

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 [(C<sub>5</sub>H<sub>5</sub>)<sub>3</sub>-Gd(OC<sub>4</sub>H<sub>8</sub>) (Rogers, Bynum & Atwood, 1980), (C<sub>5</sub>H<sub>5</sub>)<sub>3</sub>Y(OC<sub>4</sub>H<sub>8</sub>), (C<sub>5</sub>H<sub>5</sub>)<sub>3</sub>La(OC<sub>4</sub>H<sub>8</sub>) (Rogers, Atwood, Emad, Sikora & Rauch, 1981), and (C<sub>5</sub>H<sub>5</sub>)<sub>3</sub>-Nd(CNC<sub>6</sub>H<sub>11</sub>) (Burns & Baldwin, 1976), this represents the first structurally characterized organometallic tertiary phosphine complex of Ce.

Although the title complex and [U(CH<sub>3</sub>C<sub>5</sub>H<sub>4</sub>)P(CH<sub>3</sub>)<sub>3</sub>] 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 (CH<sub>3</sub>C<sub>5</sub>H<sub>4</sub>)<sub>3</sub>U(OC<sub>4</sub>H<sub>8</sub>) (Wasserman, Zozulin, Moody, Ryan & Salazar, 1983).

The published U<sup>III</sup> and Ce<sup>III</sup> ionic radii (Shannon & Prewitt, 1969) show the U<sup>III</sup> radius to be 0.03 Å larger than the Ce<sup>III</sup> 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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#### References

- BRENNAN, J. & ZALKIN, A. (1985). *Acta Cryst.* C41, 1038–1040.  
 BURNS, J. H. & BALDWIN, W. H. (1976). *J. Organomet. Chem.* 120, 361–367.  
*International Tables for X-ray Crystallography* (1974). Vol. IV. Table 2.2, pp. 71–102. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)  
 JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.  
 ROGERS, R. D., ATWOOD, J. L., EMAD, A., SIKORA, D. J. & RAUCH, M. D. (1981). *J. Organomet. Chem.* 216, 383–392.  
 ROGERS, R. D., BYNUM, R. V. & ATWOOD, J. L. (1980). *J. Organomet. Chem.* 192, 65–73.  
 SHANNON, R. D. & PREWITT, C. T. (1969). *Acta Cryst.* B25, 925–945.  
 WASSERMAN, H. J., ZOZULIN, A. J., MOODY, D. C., RYAN, R. R. & SALAZAR, K. V. (1983). *J. Organomet. Chem.* 254, 305–311.

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

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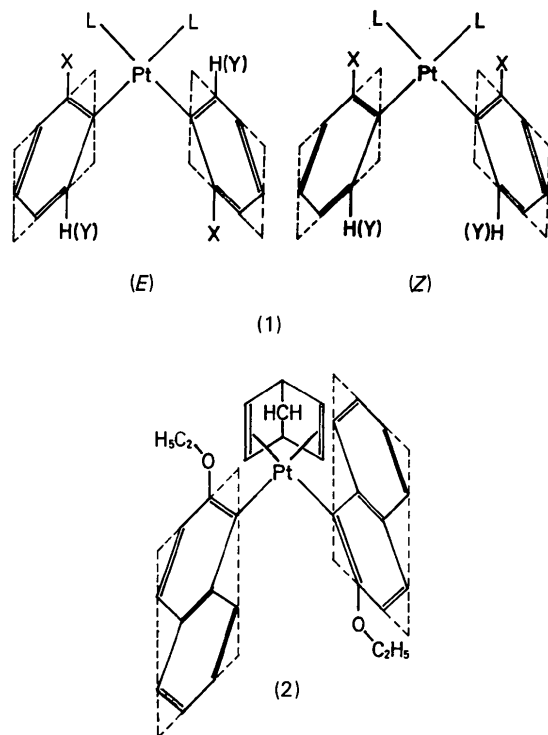
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**Abstract.** [Pt(C<sub>7</sub>H<sub>8</sub>)(C<sub>12</sub>H<sub>11</sub>O)<sub>2</sub>],  $M_r = 629.66$ , monoclinic,  $P2_1/n$ ,  $a = 14.739$  (6),  $b = 18.102$  (6),  $c = 9.445$  (5) Å,  $\beta = 96.11$  (4)°,  $V = 2505$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.668$ ,  $D_m = 1.651$  g cm<sup>-3</sup>, Mo  $K\alpha$ ,  $\lambda = 0.71069$  Å,  $\mu = 56.82$  cm<sup>-1</sup>,  $F(000) = 1240$ ,  $T = 295$  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

are – according to X-ray analysis – nearly perpendicularly oriented to the plane defined by the four valences of the  $dsp^2$ -hybridized ('square planar') platinum atom (Ertl, Debaerdemaeker & Brune, 1982; Brune, Wiege & Debaerdemaeker, 1984; Debaerdemaeker, Stapp & Brune, 1987). The introduction of one substituent into the *ortho* position of each of the two phenyl rings or of two different substituents into the two *ortho* positions of each phenyl ring should lead to the formation of *E,Z* atropisomers. It will be possible to isolate them if the energy barrier of the torsion about the platinum–phenyl bonds is high enough with respect to  $kT$ . Actually such atropisomers could be detected by  $^1\text{H}$  NMR spectroscopy in compounds of this type in which the two *ortho* positions of each phenyl ring were substituted by structurally different alkoxy groups (Laube, 1984). The lifetimes of these isomers with respect to conformer isomerization increased as expected with increasing van der Waals volumes of the substituents. Nevertheless, the isolation of the *E,Z* isomers failed as a consequence of a still too low energy barrier. Owing to the bulky 2-ethoxynaphth-1-yl ligands {2,3,5,6- $\eta^4$ -bicyclo[2.2.1]hepta-2,5-diene}bis(2-ethoxynaphth-1-yl)platinum(II), which has recently been synthesized (Weisemann & Brune, 1986), should have a higher energy barrier. Despite the possibility of the formation of *E,Z* atropisomers, only one isomer was isolated. Here we describe the structure of this isomer to which the *E* orientation (2) of the two naphthyl ligands has been assigned. No *Z* isomer could be detected, nor is there any thermal *E-Z* isomerization observable.



**Experimental.** Crystals (approximately  $0.5 \times 0.2 \times 0.2$  mm) were obtained by very slow evaporation of a  $\text{CH}_2\text{Cl}_2$  solution of the title compound. Density by flotation in  $\text{CCl}_4/\text{CH}_2\text{I}_2$ . Phillips PW 1100 four-circle diffractometer, Mo  $K\alpha$  radiation, graphite monochromator,  $\theta-2\theta$  scan. 4339 reflections measured, 3139 observed [ $F > 2.5\sigma(F)$ ],  $-16 < h < 16$ ,  $0 < k < 20$ ,  $0 < l < 10$ ,  $\theta_{\text{max}} = 25^\circ$ . The intensity of three standards did not vary during the period of measurement. The cell parameters were obtained from the refinement of 25 reflections ( $9.0 < \theta < 23.0^\circ$ ). Empirical absorption correction (Walker & Stuart, 1983), transmission factors 1.346–0.565. The structure was solved using the random-phase approach (Debaerdemaeker & Woolfson, 1983) and the XMY84 program (Debaerdemaeker, 1984). The structure was refined by full-matrix least squares on  $F$ , first with isotropic and then with anisotropic temperature parameters, using unit weights (Sheldrick, 1976) until the parameter shifts were less than the corresponding standard deviation; H atoms were ignored. Final  $R = 0.055$  for 3139 reflections and 307 parameters.  $\Delta/\sigma = 0.01$ , max. peak in final difference map  $0.7 e \text{ \AA}^{-3}$ . Scattering factors of Cromer & Mann (1968) and Doyle & Turner (1968).

**Discussion.** Final atomic coordinates and equivalent isotropic thermal parameters are given in Table 1, selected interatomic distances and angles in Table 2.\* In order to demonstrate the geometry more clearly, two different views and the atomic numbering are depicted in Figs. 1 and 2.

The C(1) and C(1') atoms of the two naphthyl ligands [C(1) and C(13) according to the numbering in Fig. 2], the centers of the double bonds in the bicyclo[2.2.1]hepta-2,5-diene [C(26)=C(27) and C(29)=C(30)] and the Pt atom lie in a plane. They form an approximately 'square planar' coordination sphere with nearly  $dsp^2$ -hybridized Pt. The angle defined by the two double-bond centers and the Pt atom is  $70.4(5)^\circ$  and thus markedly smaller than  $90^\circ$  as a consequence of the rigid bicycloheptadiene chelate, whereas the angle between the bonds from Pt to the two naphthyl ligands is close to the normal  $90^\circ$ , which may be surprising considering the fact that the space left by the small bicycloheptadiene ligand should lead to an enlarged angle between the Pt atom and the bulky naphthyl groups.

The lengths of the bonds from Pt to the naphthalene C(1) and C(13) atoms differ significantly. No such differences have been observed previously in *cis*-bis(phenyl)platinum(II) compounds (Ertl, Debaer-

\* Lists of structure factors, anisotropic thermal parameters, and bond distances and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43423 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic coordinates for non-hydrogen atoms and equivalent isotropic thermal parameters with e.s.d.'s in parentheses

	x	y	z	$\langle U \rangle^*$ (Å <sup>2</sup> )
Pt	0.4407 (1)	0.2585 (1)	0.2138 (1)	0.045 (1)
O(1)	0.3988 (10)	0.1164 (7)	0.3713 (14)	0.097 (17)
O(2)	0.5927 (7)	0.3685 (6)	0.1678 (13)	0.081 (14)
C(1)	0.4717 (8)	0.2345 (8)	0.4214 (16)	0.061 (15)
C(2)	0.4482 (13)	0.1629 (10)	0.4734 (21)	0.083 (22)
C(3)	0.4693 (13)	0.1386 (12)	0.6179 (23)	0.095 (25)
C(4)	0.5125 (14)	0.1887 (15)	0.7146 (23)	0.097 (28)
C(5)	0.5351 (10)	0.2582 (13)	0.6728 (17)	0.079 (20)
C(6)	0.5735 (14)	0.3076 (19)	0.7730 (25)	0.125 (35)
C(7)	0.5931 (16)	0.3795 (19)	0.7326 (29)	0.128 (37)
C(8)	0.5753 (14)	0.4017 (13)	0.5865 (23)	0.109 (29)
C(9)	0.5363 (10)	0.3529 (10)	0.4853 (21)	0.078 (20)
C(10)	0.5136 (9)	0.2778 (10)	0.5249 (15)	0.068 (17)
C(11)	0.3768 (16)	0.0410 (9)	0.3995 (26)	0.109 (29)
C(12)	0.3332 (16)	0.0089 (11)	0.2658 (30)	0.121 (33)
C(13)	0.5738 (10)	0.2382 (9)	0.1687 (14)	0.063 (16)
C(14)	0.6296 (9)	0.2990 (10)	0.1564 (15)	0.066 (17)
C(15)	0.7219 (12)	0.2910 (13)	0.1278 (18)	0.089 (24)
C(16)	0.7576 (12)	0.2256 (15)	0.1077 (20)	0.094 (27)
C(17)	0.7015 (13)	0.1597 (13)	0.1117 (17)	0.088 (24)
C(18)	0.7332 (19)	0.0884 (20)	0.0872 (24)	0.131 (40)
C(19)	0.6804 (24)	0.0278 (17)	0.0970 (29)	0.134 (43)
C(20)	0.5868 (19)	0.0339 (11)	0.1306 (21)	0.106 (29)
C(21)	0.5506 (13)	0.1043 (9)	0.1540 (18)	0.080 (21)
C(22)	0.6084 (12)	0.1684 (10)	0.1491 (18)	0.072 (20)
C(23)	0.6486 (15)	0.4338 (12)	0.1641 (24)	0.106 (28)
C(24)	0.5865 (17)	0.4965 (12)	0.1868 (27)	0.120 (32)
C(25)	0.3147 (11)	0.3630 (8)	0.0891 (17)	0.068 (17)
C(26)	0.3929 (10)	0.3227 (11)	0.0182 (15)	0.072 (19)
C(27)	0.3688 (10)	0.2525 (10)	-0.0103 (14)	0.069 (16)
C(28)	0.2700 (10)	0.2462 (10)	0.0414 (15)	0.074 (18)
C(29)	0.2877 (9)	0.2549 (9)	0.2076 (15)	0.064 (16)
C(30)	0.3145 (9)	0.3261 (9)	0.2365 (15)	0.062 (16)
C(31)	0.2298 (10)	0.3256 (10)	0.0032 (17)	0.074 (18)

$$* \langle U \rangle = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

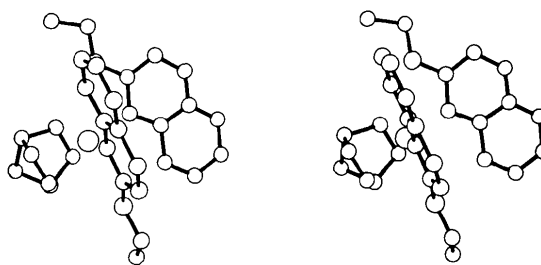


Fig. 1. Stereographic projection of the molecule.

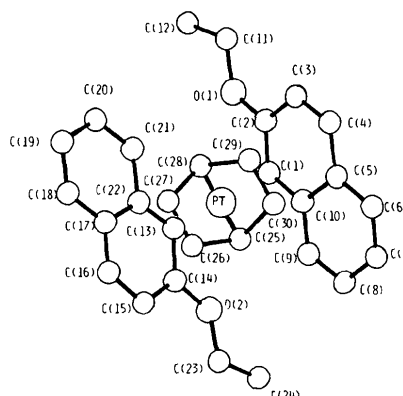


Fig. 2. Projection of the molecule approximately perpendicular to the plane defined by the four valences of Pt<sup>II</sup>.

Table 2. Selected bond distances (Å) and angles (°) with e.s.d.'s in parentheses

Pt—C(1)	2.01 (2)	Pt—C(26)	2.23 (2)
Pt—C(13)	2.08 (2)	Pt—C(27)	2.27 (1)
Pt—Z(1)*	2.15	Pt—C(29)	2.25 (1)
Pt—Z(2)*	2.15	Pt—C(30)	2.26 (2)
C(1)—Pt—C(13)	92.3 (5)	C(1)—Pt—Z(2)*	98.2 (4)
Z(1)*—Pt—Z(2)*	70.5	C(13)—Pt—Z(1)*	99.1 (4)

\* Z(1) and Z(2) are the centers between the atoms C(26), C(27) and C(29), C(30) respectively.

demaeker & Brune, 1982; Brune, Wiege & Debaerdemaeker, 1984; Debaerdemaeker, Stapp & Brune, 1987). As there seems to be no intramolecular reason for this difference it might be caused by packing effects.

The naphthyl ligands are nearly perpendicular [83.3 (4) and 81.6 (4)°] to the plane defined by the four valences from the *dsp*<sup>2</sup> planar Pt and mutually *anti*-orientated (*E* conformation). The naphthalene rings are not distorted from planarity.

Contrary to the planar naphthalene rings, the O atoms of the ethoxy groups are distorted from the in-plane position by 0.17 (5) and 0.15 (5) Å in the direction of the normal vectors of the naphthalene planes away from the adjacent naphthyl ligand. No clear evidence for the origin of this distortion is at hand.

The distances between these two O atoms – which are potential electron donors and therefore can act as coordinating ligands – and the Pt atom are both larger than 3 Å. Hence no additional coordination between O and Pt is operative.

## References

- BRUNE, H. A., WIEGE, M. & DEBAERDEMAEKER, T. (1984). *Z. Naturforsch. Teil B*, **39**, 359–368, 907–914.
- CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.
- DEBAERDEMAEKER, T. (1984). *XY84*. Univ. of Ulm, Federal Republic of Germany.
- DEBAERDEMAEKER, T., STAPP, B. & BRUNE, H. A. (1987). *Acta Cryst.* **C43**, 473–476.
- DEBAERDEMAEKER, T. & WOOLFSON, M. M. (1983). *Acta Cryst.* **A39**, 193–196.
- DOYLE, B. & TURNER, A. (1968). *Acta Cryst.* **A24**, 390–397.
- ERTL, J., DEBAERDEMAEKER, T. & BRUNE, H. A. (1982). *Chem. Ber.* **115**, 3860–3874.
- LAUBE, G. (1984). Thesis, Univ. of Ulm, Federal Republic of Germany.
- SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
- WALKER, N. & STUART, D. (1983). *Acta Cryst.* **A39**, 158–166.
- WEISEMANN, C. & BRUNE, H. A. (1986). *J. Organomet. Chem.* **312**, 133.