

the Cu—O bond lengths are explained by the different *trans* atoms). This fact explains the shortening of the Cu—N(21) bond distance [1.991 (3) Å, *trans* to O(8)] with respect to 2.005 (3) Å observed for Cu—N(10) [*trans* O(1)]. The Cu ion is also weakly linked to O(8ⁱ) of another cation [Cu...O(8ⁱ) 2.781 (3) Å, symmetry code: (i) 2-x, 1-y, 1-z], being located at the opposite side from O(31) (Fig. 1).

The salicylaldehydato ligand is not planar. The phenyl ring is planar, with the largest deviation from the mean plane being 0.014 (6) Å; O(8) and O(1) deviate from this phenyl plane by 0.035 (4) and -0.086 (4) Å respectively. The dihedral angle between the phenyl ring and the O(1), O(8), N(10), N(21) plane is 18.6 (3)°. The 1,10-phenanthroline ligand is planar with the dihedral angle between this plane and the O(1), O(8) N(10), N(21) plane equal to 2.8 (3)°.

The mean Cu—N(phenanthroline) distance of 1.998 (7) Å is similar to that of 2.01 (1) Å observed in aqua(1,10-phenanthroline)(thiamine pyrophosphate)-copper(II) dinitrate hydrate (Aoki & Yamasaki, 1980), while it is shorter than those obtained in the *trans*-bis(1,10-phenanthroline)copper(II) complex [mean value 2.05 (1) Å; Boys, Escobar & Martinez-Carrera, 1981].

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Structure of Tris(η -methylcyclopentadienyl)(trimethylphosphine)cerium(III)

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Abstract. [Ce(CH₃C₅H₄)₃{P(CH₃)₃}], $M_r = 453.57$, monoclinic, *Cc*, $a = 14.017$ (4), $b = 9.351$ (3), $c = 16.348$ (6) Å, $\beta = 103.92$ (3)°, $V = 2080$ (3) Å³, $Z = 4$, $D_x = 1.448$ (3) g cm⁻³, Mo $K\alpha$, $\lambda(\alpha_1) = 0.70930$ Å, $\mu = 23.0$ cm⁻¹, $F(000) = 916$, $T = 296$ K, $R = 0.024$ for 1232 reflections [$F^2 > \sigma(F^2)$]. The structure consists of Ce centered monomolecular units in which the Ce atom is coordinated in a pentahapto fashion to three cyclopentadiene rings and to the phosphorus atom of the trimethylphosphine molecule. The average Ce—C distance is 2.82 (4) Å and the Ce—P distance is 3.072 (4) Å.

Introduction. Recently we reported the structure of [U(CH₃C₅H₄)₃P(CH₃)₃] (Brennan & Zalkin, 1985) as part of a study of the relative affinity of Lewis bases

toward (CH₃C₅H₄)₃U. A parallel experiment using [Ce(CH₃C₅H₄)₃P(CH₃)₃] is being performed to study what effect a different metal atom has on the molecular structure and chemistry. 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 [Ce(CH₃C₅H₄)₃P(CH₃)₃], which is isomorphous with the uranium complex.

Experimental. Yellow air-sensitive needles of the phosphine complex were prepared by reacting [Ce(CH₃C₅H₄)₃OC₄H₈], isolated from the reaction of CeCl₃ with three equivalents of NaCH₃C₅H₄ in tetrahydrofuran, with P(CH₃)₃ in diethyl ether and crystallizing from diethyl ether 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 $0.18 \times 0.18 \times 0.17$ mm with six faces; modified Picker automatic diffractometer, graphite monochromator; cell dimensions from 20 reflections, $21 < 2\theta < 36^\circ$; analytical absorption correction, range 1.37–1.54; max. $(\sin\theta)/\lambda = 0.54 \text{ \AA}^{-1}$, $h - 15$ to 15 , $k 0$ to 10 , $l - 17$ to 17 ; three standard reflections, $< 2\%$ variation in intensities from average, intensities adjusted accordingly; 2878 data, 1366 unique (including 134, $F^2 < \sigma$), $R_{\text{int}} = 0.021$; refinements started with parameters of the uranium isomorph (Brennan & Zalkin, 1985); refined on F , 206 parameters, non-methyl hydrogen atoms in calculated positions with isotropic thermal parameters, methyl hydrogen atoms not included, anisotropic thermal parameters for non-hydrogen atoms; $R = 0.032$ for 1366 reflections (0.024 for 1232 for which $F^2 > \sigma$), $wR = 0.026$, $S = 1.0$; $w = [\sigma(F)]^{-2}$, $p = 0.04$ in calculation of $\sigma(F^2)$; max. (shift/ σ) = 0.03, max. correction for extinction 1% of F , $F_{\text{corr}} = F_{\text{obs}}(1 + 3.1 \times 10^{-8}I)$; max. and min. of ΔF synthesis 0.18 and -0.24 e \AA^{-3} ; atomic f for neutral Ce, 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 orientation of the molecule in this polar structure, the full unaveraged data set was used to refine both settings, but the results showed a small difference in the R factors. On the assumption that the crystal was twinned with both orientations present in equal amounts, the data were averaged ($R_{\text{int}} = 0.021$). The f'' term of the anomalous dispersion was set to zero, and the f' term was applied as usual.

A subsequent least-squares calculation, in which the f'' term for Ce was a refinable parameter and the unaveraged data set was used, resulted in an f'' for Ce of $0.6(2) \text{ e}$ vs the *International Tables* (1974) value of 2.632 e . This translates into an estimated twinning ratio of approximately 60–40%. The positional parameters from this computation are within statistics unchanged from the values given in Table 1.* Fig. 1 is an *ORTEP* drawing of the title compound.

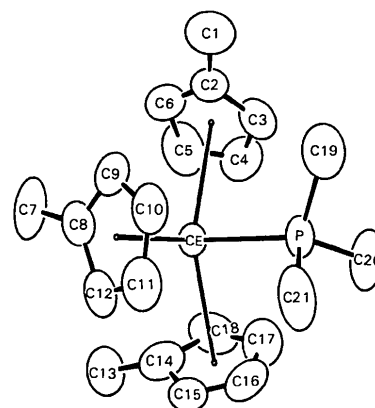
Discussion. The complex is monomolecular in the crystalline state and consists of a Ce atom coordinated to the three methylcyclopentadienyl groups in a pentahapto bonding mode and to the P atom of the trimethylphosphine molecule in a distorted trigonal

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters, deviations from least-squares planes, distances and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43451 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic parameters

$$B_{\text{eq}} = \frac{1}{3} \sum_i \sum_j B_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x $\frac{1}{4}$	y	z $\frac{1}{4}$	$B_{\text{eq}}(\text{\AA}^2)$
Ce		0.33939 (4)		3.20
P	0.2804 (3)	0.1697 (4)	0.41521 (26)	4.79
C(1)	0.3852 (13)	0.6059 (20)	0.4224 (12)	9.01
C(2)	0.3989 (9)	0.5285 (16)	0.3429 (10)	5.19
C(3)	0.4454 (11)	0.3971 (19)	0.3426 (12)	5.83
C(4)	0.4500 (16)	0.3631 (19)	0.2595 (16)	6.10
C(5)	0.4063 (12)	0.4749 (24)	0.2089 (10)	6.56
C(6)	0.3754 (15)	0.5754 (23)	0.2638 (16)	6.32
C(7)	0.1115 (11)	0.6595 (16)	0.1293 (11)	7.20
C(8)	0.1026 (13)	0.5608 (23)	0.2020 (13)	5.07
C(9)	0.1434 (10)	0.5774 (16)	0.2873 (9)	4.82
C(10)	0.1158 (11)	0.4677 (16)	0.3350 (8)	5.32
C(11)	0.0595 (17)	0.3735 (23)	0.2753 (15)	6.48
C(12)	0.0516 (11)	0.4258 (21)	0.1973 (12)	5.72
C(13)	0.1557 (14)	0.2923 (18)	0.0147 (10)	7.46
C(14)	0.1926 (16)	0.2143 (20)	0.0931 (14)	7.14
C(15)	0.1428 (8)	0.1277 (11)	0.1423 (8)	5.45
C(16)	0.2074 (12)	0.0492 (12)	0.2044 (8)	7.27
C(17)	0.3026 (10)	0.0699 (14)	0.1941 (10)	7.09
C(18)	0.2958 (10)	0.1630 (16)	0.1259 (9)	6.88
C(19)	0.3296 (14)	0.2547 (22)	0.5212 (10)	7.78
C(20)	0.3671 (10)	0.0201 (16)	0.4248 (9)	8.51
C(21)	0.1661 (10)	0.0946 (18)	0.4348 (10)	9.74

Fig. 1. *ORTEP* drawing of the title compound; thermal ellipsoids are at 50% probability level.Table 2. Selected distances (\AA) and angles ($^\circ$)

Ce—P	3.072 (4)	Ce—C(14)	2.757 (18)
Ce—C(2)	2.875 (13)	Ce—C(15)	2.829 (10)
Ce—C(3)	2.844 (16)	Ce—C(16)	2.840 (11)
Ce—C(4)	2.779 (20)	Ce—C(17)	2.837 (10)
Ce—C(5)	2.751 (15)	Ce—C(18)	2.807 (10)
Ce—C(6)	2.797 (20)	Ce—Cp ₁ *	2.55
Ce—C(8)	2.896 (19)	Ce—Cp ₂	2.59
Ce—C(9)	2.828 (13)	Ce—Cp ₃	2.54
Ce—C(10)	2.858 (13)	P—C(19)	1.880 (18)
Ce—C(11)	2.817 (23)	P—C(20)	1.836 (13)
Ce—C(12)	2.824 (16)	P—C(21)	1.847 (13)
P—Ce—Cp ₁	97.3	Cp ₂ —Ce—Cp ₃	117.8
P—Ce—Cp ₂	98.8	C(19)—P—C(20)	98.9 (8)
P—Ce—Cp ₃	96.7	C(19)—P—C(21)	98.2 (8)
Cp ₁ —Ce—Cp ₂	118.8	C(20)—P—C(21)	106.2 (8)
Cp ₁ —Ce—Cp ₃	118.2		

* Cp₁, Cp₂ and Cp₃ represent the centers of atom groups C(2)—C(6), C(8)—C(12) and C(14)—C(18) respectively.

pyramidal arrangement with the P atom at the apex and cyclopentadienyl ring centers on the base; the plane through the cyclopentadienyl centers is 0.34 Å below the Ce atom. The angles about the Ce atom are given in Table 2. The Ce atom is 3.072 (4) Å from the P atom and 2.54 to 2.58 Å from the least-squares planes of the cyclopentadienyl rings; the average Ce—C distance is 2.82 ± 0.04 Å. There are no observed close contacts between the phosphine ligand and the Cp rings.

Although there are a number of similar trivalent lanthanide structures in the literature [(C₅H₅)₃-Gd(OC₄H₈) (Rogers, Bynum & Atwood, 1980), (C₅H₅)₃Y(OC₄H₈), (C₅H₅)₃La(OC₄H₈) (Rogers, Atwood, Emad, Sikora & Rauch, 1981), and (C₅H₅)₃-Nd(CNC₆H₁₁) (Burns & Baldwin, 1976), this represents the first structurally characterized organometallic tertiary phosphine complex of Ce.

Although the title complex and [U(CH₃C₅H₄)P(CH₃)₃] are crystallographically isomorphous there is a significant structural difference in the two molecules. The angles made by the four ligands about the metal atom are close to being tetrahedral in the U complex [average Cp—U—Cp angles 112 (7)°; average P—U—Cp angle 106.4 (9)°] and trigonal pyramidal in the Ce complex [average Cp—Ce—Cp angle 118 (1)°; average P—Ce—Cp angle 98.1 (1)°]. These Ce angles are within a degree of the comparable angles in (CH₃C₅H₄)₃U(OC₄H₈) (Wasserman, Zozulin, Moody, Ryan & Salazar, 1983).

The published U^{III} and Ce^{III} ionic radii (Shannon & Prewitt, 1969) show the U^{III} radius to be 0.03 Å larger than the Ce^{III} radius. Assuming a purely ionic model,

this structure indicates the reverse to be true. The average Ce—Cp distance [2.56 (3) Å] is larger than the average U—Cp distance [2.52 (2) Å] by an amount that is barely significant. However, the Ce—P distance [3.072 (4) Å] is a full 0.1 Å larger than the U—P distance [2.972 (6) Å]. Further structural studies are currently under way to ascertain the nature of this discrepancy.

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(2,3,5,6- η^4 -Bicyclo[2.2.1]hepta-2,5-diene)-(E)-bis(2-ethoxynaphth-1-yl)platinum(II)

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Abstract. [Pt(C₇H₈)(C₁₂H₁₁O)₂], $M_r = 629.66$, monoclinic, $P2_1/n$, $a = 14.739$ (6), $b = 18.102$ (6), $c = 9.445$ (5) Å, $\beta = 96.11$ (4)°, $V = 2505$ Å³, $Z = 4$, $D_x = 1.668$, $D_m = 1.651$ g cm⁻³, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 56.82$ cm⁻¹, $F(000) = 1240$, $T = 295$ K, final $R = 0.055$ for 3139 observed reflections. The C(1) and C(13) atoms of the naphthyl ligands and the centers of

the double bonds C(26)=C(27) and C(29)=C(30) lie in a plane around the Pt atom. The two naphthyl ligands are nearly perpendicular (83.3 and 81.6°) to this plane and oriented *anti* to one another (*E* conformation).

Introduction. In compounds of the type *cis*-bis(phenyl)bis(ligand)platinum(II) (1) the two phenyl rings