

(2,6-Bis[1-[4-(dimethylamino)phenyl-imino]ethyl]pyridine)dichlorido(triphenylphosphine- κP)ruthenium(II): a zigzag chain of fused centrosymmetric $R_2^2(12)$ ringsNamik Özdemir,^{a*} Muharrem Dinçer,^a Osman Dayan^b and Bekir Çetinkaya^c^aDepartment of Physics, Arts and Sciences Faculty, Ondokuz Mayıs University, 55139 Samsun, Turkey, ^bDepartment of Chemistry, Arts and Sciences Faculty, Çanakkale Onsekiz Mart University, 17100 Çanakkale, Turkey, and ^cDepartment of Chemistry, Science Faculty, Ege University, 35100 Izmir, Turkey
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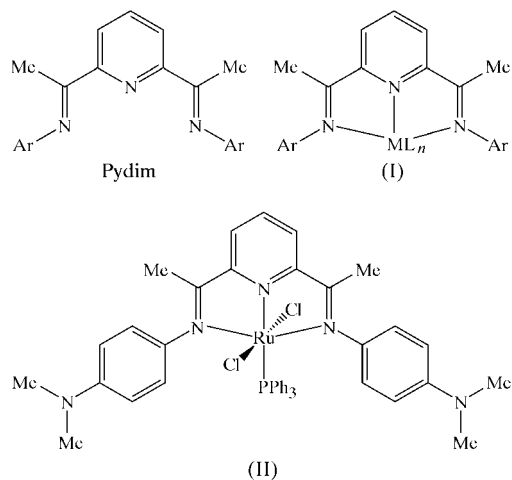
The title compound, $[\text{RuCl}_2(\text{C}_{25}\text{H}_{29}\text{N}_5)(\text{C}_{18}\text{H}_{15}\text{P})]$, a transfer hydrogenation catalyst, is supported by an N,N',N'' -tridentate pyridine-bridged ligand and triphenylphosphine. The Ru^{II} centre is six-coordinated in a distorted octahedral arrangement, with the two Cl atoms located in the axial positions, and the pyridine (py) N atom, the two imino N atoms and the triphenylphosphine P atom located in the equatorial plane. The two equatorial $\text{Ru}-\text{N}_{\text{imino}}$ distances (mean 2.093 Å) are substantially longer than the equatorial $\text{Ru}-\text{N}_{\text{py}}$ bond [1.954 (4) Å]. It is observed that the $\text{N}_{\text{imino}}-\text{M}-\text{N}_{\text{py}}$ bond angle for the five-membered chelate rings of 2,6-bis(imino)pyridine-based complexes is inversely related to the magnitude of the $\text{M}-\text{N}_{\text{py}}$ bond. The title structure is stabilized by intra- and intermolecular $\text{C}-\text{H}\cdots\text{Cl}$ hydrogen bonds, as well as by intramolecular $\pi-\pi$ stacking interactions between the aromatic rings belonging to the triphenylphosphine ligand and the dimethylaminophenyl fragment. The intermolecular hydrogen bonds form an $R_2^2(12)$ ring and a zigzag chain of fused centrosymmetric rings running parallel to the [100] direction.

Comment

Pydim [2,6-bis(imino)pyridine] complexes of the form of (I) display a range of catalytic activity. For example, iron and cobalt complexes have been used in alkene polymerization reactions (Small *et al.*, 1998; Tellmann *et al.*, 2005; Bryliakov *et al.*, 2004; Ionkin *et al.*, 2006). Ruthenium complexes have been studied for potential applications, such as optical sensors and chemical catalysis (Bianchini & Lee, 2000; Ertekin *et al.*, 2003; Çetinkaya *et al.*, 1999; Dayan & Çetinkaya, 2007). More

recently, Ru^{II} complexes have been used for transfer hydrogenation reactions of ketones (Dayan & Çetinkaya, 2007).

While Ru^{II} -pydim complexes have been examined extensively, reports of the structural properties of these compounds are rare in the literature (Ertekin *et al.*, 2003; Özdemir *et al.*, 2007). The necessity of auxiliary ligand L in our $[\text{RuCl}_2(\text{N},\text{N}',\text{N}''-L)]$ system (Çetinkaya *et al.*, 1999) prompted us to investigate the influence of PPh_3 . Therefore, a single-crystal X-ray structure analysis has been carried out on the title complex, (II).



The molecular structure of complex (II) and the atom-labelling scheme are shown in Fig. 1. Selected geometric parameters are summarized in Table 1. The mononuclear molecule contains an $(N^1,N^{1'}E,N^2,N^{2'}E)-N^1,N^{1'}-[1,1'-(\text{pyridine-2,6-diyl})\text{diethylidene}]bis(N^4,N^4\text{-dimethylbenzene-1,4-diamine})$ ligand with an Ru^{II} metal centre, one triphenylphosphine ligand and two Cl ligands. The pydim ligand, with its two imine groups in *ortho* positions with respect to the pyridine N atom, behaves as a symmetrical N,N',N'' -tridentate chelate. The Ru^{II} ion is six-coordinated by two imino N atoms, one pyridine N atom, one triphenylphosphine P atom and two Cl atoms (Fig. 1). The Ru1/N1/C1/C16/N4 and Ru1/N1/C5/C6/N2 chelate rings are planar, and the maximum deviations from their planes are 0.028 (4) and -0.040 (3) Å, respectively, for atoms C1 and N1. These two chelate rings make a small dihedral angle of 2.74 (3)° with one another, indicating that they are nearly coplanar.

The local structure around the Ru^{II} ion is that of an octahedron, of which the equatorial plane is formed by three N atoms from the pydim ligand (N1, N2 and N4) and the P atom of the triphenylphosphine ligand (P1). The axial positions in the octahedron are occupied by two Cl atoms (Cl1 and Cl2). As can be seen from the *trans* angles, which range from 154.96 (19) to 175.78 (15)°, and the *cis* angles, which range from 77.60 (18) to 102.62 (14)°, the coordination octahedron around the Ru^{II} ion can be visualized as being distorted, with the major distortion arising *via* the $\text{N2}-\text{Ru1}-\text{N4}$ angle [154.96 (19)°]. This angle is considerably smaller than the ideal angle of 180° . The $\text{N1}-\text{Ru}-\text{P1}$ angle, involving the pyridine N and triphenylphosphine P atoms, is normal at 175.78 (15)°. The $\text{Ru}-\text{N2}$ and $\text{Ru}-\text{N4}$ bond lengths are comparable to the

reported values for $[\text{RuCl}_2(\text{pybox-dihydro})(\text{C}_2\text{H}_4)]$ [pybox is bis(hydrooxazolyl)pyridine; Nishiyama *et al.*, 1995]. However, the $M\text{--N}_{\text{py}}$ bond [1.954 (4) Å] is somewhat shorter than the $M\text{--N}_{\text{imino}}$ bonds, the formal double-bond character of the imino linkages $\text{N}2=\text{C}6$ and $\text{N}4=\text{C}16$ having been retained [$\text{C}=\text{N} = 1.310$ (6) and 1.320 (6) Å, respectively]. When the ruthenium–phosphine distance is compared with the six-coordinate complexes reported in the literature [2.337 (3), 2.3451 (12) and 2.2384 (2) Å; Abbenhuis *et al.*, 1998], it is seen that the ruthenium–phosphine distance in the solid-state structure of (II) is lengthened significantly to 2.3890 (14) Å, pointing to a weaker $\text{Ru}\text{--}\text{P}$ interaction. This observation is attributed to steric effects of the groups bonded to the imino N atoms.

Previously, we have reported the closely related compound $[\text{RuCl}_2(\text{pydim})\text{CH}_3\text{CN}]$ (Ar = 4-MeOC₆H₄; Çetinkaya *et al.*, 1999), (III). The geometries of the N,N',N'' -tridentate ligands in (II) and (III) are very similar. However, the comparison between these structures reveals differences caused by the transition from $L = \text{MeCN}$ to $L = \text{PPh}_3$. The $\text{Ru}\text{--}\text{N}_{\text{py}}$ distance in (II) is significantly longer than the corresponding value in (III) [1.906 (7) Å]. This reflects the steric congestion around the ruthenium centre and also the greater *trans* influence of PPh_3 ; it appears that the stronger π -acceptor ability of PPh_3 , in comparison with MeCN, allows it to compete more effectively with the *trans* pyridyl unit for Ru electron density, and therefore the $\text{Ru}\text{--}\text{N}_{\text{py}}$ bond becomes weakened and extended in complex (II) when compared with that in (III) (Coe & Glenwright, 2000). The planes of the benzene rings substituted on the bis(imino)pyridine ligand backbone are inclined to the plane of the backbone at 55.11 (20) and 77.87 (19)° for the C8–C13 and C18–C23 rings, respectively, while the dihedral angle between the two benzene planes is 67.90 (17)°. The geometries at the imino N-atom centres are all trigonal planar, the sums of the three bond angles around these centres being 359.8 and 359.9°, and none of the atoms is more than *ca* 0.03 Å out of its associated RuC_2 plane.

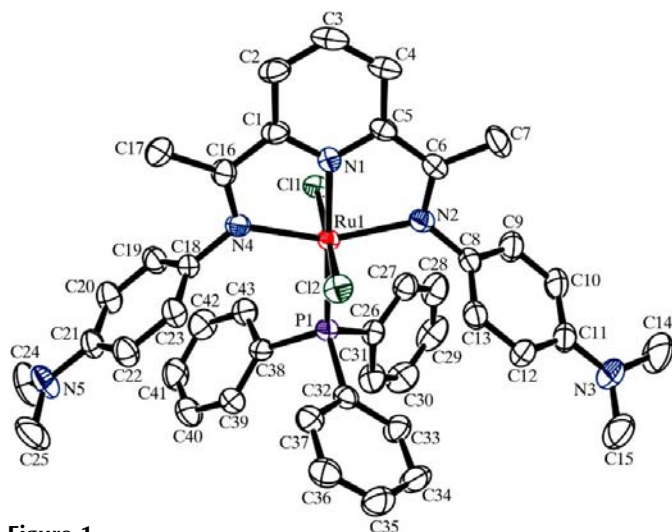


Figure 1

A view of (II), showing 30% probability displacement ellipsoids and the atom-numbering scheme. H atoms have been omitted for clarity.

There are several structures reported in the literature containing various transition metal complexes of pydim ligands (Britovsek *et al.*, 1999; Dias *et al.*, 2000; Nakayama *et al.*, 2005; Humphries *et al.*, 2005). Inspection of the $M\text{--}\text{N}$ bond distances in (II) and in these examples indicates that the two $M\text{--}\text{N}_{\text{imino}}$ bonds are *ca* 0.1–0.2 Å longer than the corresponding $M\text{--}\text{N}_{\text{py}}$ bond within each metal–tridentate chelate unit. Furthermore, it is observed that the $\text{N}_{\text{imino}}\text{--}\text{M}\text{--}\text{N}_{\text{py}}$ bond angle for the five-membered chelate rings of pydim complexes is inversely related to the magnitude of the $M\text{--}\text{N}_{\text{py}}$ bond, as expected. As the $M\text{--}\text{N}_{\text{py}}$ distance increases from 1.833 (3) Å for $[\text{CoMe}(\text{pydim})]$ (Ar = 2,6-*i*-Pr₂C₆H₃; Humphries *et al.*, 2005) to 1.911 (3) Å for $[\text{RhMe}(\text{pydim})](\text{OTf})_2$ (Ar = 2,6-*i*-Pr₂C₆H₃; OTf is trifluoromethanesulfonate; Dias *et al.*, 2000) to 1.954 (4) Å for (II) to 2.001 (3) Å for $[\text{CrCl}_3(\text{pydim})]$ (Ar = C₆F₅; Nakayama *et al.*, 2005) to 2.110 (6) Å for $[\text{FeCl}_2(\text{pydim})]$ (Ar = 2,4,6-Me₃C₆H₂; Britovsek *et al.*, 1999), the corresponding inner ‘bite’ angle decreases continually from 81.17 (average) to 79.8 (average) to 77.62 (average) to 76.6 (average) to 72.8° (average), respectively.

Examination of the structure with *PLATON* (Spek, 2003) reveals that there is an intramolecular $\pi\text{--}\pi$ stacking interaction between the C18–C23 and C38–C43 rings, with a distance of 3.636 (10) Å between the ring centroids and a perpendicular distance of 3.353 (12) Å between the rings. In the molecular structure of (II), three intramolecular interactions are observed between the benzene H atoms and the Cl atoms (Table 2), which lead to the formation of six-membered rings with graph-set descriptor $S(6)$ (Bernstein *et al.*, 1995). In the crystal structure of (II), pyridine atom C2 in the molecule at (x, y, z) acts as a hydrogen-bond donor to atom Cl2 in the molecule at $(1 - x, -y, 1 - z)$, so forming a centrosymmetric $R_2^2(12)$ ring centred at $(\frac{1}{2}, 0, \frac{1}{2})$. Similarly, pyridine atom C4 in the molecule at (x, y, z) acts as a hydrogen-bond donor to atom Cl1 in the molecule at $(2 - x, -y, 1 - z)$, so forming a

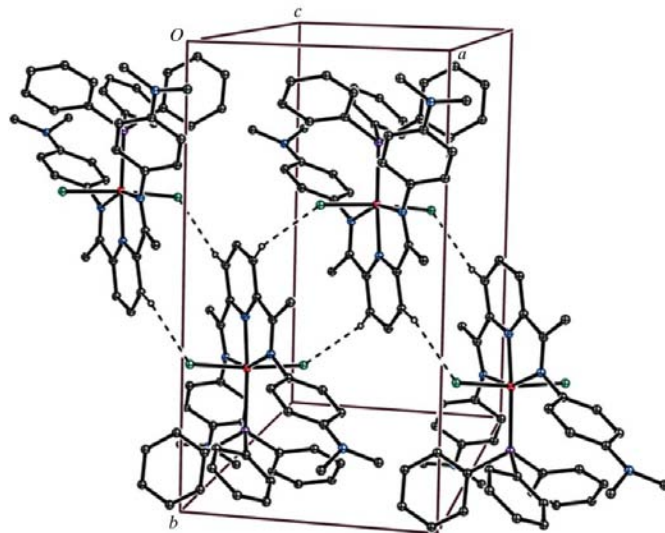


Figure 2

Part of the crystal structure of (II), showing the formation of a zigzag chain of fused centrosymmetric $R_2^2(12)$ rings along [100]. For clarity, only H atoms involved in hydrogen bonding have been included.

second centrosymmetric $R_2^2(12)$ ring motif centred at $(1, 0, \frac{1}{2})$. Propagation by inversion and translation of these two interactions generates a zigzag chain of fused rings running parallel to the $[100]$ direction (Fig. 2). The full geometry of the intra- and intermolecular interactions is given in Table 2.

Experimental

The title complex was synthesized according to a literature method (Dayan & Çetinkaya, 2007) and X-ray quality crystals were grown from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ (20 ml, 1:3 *v/v*).

Crystal data

$[\text{RuCl}_2(\text{C}_{25}\text{H}_{29}\text{N}_5)(\text{C}_{18}\text{H}_{15}\text{P})]$	$V = 3907.8 (4) \text{ \AA}^3$
$M_r = 833.77$	$Z = 4$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 10.2192 (5) \text{ \AA}$	$\mu = 0.62 \text{ mm}^{-1}$
$b = 18.3059 (13) \text{ \AA}$	$T = 296 \text{ K}$
$c = 20.9425 (12) \text{ \AA}$	$0.72 \times 0.28 \times 0.04 \text{ mm}$
$\beta = 94.089 (4)^\circ$	

Data collection

Stoe IPDSSI diffractometer	24010 measured reflections
Absorption correction: integration (<i>X-RED32</i> ; Stoe & Cie, 2002)	6869 independent reflections
$T_{\min} = 0.893$, $T_{\max} = 0.978$	3478 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.121$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.052$	471 parameters
$wR(F^2) = 0.075$	H-atom parameters constrained
$S = 0.91$	$\Delta\rho_{\max} = 0.37 \text{ e \AA}^{-3}$
6869 reflections	$\Delta\rho_{\min} = -0.44 \text{ e \AA}^{-3}$

Table 1

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

Ru1—N4	2.067 (4)	Ru1—Cl2	2.4034 (17)
Ru1—N2	2.119 (4)	Ru1—Cl1	2.4106 (17)
N1—Ru1—N4	77.64 (17)	N2—Ru1—Cl2	87.50 (12)
N1—Ru1—N2	77.60 (18)	P1—Ru1—Cl2	94.54 (6)
N4—Ru1—N2	154.96 (19)	N1—Ru1—Cl1	84.93 (14)
N1—Ru1—P1	175.78 (15)	N4—Ru1—Cl1	88.13 (13)
N4—Ru1—P1	102.35 (12)	N2—Ru1—Cl1	93.32 (12)
N2—Ru1—P1	102.62 (14)	P1—Ru1—Cl1	90.85 (5)
N1—Ru1—Cl2	89.68 (14)	Cl2—Ru1—Cl1	174.23 (5)
N4—Ru1—Cl2	88.73 (13)		

Table 2

Hydrogen-bond geometry (\AA , $^\circ$).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C43—H43 \cdots Cl1	0.93	2.78	3.587 (6)	145
C13—H13 \cdots Cl2	0.93	2.73	3.518 (6)	143
C27—H27 \cdots Cl1	0.93	2.72	3.343 (7)	126
C2—H2 \cdots Cl2 ⁱ	0.93	2.79	3.580 (6)	144
C4—H4 \cdots Cl1 ⁱⁱ	0.93	2.81	3.588 (6)	142

Symmetry codes: (i) $-x + 1, -y, -z + 1$; (ii) $-x + 2, -y, -z + 1$.

H atoms were positioned geometrically and treated using a riding model, fixing the C—H bond lengths at 0.96 and 0.93 \AA for CH_3 and

aromatic CH groups, respectively. The $U_{\text{iso}}(\text{H})$ values were constrained as $1.2U_{\text{eq}}$ ($1.5U_{\text{eq}}$ for methyl groups) of the pivot atom. Riding methyl H atoms on atoms C7 and C17 were allowed to rotate freely during refinement using the AFIX 137 command of *SHELXL97* (Sheldrick, 1997). Other methyl H atoms were placed in geometrically idealized positions using the *SHELXL97* HFIX 33 command and constrained to ride on their parent atoms.

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED32* (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *PLATON* (Spek, 2003).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: HJ3041). Services for accessing these data are described at the back of the journal.

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