

A 1,2,4-diazaphospholane complex of rhodium

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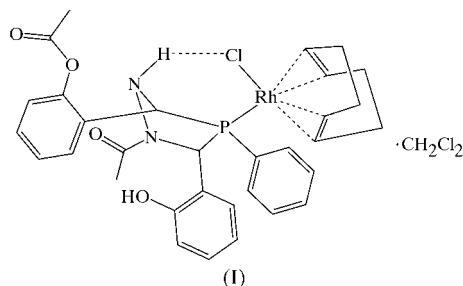
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The crystal structure of a prospective olefin catalyst, namely [2-[1-acetyl-5-(2-hydroxyphenyl)-4-phenyl-1,2,4-diazaphospholan-3-yl]phenyl acetate- κ P]chloro(η^4 -cycloocta-1,5-diene)rhodium(I) dichloromethane solvate, $[\text{RhCl}(\text{C}_8\text{H}_{12})(\text{C}_{24}\text{H}_{23}\text{N}_2\text{O}_4\text{P})]\cdot\text{CH}_2\text{Cl}_2$, has been determined at 173 K. The five-membered heterocycle of the phosphine ligand is in a slightly distorted twist conformation. An intramolecular $\text{N1}\cdots\text{H1}\cdots\text{Cl1}$ 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).



Compound (I) is a rhodium(I) complex where the metal centre is formally in a square-planar coordination environ-

ment. The ligands about Rh are a multiply substituted 1,2,4-diazaphospholane, Cl^- and cycloocta-1,5-diene (COD). While the $\text{Rh}-\text{Cl1}$ and $\text{Rh}-\text{P}$ distances (Table 1) are typical, statistically significant differences are observed between the corresponding $\text{Rh}-\text{olefin} [\text{Rh}-\text{centroid}(\text{C}=\text{C})]$ bonds of COD in (I). The $\text{Rh}-\text{olefin}$ distance *trans* to P [2.108 (2) Å] is 0.104 Å longer than the $\text{Rh}-\text{olefin}$ 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 $\text{Rh}-\text{olefin}$ bonds *trans* to P average 2.12 (3) Å. However, when the *trans* ligand is Cl^- , the average $\text{Rh}-\text{olefin}$ distance is 1.99 (2) Å for 40 compounds containing 48 relevant bonds. The disparity observed between the $\text{Rh}-\text{olefin}$ bonds in (I) is due to the differing *trans* influence effects of P, a strong σ donor, compared with Cl^- , a weak π and σ donor (Miessler & Tarr, 1999). Additionally, the $\text{C1}=\text{C2}$ distance is 0.03 Å shorter than the $\text{C5}=\text{C6}$ 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 φ_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 $\text{N1}-\text{H1}\cdots\text{Cl1}$ 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

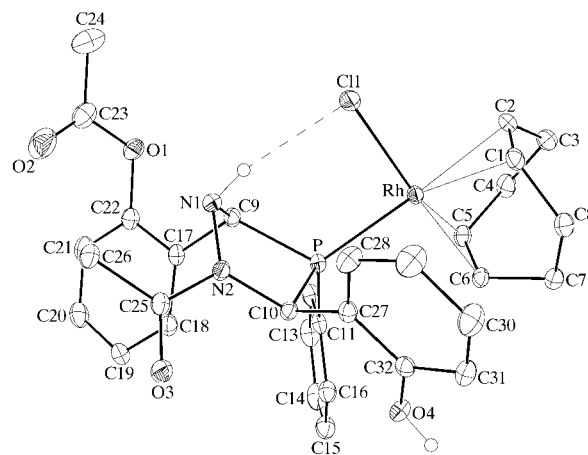


Figure 1

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.

(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 CH₂Cl₂ solution of the multiply substituted 1,2,4-diazaphospholane ligand was treated with 0.5 equivalents of [RhCl(cycloocta-1,5-diene)]₂ in CH₂Cl₂ 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 CH₂Cl₂ and hexanes (5:1) at room temperature. Spectroscopic analysis, ¹H NMR (CDCl₃, δ): 1.6 (*m*, 4H, CH₂), 1.94 (*b*, 1H), 2.07 (*s*, 3H, CH₃), 2.15 (*b*, 1H), 2.34 (*b*, 2H), 2.57 (*s*, 3H, CH₃), 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); ³¹P{¹H} NMR (CDCl₃, δ): 67.4 (*d*, *J*_{Rh–P} = 157.4 Hz).

Crystal data

[RhCl(C₈H₁₂)(C₂₄H₂₃N₂O₄P)]·
CH₂Cl₂
M_r = 765.88
Triclinic, *P*1
a = 11.6420 (5) Å
b = 11.8755 (5) Å
c = 12.7087 (6) Å
α = 102.261 (10)°
β = 103.030 (10)°
γ = 95.789 (10)°
V = 1652.21 (17) Å³

Z = 2
D_x = 1.539 Mg m^{−3}
Mo *K*α radiation
Cell parameters from 5120
reflections
θ = 2.0–25.0°
μ = 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
ω 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* > 2σ(*I*)
*R*_{int} = 0.029
θ_{max} = 26°
h = −14 → 13
k = −14 → 14
l = 0 → 15
Intensity decay: <1%

Refinement

Refinement on *F*²
R [*F*² > 2σ(*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

$$w = 1/[\sigma^2(F_o^2) + (0.0486P)^2 + 0.8831P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\max} < 0.001$$

$$\Delta\rho_{\max} = 0.80 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.45 \text{ e } \text{\AA}^{-3}$$

Table 1

Selected bond distances (Å).

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

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
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.

References

- Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
- Bruker (2000). *SHELXTL-NT* (Version 6.10) and *SADABS* (Version 2.03). Bruker AXS Inc., Madison, Wisconsin, USA.
- Bruker (2001). *SAINT* (Version 6.22) and *SMART* (Version 5.622). Bruker AXS Inc., Madison, Wisconsin, USA.
- Burk, M. J., Bienewald, F., Challenger, S., Derrick, A. & Ramsden, J. A. (1999). *J. Org. Chem.* **64**, 3290–3298.
- Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
- Landis, C. R., Jin, W. C., Owen, J. S. & Clark, T. P. (2001). *Angew. Chem. Int. Ed.* **40**, 3432–3434.
- March, J. (1992). *Advanced Organic Chemistry: Reactions, Structure and Mechanism*, 4th ed., pp. 82–140. New York: John Wiley & Sons.
- Miessler, G. L. & Tarr, D. A. (1999). *Inorganic Chemistry*, 2nd ed., pp. 383–421. Upper Saddle River: Prentice-Hall.
- Sawamura, M. & Ito, Y. (1992). *Chem. Rev.* **92**, 857–871.