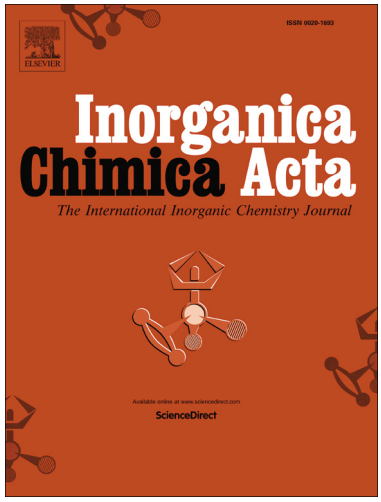

Research paper

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Yana A. Gur'eva, Igor N. Alekseev, Irina A. Dvornikova, Olga A. Zalevskaya, Aleksandr V. Kuchin

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Synthesis and characterization of new palladium complexes based on polydentate chiral Schiff base and amines ligands derived from (+)-2-hydroxypinan-3-one

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Abstract

Seven novel palladium complexes of the type $[Pd(HL)Cl_2]$ and [Pd(L)Cl] containing chiral pinane ligands (HL= 3-[(2-aminoethyl)imino]-pinane-2-ol; 3,3'-(ethylenediimino)*bis*-pinane-2-ol; *cis*-3-(2-aminoethylamino)-pinane-2-ol; *cis*-3,3'(ethylenediamino)bis-pinane-2-ol; *trans*-3,3'(ethylenediamino)bis-pinane-2-ol; 3-[2-(2-hydroxybenzylamino)ethylamino]-pinane-2-ol; L=3-[2-(3,5-di-*tert*-butyl-2-hydroxybenzylidene)amino)ethylimino]pinane-2-ol)) were synthesized in good yields from the direct reaction of chiral nitrogen ligands with Li_2PdCl_4 in MeOH. These synthesized complexes were characterized by means of elemental analysis, FT-IR, multidimensional and multinuclear NMR spectroscopic methods.

Keywords*:* Palladium complexes; chiral pinane ligands; diimines; diamines; ligands of salen type, chelate complexes, NMR

1. Introduction

It is known that derivatives of ethylenediamine are widely used in inorganic and coordination chemistry as ligands in the synthesis of complexes of various transition metals [1-5], including palladium and platinum [6-8]. Derivatives of ethylenediamine containing chiral terpene fragments, are well proven as effective chiral ligands in asymmetric catalysis [9-11]. In recent time, α-pinene nitrogen derivatives have been used as substrates in the synthesis of enantiomerically pure compounds [12,13], chiral auxiliaries [14, 15], and ligands for asymmetric synthesis [16–20]. Platinum and palladium complexes, containing diamines ligands, have been extensively studied and used in oncological practice [21-25]. Palladium complexes with different ligands show high antibacterial activity [26-29].

During the last two decades, many palladium complexes were tested practically in all the areas of classic palladium catalysis [30-38]. Especially impressing achievements are related to the catalysis by palladium complexes of Heck and cross-coupling reactions [39-42].

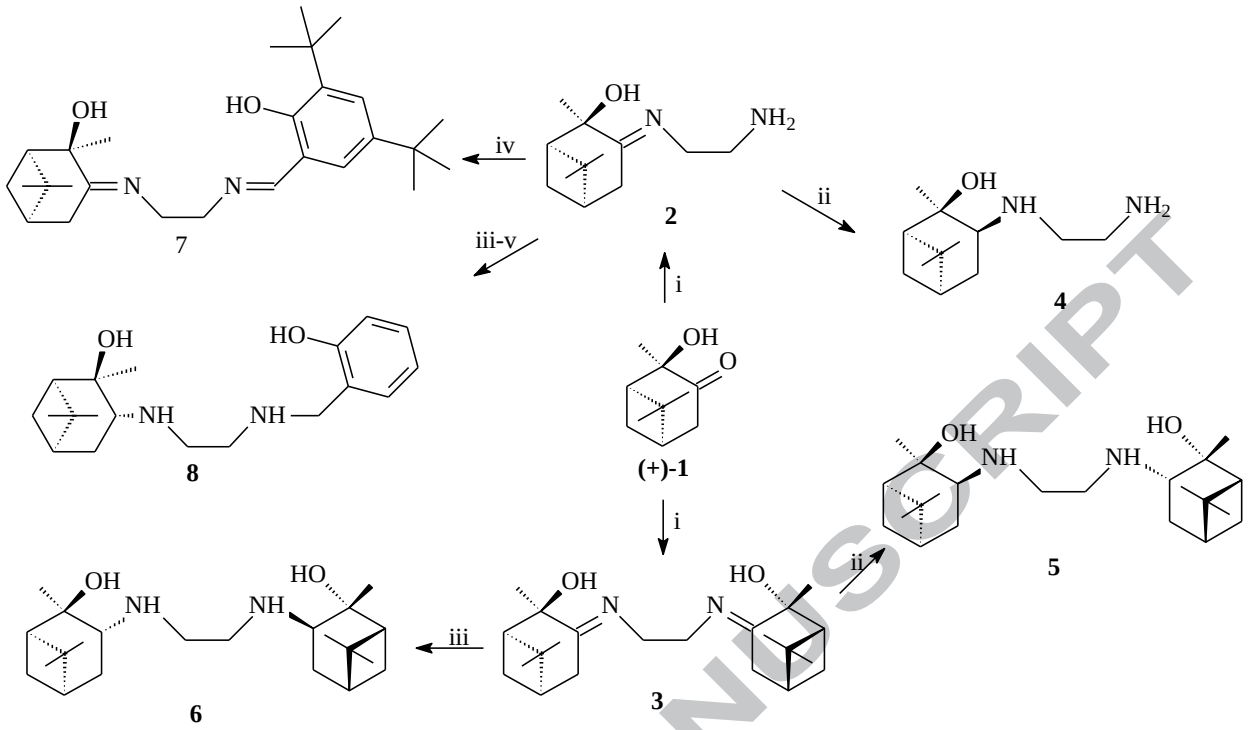
The simplicity of synthesis of these complexes draw the attention of chemists annually synthesized and tested hundreds of complex compounds of platinum and palladium with a variety of ligands. From these points of view, the development of methods of synthesis and structure investigation of new chiral palladium complexes is highly promising. Natural bicyclic monoterpenes, are available as both enantiomers are chiral building blocks as ligands for the synthesis of new palladium complexes. In this article we would like to report for the first time synthesis and structural studies of palladium complexes with chiral terpen polydentate ligands Schiff base derivatives of ethylenediamine and (+)-2-hydroxypinan-3-one.

3. Results and Discussion

Chiral ligands, derivatives of ethylenediamine and (+)-2-hydroxypinan-3-one **1** – monoimin **2**, diimin **3**, unsymmetrical diamin **4**, symmetrical *cis,cis*- and *trans,trans*-diamines **5,6**, unsymmetrical diimin **7** and diamin **8** were prepared to the method described earlier [20,43]. As starting compound for the synthesis of these chiral ligands (scheme 1) used (+)-2-hydroxypinan-3-one **1,** which was prepared by oxidation of α-pinene with $KMnO_4$ [44]. In the first step, monoimine **2** was synthesized in 79% yield by heating a solution of ketole **1** and a 20-fold excess of ethylenediamine in benzene in the presence of $F_3B{\times}OEt_2$ and molecular sieves. C_2-symmetrical *bis*-imine **3** was prepared in 51% yield by the reaction of ketole **1** with a three-fold excess of ethylenediamine. Next, the reduction imine **2** with $LiAlH_4$ in diethyl ether gave *cis-3*-aminopinan-2-ol **4** in 67% yield. Similarly by the reduction diimine **3** with $LiAlH_4$ in diethyl ether and $NaBH(AcO)_3$ in propan-2-ol *cis*- **5** and *trans*-amines **6** were obtained in 76 and 82% yields corresponding.

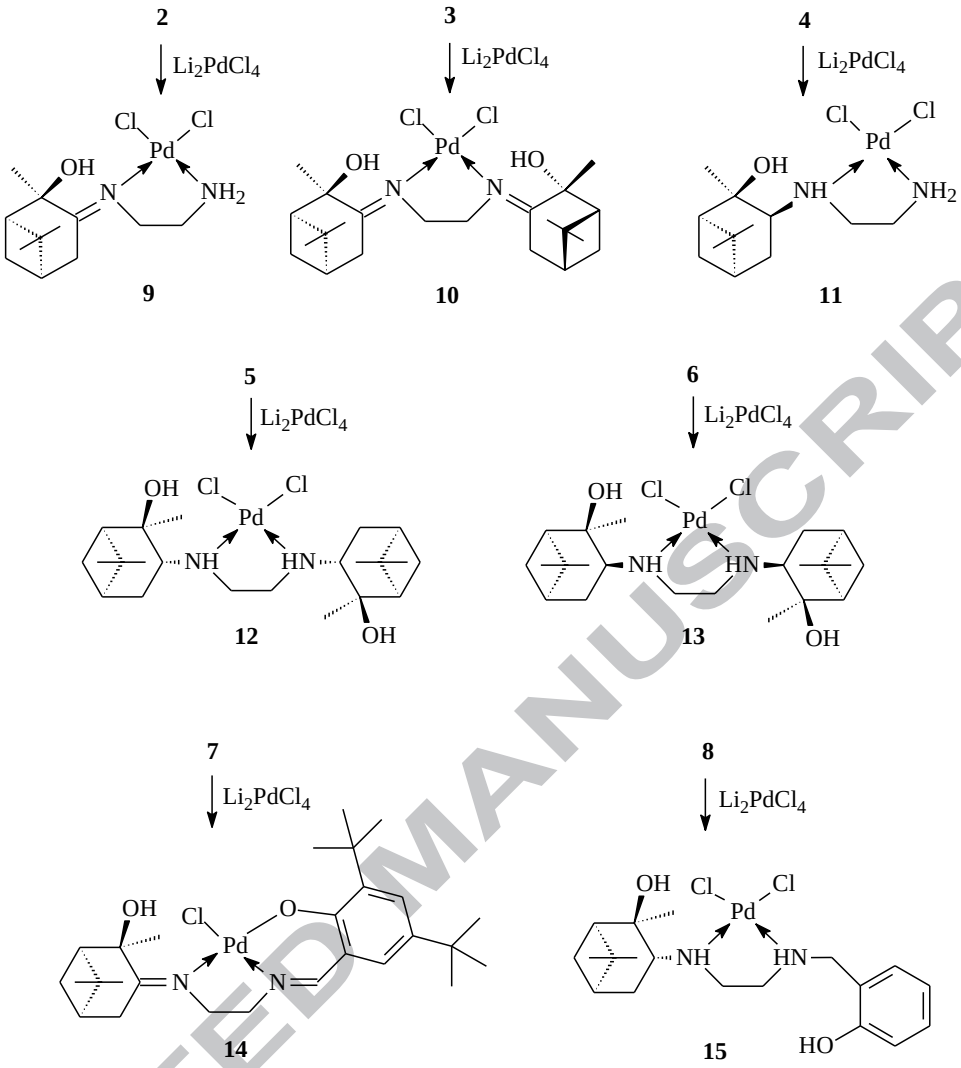
The reaction of monoimine **2** with salicylaldehyde and 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde in MeOH at room temperature gave unsymmetrical dihydroxydiimine in 93-95% yield (after crystallization). The reduction of the C=N bond with $NaBH_4$ in MeOH afforded unsymmetrical diamine **8** with 75% yield.

The chiral pinane ligands **2-8** were used as obtained in the reaction with Li_2PdCl_4 in MeOH to give complexes **9-15** with 65-98% yield, air stable pale yellow powders (scheme 2).



(i) $H_2N(CH_2)_2NH_2$, PhH, $F_3B{\times}OEt_2$, molecular sieves 4Å, 80°C; (ii) $LiAlH_4$, Et_2O, 20°C; (iii) $Na(OAc)_3BH$, *i*-PrOH, 20°C; (iv) aldehyde, MeOH, 20°C; (v) $NaBH_4$, MeOH, 20°C.

Scheme 1. Synthesis of chiral pinane ligands (**2**-**8**)



Scheme 2. Synthesis of palladium complexes (**9-15**)

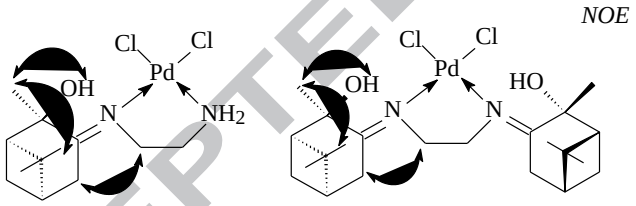
The structures of the seven new complexes **9-15** were determined using NMR (^{1}H, ^{13}C), IR-spectroscopy data and were confirmed by elemental analyses. The assignment of the signals in NMR spectra has been performed by the use of 2D (^{1}H, ^{1}H) COSY, NOESY, (^{1}H, ^{13}C), HSQC, HMBC techniques. NMR data of all complexes, their ligands and numbering of atoms used for NMR assignment presented in Tables 1-3 below, the arrows show characteristic NOE interactions.

Tables 1-3. NMR data complexes **9-15** and their ligands

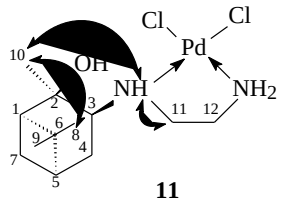
N	**9** – Acetone-d6 Ligand		**9** – Acetone-d6 Complex		**10** - $CDCl_3$ Ligand		**10** - $CDCl_3$ Complex*		**11*** - DMSO-d6 Ligand		**11*** - DMSO-d6 Complex	
	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H
1	50.4	2.08 m	53.0	2.01 m	50.5	2.08 m	52.5	2.13 dd J=5.5, 6.5	54.1	1.92 dd J=5.6, 5.9	54.9	1.66 dd J=5.4, 5.6
2	76.3	-	76.1	-	76.4	-	**	-	71.5	-	76.0	-
3	176.9	-	188.4	-	176.4	-	**	-	57.5	2.80 m	57.8	4.01 dd J=8.5, 8.7
4	33.7	2.50-2.55 m 2H	36.1	3.0-3.1 m 2H	33.7	2.55-2.68 m 4H	37.8	2.80-2.95 m 4H	37.9	1.27 ddd J=2.5, 5.6, 13.5 2.45 m J=13.5	29.8	2.20 m 2.38 m
5	38.3	2.06 m	38.1	2.04 m	38.5	2.06 m	37.7	2.06 m 2H	40.4	1.83 m J=5.6, 5.9	40.9	1.97 m
6	38.5	-	43.0	-	38.4	-	**	-	38.3	-	39.1	-
7	28.2	1.56 d J=10.5 2.35 m	26.9	1.60 d J=10.6 2.24 m	28.2	1.58 d J=10.6 2.35 m	26.8	1.78 d J=11 2.32 m	28.1	1.23 d J=10 2.07 dddd J=2.5, 5.6, 5.9, 10	27.9	1.28 d J=9.8 2.05 m
8	22.9	0.86 s	22.4	0.90 s	22.9	0.87 s	22.4	0.67 s	24.0	0.92 s	23.9	0.88 s
9	27.3	1.34 s	26.2	1.35 s	27.4	1.34 s	26.2	1.29 s	27.9	1.20 s	28.3	1.21 s
10	28.3	1.49 s	28.9	2.57 s	28.4	1.47 s	28.4	2.54 s	31.3	1.21 s	30.5	1.25 s
11	53.3	3.31 t J=5.7	60.8	4.25 dd J=3.6, 12.5 4.45 ddd J=5.0, 5.6, 12.5	51.4	3.55-3.70 m, 4H	55.2	3.94 d J=8.8 2H 4.79 d J= 8.8 2H	52.9	2.65-2.75 m 2H	50.0	2.68 m 3.08 m
12	42.6	3.00 tt J=5.4, 5.7	43.2	2.67 m 2.97 m					41.8	2.74-2.83 m 2H	46.4	2.26 m 2.65 m
OH	-	2.13 br 3H	-	5.76 s	-	3.07 s	-	5.44 s	-	2.25 very br 4H	-	4.57 s
NH	-		-	4.81 br 1H 5.00 br 1H	-	-	-	-	-		-	4.72, 4.90 br NH_2 6.09 br NH

* - signal ^{13}C was obtained from spectrum HSQC

** - signal not detected



9 **10**

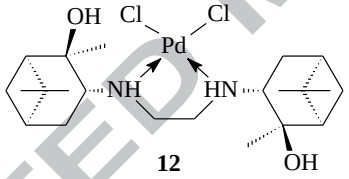


11

N	**12** - DMSO-d6						**13** - $CDCl_3$					
	Ligand		Complex Fragment-1		Complex Fragment-2		Ligand		Complex Fragment-1		Complex Fragment-2	
	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H
1	55.6	1.90 m	56.7	1.7 m	55.8	1.6 m	54.1	2.00 dd J=5.6, 5.8	54.9	2.01 dd J=5.5, 5.7	55.3	1.79 dd J=5.0, 5.5
2	77.6	-	76.4	-	76.1	-	71.8	-	73.5	-	73.5	-
3	60.7	3.16 dd J=8.6, 8.8	63.2	4.05 dd J=9.6, 10	61.1	3.35 m	57.3	2.90 m	57.4	4.42 m	65.4	2.97 m
4	33.1	2.28-2.38 m 4H	33.1	2.6-2.7 2H	28.0	2.02 m 2.75 m	38.1	1.33 m J=13 2.54 m J=13	29.2	2.22 m 2.72 dd J=11, 13	40.4	2.82 dd J=11.4 4.25 dd J=6.2, 11.4
5	40.3	1.99 m 2H	40.3	2.0 m	40.2	2.0 m	40.5	1.91 m	40.7	2.10 m	41.1	2.15 m
6	39.1	-	*	-	*	-	38.4	-	39.1	-	39.3	-
7	28.2	1.62 d J=10.2 2.14 m	24.9	1.54 d J=10 2.02 m	24.6	1.65 d J=11 2.02 m	28.2	1.30 d J=10 2.15 m	27.5	1.43 d J=11 2.20 m	28.0	1.92 d J=11 2.20 m
8	23.1	0.91 s	23.8	0.81 s	23.5	0.92 s	24.1	1.00 s	23.7	1.01 s	24.5	1.08 s
9	27.7	1.26 s	28.0	1.19 s	28.3	1.22 s	28.0	1.28 s	28.0	1.33 s	28.1	1.30 s
10	24.9	1.38 s	24.6	1.24 s	26.9	1.34 s	31.3	1.29 s	31.0	1.42 s	29.2	1.25 s
11	48.5	2.81 br m 2H 2.96 br m 2H	46.1	2.6 m 2H 3.13 m 2H	55.1	2.9 m 2H 3.4 m 2H	49.5	2.80-2.85 m 4H	50.1	3.03 m 3.48 m	60.4	2.27 m 4.48 m
OH	-	2.02 br 4H	-	5.12 d J=9.6	-	6.68 br	-	**	-	6.21 br d J=6.5	-	6.50 br s
NH	-		-	4.70 s	-	4.30 s	-	**	-	1.90 s	-	3.74 s

* - signal is under the DMSO ~40 ppm

** - signal not found in $CDCl_3$



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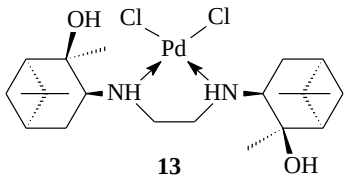
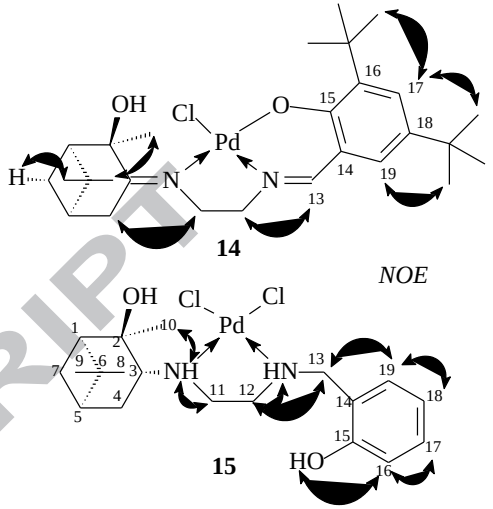


13

N	**14** – $CDCl_3$ Ligand		**14** – $CDCl_3$ Complex*		**15** – DMSO-d6 Ligand		**15** – DMSO-d6 Complex	
	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H
1	50.3	2.05 dd J=5.4, 5.8	52.9	2.13 dd J=5.7, 6.0	55.6	1.89 dd J=5.5, 5.6	56.7	1.58 dd J=5.6, 5.7
2	76.5	-	76.1	-	77.6	-	75.9	-
3	177.3	-	189.7	-	60.5	3.12 dd J=8.8, 9.2	60.6	2.70 m
4	33.7	2.47-2.61 m 2H	38.0	2.90 br 2H	33.1	1.41 dd J=8.5, 14 2.32 ddd J=5.0, 9.6, 14	32.4	2.25 m 2H
5	38.4	2.02 m	38.2	2.07 m	40.2	1.96 m	40.2	1.76 m
6	35.0	-	37.4	-	39.2	-	39.3	-
7	28.1	1.49 d J=10.3 2.31 m	27.1	1.76 d J=10.8 2.33 m	24.7	1.59 d J=10.0 2.14 m	24.1	1.30 d J=10 1.90 m
8	22.7	0.70 s	22.9	0.84 s	23.1	0.91 s	23.6	0.74 s
9	27.4	1.26 s	26.7	1.36 s	27.6	1.27 s	28.8	1.14 s
10	28.4	1.45 s	28.6	2.54 s	24.8	1.37 s	24.7	1.21 s
11	59.7	3.86-4.06 m 2H	59.4	4.18 dd J=3.0, 12 4.49 ddd J=4.3, 4.7, 12	48.4	2.74-3.02 m 4H	54.2	2.73 m 1H 3.24 m 1H
12	50.9	3.58-3.77 m 2H	58.6	3.52 ddd J=3.0, 4.7, 13 3.63 dd J=4.7, 13	47.2		48.6	2.35 m 1H 2.78 m 1H
13	167.0	8.38 s	159.7	7.50 s	52.4	4.05 s 2H	48.2	3.67 d J=12.5 3.87 dd J=4.7, 12.5
14	117.8	-	118.7	-	122.5	-	122.1	-
15	158.2	-	161.1	-	158.2	-	156.6	-
16	140.0	-	140.6	-	116.5	6.86 d J=7.8	115.6	6.89 d J=8.1
17	126.8	7.39 d J=2.4	131.0	7.44 d J=1.9	128.7	7.20 J=7.6, 7.8	129.9	7.20 dd J=7.8, 8.1
18	136.6	-	137.2	-	119.0	6.80 dd J=7.2, 7.6	119.6	6.95 dd J=7.2, 7.8
19	125.8	7.10 d J=2.4	126.9	6.96 d J=1.9	128.4	7.03 J=7.2	133.1	8.22 d J=7.2
OH	-	2.71 s (C2)	-	6.19 s (C2)	-	4.20 br 4H	-	4.30 s (C2) 9.73 s (C15)
NH	-	-	-	-	-		-	5.11 br d J=10 (C11) 6.56 br (C12)



HMBC (**14**): H10-C3, CH_3(t-Bu-16)-C16, CH_3(t-Bu-18)-C18, CH_3(t-Bu-16)-C(t-Bu-16), CH_3(t-Bu-18)-C(t-Bu-18).

HMBC (**15**): H19-C13, 15OH-C14, 15OH-C15, 2OH-C3, H13-C14, H10-C3, H10-C2.

* - additional signals for **14**

t-Bu-16: ^{13}C - 35.8 (C)+29.5 ($3CH_3$), ^{1}H - 1.45 s (9H); t-Bu-18: ^{13}C - 33.9 (C)+31.3 ($3CH_3$), ^{1}H - 1.28 s (9H) (complex).

t-Bu-16: ^{13}C - 35.0 (C)+29.4 ($3CH_3$), ^{1}H - 1.45 s (9H); t-Bu-18: ^{13}C - 34.1 (C)+31.5 ($3CH_3$), ^{1}H - 1.33 s (9H) (ligand).

In the formation of imine-amine complex **9** compared to the ligand, we observed a downfield shift the signal C3 by 11 ppm and 7 ppm C11. Additionally, in the spectrum of ^{1}H for amino-ethylene fragment in the ligand are observed in the expected triplet (2H, H-11) and a triplet of triplets (2H, H-12) and the broad signal of NH_2 protons, and in the complex with the formation of five-membered cycle is fixed configuration of all six protons amino-ethylene fragment, which leads to differentiation of all signals protons.

The study of the complex **10** spectra showed the presence of only one set of signals in NMR spectra, which indicates the symmetry of the molecule. The slightest asymmetry leads to a double set of signals that we observed in the complexes **12** and **13**.

In the spectrum of complex **10** a downfield shift signal C11 at 4 ppm has been observed, but also strong changes in the representation of signals ^{1}H of the ethylene bridge: multiplet in ligand at 3.55-3.70 ppm of 4H, and in the complex the doublet of 2H at 3.94 ppm (J=8.8 Hz) and a doublet of 2H at 4.79 ppm (J=8.8 Hz) for the two pairs of nonequivalent geminal protons.

For ethylene-diamine complex **11** there are several other NMR spectra changes in comparison with the ligand associated with the formation of a new chiral centre on the nitrogen atom – shift of the C2 signal downfield by 4.5 ppm, the signal of H-3 change the multiplicity of the signals and shifted downfield by 1.2 ppm. The signal C4 is shifted to the opposite in a strong field by 8 ppm, there have been changes and the signals of both protons on it. The changes in signals aminoethylene fragment are similar to those in the complex **9**.

Is of interest the formation of chelate complex **15**, in which coordination is only for amino groups, phenolic OH-group is not involved. Described the formation of salen-type complex from the corresponding ligand, but with ethylene-diimine bridge [45]. We can assume that the complexation with ethylene-diimine bridges in the presence of OH-group in ortho-position in the aromatic ring is mainly the salen-type proceeded.

In the structure **14** hydroxyl group of the aromatic ring failed to be detected by spectroscopic methods, at the same time, there has been a shift signal C15-O in the spectrum ^{13}C downfield by 3 ppm compared to the ligand, which is typical during the transition from alcohol to ether. Opposite the compound **15** we do not observe a shift signal C15-O compared with the ligand, but seen far H-C interaction HO-C15 and HO-C14 in the HMBC NMR spectra.

IR data for terpen ligands and corresponding complexes are given in table 4. Thus, the IR data of compounds **9-15** demonstrated the presence of the group of bands relating to the vibrations of C=N, OH, NH, NH_2, the appearance of intense bands 345-305 cm^{-1} relating to the vibrations of Pd-Cl bonds. In the IR spectra of palladium complexes **9**, **10** and **14**, containing imines ligands, we observed that the stretching vibrations of C=N group shift to lower frequencies (from 1658,1664 and 1631 cm^{-1} in spectra of imines to 1612, 1645 and 1618 cm^{-1} in spectra of complexes), that indicates the participation

imino-group in coordination with palladium. The same pattern is observed for the complexes **11**, **12**, **13** and **15**, containing diamines ligands (in the IR spectra of the palladium complexes observed low-frequency shift of the stretching vibrations of NH and NH_2 groups).

Table 4. Selected vibrational wavenumbers (cm^{-1}) in IR spectra of ligands L^2-L^8 and complexes **9-15**

L^2	**9**	L^3	**10**	L^4	**11**	L^5	**12**	Assignment
3368	3379	3284	3298	3504	3443	3292	3439	ν (OH-terp)
3296	3219	-	-	3442, 3423	3395, 3327	3253	3167	ν (NH_2), ν (NH)
1658	1612	1664	1645	-	-	-	-	ν (C=N)
1596	1572	-	-	1471,1369	1496, 1362	1454	1476	δ (NH_2), δ (NH)
L^6	**13**	L^7	**14**	L^8	**15**	Assignment		
3350	3445	3404	3304	3313	3296	ν (OH-terp)		
3296	3423	-	-	3311	3285	ν (NH_2), ν (NH)		
-	-	1631	1618	-	-	ν (C=N)		
1473	1469	-	-	1591	1567	δ (NH_2), δ (NH)		
-	-	3415	-	3392	3382	ν (OH-phenol)		

IR data of complex **14** demonstrated the disappearance of the band 3415 cm^{-1} corresponding to the phenolic hydroxyl group while going from diimin **7** to complex **14** which together with the data of NMR spectroscopy for this complex confirms the involvement of phenolic hydroxyl groups to coordinate with palladium and formation of the salen-type complex.

2. Experimental

Materials and methods

All reactions for the synthesis of the complexes (**9-15**) were done using standard Schlenk type flasks and were carried out under air atmosphere. The solvents used were of analytical grade. All reagents and solvents were purchased from Sigma-Aldrich, Merck and Fluka. The NMR experiments were carried out using a Bruker AVANCE-II-300 spectrometer operating at 300.17 MHz for ^1H and 75.48 MHz for ^{13}C. ^1H chemical shift data are given in units δ relative TMS calibrated with residual protonic solvent ($CHCl_3$ at 7.26, DMSO at 2.52 and acetone-d6 at 2.08 ppm). The multiplicity of a signal is indicated as follows: br, broad; s, singlet; d, doublet; m multiplet; dd, doublet of doublets. ^{13}C chemical shifts are given relative TMS calibrated to the solvent, $CDCl_3$ at 77.07, DMSO-d6 at 40.04 and acetone-d6 at 30.6 ppm. ^1H and ^{13}C chemical shifts were measured and assigned by 2D experiments. 2D inverse proton detected homonuclear ^1H–^1H (COSY, NOESY) and heteronuclear shift correlation spectra, HSQC (^1H-^{13}C) and HMBC (^1H-^{13}C) were obtained using standard pulse sequence from the Bruker library. The coupling constants (*J*) were given in Hz. The FT-IR spectra of the synthesized novel complexes were recorded in the 200-4000 cm^{-1} region on FT-IR spectrometer Shimadzu IR Prestige 21 on thin films or KBr tablets. Optical rotations were obtained with

automatized digital polarimeter Optical Activity PolAAr 3001 (England). Melting points were determined with Gallencamp-Sanyo apparatus. Elemental analyses were performed by using EA 1110 CHNS-O apparatus.

*Synthesis of complex **9***

A suspension of $PdCl_2$ (0.2 g; 1.0 mmol) and LiCl (0.1 g; 2.0 mmol) in MeOH (5 mL) was refluxed for 1 h on a water bath. A dark red solution of Li_2PdCl_4 was added to a solution of chiral pinane ligand **2** (1.0 mmol) in methanol (4 mL), the mixture was stirred at room temperature for 5 h. The solvent was removed under reduced pressure, the residue was dissolved in benzene and purified by chromatography (SiO_2, eluent benzene-acetone, 50 : 1). The solvents were removed under reduced pressure. The product was washed with diethyl ether (3-8 mL) and dried under vacuum. Yellow powder was obtained; yield: 66%; m.p.: 215-216 ºC.

Elemental analysis calcd. (%) for $C_{12}H_{22}Cl_2N_2OPd$ (386.40 g/mol): C 37.2, H 5.7, N 7.2.; found: C 37.1, H 5.4, N 7.0; $[\alpha]_D^{25}$ +105.3 (c 0.1, acetone).

*Synthesis of complex **10***

According to the same conditions and procedure for the **9** complex, the **10** complex was prepared from chiral pinane ligand **3** (0.1 g, 0.3 mmol) and Li_2PdCl_4 (0.1 g, 0.3 mmol) in MeOH (5 mL) at 24 ºC for 6 h. A yellow powder was obtained; yield: 68 %; m.p.: 120-121 ºC.

Elemental analysis calcd. (%) for $C_{22}H_{36}Cl_2N_2O_2Pd$ (536.40 g/mol): C 49.2, H 6.7, N 5.2; found: C 48.8, H 6.5, N 4.8; $[\alpha]_D^{25}$ +44.7 (*c* 0.1, $CHCl_3$).

*Synthesis of complex **11***

According to the same conditions and procedure for the **9** complex, the **11** complex was prepared from chiral pinane ligand **4** (0.05 g, 0.2 mmol) and Li_2PdCl_4 (0.06 g, 0.2 mmol) in MeOH (5 mL) at 24 ºC for 3 h. A yellow powder was obtained; yield: 84 %; m.p.: 182-183 ºC.

Elemental analysis calcd. (%) for $C_{12}H_{24}Cl_2N_2OPd$ (388.40 g/mol): C 37.1, H 6.2, N 7.2; found: C 37.3, H 6.5, N 7.0; $[\alpha]_D^{25}$ +85.3 (*c* 0.1, $CHCl_3$).

*Synthesis of complex **12***

According to the same conditions and procedure for the **9** complex, the **12** complex was prepared from chiral pinane ligand **5** (0.05 g, 0.1 mmol) and Li_2PdCl_4 (0.03 g, 0.1 mmol) in MeOH (5 mL) at 24 ºC for 4 h. A yellow powder was obtained; yield: 98 %; m.p.: 152-153 ºC.

Elemental analysis calcd. (%) for $C_{22}H_{40}Cl_2N_2O_2Pd$ (540.40 g/mol): C 48.9, H 7.4, N 5.2; found: 48.5, H 7.2, N 4.9; $[\alpha]_D^{25}$ -116.0 (*c* 0.1, $CHCl_3$).

*Synthesis of complex **13***

According to the same conditions and procedure for the **9** complex, the **13** complex was prepared from chiral pinane ligand **6** (0.06 g, 0.2 mmol) and Li_2PdCl_4 (0.05 g, 0.2 mmol) in MeOH (5 mL) at 24 ºC for 6 h. A yellow powder was obtained; yield: 97 %; m.p.: 155-156 ºC.

Elemental analysis calcd. (%) for $C_{22}H_{40}Cl_2N_2O_2Pd$ (540.40 g/mol): C 48.9, H 7.4, N 5.2; found: 48.6, H 7.1, N 5.0; $[\alpha]_D^{25}$ +147.8 (*c* 0.2, $CHCl_3$).

*Synthesis of complex **14***

According to the same conditions and procedure for the **9** complex, the **14** complex was prepared from chiral pinane ligand **7** (0.05 g, 0.1 mmol) and Li_2PdCl_4 (0.03 g, 0.1 mmol) in MeOH (5 mL) at 24 ºC for 3 h. A red powder was obtained; yield: 70 %; m.p.: 177-178 ºC.

Elemental analysis calcd. (%) for $C_{27}H_{41}ClN_2O_2Pd$ (566.40 g/mol): C 57.2, H 7.2, N 4.9; found: 56.9, H 6.9, N 4.6; $[\alpha]_D^{26}$ +272.5 (c 0.1, $CHCl_3$).

*Synthesis of complex **15***

According to the same conditions and procedure for the **9** complex, the **15** complex was prepared from chiral pinane ligand **8** (0.06 g, 0.2 mmol) and Li_2PdCl_4 (0.05 g, 0.2 mmol) in MeOH (5 mL) at 24 ºC for 3 h. A yellow powder was obtained; yield: 52 %; m.p.: 175-176 ºC.

Elemental analysis calcd. (%) for $C_{19}H_{30}Cl_2N_2O_2Pd$ (494.40 g/mol): C 46.1, H 6.1, N 5.7; found: 45.8, H 5.9, N 5.4; $[\alpha]_D^{25}$ -27.7 (c 0.1, $CHCl_3$).

4. Conclusion

In summary, seven novel palladium(II) complexes with chiral pinane ligands were obtained by the direct reaction of Li_2PdCl_4 with 3-[(2-aminoethyl)imino]-pinane-2-ol, 3,3'-(ethylenediimino)*bis*-pinane-2-ol, *cis*-3-(2-aminoethylamino)-pinane-2-ol, *cis*-3,3'(ethylenediamino)bis-pinane-2-ol, *trans*-3,3'(ethylenediamino)bis-pinane-2-ol, 3-[2-(2-hydroxybenzylamino)ethylamino]-pinane-2-ol, 3-[2-(3,5-di-*tert*-butyl-2-hydroxybenzylidene)amino)ethylimino]pinane-2-ol in MeOH in a molar ratio of 1:1 in good yields. On the basis of the FT-IR, NMR spectra and elemental analysis of the ligands and the corresponding Pd(II) complexes, we concluded that the ligands are bidentately and tridentate coordinated to the palladium(II) ion.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica..... .

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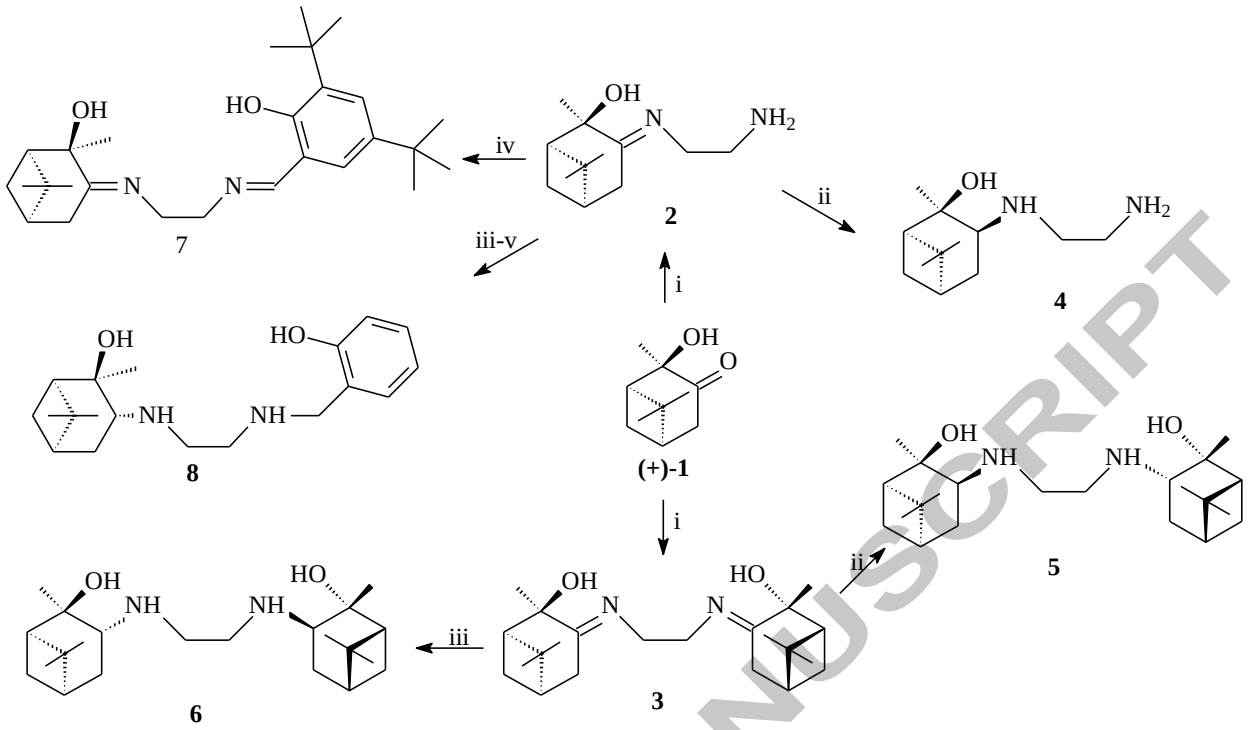
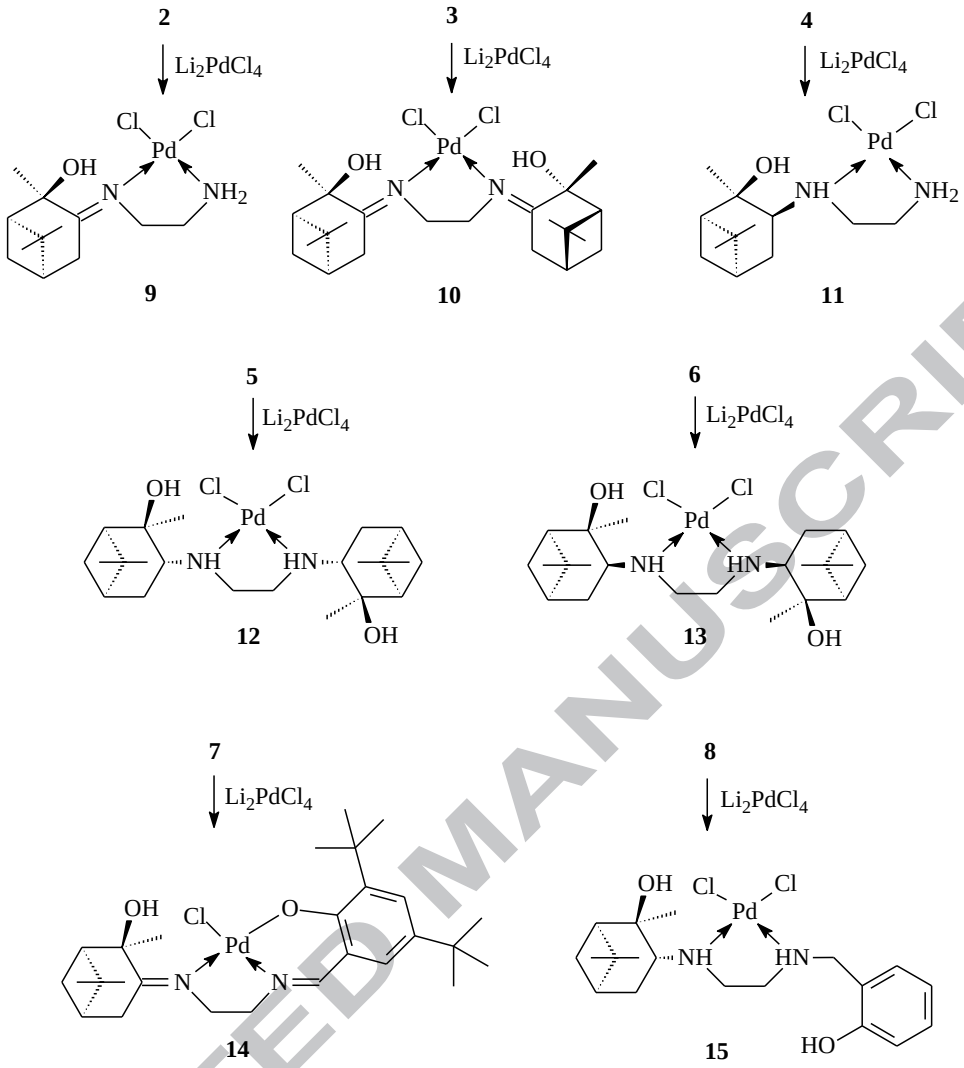
Seven novel palladium complexes containing chiral pinane ligands were synthesized.

Their structures were characterized by elemental analysis and spectroscopic methods.



(i) $H_2N(CH_2)_2NH_2$, PhH, $F_3B{\times}OEt_2$, molecular sieves 4Å, 80°C; (ii) $LiAlH_4$, Et_2O, 20°C; (iii) $Na(OAc)_3BH$, *i*-PrOH, 20°C; (iv) aldehyde, MeOH, 20°C; (v) $NaBH_4$, MeOH, 20°C.

Scheme 1. Synthesis of chiral pinane ligands (**2-8**)



Scheme 2. Synthesis of palladium complexes (**9-15**)