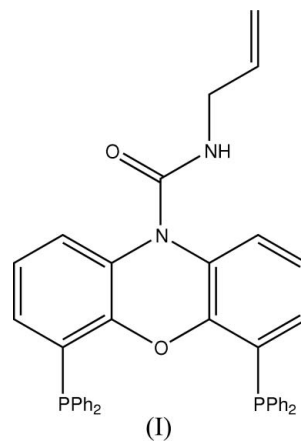


***N*-Allyl-4,6-bis(diphenylphosphino)phenoxazine-10-carboxamide****Stefan Ricken, Markus Schürmann, Hans Preut\* and Peter Eilbracht**Fachbereich Chemie, Universität Dortmund,  
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uch002@uxp1.hrz.uni-dortmund.de**Key indicators**Single-crystal X-ray study  
 $T = 291$  K  
Mean  $\sigma(\text{C}-\text{C}) = 0.003$  Å  
Disorder in main residue  
 $R$  factor = 0.044  
 $wR$  factor = 0.093  
Data-to-parameter ratio = 17.9For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.

In the title compound,  $\text{C}_{40}\text{H}_{32}\text{N}_2\text{O}_2\text{P}_2$ , used as a nixantphos-type ligand in homogeneous catalysis, the central phenoxazine ring system deviates markedly from planarity, the dihedral angle between the two halves being  $38.14(3)^\circ$ . The intramolecular  $\text{P} \cdots \text{P}$  distance is  $4.2400(7)$  Å.

Received 29 May 2006  
Accepted 30 May 2006**Comment**

The title compound, (I) (Fig. 1), is a diphosphine ligand used for highly regioselective hydroformylation reactions. Hydroformylation, the most important homogeneously catalysed industrial reaction, usually 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 and co-workers have 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 ongoing studies (Ricken, Osinski, Schürmann *et al.*, 2006) evaluating different attachment routes by connecting a polymer with the N-atom anchor in the nixantphos [ $\text{C}_{36}\text{H}_{27}\text{NOP}_2$ ; 4,6-bis(diphenyl-phosphino)phenoxazine] ligand, compound (I) with a functionalized alkyl side chain was prepared from nixantphos with allyl isocyanate to give the corresponding product of the addition. According to preliminary results, this compound was found to be a good ligand with regard to *n*-selectivity in the hydroformylation reaction of 1-octene (Ricken, Osinski, Eilbracht & Haag, 2006). A crystal structure determination of (I) has now been carried out for the determination of important structural parameters, such as the cone angle and the flexibility range of the natural bite

angle (Claver & van Leeuwen, 2000). It reveals the P...P distance in (I) to be 4.2400 (7) Å, hence a little larger than the value of 4.080 Å in xantphos [C<sub>39</sub>H<sub>32</sub>OP<sub>2</sub>; 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene; Kranenburg *et al.*, 1995]; the resulting wider bite angle in the corresponding chelate is supposed to affect the selectivity of the catalyst. The central phenoxazine ring system in (I) deviates markedly from planarity, the dihedral angle between the two halves (atoms C5–C10/N2/O2 and C11–C16/N2/O2) being 38.14 (3)°.

## Experimental

A mixture of nixantphos (0.5 g, 0.906 mmol) and allyl isocyanate (0.5 g, 6 mmol) in toluene was heated under reflux for 1 d under Ar. Next, the reaction mixture was stirred at room temperature for 6 h, the solvent was evaporated and the residue was purified by chromatography [from cyclohexane/dichloromethane (1:1) to dichloromethane] followed by crystallization from dichloromethane/ethanol (10:1 → 1:1 v/v). Yield 0.472 g (82%) of colourless crystals, m.p. 451–452 K.

### Crystal data

C <sub>40</sub> H <sub>32</sub> N <sub>2</sub> O <sub>2</sub> P <sub>2</sub>	$V = 1664.1 (2) \text{ \AA}^3$
$M_r = 634.62$	$Z = 2$
Triclinic, $P\bar{1}$	$D_x = 1.267 \text{ Mg m}^{-3}$
$a = 11.3740 (7) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 12.5567 (8) \text{ \AA}$	$\mu = 0.17 \text{ mm}^{-1}$
$c = 13.1164 (12) \text{ \AA}$	$T = 291 (1) \text{ K}$
$\alpha = 115.644 (4)^\circ$	Block, colourless
$\beta = 97.432 (5)^\circ$	$0.50 \times 0.30 \times 0.16 \text{ mm}$
$\gamma = 92.527 (4)^\circ$	

### Data collection

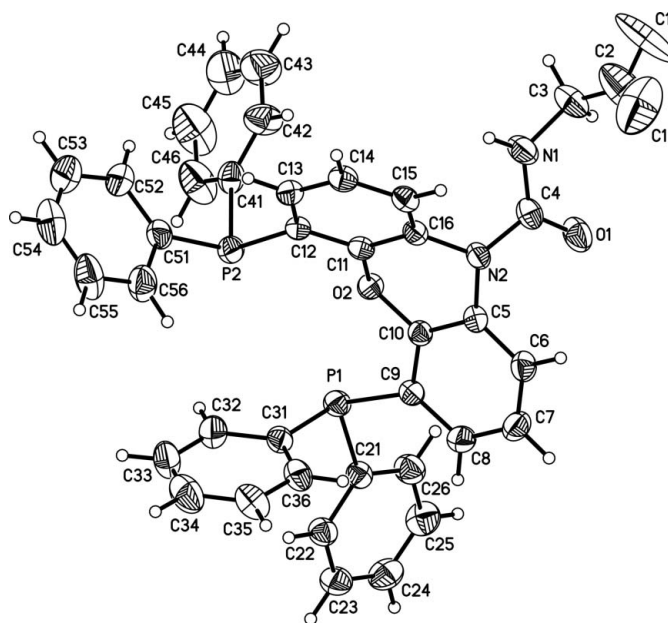
Nonius KappaCCD diffractometer	7593 independent reflections
$\omega$ scans	3761 reflections with $I > 2\sigma(I)$
Absorption correction: none	$R_{\text{int}} = 0.032$
26936 measured reflections	$\theta_{\text{max}} = 27.6^\circ$

### Refinement

Refinement on $F^2$	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.044$	$w = 1/[\sigma^2(F_o^2) + (0.0298P)^2]$
$wR(F^2) = 0.093$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.04$	$(\Delta/\sigma)_{\text{max}} = 0.002$
7593 reflections	$\Delta\rho_{\text{max}} = 0.29 \text{ e \AA}^{-3}$
424 parameters	$\Delta\rho_{\text{min}} = -0.25 \text{ e \AA}^{-3}$

H atoms were placed in calculated positions, with C–H = 0.93–0.97 Å and N–H = 0.86 Å, and were refined as riding, with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ . The position C1 is disordered over two positions with equal occupancies of 0.50. The displacement ellipsoids of the two components of C1 perhaps reflect further, unmodelled, disorder.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* and *SCALEPACK*; program(s) used to solve



**Figure 1**

The molecular structure of (I), with displacement ellipsoids shown at the 30% probability level (arbitrary spheres for the H atoms). Both components of the disordered =CH<sub>2</sub> group are shown; H atoms of this group have been omitted.

structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL-Plus* (Sheldrick, 1991); software used to prepare material for publication: *SHELXL97*, *PARST95* (Nardelli, 1995) and *PLATON* (Spek, 2003).

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