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Synthesis, characterization and X-ray structure of *N*-2-pyridylmethylidene-1-phenylethylamine–$PdCl_2$ complexes

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Abstract

The $PdCl_2$ complexes with imines derived from reactions of 2-pyridinealdehyde with (*R*)-, (*S*)- and racemic 1-phenylethylamine have been synthesized and characterized by various physico-chemical methods. The (*R*)-**1** and (*S*)-**1** palladium complexes obtained from the (*R*)- and (*S*)- ligands were optical antipodes and differed only by the optical rotation sign and opposite circular dichromism spectra. Two crystals **I** and **II** resulted from these complexes were studied by the X-ray analysis. The first structure turned out to be racemic (it had the centrosymmetric space group $P2_1/c$) while the second one (space group $P2_1$) contained the molecules of a single enantiomer. The *cis* chelate coordination of the organic ligand and almost square-planar coordination geometry was found for both crystals. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Optically active Schiff base; Palladium(II) complex; Structure

1. Introduction

Complexes of transition metals with optically active ligands, including Schiff bases, have been used as chiral inductors in a large number of asymmetric catalytic processes [1–3]. Optically active (*R*)- and (*S*)-*N*-2-pyridylmethylidene-1-phenylethylamine (named in Ref. [1] as 2-pyridinal-1-phenylethylimine (PPEI)) was found to be an efficient ligand of Rh(I) and Ir(I) complexes for enantioselective hydrosilylation and hydrogen transfer reduction, respectively [4–7]. The complexes of this ligand with a number of transition metals were known earlier: the tetragonal pyramidal compounds $[M(\eta^5\text{-}C_5H_5)(PPEI)(CO)_2]PF_6$ (M = V [8], Mo and W [9–11]) and the analogous cobalt derivatives [12]. The structure of one of them was determined by X-ray analysis [11]. The structure of this ligand complex with one metal of the platinum group was previously reported [6]: PPEI-(COD)IrI, synthesized from (*S*)-PPEI, $[Ir(COD)Cl]_2$ and NaI (COD = *cis,cis*-1,5-cyclooctadiene).

In a continuation of our studies [13–16] in the area of asymmetric catalysis (hydrosilylation and hydrogen transfer reduction of ketones and trimethylsilylcyanation of aldehydes in the presence of $RhCl_3$, $[Rh(COD)Cl]_2$, $AlCl_3$ complexes with the optically active *N,N′*-bi- and *N,N′,N″*-tridentate chelating ligands based on the pyridine framework) and taking into account our prior interest in palladium(II) complex catalysts [17] we are reporting herein the preparation and investigation of $PdCl_2$ complexes with PPEI. Reports in recent literature on the studies concerning the structures of complexes with the pairs of enantiomers are scarce. In this work we have synthesized and studied the palladium complexes with (*R*)-, (*S*)- and racemic ligands.

2. Results and discussion

2.1. Synthesis and characterization of the PPEI ligands and the (R)-1, (S)-1 and racemic 1 complexes

The above named complexes were prepared from $K_2[PdCl_4]$ [18] and the corresponding PPEI [4] (Scheme 1).

Three prepared complexes and the (*R*)-, (*S*)-PPEI ligands were investigated by means of IR, UV, CD, MS, ^{1}H-NMR, determination of optical rotation and elemental analysis. The IR and ^{1}H-NMR spectra are

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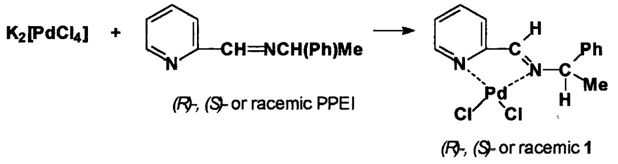

Scheme 1. Synthesis of complexes **1**.

Table 1
IR spectra in the 1490–1800 cm^{-1} region

Compound	Assignments (ν, cm^{-1}) [a]			
	Pyridine ring			C=N
PPEI	1495 s	1570 s	1590 s	1650 s
1 [b]	1498 m	1600 m	1623 w	1687 m, br s
$\Delta\nu$	+3	+30	+33	+37

[a] According to [19]; s-strong, m-medium, w-weak, br – broad.
[b] The identical spectra of (*R*)-, (*S*)- and racemic **1** were found.

listed in Tables 1 and 2. ^{1}H-NMR spectra of the PPEI ligands were comparable with that given in [4] for the (*S*)-isomer. The comparison of the spectra of the ligands with the spectra of the complexes evidenced for the coordination of Pd atom with N atoms of pyridine and imine groups as expected.

It is worthy to note the changes in the sign and optical rotation value observed in amine–imine-complex consecutive transformations (Table 3). The PPEI obtained by condensation, e.g. of (*R*)-(+)-PEA with 2-pyridinecarbaldehyde was levorotary while the complexation with $PdCl_2$ changed the sign of optical rotation, and also increased the optical rotation value. However, it is not a general rule for conversions of all optically active amines in condensations and complexations, as was affirmed in Ref. [21]. The signs of optical rotation of some primary amines remain unchanged after the condensation with aldehyde [22].

Table 3
Specific optical rotation of amines, imines and complexes **1**

Compound	$[\alpha]^{20}_{546}$ (°)	Conditions
(*R*)-PEA [a]	+35 [20]	$c = 10$, ethanol
(*R*)-PPEI	− 55	$c = 10$, acetone
(*R*)-**1**	+140	$c = 1$, chloroform
(*S*)-PEA	−35 [20]	$c = 10$, ethanol
(*S*)-PPEI	+56 [b]	$c = 10$, acetone
(*S*)-**1**	−140	$c = 1$, chloroform

[a] PEA-1-phenylethylamine.
[b] $[\alpha]^{20}_{546} = +55.7°$ ($c = 51.0$, acetone) [4].

The CD spectra of both (*R*)- and (*S*)- complexes shown in Fig. 1 confirm that these coordination compounds are optical antipodes. All optically active bands could also be followed up in the UV spectra, which were identical for two enantiomers.

2.2. Molecular and crystal structure

Single crystals **I** and **II**, suitable for X-ray structure determination were obtained from (*R*)-**1** and (*S*)-**1** complexes, respectively. The attempts to prepare a crystal of a complex synthesized from racemic PPEI suitable for X-ray analysis were not successful. The structure of the palladium complexes **I** and **II** are shown in Figs. 2–4. The selected bond distances and angles of the crystal **I** are given in Table 4. Contrary to expectation the crystals afforded from two optical antipodes in the same conditions were not antipodes. It turned out that crystal **I** obtained from (*R*)-**1** was racemic (centrosymmetric space group $P2_1/c$), while crystal **II** grown from (*S*)-**1** contained the molecules of one enantiomer (non-centrosymmetric space group $P2_1$).

The X-ray study of the crystals **I** and **II** confirmed the *cis* chelate coordination of the ligand and almost square-planar coordination geometry. In structure **I** the

Table 2
^{1}H-NMR (360 MHz, $CDCl_3$, TMS, 303 K; δ in ppm, J in Hz)

Compound	CH_3	$CHCH_3$	C_6H_5	Pyridine ring				CH = N
				H-3	H-4	H-5	H-6	
PPEI	1.61 d $J = 6.9$	4.64 q $J = 6.9$	7.2–7.5 m	8.09 ddd $J_1 = 7.7$ $J_2 = 1.4$ $J_3 = 1.0$	7.72 m $J_1 = 7.7$ $J_2 = 1.7$	7.29 ddd $J_1 = 7.7$ $J_2 = 4.9$ $J_3 = 1.4$	8.63 m $J_1 = 4.9$ $J_2 = 1.7$ $J_3 = 1.0$	8.46 m $J < 1.0$
1 [a]	1.85 d $J = 6.9$	5.99 q $J = 6.9$	7.3–7.5 m	7.90 m $J = 7.6$	8.09 m $J_1 = 7.6$ $J_2 = 1.5$	7.64 ddd $J_1 = 7.6$ $J_2 = 5.6$ $J_3 = 1.5$	9.23 m $J_1 = 5.6$ $J_2 = 1.5$	8.03 m $J < 1.0$

[a] The identical spectra of (*R*)-, (*S*)- and racemic **1** were found.

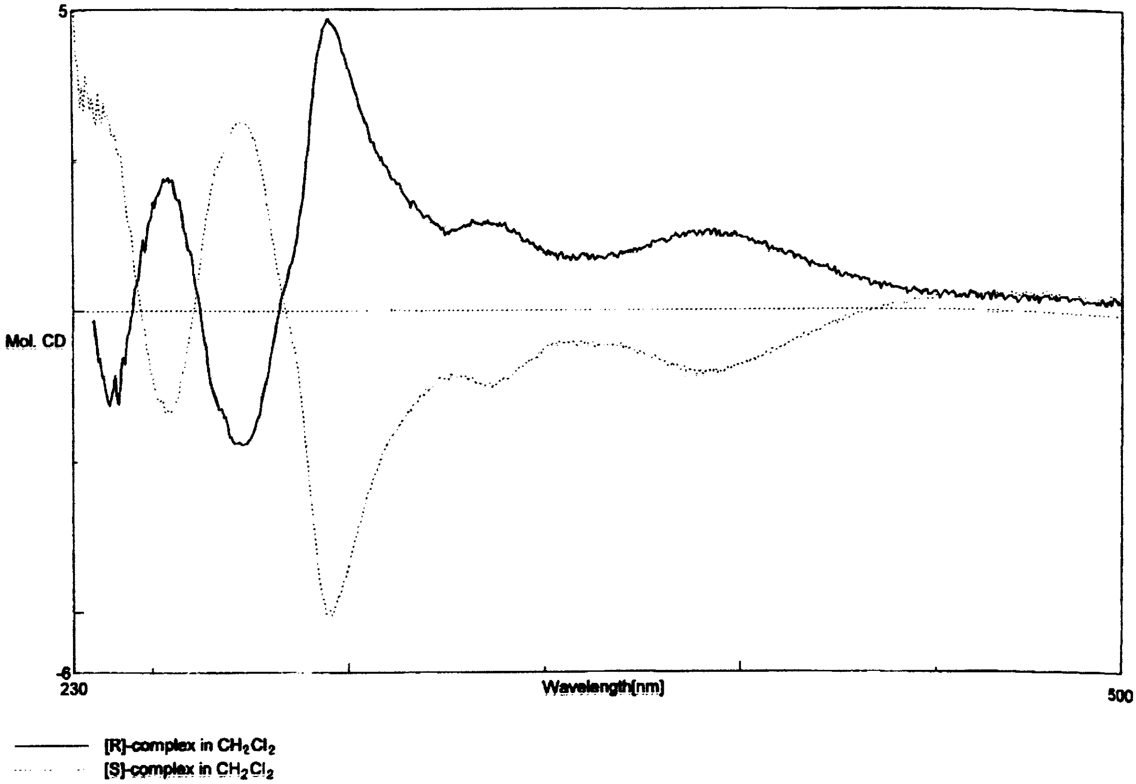

Fig. 1. CD spectra of (*R*)-**1** and (*S*)-**1** complexes.

Pd–Cl1 (2.286(2) Å) distance was longer than Pd–Cl2 (2.270(2) Å). In turn Pd–N1 (2.014(5) Å) was slightly shorter than Pd–N2 (2.032(4) Å). The smallest bond angle at Pd atom was N1–Pd–N2 = 80.7(2)°. The sum of bond angles around Pd atom was just 360°. Pyridine plane formed a dihedral angle of 6.1° with the coordination plane. The phenyl ring was turned out from the coordination plane by a dihedral angle of 74.8°.

In crystal the molecular fragments of complex **1** formed stacks with Pd–Pd intermolecular distances of 4.376 Å. Channels between the stacks were filled with 1,4-dioxane molecules fixed close to each other by two electron-rich phenyl groups from the adjacent stacks (Fig. 3). Possibly, the solvate molecules stabilized the centrosymmetric structure of the crystal **I**.

In the structure of the crystal **II** three independent molecules (a, b, c) have been found in the asymmetric unit cell (Fig. 4). Insufficient accuracy of refinement for crystal **II**, resulting from the poor quality of the crystals used, does not permit the discussion of its geometry in detail. However, it is worth noting that all three molecules had the same absolute configuration with respect to the asymmetric atom C(7) and differed in the orientation of the phenyl rings. The solvate molecules were absent in the structure of crystal **II**.

Thus, two (*R*)-**1** and (*S*)-**1** palladium complexes synthesized from the known PPEI ligand were optical antipodes differing only by the optical rotation sign and opposite circular dichromism spectra. However, the X-ray analysis of crystals **I** and **II** obtained from these two complexes by their recrystallization under the same conditions from chloroform–hexane–1,4-dioxane at ambient temperature has revealed that one of them was racemic while another contained the molecules of a single enantiomer. It shows that optical antipodes may have different tendencies to racemization. Possibly, easy racemization of some complexes is a reason for their low enantiomeric selectivity in catalytic processes.

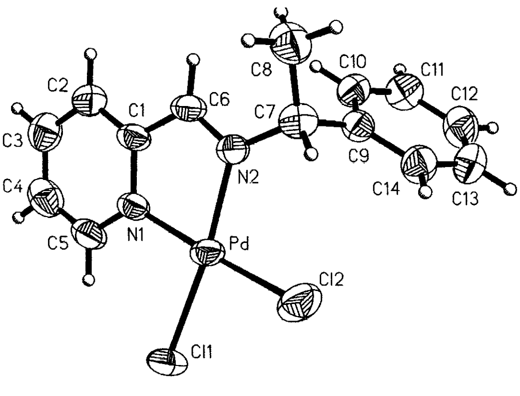

Fig. 2. Molecular structure of the crystal **I**.

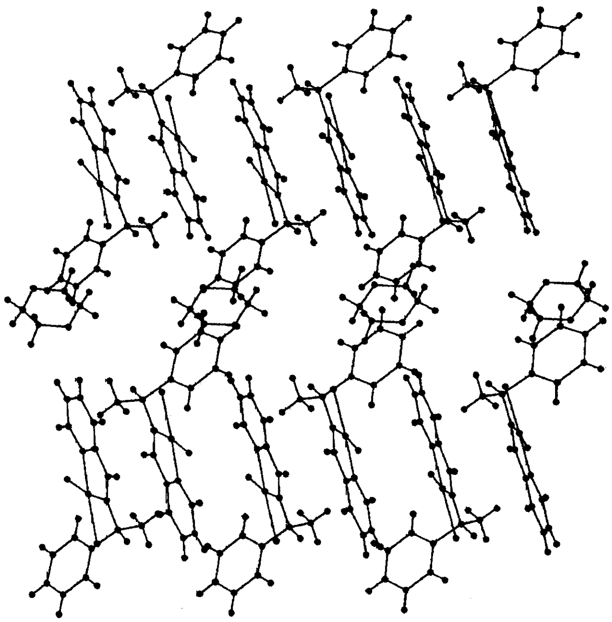

Fig. 3. Diagram of the crystal packing for **I** (**1**.1/2 1,4-dioxane solvate).

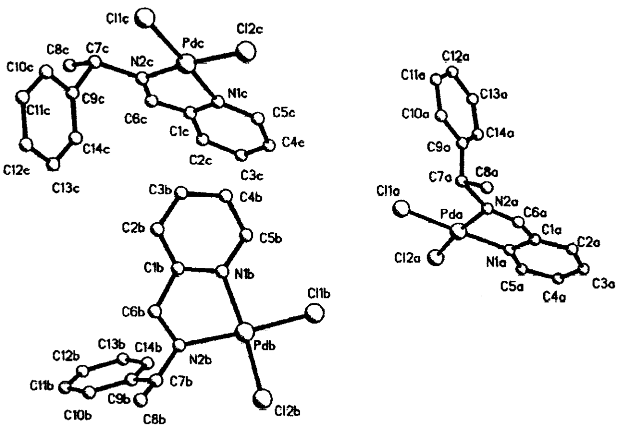

Fig. 4. Molecular structure of the crystal **II**.

Table 4
Selected geometric data for crystal **I**

Bond distances (Å)			
Pd–N1	2.014(5)	Pd–Cl2	2.270(2)
Pd–N2	2.032(4)	Pd–Cl1	2.286(2)
Bond angles (°)			
N1–Pd–N2	80.7(2)	C5–N1–Pd	129.2(4)
N1–Pd–Cl2	176.3(1)	C1–N1–Pd	113.2(3)
N2–Pd–Cl2	95.9(1)	C6–N2–Pd	113.0(4)
N1–Pd–Cl1	93.1(1)	C7–N2–Pd	125.8(3)
N2–Pd–Cl1	173.4(1)	Cl1–Pd–Cl2	90.3(8)

3. Experimental

3.1. General methods and materials

The following instruments were used to characterize the compounds: Perkin–Elmer 580 B IR spectrometer; Bruker AM-360 (360 MHz) NMR spectrometer, $CDCl_3$ as a solvent, TMS as an internal standard; Kratos MS-25 GC–MS (70 eV) spectrometer and MS-50 (70 eV) mass spectrometer. All starting chemicals were purchased from Fluka or Merck and were of commercial grade.

3.2. CD and UV study

Two enantiomeric (*R*)-**1** and (*S*)-**1** complexes were investigated by means of circular dichromism (CD) spectroscopy in CH_2Cl_2. The spectra were measured on a Dichrograph J700 (Jasco) within the wavelength range of 200–500 nm at 22–25°C. The Dichrograph was calibrated by the standards of epiandrosterone and 10-camphorsulphonic acid. To record the spectra quartz cells of Helma were used: 0.01 cm for the spectral range 230–500 nm and 0.005 cm for the range 200–350 nm. The concentration of the solutions was 10^{-2}–10^{-3} M. The molar ellipticity [θ] was measured as degree cm^2 dmol^{-1}. The UV spectra were recorded on the spectrophotometer Lambda2-S (Perkin–Elmer) within the wavelength range of 200–600 nm; the same quartz cells as for recording of CD spectra were used.

3.3. X-ray crystallographic study

Two single crystals **I** and **II** obtained from (*R*)-**1** and (*S*)-**1**, respectively, were studied by the X-ray analysis. The data were collected on a Syntex $P2_1$ automatic diffractometer (Mo–K_α radiation, graphite monochromator) by $\theta/2\theta$ method. The cell constants were obtained from the least-squares refinement on the setting angles of 20 reflections in the range of $20 < 2\theta < 25°$. No absorbtion correction was used. Crystallographic data for both structures are given in Table 5. The structures were solved by a direct method using the program SHELXS-86 [23] and refined by the full-matrix least-squares method on F^2 (SHELXL-93) [24] anisotropically for non-hydrogen atoms. H atoms were constrained to ride on the adjacent non-H atoms.

3.4. $K_2[PdCl_4]$ and PPEI (*R*-, *S*- and racemic)

$K_2[PdCl_4]$ and PPEI (*R*-, *S*- and racemic) were obtained using the slightly modified methods described in Refs. [4,18]. Mass spectra of PPEI: MS (70 eV), *m*/*z* (%): 210 (12) [M^+], 195 (51) [$M^+ - CH_3$], 133 (10) [$M^+ - C_6H_5$], 105 (100) [C_5H_4N–CH=N^+], 92 (18), 79 (22), 78 (15) [$C_5H_4N^+$], 77 (28) [$C_6H_5^+$], 65 (12), 51 (21), 39 (13), 28 (22). For other data, see Tables 1–3.

Table 5
Crystal data and structure refinement for **I** and **II**

	I	**II**
Empirical formula	$C_{14}H_{14}N_2PdCl_2\cdot\frac{1}{2}$1,4-dioxane	$3C_{14}H_{14}N_2PdCl_2$
Formula weight	431.62	1162.83
Crystal system	Monoclinic	Monoclinic
Color	Light orange	Dark orange
Space group	$P2_1/c$	$P2_1$
Crystal size (mm)	$0.25\times0.30\times0.75$	Shapeless
a (Å)	14.795(9)	14.608(3)
b (Å)	7.627(4)	8.495(2)
c (Å)	16.409(10)	18.765(4)
β (°)	111.41(5)	103.34(3)
V (Å^3)	1723.8	2265.8(4)
Z	4	6
D_{calc} (Mg m^{-3})	1.663	1.704
$2\theta_{max}$ (°)	47.14	50.14
Number of independent reflections	2535	3523
Number of reflections with $J>2\sigma(J)$	2277	3002
R_{inf}	0.033	0.056
Number of parameters	200	505
R	0.044	0.147
R_w	0.103	0.337

*3.5. (R)-(+)-(N-2-Pyridylmethylidene-1-phenylethylamine)palladium(II)dichloride ((R)-**1**)*

The $K_2[PdCl_4]$ (0.33 g, 1 mmol) solution in water (10 ml) was treated with a slight excess of (R)-PPEI (0.22 g, 1.05 mmol) in 10 ml 1,4-dioxane. The product precipitated after 8 h stirring at ambient temperature. The precipitate was filtered off, washed with water, then acetone and hexane, and dried in a vacuum-excitator. Complex (R)-**1** (0.33 g, 85%) was prepared as a microcrystalline yellow substance (m.p. 186–188°C (decomposition)), the further investigations revealed that this compound was stable in air and water. The complexes (S)-**1** and racemic **1** obtained in this manner had the m.p. 184–185 and 189–201°C, respectively. The attempts to obtain the MS (EI, FAB) spectra of $PdCl_2$–PPEI complexes were not successful; decomposition of complex molecules took place. The characteristics of the complexes synthesized are given in Tables 1–3. The results of the elemental analysis for all three complexes were found in good agreement with the calculated data. Single orange crystals **I** and **II**, suitable for the X-ray diffraction analysis were obtained by recrystallization of (R)-**1** and (S)-**1** complexes from 1:1:0.1 chloroform–hexane–1,4-dioxane for 10 h at ambient temperature.

4. Supplementary material

The crystallographic data (excluding structure factors) for the structures reported in this paper were deposited with the Cambridge Crystallographic Center. The deposition numbers are CCDC 114914 and 114915. The copies of these data can be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: teched@chemcrys.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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