difference map was of height 0·89 e Å^{-3} at 1·05 Å from Cu atom. No correction for secondary extinction. Atomic scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974). Computer programs from *UCLA Crystallographic Computing Package* (Strouse, 1981).

Discussion. (Methylcyclopentadienyl)(triphenylphosphine)copper(I) crystallizes in monomeric units consisting of an (η-$CH_3C_5H_4$)Cu fragment bonded to a PPh_3 moiety, such that the geometry around the P is roughly tetrahedral. A view of the molecule providing the numbering scheme is given in Fig. 1. Fractional atomic coordinates are listed in Table 1, and selected bond distances and angles are presented in Table 2.† A comparison of the structures of (C_5H_5)$CuPPh_3$, (C_5H_5)$CuPEt_3$, and ($CH_3C_5H_4$)$CuPPh_3$ is given in Table 3.

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† Lists of observed and calculated structure factor amplitudes, anisotropic thermal parameters, equations of least-squares planes and all bond distances and angles involving non-H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42121 (25 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

0108-2701/85/071036-03\$01.50

The geometry of the individual sections of the molecule is typical for such units and requires only brief comment. The methylcyclopentadienyl ring is highly regular; all atoms of the C_5 ring are within 0·002 Å of the least-squares plane and all C—C bond distances are equal within error limits [average length 1·402 (9) Å]. The methyl group is displaced by 0·10 Å out of the five-C-atom plane and away from the metal ($\alpha = 4{\cdot}0°$). The triphenylphosphine moiety is unexceptional [average C—C = 1·379 (8) Å] and all phenyl atoms are within 0·014 Å of their respective least-squares planes.

A comparison of the structures of the three (RC_5H_4)-CuPR'_3 species (R = Me, H; R' = Ph, Et) reveals a considerable degree of uniformity among them. The three Cu—ring-centroid distances are very similar and do not differ by more than 0·02 Å from the mean separation of 1·88 Å. All three Cu—P distances are shorter than those found in the $[(PR_3)_nCuL]_m$ phosphine species (2·22–2·28 Å) [R = Ph, $L = BH_4$, $n = 2$, $m = 1$ (Lippard & Melmed, 1967); R = Ph, $L = NO_3$, $n = 2$, $m = 1$ (Messmer & Palenik, 1969); R = Me, L = C≡CPh, $n = 1$, $m = 4$ (Corfield & Shearer, 1966)], but longer than that discovered in $ReCu(C_2C_6F_5)_2(CO_3)(PPh_3)_2$ [2·01 (1) Å] (Abu Salah, Bruce & Redhouse, 1974). It is possible to formulate the latter complex as the ion pair $[Cu(PPh_3)]^+$-$[Ru(C_2C_6F_5)_2(CO)_3(PPh_3)]^-$, which may account for the bond shortening.

A trend is evident in the ring-centroid—Cu—P angles of the (RC_5H_4)CuPR'_3 compounds which correlates with the increasing bulk of the phosphine and cyclopentadienyl ligands. The nearly perfect linearity in (C_5H_5)CuPEt$_3$ (179·9°) decreases to 175·2° in (C_5H_5)CuPPh$_3$, and with the addition of a methyl group to the cyclopentadienyl ring the angle closes slightly more (173·1°). In the latter complex, there are no intramolecular ring contacts significantly shorter than the sum of the appropriate van der Waals radii (Pauling, 1960), and the additional bending presumably occurs because of crystal-packing forces.

We thank the Division of Basic Energy Sciences of the Department of Energy and the Alfred P. Sloan Foundation for a Research Fellowship (to WJE) for support of this research, and Professor R. J. Doedens for helpful advice.

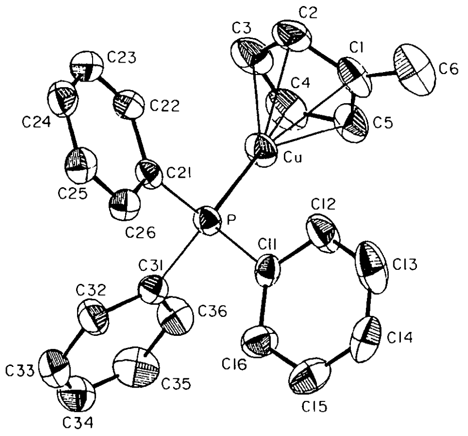

Fig. 1. *ORTEP* drawing (Johnson, 1965) of ($CH_3C_5H_4$)CuPPh$_3$. Thermal ellipsoids have been drawn at the 35% probability level; H atoms have been omitted.

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters for* ($CH_3C_5H_4$)CuPPh$_3$

$U_{eq} = \frac{1}{3}$(trace of orthogonalized U_{ij} matrix).

	x	y	z	$U_{eq} \times 10^4$ (Å^2)
Cu	0·20191 (3)	0·10819 (8)	0·86076 (3)	612 (6)
P	0·31144 (7)	0·0515 (2)	0·85706 (6)	451 (9)
C(1)	0·1344 (3)	0·2675 (8)	0·8986 (3)	703 (52)
C(2)	0·1300 (4)	0·1215 (9)	0·9206 (3)	835 (61)
C(3)	0·0983 (3)	0·0271 (9)	0·8773 (4)	854 (61)
C(4)	0·0826 (3)	0·1082 (10)	0·8284 (3)	805 (55)
C(5)	0·1051 (3)	0·2585 (8)	0·8413 (3)	731 (53)
C(6)	0·1595 (5)	0·4061 (10)	0·9306 (4)	1162 (81)
C(11)	0·3721 (2)	0·2157 (6)	0·8617 (2)	479 (36)
C(12)	0·3662 (3)	0·3253 (8)	0·8991 (3)	753 (52)
C(13)	0·4083 (4)	0·4544 (8)	0·9040 (4)	963 (65)
C(14)	0·4572 (3)	0·4765 (7)	0·8720 (3)	751 (53)
C(15)	0·4647 (4)	0·3679 (8)	0·8352 (3)	802 (56)
C(16)	0·4225 (3)	0·2346 (7)	0·8303 (2)	686 (48)
C(21)	0·3580 (3)	−0·0669 (6)	0·9147 (2)	448 (35)
C(22)	0·3151 (3)	−0·1437 (6)	0·9446 (2)	566 (42)
C(23)	0·3483 (3)	−0·2305 (7)	0·9899 (3)	677 (49)
C(24)	0·4243 (4)	−0·2446 (7)	1·0038 (2)	660 (47)
C(25)	0·4669 (3)	−0·1732 (7)	0·9753 (2)	602 (42)
C(26)	0·4343 (3)	−0·0824 (6)	0·9300 (2)	519 (38)
C(31)	0·3214 (2)	−0·0464 (6)	0·7951 (2)	461 (35)
C(32)	0·3761 (3)	−0·1488 (7)	0·7941 (3)	665 (47)
C(33)	0·3799 (4)	−0·2196 (8)	0·7460 (3)	807 (60)
C(34)	0·3289 (4)	−0·1873 (8)	0·6975 (3)	774 (57)
C(35)	0·2753 (4)	−0·0848 (9)	0·6984 (3)	873 (59)
C(36)	0·2703 (3)	−0·0130 (8)	0·7457 (3)	705 (50)

Table 2. *Selected bond lengths* (Å) *and angles* (°) *in* ($CH_3C_5H_4$)CuPPh$_3$

Cu—P	2·131 (1)	P—Cu—C(1)	143·9 (2)
Cu—C(1)	2·247 (6)	P—Cu—C(2)	141·0 (2)
Cu—C(2)	2·240 (6)	P—Cu—C(3)	146·1 (2)
Cu—C(3)	2·195 (6)	P—Cu—C(4)	152·9 (2)
Cu—C(4)	2·183 (6)	P—Cu—C(5)	151·5 (2)
Cu—C(5)	2·206 (5)	C(1)—Cu—C(3)	61·2 (3)
C(1)—C(6)	1·481 (10)	C(1)—Cu—C(4)	62·0 (2)
P—C(11)	1·833 (5)	C(2)—Cu—C(4)	61·7 (3)
P—C(21)	1·827 (5)	C(2)—Cu—C(5)	61·6 (3)
P—C(31)	1·826 (5)	C(3)—Cu—C(5)	61·7 (3)
		Cu—P—C(11)	113·3 (2)
		Cu—P—C(21)	112·6 (2)
		Cu—P—C(31)	116·3 (2)
		C(11)—P—C(21)	103·6 (2)
		C(11)—P—C(31)	104·1 (2)
		C(21)—P—C(31)	105·7 (2)

Table 3. *Comparison of* (RC_5H_4)CuPR'_3 *structures*

Complex	(C_5H_5)CuPEt$_3$	(C_5H_5)CuPPh$_3$	($CH_3C_5H_4$)CuPPh$_3$
Cu—P (Å)	2·136 (9)	2·135 (1)	2·131 (1)
Cu—C (ave., Å)	2·24 (3)	2·211 (3)	2·214 (6)
Cu—ring centroid (Å)	1·90 (6)	1·863 (9)	1·865 (9)
Centroid—Cu—P (°)	179·9	175·2	173·1
P—C (ave., Å)	1·88 (5)	1·829 (2)	1·829 (5)
Reference	(*a*)	(*b*)	(*c*)

References: (*a*) Delbaere, McBride & Ferguson (1970). (*b*) Cotton & Takats (1970). (*c*) This work.

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Acta Cryst. (1985). C**41**, 1038–1040

Structure of Tris(η-methylcyclopentadienyl)(trimethylphosphine)uranium(III), $[U(CH_3C_5H_4)_3\{P(CH_3)_3\}]$

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(*Received* 10 *September* 1984; *accepted* 14 *March* 1985)

Abstract. $M_r = 551{\cdot}5$, monoclinic, Cc, $a = 13{\cdot}949\ (5)$, $b = 9{\cdot}280\ (4)$, $c = 16{\cdot}194\ (6)$ Å, $\beta = 104{\cdot}09\ (4)°$, $V = 2033\ (3)$ Å^3, $Z = 4$, $D_x = 1{\cdot}801\ (3)$ g cm^{-3}, Mo $K\alpha$, $\lambda(\alpha_1) = 0{\cdot}70930$ Å, $\mu = 76{\cdot}4$ cm^{-1}, $F(000) = 1052$, $T = 296$ K, $R = 0{\cdot}024$ for 1568 reflections ($F^2 > 2\sigma$). The structure consists of U-centered monomolecular units in which the U atom is coordinated in a pentahapto fashion to three cyclopentadiene rings and to the P atom of the trimethylphosphine molecule. The average U—C distance is 2·79 ±0·06 Å and the U—P distance is 2·972 (6) Å.

Introduction. We are currently studying the relative affinity of Lewis bases toward $(CH_3C_5H_4)_3U$. Interligand contacts influence the ability of a ligand to coordinate to a metal ion and must be considered when comparing ligand basicities. As part of this study we report here the X-ray structure of $(CH_3C_5H_4)_3U\{P(CH_3)_3\}$.

Experimental. Red, air-sensitive needles of the phosphine complex were prepared by reacting UCl_3 (Andersen, 1979) with $Na(CH_3C_5H_4)$ in tetrahydrofuran (THF), adding $P(CH_3)_3$, and crystallizing from pentane at 253 K. Crystals were sealed inside quartz capillaries because of their reactivity in the atmosphere, and no measured density is reported for the same reason. Crystal 0·15 × 0·23 × 0·38 mm with 9 faces; modified Picker automatic diffractometer, graphite monochromator; cell dimensions from 31 reflections, $20° < 2\theta < 27°$; analytical absorption correction, range 2·78 to 3·41; max. $(\sin\theta)/\lambda = 0{\cdot}60$ Å^{-1}, h −16 to 16, k 0 to 11, l −19 to 19; three standard reflections, <2% variation in intensities from average, intensities adjusted accordingly; 3650 data, 1798 unique (including 230, $F^2 < 2\sigma$), $R_{\rm int} = 0{\cdot}029$; structure solved by Patterson and Fourier methods, refined on F, 207 parameters, non-methyl H atoms in calculated positions with isotropic thermal parameters, methyl H atoms not included, anisotropic thermal parameters for non-hydrogen atoms, ring C—C and C—CH_3 bond distances restrained; $R = 0{\cdot}033$ for 1798 reflections (0·024 for 1568 for which $F^2 > 2\sigma$), $wR = 0{\cdot}032$, $S = 1{\cdot}07$; $w = [\sigma(F)]^{-2}$, $p = 0{\cdot}05$ in calculation of $\sigma(F^2)$; max. $(\Delta/\sigma) = 0{\cdot}08$; max. correction for extinction 3% of F, $F_{\rm corr} = F_{\rm obs}(1 + 4{\cdot}0 \times 10^{-8} I)$; max. and min. of ΔF synthesis 0·34 and −0·37 e Å^{-3}; atomic f for neutral U, P and C, and spherical bonded H from *International Tables for X-ray Crystallography* (1974); local unpublished programs and *ORTEP* (Johnson, 1965).

In an effort to determine the absolute configuration of the molecule, the full unaveraged data set was used to refine both enantiomorphic structures, but the results showed no significant differences in the R factors for the two structures. The Friedel pairs of selected reflections with large differences were investigated, but again there was no significant correlation with the observed data. On the assumption that the crystal was twinned with both enantiomers present in equal amounts, the data were averaged. The f'' term of the anomalous dispersion was set to zero, and the f' term was applied as usual.

0108-2701/85/071038-03\$01.50