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[(*R*)-2,2′-Bis(diphenylphosphino)-1,1′-binaphthyl-κ^2P,P']chlorohydrido{(*S*)-2-methyl-1-[(4*R*,5*R*)-4-methyl-5-phenyl-4,5-dihydrooxazol-2-yl]propan-1-amine-κ^2N,N'}ruthenium(II) benzene solvate: an active ketone hydrogenation catalyst

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In the title complex, $[RuClH(C_{14}H_{20}N_2O)(C_{44}H_{32}P_2)]\cdot C_6H_6$, the Ru^{II} ion is in a slightly distorted coordination environment. One of the amino H atoms is involved in a weak intramolecular N—H···Cl interaction (H···Cl = 2.71 Å), while the other is involved in an intramolecular N—H···π(arene) interaction (NH···*Cg* = 2.62 Å, where *Cg* is the centroid of a benzene ring).

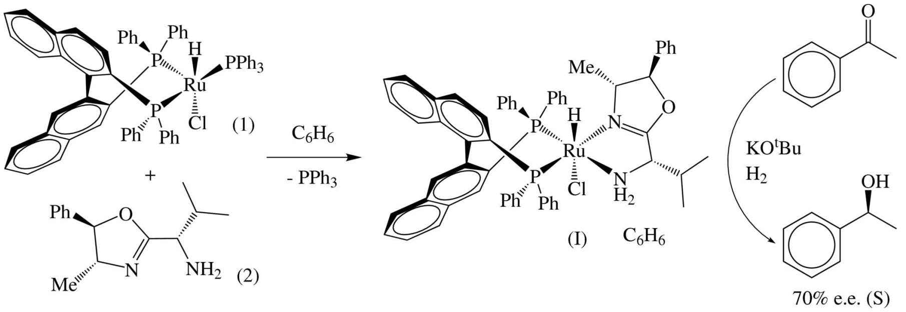
Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.007 Å
R factor = 0.051
wR factor = 0.129
Data-to-parameter ratio = 16.6

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

Catalytic asymmetric hydrogenation of ketones and imines represents a valuable process for the preparation of chiral alcohols and amines. Ohkuma *et al.* (1995) and Doucet *et al.* (1998) have developed an excellent class of ruthenium catalysts of the type $RuCl_2$(diphosphine)(diamine) which are efficient, selective and modular for the hydrogenation of a wide range of ketones. Our research effort and that of others subsequently demonstrated that these catalysts are also very effective for the hydrogenation of imines (Abdur-Rashid, Faatz *et al.*, 2001; Abdur-Rashid, Lough & Morris, 2001; Cobley & Henschke, 2003). Extensive mechanistic investigations of the catalytic reaction showed that the NH groups of the diamine ligand participate in the catalytic process and account for the enhanced activity of this class of catalysts (Abdur-Rashid, Faatz *et al.*, 2001; Abdur-Rashid, Lough & Morris, 2001). We have now extended this study to complexes of the type RuX_2(diphosphine)(amino-oxazoline) (where X = Cl, H) on the premise that the NH groups of the amino-oxazoline ligand (Rajaram & Sigman, 2002) will be non-innocent and will facilitate the catalytic hydrogenation of ketones.



The title compound, (I), was prepared by the reaction of a stoichiometric mixture of $RuHCl$(*R*-binap)(PPh_3), (1) [where *R*-binap = (*R*)-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl], and the aminooxazoline ligand (2). Catalytic hydrogenation (3 atm. H_2 gas, room temperature) of acetophenone using (I) as a catalyst in the presence of KO^{t}Bu (substrate:catalyst:base =

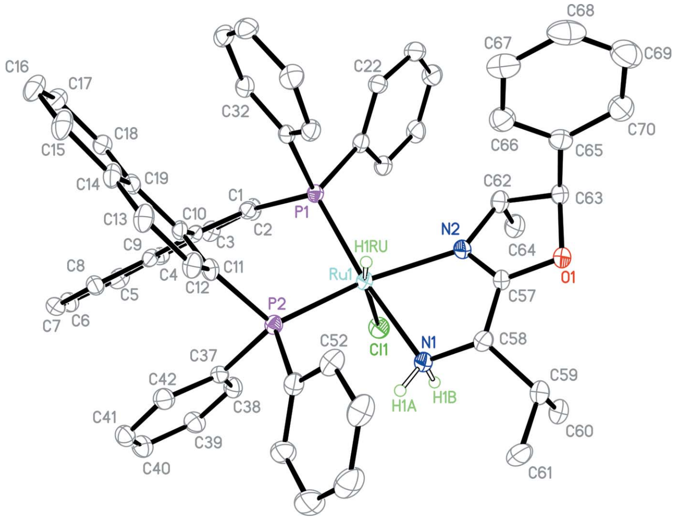


Figure 1
The molecular structure of (I). Displacement ellipsoids are at the 30% probability level. The benzene solvent molecule and H atoms bonded to C atoms are not shown.

2500:1:10) in 2-propanol resulted in 80% conversion of the ketone to the alcohol in 70% e.e. (*S*) after 8 h (see scheme).

The molecular structure of the complex (I) is shown in Fig. 1 and selected bond lengths and angles are given in Table 1. The Ru^{II} ion is in a slightly distorted octahedral coordination environment. For a comparison of geometric parameters, previously published structures of Ru^{II} hydride complexes with a $RuCl(H)N_2P_2$ coordination center are available (Guo *et al.*, 2004; Li *et al.*, 2004; Abbel *et al.*, 2005; Abdur-Rashid, Abbel *et al.*, 2005; Abdur-Rashid, Guo *et al.*, 2005; Abdur-Rashid *et al.*, 2002; Guo *et al.*, 2005). In (I), one of the amino H atoms is involved in a weak intramolecular N—H···Cl interaction, while the other is involved in a weak N—H···π(arene) interaction (Table 2). A single intramolecular C—H···π(arene) interaction is also present, but there are no direction-specific intermolecular interactions.

Experimental

Tetrahydrofuran (10 ml) was added to a mixture of RuHCl(*R*-binap)(PPh_3) (250 mg, 0.24 mmol) and the aminooxazoline ligand (60 mg, 0.26 mmol). The resulting yellow solution was stirred for 2 h under Ar. The mixture was concentrated to 2 ml under reduced pressure and hexanes were added. The yellow suspension that formed was stirred vigorously for 2 h. It was then filtered off, washed with hexanes and dried under vacuum. X-ray diffraction quality single crystals were grown by slow diffusion of hexanes into a solution of (I) in benzene (yield: 216 mg, 89%).

Crystal data

$[RuClH(C_{14}H_{20}N_2O)(C_{44}H_{32}P_2)]\cdot C_6H_6$
$M_r = 1070.59$
Monoclinic, *C*2
$a = 24.9502\ (6)$ Å
$b = 10.7366\ (3)$ Å
$c = 19.4560\ (4)$ Å
$\beta = 96.9779\ (16)^\circ$
$V = 5173.4\ (2)$ Å^3
$Z = 4$
$D_x = 1.375$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.46$ mm^{-1}
$T = 150\ (1)$ K
Block, orange
0.22 × 0.12 × 0.10 mm

Data collection

Bruker–Nonius KappaCCD diffractometer
φ scans and ω scans with κ offsets
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)
$T_{min} = 0.928$, $T_{max} = 0.957$
20470 measured reflections
10692 independent reflections
9051 reflections with $I > 2\sigma(I)$
$R_{int} = 0.058$
$\theta_{max} = 27.6^\circ$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.051$
$wR(F^2) = 0.129$
$S = 1.04$
10692 reflections
645 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0653P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.48$ e Å^{-3}
$\Delta\rho_{min} = -1.12$ e Å^{-3}
Extinction correction: *SHELXTL/PC*
Extinction coefficient: 0.0015 (3)
Absolute structure: Flack (1983), 4433 Friedel pairs
Flack parameter: −0.05 (3)

Table 1
Selected geometric parameters (Å, °).

Ru1—H1RU	1.71 (6)	O1—C57	1.338 (5)
Ru1—N1	2.186 (3)	O1—C63	1.489 (6)
Ru1—N2	2.202 (4)	N2—C57	1.286 (6)
Ru1—P2	2.2418 (10)	N2—C62	1.488 (6)
Ru1—P1	2.2434 (10)	C62—C63	1.554 (7)
Ru1—Cl1	2.5661 (12)		
H1RU—Ru1—N1	83.6 (17)	N2—Ru1—P1	100.40 (10)
H1RU—Ru1—N2	88.3 (18)	P2—Ru1—P1	91.39 (4)
N1—Ru1—N2	73.71 (13)	H1RU—Ru1—Cl1	165.3 (17)
H1RU—Ru1—P2	77.1 (18)	N1—Ru1—Cl1	81.75 (11)
N1—Ru1—P2	93.60 (10)	N2—Ru1—Cl1	87.38 (11)
N2—Ru1—P2	161.78 (10)	P2—Ru1—Cl1	104.00 (5)
H1RU—Ru1—P1	93.3 (17)	P1—Ru1—Cl1	101.29 (4)
N1—Ru1—P1	173.36 (11)		

Table 2
Hydrogen-bond geometry (Å, °).

*Cg*1 and *Cg*2 are the centroids defined by ring atoms C51–C56 and C21–C26, respectively.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*B*···Cl1	0.92	2.71	3.123 (4)	109
N1—H1*A*···*Cg*1	0.92	2.62	3.487 (5)	157
C62—H62*A*···*Cg*2	1.00	2.63	2.482 (6)	143

All H atoms, except for the hydride H atom, were placed in calculated positions with C—H = 1.00 (methine CH), 0.98 (methyl CH_3) and 0.95 Å (aromatic CH) and N—H = 0.92 Å. They were included in the refinement in the riding-model approximation with $U_{iso}(H) = 1.2U_{eq}(C,N)$ or $U_{iso}(H) = 1.5U_{eq}(C_{methyl})$. The hydride H atom (H1RU) was refined independently with free coordinates and isotropic displacement parameter. The two residuals greater than 1.0 e Å^{-3} in the final difference map are 1.48 and 1.39 e Å^{-3} and these are located within 1.2 Å of Ru1. The deepest hole is 0.89 Å from Ru1.

Data collection: *COLLECT* (Nonius, 2002); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXTL/PC* (Sheldrick, 2001); molecular graphics: *SHELXTL/PC*; software used to prepare material for publication: *SHELXTL/PC*.

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