

[4-(Diphenylphosphino)-9,9-dimethylxanthen-5-yl]-diphenylphosphine oxide toluene hemisolvate

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Key indicators

Single-crystal X-ray study

T = 150 K

Mean $\sigma(\text{C}-\text{C}) = 0.005 \text{ \AA}$

H-atom completeness 99%

Disorder in solvent or counterion

R factor = 0.058

wR factor = 0.168

Data-to-parameter ratio = 13.7

For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

In the title compound, $\text{C}_{39}\text{H}_{32}\text{O}_2\text{P}_2 \cdot 0.5\text{C}_7\text{H}_8$, there are two distinct phosphorus centers. The P—C bond lengths around the diphenylphosphino group are around 0.04 Å larger than those in the phosphine oxide moiety. This corresponds to smaller C—P—C bond angles of 101.2 (15)° compared to 108.4 (9)° for the latter. The rigid dibenzopyran backbone is folded at an angle of 158.9 (1)°.

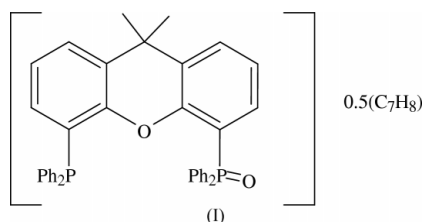
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Comment

The title structure, (I), is similar to the bis(diphenylphosphino) derivative, (II) (Hillebrand *et al.*, 1995; Kranenburg *et al.*, 1995), and the bis(methylphenylphosphine) oxide compound (Hamada *et al.*, 1997). The atoms in the xanthane backbone of (I) do not have the symmetry associated with (II), but are folded at a similar angle, 158.9 (1)° [*cf.* 156.6° in (II)], due to the steric congestion between the diphenylphosphine groups and the xanthane unit.



The geometry around each P atom is distinct due to the different oxidation states: the P—C bond distances [mean 1.802 (11) Å] around P1, formally P^V, are shorter than those at P2 [P^{III}; mean 1.843 (6) Å]. The C—P1—C bond angles tend towards tetrahedral [average 108.4 (9)°] whilst the corresponding ones around P2 are more acute [average 101.2 (15)°].

The lone pair and oxide group on the P atoms in (I) have an in-out orientation, whereas in (II), the lone pairs point towards each other (in-in), so that only a small adjustment is required for metal chelation (Kranenburg *et al.*, 1995). This can be correlated with the distance between the P atoms which increases from 4.045 (1) Å in (II) to 4.693 (2) Å in (I).

The asymmetry of the ligand is also shown by the C—C—P angles at the substituted C atoms of the xanthane unit, namely C2 and C8. In (I), the angle deformation is again dependent on the nature of the phosphine; thus, those around C2 are 113.4 (2) and 129.2 (2)° (for P1), whilst around C8 are 120.9 (2) and 121.6 (2)° (for P2). In the (more) symmetric ligand (II), the C—C—P angles are 118.4 (2) and 125.1 (3)°, *i.e.* the reverse situation is present.

Experimental

The title compound was obtained as a by-product in the attempted synthesis of (xantphos)nickel dicyanide. Colorless crystals were obtained by recrystallization from toluene of a solution containing styrene and cyclooctadiene.

Crystal data

$C_{39}H_{32}O_2P_2 \cdot 0.5C_7H_8$
 $M_r = 640.15$
 Triclinic, $P\bar{1}$
 $a = 10.7700$ (11) Å
 $b = 11.1547$ (11) Å
 $c = 15.941$ (3) Å
 $\alpha = 91.088$ (11)°
 $\beta = 102.471$ (11)°
 $\gamma = 116.993$ (7)°
 $V = 1651.1$ (4) Å³

$Z = 2$
 $D_x = 1.288$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 25 reflections
 $\theta = 9.9$ – 13.9 °
 $\mu = 0.17$ mm⁻¹
 $T = 150$ (2) K
 Wedge, colorless
 $0.40 \times 0.28 \times 0.18$ mm

Data collection

Nonius CAD-4 diffractometer
 ω scans
 6185 measured reflections
 5855 independent reflections
 4099 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.053$
 $\theta_{max} = 25.1$ °

$h = -12 \rightarrow 11$
 $k = 0 \rightarrow 13$
 $l = -18 \rightarrow 18$
 3 standard reflections
 frequency: 60 min
 intensity decay: <1%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.058$
 $wR(F^2) = 0.168$
 $S = 1.01$
 5855 reflections
 427 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0952P)^2 + 0.4293P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} < 0.001$
 $\Delta\rho_{max} = 0.51$ e Å⁻³
 $\Delta\rho_{min} = -0.46$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

P1–O2	1.488 (2)	P2–C8	1.848 (3)
P1–C2	1.809 (3)	P2–C25	1.844 (3)
P1–C13	1.790 (3)	P2–C31	1.837 (3)
P1–C19	1.808 (3)		
O2–P1–C2	110.04 (14)	C31–P2–C8	100.80 (15)
O2–P1–C13	111.59 (14)	C31–P2–C25	102.83 (15)
O2–P1–C19	110.03 (14)	C1–C2–P1	129.2 (2)
C13–P1–C2	107.61 (14)	C3–C2–P1	113.4 (2)
C19–P1–C2	109.31 (15)	C7–C8–P2	120.9 (2)
C13–P1–C19	108.21 (15)	C9–C8–P2	121.6 (2)
C25–P2–C8	99.94 (14)		

Aromatic H atoms were constrained and allowed to ride on their C atoms with $U_{iso}(H) = 1.2U_{eq}(C)$. The methyl H atoms were constrained to an ideal geometry with $U_{iso}(H) = 1.5U_{eq}(C)$, and allowed to rotate freely about the C–C bonds. The toluene solvent was located near an inversion centre, so the methyl group was disordered over two sites, and refined with a site-occupancy factor of 50%. The H atom, at the same position as the disordered methyl group, was not refined.

Data collection: locally modified *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *SET4* (de Boer & Duisenberg, 1984); data

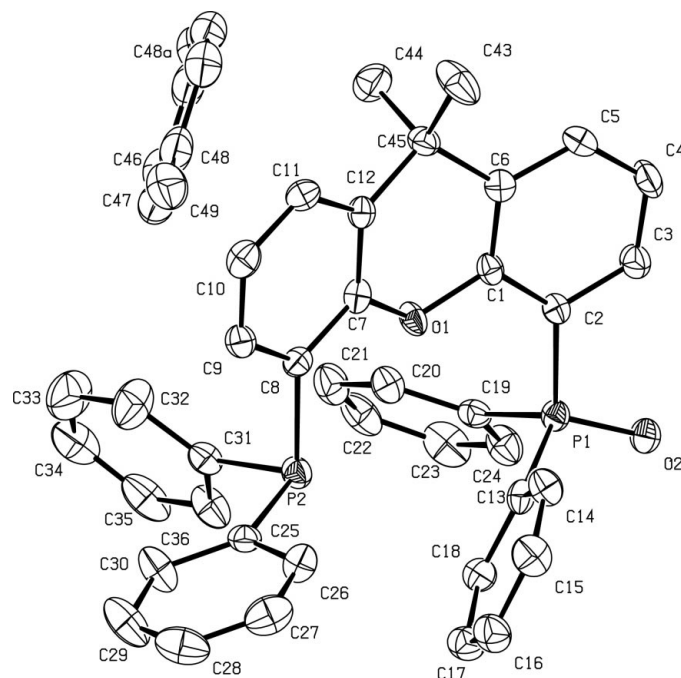


Figure 1

PLATON/ORTEP representation (Spek, 2000) of (I) with displacement ellipsoids at 50% probability level. H atoms have been omitted for clarity.

reduction: *HELENA* (Spek, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2000); software used to prepare material for publication: *PLATON* (Spek, 2000).

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