

Methyl 3-[4,6-bis(diphenylphosphino)-phenoxazin-10-yl]propionate

Stefan Ricken, Piotr W. Osinski,
Markus Schürmann, Hans Preut*
and Peter EilbrachtFachbereich Chemie, Universität Dortmund,
Otto-Hahn-Strasse 6, 44221 Dortmund,
GermanyCorrespondence e-mail:
uch002@uxp1.hrz.uni-dortmund.de

Key indicators

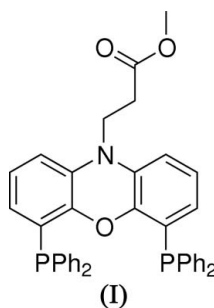
Single-crystal X-ray study
 $T = 291\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.006\text{ \AA}$
Disorder in main residue
 R factor = 0.038
 wR factor = 0.088
Data-to-parameter ratio = 14.3For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

In the title compound, $\text{C}_{40}\text{H}_{33}\text{NO}_3\text{P}_2$, used as a nixantphos-type ligand in homogeneous catalysis, the central phenoxazine ring system is nearly planar. The most important feature of the molecule is the intramolecular $\text{P}\cdots\text{P}$ distance of 4.2346 (13) Å. The angles involving the P atoms are in the range 100.90 (13)–103.40 (16)°.

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Comment

The title compound, (I), is a diphosphine ligand used for highly regioselective hydroformylation reactions. The hydroformylation reaction, the most important homogeneously catalysed reaction, produces a mixture of linear and branched aldehydes from olefins, carbon monoxide and hydrogen (Claver & van Leeuwen, 2000). In order to achieve high selectivity towards the formation of one product, appropriate ligands have to be employed. Van Leeuwen has pioneered the use of xanthene- and phenoxazine-based diphosphine ligands (Kranenburg *et al.*, 1995; van der Veen *et al.*, 1998), which give extremely regioselective rhodium catalysts that produce linear aldehydes.



As part of our investigation aimed at evaluating different attachment routes by connecting a polymer with the nitrogen anchor in the nixantphos ligand, the title new ligand was prepared from nixantphos with methyl acrylate to give the corresponding product of the Michael addition. According to preliminary results, this compound was found to be superior over nixantphos as a ligand with regard to *n*-selectivity in the hydroformylation reaction of 1-octene (Ricken *et al.*, 2006). It was believed that the crystal structure determination of this compound might allow for the determination of important ligand factors, such as the cone angle and the flexibility range of the natural bite angle (Claver & van Leeuwen, 2000). The structural analysis reveals the $\text{P}\cdots\text{P}$ distance to be 4.2346 (13) Å, longer than in xantphos (4.080 Å; Kranenburg *et al.*, 1995); the resulting wider bite angle in the corresponding chelate is supposed to affect the selectivity of the catalyst.

Experimental

To a stirred suspension of 2.5 g of nixantphos (4.54 mmol) and 8 ml of methyl acrylate (97 mmol, 21 equivalents) a solution of 0.2 g of NBu_4Br (0.62 mmol) and 40 mg of NaOMe (0.7 mmol, 16%) in 2 ml of methanol was added through a syringe. The mixture was heated and stirred under reflux for 2 h. After that, thin-layer chromatography showed very little substrate left (cyclohexane/acetone, 4:1 v/v). Water (50 ml) was added and the mixture was extracted with 3×20 ml of dichloromethane. The combined organic phases were dried over MgSO_4 , filtered, evaporated, and dried with an oil pump. Crystallization (dichloromethane/ethanol, 1:1 to 1:10 v/v) yielded 1.81 g (62%) of pale-yellow crystals (m.p. 477–478 K). MS (FAB + LR): m/z (%) = 638 (M^+), (1/5); exact mass (FAB + HR): 637.1968 (M^+); calculated for $\text{C}_{40}\text{H}_{33}\text{O}_3\text{NP}_2$: 637.1936. Elemental analysis found: C 74.8, H 5.2, N 2.1%; $\text{C}_{42}\text{H}_{38}\text{O}_3\text{NP}_2$ requires: C 75.3, H 5.2, N 2.2%.

Crystal data

$\text{C}_{40}\text{H}_{33}\text{NO}_3\text{P}_2$	$V = 1669.5 (5) \text{ \AA}^3$
$M_r = 637.61$	$Z = 2$
Triclinic, $P\bar{1}$	$D_x = 1.268 \text{ Mg m}^{-3}$
$a = 10.431 (2) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 11.354 (2) \text{ \AA}$	$\mu = 0.17 \text{ mm}^{-1}$
$c = 15.337 (3) \text{ \AA}$	$T = 291 (1) \text{ K}$
$\alpha = 68.961 (6)^\circ$	Plate, pale yellow
$\beta = 84.619 (10)^\circ$	$0.26 \times 0.16 \times 0.08 \text{ mm}$
$\gamma = 80.182 (9)^\circ$	

Data collection

Nonius KappaCCD diffractometer	6052 independent reflections
ω scans	2007 reflections with $I > 2\sigma(I)$
Absorption correction: none	$R_{\text{int}} = 0.033$
21372 measured reflections	$\theta_{\text{max}} = 25.4^\circ$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.038$	$w = [\exp(4.2(\sin\theta/\lambda)^2)]/[\sigma^2(F_o^2)]$
$wR(F^2) = 0.088$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.01$	$\Delta\rho_{\text{max}} = 0.22 \text{ e \AA}^{-3}$
6052 reflections	$\Delta\rho_{\text{min}} = -0.15 \text{ e \AA}^{-3}$
424 parameters	

H atoms were placed in calculated positions, with C–H = 0.93–0.97 Å, and were refined as riding, with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for methyl groups and $1.2U_{\text{eq}}(\text{C})$ for others; the methyl groups were allowed to rotate but not to tip. Atom O3 is disordered over two positions with occupancies of 0.50.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO/SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO/SCALEPACK*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL-Plus*

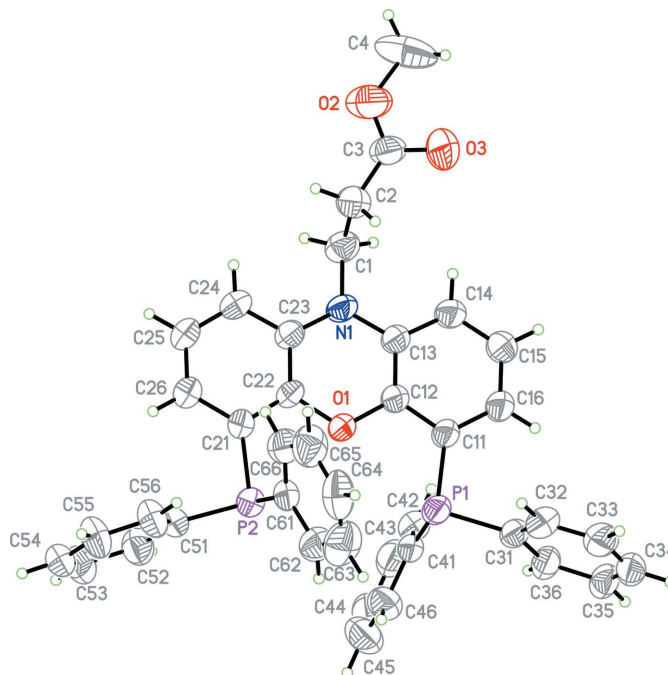


Figure 1

The molecular structure of the title compound, showing the labelling of all non-H atoms. Displacement ellipsoids are shown at the 30% probability level. Only one component of the disordered atom O3 is shown.

(Sheldrick, 1991); software used to prepare material for publication: *SHELXL97*, *PARST95* (Nardelli, 1995) and *PLATON* (Spek, 2003).

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