

**[(*R,R*)-1-(*N*-Benzylideneamino)-2-(diphenylphosphino)cyclohexane- $\kappa^2$ *N,P*]-dichloro(triphenylphosphine- $\kappa$ *P*)ruthenium(II)**

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The title compound, [RuCl<sub>2</sub>(C<sub>18</sub>H<sub>15</sub>P)(C<sub>25</sub>H<sub>26</sub>NP)], crystallizes with two molecules in the asymmetric unit. The coordination geometry is a distorted square pyramid, with the P atom of the –PPh<sub>2</sub> moiety at the apical position. This is the first reported structure determination of a compound containing the (*R,R*)-1-(*N*-benzylideneamino)-2-(diphenylphosphino)cyclohexane ligand.

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### Key indicators

Single-crystal X-ray study

*T* = 150 K

Mean  $\sigma$ (C–C) = 0.011 Å

*R* factor = 0.051

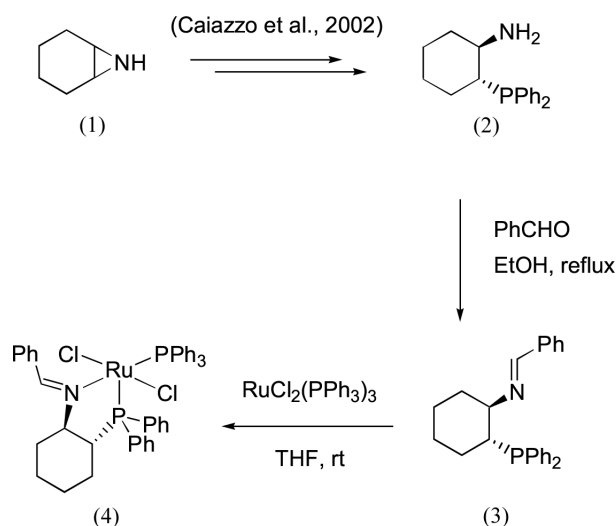
w*R* factor = 0.118

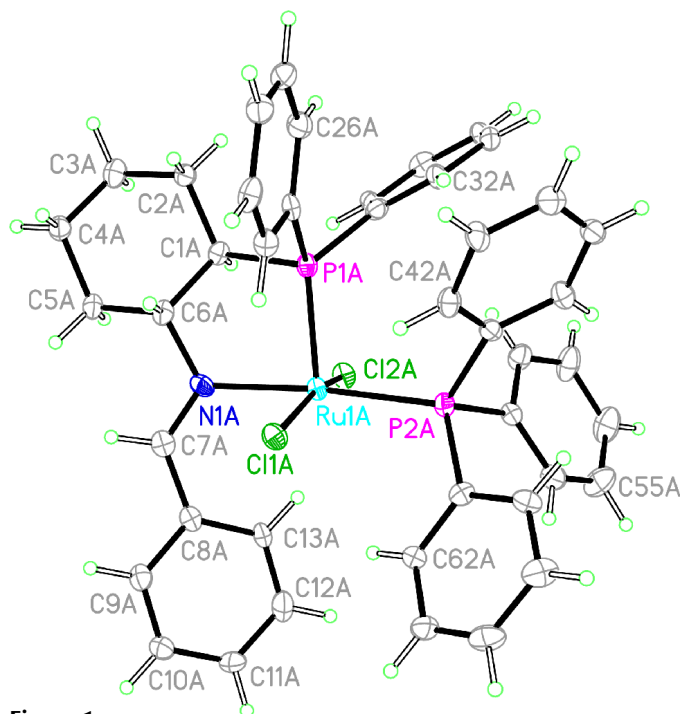
Data-to-parameter ratio = 13.6

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

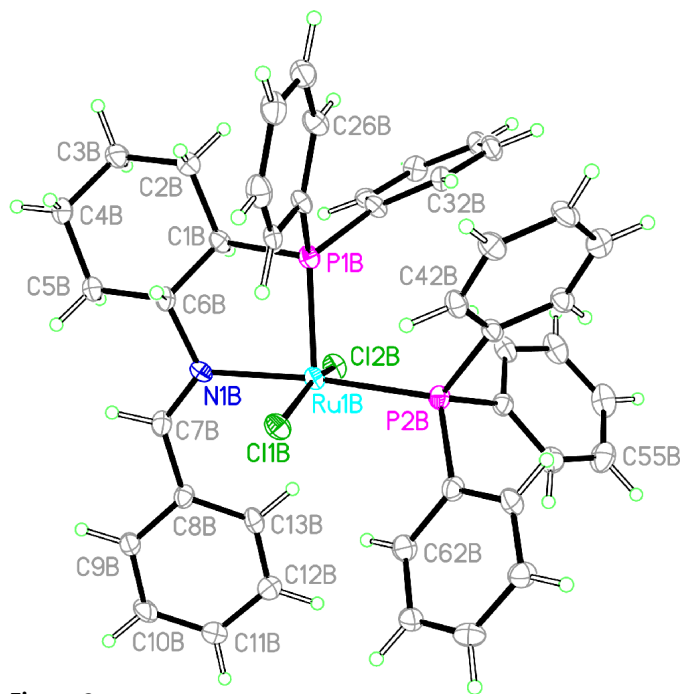
### Comment

Iminophosphine ligands are characterized by interesting mixed properties derived from the simultaneous presence of the hard nitrogen and the soft phosphorus sites (Drent *et al.*, 1993; Dekker *et al.*, 1992). They have recently been used in a variety of catalytic processes, involving both Pd<sup>II</sup> (Van den Beuken *et al.*, 1998; Scrivanti *et al.*, 2001) and Ru<sup>II</sup> (Crochet *et al.*, 2003; 2001). In particular, Ru complexes containing different *N*-(2'-diphenylphosphinobenzylidene)alkylamine ligands have been synthesized and employed in the transfer hydrogenation of acetophenone in 2-propanol (Crochet *et al.*, 2003, 2001). We have recently prepared, starting from readily available 7-azabicyclo[4.1.0]heptane, (1), a new optically active P–N ligand, (*R,R*)-1-amino-2-diphenylphosphinocyclohexane, (2) (Caiazzo *et al.*, 2002). The iminophosphine (*R,R*)-1-(*N*-benzylideneamino)-2-(diphenylphosphino)cyclohexane, (3), can be easily obtained from the reaction between the above P–N cyclohexane ligand and benzaldehyde in ethanol (see Scheme). Here we report the synthesis and the X-ray analysis of (4), the first reported complex containing the ligand (3).





**Figure 1**  
View of molecule *A* of (4), with the crystallographic labeling scheme. Displacement ellipsoids are drawn at the 30% probability level.



**Figure 2**  
View of molecule *B* of (4), with the crystallographic labeling scheme. Displacement ellipsoids are at the 30% probability level.

The reaction between (3) and an equimolar amount of  $\text{RuCl}_2(\text{PPh}_3)_3$  in tetrahydrofuran at room temperature affords the compound (4) in good yield. In the crystal structure of (4), there are two molecules in the asymmetric unit, *A* and *B* (Figs. 1 and 2). Analogously to the precursor  $\text{RuCl}_2(\text{PPh}_3)_3$  (La Placa & Ibers, 1965) and to similar structures (Crochet *et al.*, 2001), the coordination geometry of compound (4) can be

described as a distorted square pyramid, with the P atom (P1) of the  $-\text{PPh}_2$  moiety at the apical position. The base of the pyramid is formed by the two Cl atoms, *trans* to each other [with a  $\text{Cl1}-\text{Ru1}-\text{Cl2}$  angle of  $164.70(7)$  and  $163.65(6)^\circ$  for molecules *A* and *B*, respectively], and the N atom of the imino group in a *trans* position to the P atom of the  $\text{PPh}_3$  moiety [ $\text{N1}-\text{Ru}-\text{P2} = 173.58(16)$  and  $174.55(16)^\circ$ ]. The Ru atom is displaced by  $0.264(1)$  and  $0.280(1)$  Å in molecules *A* and *B*, respectively, towards atom P1 from the weighted least-squares plane formed by  $\text{N1}/\text{P2}/\text{Cl1}/\text{Cl2}$ . Unlike the similar previously reported structures, where the N atom and the P atom in the ligand are bound to an aromatic ring, the metallacycle formed by the ligand (3) is not planar, owing to the geometry of the cyclohexane ring. In the metallacycle, an analysis (Cremer & Pople, 1975) of the puckering of the five-membered ring ( $\text{Ru1}/\text{N1}/\text{C6}/\text{C1}/\text{P1}$ ) gives  $Q_t$  of  $0.484(6)$  and  $0.479(6)$  Å for molecules *A* and *B*, respectively. In molecule *A*, the conformation of that ring is ‘envelope’, with a local pseudo-mirror passing through  $\text{C1A}$  and the mid-point of the  $\text{N1A}-\text{Ru1A}$  bond, while in molecule *B* the conformation is ‘half-chair’, with a local pseudo-twofold axis passing through  $\text{Ru1B}$  and the mid-point of the  $\text{C1B}-\text{C6B}$  bond (Duax *et al.*, 1976). The bond lengths in each of the independent molecules are the same within experimental error, and are, in turn, similar to those in the previously reported structure  $\text{RuCl}_2(\kappa^2\text{-}2\text{-Ph}_2\text{PC}_6\text{H}_4\text{C}=\text{NtBu})(\text{PPh}_3)$  (Crochet *et al.*, 2001); selected values are reported in Table 1.

## Experimental

To a solution of  $\text{RuCl}_2(\text{PPh}_3)_3$  (259 mg, 0.27 mmol) in 30 ml of dry and deoxygenated tetrahydrofuran, (*R,R*)-2- $\text{Ph}_2\text{PC}_6\text{H}_{10}\text{N}=\text{CHPh}$ , (3) (100 mg, 0.27 mmol), was added and the resulting mixture stirred at room temperature for 24 h. The solvent was removed and the dark-green residue washed 4 times with a mixture of hexanes/diethyl ether (1:1) and dried under vacuum. Compound (4) was obtained as a dark-green solid (163 mg, 75%). Suitable crystals for X-ray analysis were obtained by slow diffusion of hexanes into a concentrated toluene solution of (4).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ): 9.14 (*d*,  $J = 9.3$  Hz, 1H), 8.07 (*t*,  $J = 9.2$  Hz, 2H), 7.54 (*t*,  $J = 6.6$  Hz, 1H), 7.39–6.98 (*m*, 27H), 4.15 (*m*, 1H), 3.22 (*m*, 1H), 2.94 (*m*, 1H), 1.96 (*m*, 3H), 1.64 (*m*, 1H), 1.26 (*m*, 2H), 0.60 (*m*, 1H).  $^{31}\text{P}$  NMR (121.5 MHz,  $\text{CDCl}_3$ ): 86.6 (*d*,  $J = 34.8$  Hz), 43.5 (*d*,  $J = 34.8$  Hz).

### Crystal data

$[\text{RuCl}_2(\text{C}_{18}\text{H}_{15}\text{P})(\text{C}_{25}\text{H}_{26}\text{NP})]$   
 $M_r = 805.68$   
 Monoclinic,  $P2_1$   
 $a = 14.6010(5)$  Å  
 $b = 16.9630(7)$  Å  
 $c = 14.7430(7)$  Å  
 $\beta = 90.8570(14)^\circ$   
 $V = 3651.1(3)$  Å<sup>3</sup>  
 $Z = 4$

$D_x = 1.466$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 Cell parameters from 55428 reflections  
 $\theta = 2.6\text{--}25.0^\circ$   
 $\mu = 0.70$  mm<sup>-1</sup>  
 $T = 150(1)$  K  
 Plate, dark green  
 $0.12 \times 0.10 \times 0.04$  mm

### Data collection

Nonius KappaCCD diffractometer  
 $\varphi$  scans and  $\omega$  scans with  $\kappa$  offsets  
 Absorption correction: multi-scan (SORTAV; Blessing, 1995)  
 $T_{\min} = 0.893$ ,  $T_{\max} = 0.974$   
 21972 measured reflections  
 12013 independent reflections

9236 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.082$   
 $\theta_{\max} = 25.1^\circ$   
 $h = -17 \rightarrow 17$   
 $k = -17 \rightarrow 20$   
 $l = -15 \rightarrow 17$

## Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2)]$
$R[F^2 > 2\sigma(F^2)] = 0.051$	$(\Delta/\sigma)_{\max} = 0.002$
$wR(F^2) = 0.118$	$\Delta\rho_{\max} = 0.87 \text{ e } \text{\AA}^{-3}$
$S = 0.98$	$\Delta\rho_{\min} = -0.67 \text{ e } \text{\AA}^{-3}$
12013 reflections	Absolute structure: (Flack, 1983),
883 parameters	5320 Friedel pairs
H-atom parameters constrained	Flack parameter = 0.02 (3)

Table 1

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

Ru1A–N1A	2.115 (6)	Ru1B–N1B	2.119 (6)
Ru1A–P1A	2.2046 (18)	Ru1B–P1B	2.2027 (18)
Ru1A–P2A	2.3386 (18)	Ru1B–P2B	2.3280 (18)
Ru1A–Cl1A	2.3833 (18)	Ru1B–Cl2B	2.3891 (18)
Ru1A–Cl2A	2.3991 (18)	Ru1B–Cl1B	2.3985 (18)
N1A–C7A	1.288 (9)	N1B–C7B	1.296 (8)
N1A–Ru1A–P1A	84.89 (16)	N1B–Ru1B–P1B	85.31 (15)
N1A–Ru1A–P2A	173.58 (16)	N1B–Ru1B–P2B	174.55 (16)
P1A–Ru1A–P2A	100.02 (7)	P1B–Ru1B–P2B	99.59 (6)
N1A–Ru1A–Cl1A	84.18 (15)	N1B–Ru1B–Cl2B	87.58 (16)
P1A–Ru1A–Cl1A	103.87 (7)	P1B–Ru1B–Cl2B	90.36 (7)
P2A–Ru1A–Cl1A	90.59 (7)	P2B–Ru1B–Cl2B	94.74 (7)
N1A–Ru1A–Cl2A	90.18 (16)	N1B–Ru1B–Cl1B	86.70 (16)
P1A–Ru1A–Cl2A	89.72 (7)	P1B–Ru1B–Cl1B	104.41 (7)
P2A–Ru1A–Cl2A	93.96 (7)	P2B–Ru1B–Cl1B	89.74 (7)
Cl1A–Ru1A–Cl2A	164.70 (7)	Cl2B–Ru1B–Cl1B	163.65 (6)

All H atoms were placed in calculated positions, with C–H distances ranging from 0.95 to 1.00  $\text{\AA}$ , and included in the refinement in riding-motion approximation, with  $U_{\text{iso}} = 1.2U_{\text{eq}}$  of the carrier atom.

Data collection: COLLECT (Nonius, 1997–2002); cell refinement: DENZO-SMN (Otwinowski & Minor, 1997); data reduction:

DENZO-SMN; program(s) used to solve structure: SHELXTL (Sheldrick, 2001); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

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## References

- Blessing, R. H. (1995). *Acta Cryst.* **A51**, 33–38.
- Caiazza, A., Dalili, S. & Yudin, A. K. (2002). *Org. Lett.* **4**, 2597–2600.
- Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
- Crochet, P., Gimeno, J., Borge, J. & García-Granda, S. (2003). *New J. Chem.* **27**, 414–420.
- Crochet, P., Gimeno, J., García-Granda, S. & Borge, J. (2001). *Organometallics*, **20**, 4639–4377.
- Dekker, G. P. C. M., Buijs, A., Elsevier, C. J., Vrieze K., van Leeuwen, P. W. N. M., Smeets W. J. J., Spek, A. L., Wang, Y. F. & Stam, C. H. (1992). *Organometallics*, **11**, 1937–1948.
- Drent, E., Arnoldy, P. & Budzelaar, P. H. M. (1993). *J. Organomet. Chem.* **455**, 247–253.
- Duax, W. L., Weeks, C. M. & Rohrer, D. C. (1976). *Topics in Stereochemistry*, Vol. 9, edited by N. L. Allinger and E. L. Eliel, pp. 271–383. New York: John Wiley.
- Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
- La Placa, S. J. & Ibers, J. A. (1965). *Inorg. Chem.* **4**, 778–783.
- Nonius (1997–2002). COLLECT. Nonius BV, Delft, The Netherlands.
- Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr and R. M. Sweet, pp. 307–326. New York: Academic Press.
- Scrivanti, A., Matteoli, U., Beghetto, V., Antonaroli, S., Scarpelli, R. & Crociani, B. (2001). *J. Mol. Cat. A Chem.* **170**, 51–56.
- Sheldrick, G. M. (2001). SHELXTL/PC. Version 6.12 Windows NT Version. Bruker AXS Inc., Madison, Wisconsin, USA.
- Van den Beuken, E. K., Smeets, W. J. J., Spek, A. L. & Feringa, B. L. (1998). *Chem. Commun.* pp. 223–224.