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# A 1,2,4-diazaphospholane complex of rhodium

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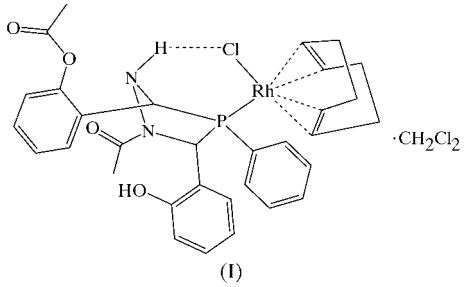
The crystal structure of a prospective olefin catalyst, namely {2-[1-acetyl-5-(2-hydroxyphenyl)-4-phenyl-1,2,4-diazaphospholan-3-yl]phenyl acetate-$\kappa P$}chloro($\eta^4$-cycloocta-1,5-diene)rhodium(I) dichloromethane solvate, $[RhCl(C_8H_{12})(C_{24}H_{23}N_2O_4P)]\cdot CH_2Cl_2$, has been determined at 173 K. The five-membered heterocycle of the phosphine ligand is in a slightly distorted twist conformation. An intramolecular N1—H1···Cl1 hydrogen bond contributes to the adopted conformation and may additionally participate in secondary interactions with substrates during catalysis.

## Comment

Rhodium complexes utilizing chiral phosphine ligands, such as 1,2-bis[(2*R*,5*R*)-2,5-dimethylphospholano]benzene [(*R*,*R*)-Me-DuPHOS], have become important compounds in catalyzing highly enantioselective asymmetric hydrogenation reactions (Burk *et al.*, 1999). In this study, the title complex of rhodium coordinated by 1,2,4-diazaphospholane, (I), which is a structural analogue of DuPHOS, has been successfully synthesized and structurally characterized. Diazaphospholane-based phosphine ligands are a potentially attractive class of ligand in catalyst development, because these compounds are readily synthesized and easily varied (Landis *et al.*, 2001).




(I)

Compound (I) is a rhodium(I) complex where the metal centre is formally in a square-planar coordination environment. The ligands about Rh are a multiply substituted 1,2,4-diazaphospholane, $Cl^-$ and cycloocta-1,5-diene (COD). While the Rh—Cl1 and Rh—P distances (Table 1) are typical, statistically significant differences are observed between the corresponding Rh–olefin [Rh–centroid(C═C)] bonds of COD in (I). The Rh–olefin distance *trans* to P [2.108 (2) Å] is 0.104 Å longer than the Rh–olefin separation *trans* to Cl [2.004 (2) Å]. In 85 compounds containing 161 relevant bonds reported in the Cambridge Structural Database (CSD, Version 5.23; Allen, 2002), the corresponding values for Rh–olefin bonds *trans* to P average 2.12 (3) Å. However, when the *trans* ligand is $Cl^-$, the average Rh–olefin distance is 1.99 (2) Å for 40 compounds containing 48 relevant bonds. The disparity observed between the Rh–olefin bonds in (I) is due to the differing *trans* influence effects of P, a strong $\sigma$ donor, compared with $Cl^-$, a weak $\pi$ and $\sigma$ donor (Miessler & Tarr, 1999). Additionally, the C1═C2 distance is 0.03 Å shorter than the C5═C6 distance (Table 1). However, these distances fall in the expected range for coordinated olefins.

The conformation of the five-membered heterocycle P/C9/N1/N2/C10 in (I) was characterized according to Cremer & Pople (1975). Typically, the most stable spatial arrangement of five-membered rings such as cyclopentane is either the twist or the energetically similar envelope conformation, and the most favorable combination of steric, electronic and non-bonding interactions determines the adopted conformation (March, 1992). The generalized puckering coordinates $q_2$ [0.472 (2) Å] and $\varphi_2$ [56.6 (3)°] suggest that the spatial arrangement of the ring atoms in (I) is essentially the twist form $^3T_2$, with a very minor contribution of the envelope $^3E$ form, where atom N1 acts as the 'flap' atom of the envelope.

The twist conformation of the ring in (I) is stabilized by an intramolecular N1—H1···Cl1 hydrogen-bonding interaction (Table 2). The corresponding values for 105 compounds with 130 similar hydrogen bonds reported in the CSD average 3.24 (9) Å and 162 (7)°. Therefore, the distance observed in

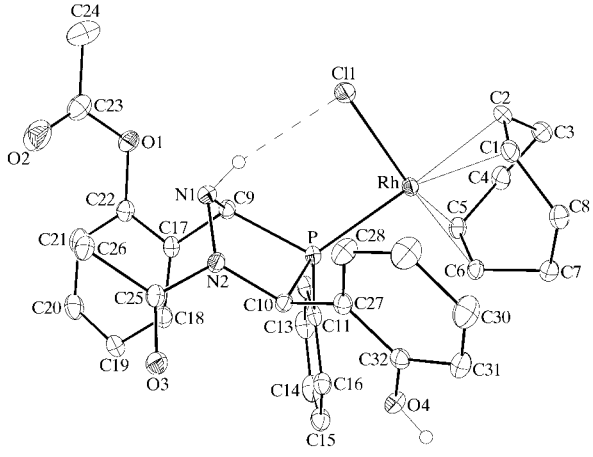



**Figure 1**
A view of the molecular structure of (I). Displacement ellipsoids are drawn at the 30% probability level and all H atoms except for H1 and H4 have been omitted for clarity.

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(I) is indicative of a relatively strong hydrogen bond. The observed N1—H1···Cl1 hydrogen bond may also play a role in the future development of this class of catalysts, due to possible participation in 'secondary interactions'. Such interactions have been proposed to be potentially important in increasing enantioselectivity by forming non-bonding contacts with the reacting substrates (Sawamura & Ito, 1992). Steric interactions also contribute to the conformation adopted by (I), as the majority of the bulky ring substituents occupy pseudo-equatorial positions. Additionally, ester atoms O1, O2, C23 and C24 are nearly perpendicular to the phenyl ring (atoms C17–C22), to mitigate steric repulsion between atoms O2 and H21.

In the lattice of (I), there are intermolecular hydrogen-bonding interactions between symmetry-related molecules. These O4—H4···O3($-x$, $1-y$, $2-z$) interactions result in the formation of dimers of rhodium complexes (Table 2). The corresponding values for 67 compounds with 74 similar hydrogen bonds in structures reported in the CSD average 2.68 (6) Å and 168 (7)°, and compare reasonably well with the O···O hydrogen bond in (I).

## Experimental

A $CH_2Cl_2$ solution of the multiply substituted 1,2,4-diazaphospholane ligand was treated with 0.5 equivalents of [RhCl(cycloocta-1,5-diene)]$_2$ in $CH_2Cl_2$ at room temperature. The mixture was stirred for 1 h and dried *in vacuo* to yield the yellow title solid, (I), in quantitative yield. Crystals suitable for X-ray structure determination were obtained by slow crystallization from $CH_2Cl_2$ and hexanes (5:1) at room temperature. Spectroscopic analysis, $^1$H NMR ($CDCl_3$, $\delta$): 1.6 (*m*, 4H, $CH_2$), 1.94 (*b*, 1H), 2.07 (*s*, 3H, $CH_3$), 2.15 (*b*, 1H), 2.34 (*b*, 2H), 2.57 (*s*, 3H, $CH_3$), 2.72 (*b*, 1H), 3.02 (*b*, 1H), 5.34 (*b*, 2H), 6.32 (*b*, 2H), 6.39 (*d*, 1H, $J$ = 8 Hz), 6.7 (*m*, 2H), 7.0 (*m*, 2H), 7.07–7.25 (*m*, 6H), 7.35 (*m*, 2H), 8.25 (*d*, 1H), 8.95 (*b*, 1H); $^{31}$P{$^1$H} NMR ($CDCl_3$, $\delta$): 67.4 (*d*, $J_{Rh-P}$ = 157.4 Hz).

*Crystal data*

$[RhCl(C_8H_{12})(C_{24}H_{23}N_2O_4P)]\cdot CH_2Cl_2$
$M_r$ = 765.88
Triclinic, $P\overline{1}$
$a$ = 11.6420 (5) Å
$b$ = 11.8755 (5) Å
$c$ = 12.7087 (6) Å
$\alpha$ = 102.261 (10)°
$\beta$ = 103.030 (10)°
$\gamma$ = 95.789 (10)°
$V$ = 1652.21 (17) Å$^3$
$Z$ = 2
$D_x$ = 1.539 Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 5120 reflections
$\theta$ = 2.0–25.0°
$\mu$ = 0.85 mm$^{-1}$
$T$ = 173 (2) K
Needle, orange
0.45 × 0.15 × 0.08 mm

*Data collection*

Bruker SMART1000 CCD area-detector diffractometer
$\omega$ scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
$T_{min}$ = 0.702, $T_{max}$ = 0.935
13 910 measured reflections
6453 independent reflections
5873 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.029
$\theta_{max}$ = 26°
$h = -14 \rightarrow 13$
$k = -14 \rightarrow 14$
$l = 0 \rightarrow 15$
Intensity decay: <1%

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.088
$S$ = 1.06
6453 reflections
403 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0486P)^2 + 0.8831P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ < 0.001
$\Delta\rho_{max}$ = 0.80 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.45 e Å$^{-3}$

**Table 1**
Selected bond distances (Å).

| | | | |
|---|---|---|---|
| Rh—P | 2.2943 (6) | C1—C2 | 1.362 (4) |
| Rh—Cl1 | 2.3856 (7) | C5—C6 | 1.392 (3) |

**Table 2**
Hydrogen-bonding geometry (Å, °).

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| O4—H4···O3$^{i}$ | 0.84 | 1.82 | 2.654 (2) | 173 |
| N1—H1···Cl1 | 0.90 (2) | 2.34 (2) | 3.167 (2) | 152 (2) |

Symmetry code: (i) $-x$, $1-y$, $2-z$.

Hydroxyl and methyl H atoms were constrained to an ideal geometry, with $U_{iso}$(H) = 1.5$U_{eq}$(O,C), and allowed to rotate freely about their C—O or C—C bonds, respectively. All other H atoms, except H1, were constrained (C—H = 0.95–1.00 Å and N—H = 0.84 Å) and allowed to ride on their C atoms, with $U_{iso}$(H) = 1.2$U_{eq}$(C). Atom H1 bonded to N1 was positioned from inspection of difference maps and refined subject to a DFIX (*SHELXTL*; Bruker, 2000) restraint of 0.90 (2) Å, with $U_{iso}$(H) = 1.2$U_{eq}$(N). A residual peak of electron density (0.80 e Å$^{-3}$) was located in a chemically unreasonable position in the vicinity of the Rh atom and considered to be noise.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Bruker, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1680). Services for accessing these data are described at the back of the journal.

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