

This study was performed through Special Coordination Funds of the Science and Technology Agency of the Japanese Government.

References

- CURTIS, N. F. (1979). *Coordination Chemistry of Macrocyclic Compounds*, edited by G. A. MELSON, pp. 219–344: New York: Plenum.
- FREEMAN, H. C. (1967). *Adv. Protein Chem.* **22**, 342–346.
- FREEMAN, H. C., MARZILLI, L. G. & MAXWELL, I. E. (1970). *Inorg. Chem.* **9**, 2408–2415.
- FREEMAN, H. C. & MAXWELL, I. E. (1970). *Inorg. Chem.* **9**, 649–655.

- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
- MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCO, J.-P. & WOOLFSON, M. M. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univ. of York, England, and Louvain, Belgium.
- MATHIESON, S. & WELSH, H. K. (1952). *Acta Cryst.* **5**, 599–604.
- OKI, H. & YONEDA, H. (1981). *Inorg. Chem.* **2**, 3875–3879.
- SAKURAI, T. & KOBAYASHI, K. (1979). *Rikagaku Kenkyusho Hokoku*, **55**, 69–77.
- SAKURAI, T., TSUBOYAMA, S. & TSUBOYAMA, K. (1980). *Acta Cryst.* **B36**, 1797–1801.
- TSUBOYAMA, S., SAKURAI, T. & TSUBOYAMA, K. (1987). *J. Chem. Soc. Dalton Trans.* pp. 721–727.
- TSUBOYAMA, S., TSUBOYAMA, K. & SAKURAI, T. (1989). *Acta Cryst.* **C45**, 669–672.

Acta Cryst. (1989). **C45**, 876–879

(8,9,10-Trinorbornadiene)[1,2,3-tris(diphenylphosphino)propane]rhodium Hexafluorophosphate

BY F. BACHECHI

Istituto di Strutturistica Chimica, CNR, Area della Ricerca di Roma, CP 10, 00016 Monterotondo St, Roma, Italy

AND J. OTT AND L. M. VENANZI

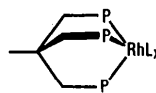
Laboratorium für Anorganische Chemie, ETH-Zentrum, CH-8092 Zürich, Switzerland

(Received 2 February 1988; accepted 28 November 1988)

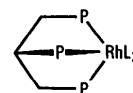
Abstract. [Rh(C₇H₈)((C₆H₅)₂PCH{CH₂P(C₆H₅)₂})₂]-[PF₆], C₄₆H₄₃F₆P₄Rh, *M_r* = 936.6, monoclinic, *P*2₁/*n*, *a* = 18.241 (7), *b* = 10.512 (5), *c* = 21.995 (7) Å, β = 104.43 (6)°, *V* = 4085 (3) Å³, *Z* = 4, *D_x* = 1.523 g cm⁻³, λ(Mo *K*α) = 0.71073 Å, μ = 6.2 cm⁻¹, *F*(000) = 1909, *T* = 293 K, *R* = 0.056 for 4512 observed reflections. The Rh atom is pentacoordinated by the P atoms of the triphosphine ligand 1,2,3-tris(diphenylphosphino)propane, C₃triphos, and by the midpoints of the coordinated double bonds of the 8,9,10-trinorbornadiene ligand, nbd. The metal coordination sphere is essentially a trigonal bipyramid with one olefinic residue in axial position and the other in equatorial position.

Introduction. In the course of an investigation on rhodium complexes with the tripod-like tridentate ligand H₃CC(CH₂PPh₂)₃, triphos, the new tripod-like ligand Ph₂PCH(CH₂PPh₂)₂, C₃triphos, was synthesized in order to study whether changes in the triphos geometry could affect the properties of triphos complexes (Ott, 1986).

The main difference between the two ligands is in the lack of a methylene group in C₃triphos, so that, on coordination to a metal centre, C₃triphos forms a rigid backbone consisting of two five- and one six-membered rings.



triphos = H₃CC(CH₂PPh₂)₃



C₃triphos = Ph₂PCH(CH₂PPh₂)₂

As in triphos, the structure of this ligand only allows small variations of the P–M–P angles from the ideal values of 90°, so that some facial coordination geometries can be obtained only with strong distortions.

The present work deals with the first structure of a complex containing the C₃triphos ligand.

Experimental. Crystals were obtained from CH₃CN/CH₃CH₂OH solution; Nicolet R3 four-circle diffractometer; graphite-monochromatized Mo *K*α radiation;

Table 1. Atomic coordinates and equivalent isotropic thermal parameters with their e.s.d.'s in parentheses

	x	y	z	$U_{eq}(\text{\AA}^2)$
Rh1	0.04531 (3)	0.03812 (5)	0.31446 (3)	0.0273 (2)
P(1)	0.0554 (1)	0.2124 (2)	0.3834 (1)	0.031 (1)
P(2)	0.1454 (1)	0.1366 (2)	0.2845 (1)	0.032 (1)
P(3)	0.0322 (1)	0.1764 (2)	0.2455 (1)	0.032 (1)
C(1)	0.0661 (5)	0.3397 (7)	0.3272 (4)	0.036 (3)
C(2)	0.1351 (5)	0.3083 (8)	0.2984 (4)	0.039 (3)
C(3)	-0.0082 (5)	0.3391 (8)	0.2763 (4)	0.042 (3)
C(6)	0.1307 (4)	0.2332 (8)	0.4549 (4)	0.04 (13)
C(7)	0.1871 (5)	0.3247 (9)	0.4626 (4)	0.04 (16)
C(8)	0.2433 (6)	0.3295 (10)	0.5190 (5)	0.06 (20)
C(9)	0.2443 (6)	0.2438 (11)	0.5648 (5)	0.06 (22)
C(10)	0.1885 (6)	0.1539 (10)	0.5586 (5)	0.06 (21)
C(11)	0.1313 (5)	0.1475 (9)	0.5031 (4)	0.05 (16)
C(12)	0.0249 (5)	0.2626 (8)	0.4127 (4)	0.04 (14)
C(13)	0.0786 (5)	0.1759 (9)	0.4204 (5)	0.05 (18)
C(14)	-0.1406 (6)	0.2136 (11)	0.4424 (5)	0.07 (23)
C(15)	0.1492 (6)	0.3376 (11)	0.4562 (5)	0.06 (22)
C(16)	-0.0966 (6)	0.4270 (10)	0.4495 (5)	0.06 (22)
C(17)	-0.0340 (5)	0.3901 (9)	0.4275 (4)	0.05 (18)
C(18)	0.2420 (4)	0.1030 (8)	0.3305 (3)	0.03 (13)
C(19)	0.2527 (5)	0.0630 (8)	0.3922 (4)	0.04 (15)
C(20)	0.3257 (6)	0.0424 (10)	0.4290 (5)	0.06 (18)
C(21)	0.3867 (6)	0.0626 (10)	0.4047 (5)	0.06 (19)
C(22)	0.3771 (6)	0.0981 (11)	0.3433 (5)	0.06 (21)
C(23)	0.3035 (5)	0.1203 (9)	0.3054 (4)	0.05 (17)
C(24)	0.1575 (4)	0.1181 (7)	0.2056 (4)	0.03 (13)
C(25)	0.1647 (5)	0.2178 (10)	0.1657 (5)	0.05 (18)
C(26)	0.1743 (7)	0.1900 (12)	0.1062 (6)	0.07 (24)
C(27)	0.1780 (6)	0.0676 (10)	0.0869 (5)	0.06 (22)
C(28)	0.1723 (5)	-0.0314 (10)	0.1258 (4)	0.06 (18)
C(29)	0.1606 (5)	-0.0076 (8)	0.1846 (4)	0.04 (17)
C(30)	-0.0296 (5)	0.1832 (8)	0.1627 (4)	0.04 (14)
C(31)	0.0440 (5)	0.2956 (9)	0.1290 (4)	0.05 (16)
C(32)	0.0470 (5)	0.2960 (9)	0.0650 (4)	0.05 (18)
C(33)	-0.0361 (6)	0.1833 (10)	0.0354 (5)	0.06 (20)
C(34)	-0.0241 (6)	0.0718 (10)	0.0688 (5)	0.06 (20)
C(35)	0.0182 (5)	0.0703 (8)	0.1330 (4)	0.05 (17)
C(36)	-0.1347 (5)	0.1544 (8)	0.2372 (4)	0.04 (15)
C(37)	-0.1750 (8)	0.2241 (13)	0.2690 (6)	0.08 (28)
C(38)	-0.2530 (11)	0.1946 (18)	0.2610 (8)	0.11 (42)
C(39)	-0.2868 (10)	0.0993 (16)	0.2232 (7)	0.10 (35)
C(40)	-0.2442 (7)	0.0300 (13)	0.1911 (6)	0.08 (26)
C(41)	0.1680 (6)	0.0566 (10)	0.1988 (5)	0.06 (20)
C(42)	0.0479 (7)	-0.2333 (11)	0.2987 (5)	0.067 (5)
C(43)	-0.0139 (6)	-0.1373 (10)	0.2744 (5)	0.053 (4)
C(44)	-0.0398 (5)	-0.0964 (8)	0.3276 (4)	0.044 (3)
C(45)	-0.0098 (6)	-0.1681 (10)	0.3824 (4)	0.059 (4)
C(46)	0.0859 (6)	-0.1089 (9)	0.3889 (5)	0.055 (4)
C(47)	0.1094 (5)	-0.1464 (8)	0.3360 (4)	0.045 (3)
C(48)	0.0213 (7)	-0.2990 (9)	0.3507 (5)	0.065 (4)
P(4)	0.1136 (2)	0.3134 (3)	0.9002 (2)	0.055 (1)
F(1)	0.0416 (5)	0.2248 (9)	0.8857 (5)	0.122 (5)
F(2)	0.1791 (5)	0.4091 (11)	0.9080 (6)	0.154 (6)
F(3)	0.0709 (6)	0.3850 (10)	0.8382 (4)	0.129 (5)
F(4)	0.1519 (5)	0.2228 (9)	0.8609 (4)	0.113 (4)
F(5)	0.0730 (5)	0.4032 (9)	0.9380 (5)	0.117 (4)
F(6)	0.1532 (7)	0.2451 (12)	0.9588 (4)	0.180 (6)

$$U_{eq} = (1/6\pi^2) \sum_i \sum_j \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j$$

crystal size 0.30 × 0.15 × 0.35 mm; unit-cell dimensions determined with 15 reflections ($20 \leq 2\theta \leq 26^\circ$); 10 600 reflections measured in the range $3 \leq 2\theta \leq 60^\circ$, $h = 0$ to 20, $k = 0$ to 11, $l = -22$ to 22; 4512 reflections with $I \geq 3\sigma(I)$ considered observed; ω -scan mode, with scan rate depending on the intensities. Three standards measured every 100 reflections, no significant change; data processed to yield values of I and $\sigma(I)$ (Bachechi, Zambonelli & Marcotrigiano, 1977); in the estimation of $\sigma(I)$ the uncertainty factor was $p = 0.028$ as calculated from the variance of the standard reflections (McCandlish, Stout & Andrews, 1975). Corrections for Lorentz and polarization. An empirical absorption correction applied using ψ scans of reflections at χ

angles about 90° ; minimum normalized transmission factors in the range 0.66–0.70. Structure solved by Patterson and Fourier methods and refined by full-matrix least-squares procedures, function $\sum w(|F_o| - |F_c|)^2$ with $w = 4F_o^2/\sigma^2(F_o^2)$ minimized. Heavier atoms, except the C atoms of the phenyl rings, with anisotropic thermal parameters and H atoms, at calculated positions, with fixed coordinates and isotropic thermal parameters (270 parameters refined). Convergence at $R = 0.056$ ($wR = 0.074$, $S = 0.28$). $(\Delta/\sigma)_{\max} = 0.04$; final difference map with $\Delta\rho$ in the range $\pm 0.30 \text{ e \AA}^{-3}$. All calculations performed on the Data General Eclipse MV8000II computer using local programs (Cerrini & Spagna, 1977). Scattering factors from *International Tables for X-ray Crystallography* (1974). Final atomic parameters of the non-hydrogen atoms are given in Table 1.*

Discussion. The crystal structure consists of discrete $[\text{Rh}(\text{nbd})(\text{C}_3\text{triphos})]^+$ (nbd = norbornadiene) cations and $[\text{PF}_6]^-$ anions with no short contacts between atoms of different ions.

A perspective view of the cationic complex is shown in Fig. 1. Table 2 lists a selection of intramolecular distances and angles with their standard deviations.

The Rh atom is five-coordinated by the three P atoms of the $\text{C}_3\text{triphos}$ ligand and by the double bonds of the chelating norbornadiene ligand. The geometry of the inner coordination sphere of the cationic complex is

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters and another view of the molecule have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51647 (27 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

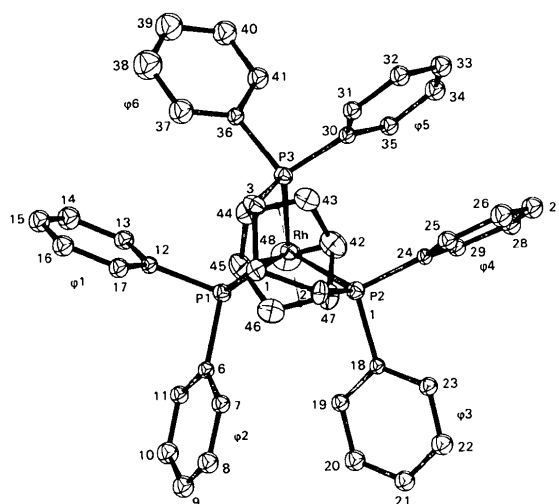


Fig. 1. Perspective view of the complex cation $[\text{Rh}(\text{nbd})(\text{C}_3\text{triphos})]^+$ along the pseudo- C_3 axis. The ellipsoids represent 30% probability.

Table 2. Selected bond lengths (Å) and angles (°)

MP(1) is the midpoint of the C(43)–C(44) double bond and *MP*(2) is the midpoint of the C(46)–C(47) double bond.

Rh–P(1)	2.357 (2)	P(2)–C(24)	1.815 (8)
Rh–P(2)	2.332 (2)	P(3)–C(3)	1.851 (9)
Rh–P(3)	2.311 (2)	P(3)–C(30)	1.836 (9)
Rh– <i>MP</i> (1)	2.068 (13)	P(3)–C(36)	1.847 (9)
Rh– <i>MP</i> (2)	2.135 (12)	C(1)–C(2)	1.578 (11)
Rh–C(43)	2.206 (11)	C(1)–C(3)	1.528 (14)
Rh–C(44)	2.171 (9)	C(42)–C(43)	1.508 (17)
Rh–C(46)	2.239 (11)	C(42)–C(48)	1.515 (18)
Rh–C(47)	2.253 (9)	C(43)–C(44)	1.432 (13)
P(1)–C(1)	1.865 (8)	C(44)–C(45)	1.516 (15)
P(1)–C(6)	1.824 (9)	C(45)–C(46)	1.495 (16)
P(1)–C(12)	1.819 (8)	C(45)–C(48)	1.581 (14)
P(2)–C(2)	1.849 (8)	C(46)–C(47)	1.392 (13)
P(2)–C(18)	1.835 (9)	C(47)–C(42)	1.520 (16)
P(1)–Rh–P(2)	84.0 (1)	Rh–P(3)–C(3)	106.9 (3)
P(1)–Rh–P(3)	82.6 (1)	Rh–P(3)–C(30)	120.9 (3)
P(1)–Rh– <i>MP</i> (1)	130.5 (4)	Rh–P(3)–C(36)	115.1 (3)
P(1)–Rh– <i>MP</i> (2)	111.3 (4)	C(3)–P(3)–C(30)	105.3 (4)
P(2)–Rh–P(3)	85.9 (1)	C(3)–P(3)–C(36)	107.1 (4)
P(2)–Rh– <i>MP</i> (1)	145.5 (4)	C(30)–P(3)–C(36)	100.5 (4)
P(2)–Rh– <i>MP</i> (2)	102.5 (4)	P(1)–C(1)–C(2)	110.0 (6)
P(3)–Rh– <i>MP</i> (1)	97.9 (4)	P(1)–C(1)–C(3)	105.3 (5)
P(3)–Rh– <i>MP</i> (2)	164.3 (4)	P(2)–C(2)–C(1)	113.3 (5)
<i>MP</i> (1)–Rh– <i>MP</i> (2)	67.6 (5)	P(3)–C(3)–C(1)	111.0 (6)
Rh–P(1)–C(1)	97.8 (3)	C(2)–C(1)–C(3)	110.7 (7)
Rh–P(1)–C(6)	124.7 (3)	C(42)–C(43)–C(44)	106.4 (9)
Rh–P(1)–C(12)	120.9 (3)	C(43)–C(44)–C(45)	104.3 (8)
C(1)–P(1)–C(6)	107.7 (4)	C(44)–C(45)–C(46)	103.0 (8)
C(1)–P(1)–C(12)	104.7 (4)	C(44)–C(45)–C(48)	101.5 (9)
C(6)–P(1)–C(12)	99.2 (4)	C(46)–C(45)–C(48)	100.5 (8)
Rh–P(2)–C(2)	105.5 (3)	C(45)–C(46)–C(47)	105.9 (9)
Rh–P(2)–C(18)	118.1 (3)	C(45)–C(48)–C(42)	92.3 (8)
Rh–P(2)–C(24)	120.9 (3)	C(46)–C(47)–C(42)	106.4 (8)
C(2)–P(2)–C(18)	102.7 (4)	C(47)–C(42)–C(43)	100.0 (8)
C(2)–P(2)–C(24)	107.7 (4)	C(47)–C(42)–C(48)	101.5 (8)
C(18)–P(2)–C(24)	100.3 (4)	C(48)–C(42)–C(43)	100.7 (9)

illustrated in Fig. 2. The arrangement around the Rh atom can be regarded as trigonal bipyramidal with P(1), P(2) and one of the olefinic double bonds occupying equatorial positions, while P(3) and the other olefinic double bond lie in axial positions.

The trigonal-bipyramidal geometry is severely distorted because of the steric requirements of both ligands. The C₃triphos ligand presents P–Rh–P angles of 82.6 (1), 84.0 (1) and 85.9 (1)°, while the nbd ligand has a bite angle, *MP*(1)–Rh–*MP*(2),* of only 68°.

The Rh–C distances are within the range expected. The distances from the Rh to the equatorial olefin C atoms [2.171 (9) and 2.206 (11) Å] are shorter than those to the axial olefin C atoms [2.239 (11) and 2.253 (9) Å]. Accordingly, the equatorial C=C distance [1.432 (13) Å] is longer than the axial C=C distance [1.392 (13) Å]. The difference between the axial and the equatorial distances fits a pattern observed in other pentacoordinate Rh- and Ir-diene complexes (Churchill & Lin, 1974; Hughes, Krishnanachari, Loch, Powell & Turner, 1977). In the related complex [Rh(nbd)(triphos)]⁺ (Bachechi, Ott & Venanzi, 1989) the coordination geometry of the Rh atom can be described as square-pyramidal with both midpoints of

the olefinic double bonds approximately in the equatorial plane. The distances from the metal to the midpoints of the coordinated double bonds [2.055 (9) and 2.115 (9) Å] are comparable with those in the C₃triphos complex [2.068 (13) and 2.135 (12) Å], but the C=C bond lengths do not present a sensible lengthening on coordination [1.334 (13) Å].

A common feature between the two complexes, which is related to the tripod-like geometry of the two triphosphine ligands, is that the nbd ligand can accommodate in the coordination sphere of the Rh-triphosphine unit only with the coordinated double bonds lying in a plane parallel to that passing through the three P atoms. A 90° rotation of the diene ligand around the Rh–C(48) direction, which maintains the two C=C bonds in the same plane, theoretically allows an interconversion from a square-pyramidal to a trigonal-bipyramidal coordination geometry and *vice versa* in both complexes, but this is actually prevented by short contacts between the H atoms of the nbd ligand and those of the phenyl rings of the triphosphine ligands.

Although the two ligands differ substantially in only one methylene group, C₃triphos seems more flexible and allows the P–Rh–P angles to close towards the axial P atom [82.6 (1), 84.0 (1) and 85.9 (1)°] so that the nbd ligand can coordinate according to a trigonal-bipyramidal geometry.

Bond distances and angles within the nbd ligand are normal. The C–C bond distances average to 1.52 Å. The bond angles of the type C(sp²)–C(sp²)–C(sp³)

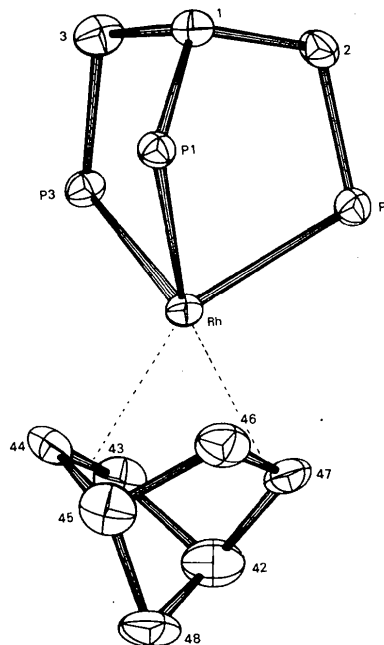


Fig. 2. Inner coordination sphere of the Rh atom. The ellipsoids represent 30% probability.

* *MP*(1) is the midpoint of C(43)–C(44) and *MP*(2) is the midpoint of C(46)–C(47).

average to 105.8° , those centred at the bridgehead C atoms average to 101.5° , and the angle centred at the carbon atom of the bridging apex, *i.e.* C(42)–C(48)–C(45), is $92.3(8)^\circ$.

The Rh–P bond distances are significantly different from one another [Rh–P(1) = $2.357(2)$, Rh–P(2) = $2.332(2)$, Rh–P(3) = $2.311(2)$ Å] and fall in the middle to high part of the Rh–P range generally observed in tertiary phosphine complexes of Rh^I.

Dimensions in the C₃triphos ligand are normal. Deviations from an ideal geometry are present in the bond angles and mainly resemble those observed for the triphos ligand in the [Rh(nbd)(triphos)]⁺ complex except for the Rh–P–C_{alkyl} angles which average 103.4° , while they average 110.0° in the triphos complex.

The relative orientations of the phenyl groups are shown in Fig. 1. The phenyl rings φ_4 and φ_5 are roughly parallel [the dihedral angle between their planes is $14.6(3)^\circ$] and give rise to a graphite-like interaction (about 3° Å spacing). This type of non-bonded interaction, which tends to occur between phenyl groups in phenylphosphines (Tolman, 1977), can only be established between φ_4 and φ_5 because they are 1,3-axial substituents in the basal part of the boat-like six-membered ring Rh–P(2)–C(2)–C(3)–P(3) (scheme, Fig. 2). The other phenyl rings, even if free to rotate, could not interact similarly: φ_1 and φ_6 are 1,3-axial substituents in the five-membered ring Rh–P(1)–C(1)–C(3)–P(3) in a twist conformation with P(1) and

C(1) at the maximum puckering; φ_2 is axial and φ_3 is bisectonal in the five-membered ring Rh–P(1)–C(1)–C(2)–P(2) in an envelope conformation with P(1) at the tip (scheme, Fig. 2). A graphite-like interaction is also observed in the triphos complex [IrCl(CO)(triphos)] (Bachechi, Janser & Venanzi, 1985).

The bond lengths and angles in the PF₆⁻ anion are normal with P–F bond lengths between 1.55 and 1.59 Å and F–P–F angles between 88 and 92° (Lang & Hope, 1976).

References

- BACHECHI, F., JANSER, P. & VENANZI, L. M. (1985). *J. Organomet. Chem.* **296**, 229–242.
 BACHECHI, F., OTT, J. V. & VENANZI, L. M. (1989). *Acta Cryst.* **C45**, 724–728.
 BACHECHI, F., ZAMBONELLI, L. & MARCOTRIGIANO, G. (1977). *J. Cryst. Mol. Struct.* **7**, 11–20.
 CERRINI, S. & SPAGNA, R. (1977). Abstr. 4th Eur. Crystallogr. Meet., Oxford, England, p. 7.
 CHURCHILL, M. R. & LIN, K. G. (1974). *J. Am. Chem. Soc.* **96**, 76–80.
 HUGHES, R. P., KRISHMANACHARI, N., LOCK, C. J. L., POWELL, J. & TURNER, G. (1977). *Inorg. Chem.* **16**, 314–319.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
 LANG, M. & HOPE, L. (1976). *Acta Cryst.* **B32**, 1547–1550.
 MCCANDLISH, L. E., STOUT, G. H. & ANDREWS, L. C. (1975). *Acta Cryst.* **A31**, 245–249.
 OTT, J. (1986). PhD Thesis. ETH Zentrum, Zürich, Switzerland.
 TOLMAN, C. A. (1977). *Chem. Rev.* **77**, 314–348.

Acta Cryst. (1989). **C45**, 879–882

Bis{4-(*n*-heptyloxy)-*N*-[*p*-(*n*-hexyloxy)phenyl]salicylideneaminato}palladium(II)

BY P. IANNELLI AND A. IMMIRZI

Dipartimento di Fisica, Università di Salerno, I-84100 Salerno, Italy

AND U. CARUSO, A. ROVIELLO AND A. SIRIGU

Dipartimento di Chimica, Università di Napoli, Via Mezzocannone 4, I-80134 Napoli, Italy

(Received 19 September 1988; accepted 19 December 1988)

Abstract. [Pd(C₂₆H₃₆NO₃)₂] (*M_r* = 927.6) is a tetra-coordinate square-planar complex of Pd^{II}, with a salicylideneaminato bidentate ligand (*L*) having two long-chain substituents, which displays thermotropic behaviour. [Pd^{II}(*L*)₂] is *trans* square planar with C₂ molecular symmetry in the crystalline state. Crystals are monoclinic, *P*2₁/*a*, *a* = 5.961 (5), *b* = 15.018 (4), *c* = 27.881 (7) Å, β = 94.80 (4)°, *V* = 2487 (2) Å³, *Z* = 2, *D_m*(floatation) = 1.25 (5), *D_x* = 1.237 g cm⁻³, λ(Cu Kα) = 1.54178 Å, μ = 35.3 cm⁻¹, *F*(000) = 984,

T = 298 K, *R* = 0.065 for 3737 observed independent reflections. The molecule has a flattened shape with the long-chain substituents in zigzag planar conformation roughly parallel to each other. The dihedral angle between the planar salicylideneaminato group and the *N*-bonded phenyl group is 62 (2)°.

Introduction. The study of the relationships between molecular structure and liquid-crystal properties of organic compounds is based on the crystal struc-