

10-(*tert*-Butyldimethylsilyl)-4,6-bis(diphenylphosphino)phenoxazinePiotr W. Osiński,<sup>a</sup> Markus Schürmann,<sup>a</sup> Hans Preut,<sup>a\*</sup> Rainer Haag<sup>b</sup> and Peter Eilbracht<sup>a</sup><sup>a</sup>Fachbereich Chemie, Universität Dortmund, Otto-Hahn-Strasse 6, 44221 Dortmund, Germany, and <sup>b</sup>Department of Chemistry, Freie Universität Berlin, Takustrasse 3, 14195 Berlin, GermanyCorrespondence e-mail:  
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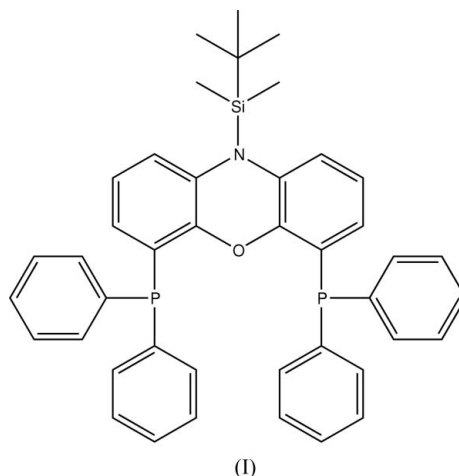
## Key indicators

Single-crystal X-ray study  
 $T = 291\text{ K}$   
Mean  $\sigma(\text{C}-\text{C}) = 0.005\text{ \AA}$   
 $R$  factor = 0.037  
 $wR$  factor = 0.079  
Data-to-parameter ratio = 15.1For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The title compound,  $\text{C}_{42}\text{H}_{41}\text{NOP}_2\text{Si}$ , used as a nixantphos-type ligand in homogeneous catalysis, crystallizes with one molecule in the asymmetric unit. The molecule has nearly mirror symmetry with N, O and Si on the pseudo-mirror plane, but it is not located on a crystallographic mirror plane. The most important feature of the molecule is the intramolecular P—P distance of 4.1453 (12) Å. The bond angles involving the P atoms are in the range 100.32 (14)–103.04 (15)°.

## Comment

The title compound, (I), is a diphosphine ligand used for highly regioselective hydroformylation reactions, one of the most important homogeneously catalysed industrial reaction types, which produce mixtures of linear and branched aldehydes from olefins, carbon monoxide and hydrogen (Claver & van Leeuwen, 2000). In order to achieve high selectivity towards formation of one product, the appropriate ligand must 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 of structural modifications of hydroformylation catalysts, the title new ligand, (I), was prepared following a modified literature procedure (Antonio *et al.*, 1989; Petrassi *et al.*, 2000; van der Veen *et al.*, 2000). According to preliminary results, this compound was found to be superior over nixantphos as a ligand with regard to selectivity (Osiński & Eilbracht, 2005). It was believed that the crystal structure determination of this compound might allow for the determination of important ligand factors, such as the

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cone angle and the flexibility range of the natural bite angle (Claver & van Leeuwen, 2000). The most important feature of the molecule is the intramolecular P···P distance of 4.1453 (12) Å, this is a little higher than in xantphos (4.080 Å) (Kranenburg *et al.*, 1995) and results in a wider bite angle.

## Experimental

At 273 K, *n*-butyllithium (16 ml of 2.5 M in hexanes, 39 mmol) was added dropwise to a stirred solution of 10-(*tert*-butyldimethylsilyl)phenoxazine (4.84 g, 16.3 mmol) and TMEDA (*N,N,N',N'*-tetramethylethylenediamine; 5.9 ml, 39 mmol) in diethyl ether (250 ml). The reaction mixture was slowly warmed to room temperature and stirred for 16 h. The maize-yellow suspension was then cooled to 273 K and a solution of chlorodiphenylphosphine (7.0 ml, 39 mmol) in hexanes (25 ml) was added dropwise. The reaction mixture decolourized and a light-brown precipitate was formed. After stirring for 16 h at room temperature, the reaction mixture was hydrolyzed with brine (concentrated, 50 ml). The water layer was removed and the organic layer was dried over MgSO<sub>4</sub>. The solvent was removed and the residue purified by chromatography (cyclohexane), followed by crystallization from dichloromethane-ethanol (ratio: from 10:1 at the beginning to 1:10 at the end). Yield 7.91 g (73%) of colourless crystals of (1), m.p. 432–433 K. Spectroscopic analysis: <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>, δ, p.p.m.): 0.26 (*s*, 6H), 0.90 (*s*, 9H), 6.63 (*d*, 2H, *J* = 7.7 Hz), 6.71 (*t*, 2H, *J* = 7.7 Hz), 6.89 (*d*, 2H, *J* = 7.7 Hz), 7.1 (*bs*, 12H), 7.5 (*bs*, 8H); <sup>13</sup>C NMR (125 MHz, C<sub>6</sub>D<sub>6</sub>, δ, p.p.m.): 0.9 (CH<sub>3</sub>), 21.7 (C), 28.7 (CH<sub>3</sub>), 124.3 (CH), 125.0 (CH), 128.2 (C), 128.3 (C), 128.4 (C), 129.4 (CH), 129.8 (*m*, CH), 136.8 (*m*, CH), 138.4 (C), 139.0 (*m*, C); <sup>31</sup>P NMR (81 MHz, CDCl<sub>3</sub>, δ, p.p.m.): –16.6; MS (FAB+ LR): *m/z* (%) = 666 (*M*)<sup>+</sup>, (20); exact mass (FAB+ HR): 665.2425 (*M*)<sup>+</sup>, calculated for C<sub>42</sub>H<sub>41</sub>ONSiP<sub>2</sub>: 665.2433.

### Crystal data

C <sub>42</sub> H <sub>41</sub> NOP <sub>2</sub> Si	<i>D</i> <sub>x</sub> = 1.191 Mg m <sup>−3</sup>
<i>M</i> <sub>r</sub> = 665.79	Mo <i>K</i> α radiation
Monoclinic, <i>P</i> 2 <sub>1</sub> / <i>n</i>	Cell parameters from 32114 reflections
<i>a</i> = 18.8748 (18) Å	<i>θ</i> = 3.2–25.0°
<i>b</i> = 10.8973 (10) Å	<i>μ</i> = 0.18 mm <sup>−1</sup>
<i>c</i> = 19.1042 (15) Å	<i>T</i> = 291 (1) K
<i>β</i> = 109.139 (5)°	Block, light yellow
<i>V</i> = 3712.2 (6) Å <sup>3</sup>	0.20 × 0.10 × 0.08 mm
<i>Z</i> = 4	

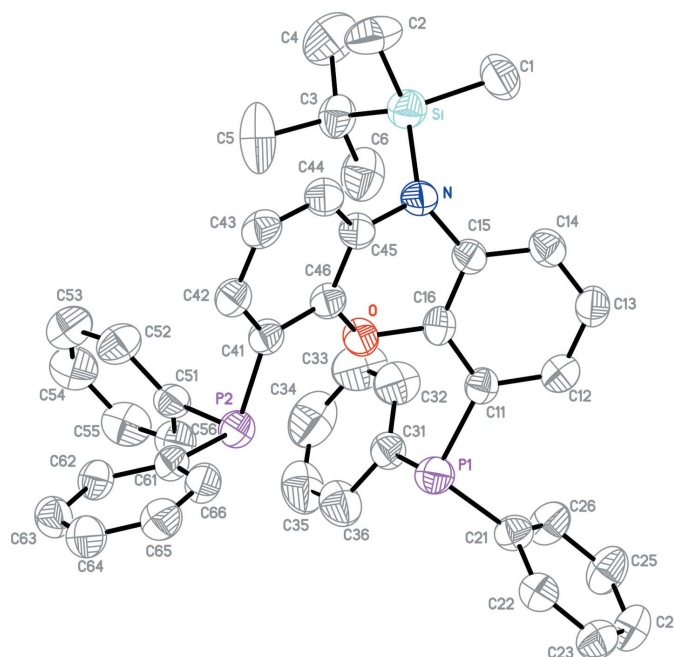
### Data collection

Nonius KappaCCD area-detector diffractometer	2229 reflections with <i>I</i> > 2σ( <i>I</i> )
<i>ω</i> scans	<i>R</i> <sub>int</sub> = 0.041
Absorption correction: none	<i>θ</i> <sub>max</sub> = 25.0°
32114 measured reflections	<i>h</i> = −22 → 22
6468 independent reflections	<i>k</i> = −12 → 12
	<i>l</i> = −22 → 21

### Refinement

Refinement on <i>F</i> <sup>2</sup>	H-atom parameters constrained
<i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )] = 0.037	<i>w</i> = [exp{4.2(sinθ/λ) <sup>2</sup> }/σ <sup>2</sup> ( <i>F</i> <sub>o</sub> <sup>2</sup> )]
<i>wR</i> ( <i>F</i> <sup>2</sup> ) = 0.079	(Δ/σ) <sub>max</sub> < 0.001
<i>S</i> = 0.99	Δρ <sub>max</sub> = 0.15 e Å <sup>−3</sup>
6468 reflections	Δρ <sub>min</sub> = −0.18 e Å <sup>−3</sup>
429 parameters	

H atoms were placed in calculated positions, with C–H = 0.93–0.96 Å, and were refined as riding, with *U*<sub>iso</sub>(H) = 1.5*U*<sub>eq</sub>(C) for methyl groups and 1.2*U*<sub>eq</sub>(C) for others; the methyl groups were allowed to rotate but not to tip.



**Figure 1**  
The molecular structure of the title compound, showing the labelling of all non-H atoms. H atoms have been omitted for clarity. Displacement ellipsoids are shown at the 30% probability level.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* and *SCALEPACK*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); 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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