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Chiral palladium complexes based on derivatives of benzylamine and 2α-hydroxypinan-3-one

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ABSTRACT

Synthesized and characterized new chiral palladium complexes, some of which contain asymmetric donor nitrogen atom. Nitrogen-containing derivatives (+) - and (-)-2α-hydroxypinan-3-one-(1R,2R,5R)-3-(benzylimino)-2,6,6-trimethylbicyclo[3.1.1]heptane-2-ol (HL^1), (1S,2S,3S,5S)-3-(benzylamino)-2,6, 6-trimethylbicyclo[3.1.1]-heptane-2-ol (HL^2), (1R,2R,5R)-3-((S)-α-methylbenzylimino)-2,6,6-trimethylbicyclo[3.1.1]-heptane-2-ol (HL^3), (1R,2R,3R,5R)-3-((S)-α-methylbenzylamino)-2,6,6-trimethylbicyclo[3.1.1]-heptane-2-ol (HL^4) -were studied as optically active ligands.

Keywords: Palladium Complexes; Cyclopalladation; Chiral Imine; Amine

1. INTRODUCTION

Chiral palladium complexes of various types are widely used in modern asymmetric synthesis, the goal of which is to obtain enantiopure compounds. Cyclopalladated complexes (CPCs) form a special group of compounds with a σ-connection palladium-carbon [1]. These complexes show reasonably high activity and thermal stability. Chiral CPCs are very successfully used in asymmetric synthesis, both as the original matrix [2-7] and as catalysts [8-12]. They have been used in NMR studies as shifting reagents [13-15] and as effective resolution agents [16-18]. This is especially significant for obtaining enantiopure phosphines, which are efficient ligands for asymmetric catalysis of transition metal complexes. Currently, the CPCs are received with different types of chirality [1]. The compounds of a variety of classes have been tested for their ability to become ligands for CPCs. However, the synthetic accessibility of chiral ligands remains an important problem.

2. EXPERIMENTAL

2.1. General

The ^1H and ^{13}C NMR spectra were recorded with a Bruker Avance-300 spectrometer operating at the frequencies 300 and 75 MHz for ^1H and ^{13}C nucleus, respectively. The measurements were carried out at ambient temperature in $CDCl_3$. Chloroform signals were used as an internal standard (δ_H 7.27 ppm, δ_C 77.00 ppm). The assignment of signals was carried out using ^{13}C NMR spectra recorded in the mode of J-modulation, and according to two-dimensional correlation spectra of $^1H\{^1H\}$ (COSY) and $^1H\{^{13}C\}$ (HSQC) and NOE experiments. IR spectra were measured in a thin layer or in KBr pellets on a device "IR Prestige 21" made by Shimadzu. Optical rotations were measured on a Kruss P3002RS polarimeter (Germany) with a 10 cm cell and were reported as follows: $[\alpha]_D^{t^\circ C}$ (concentration in g/10 mL, solvent). Elemental analyses were performed using an automatic analyzer EA 1110 CHNS-O.

All reactions were monitored on a thin layer chromatography (TLC) using Merck silica gel (70-230 mesh) and benzene acetone mixtures as eluents; the TLC spots were visualized with J_2 and $KMnO_4/H_2SO_4$. Column chromatography was carried out using Merck silica gel (70-230 mesh) and benzene acetone mixtures as eluents.

2.2. Solvents and Starting Reagents

Benzene was dried with CaCl2, refluxed with Na, and then distilled from Na. Methanol was distilled from MeONa. Hexane was distilled from Na. Palladium chloride was used without additional purification. (SC)-α-Methylbenzylamine of 99% ee was purchased from Merck and used without purification.

Imines HL1, HL3 and amines HL2, HL4 were prepared by a reported method [19].

2.3. Di-μ-Chlorobis{(1R,2R,5R)-3-(Benzylimino)-2,6,6-Trimethylbicyclo [3.1.1]Heptane-2-ol-C,N} Dipalladium(II), 1

A suspension of palladium chloride (II) (0.09 g, 0.5 mmol) and lithium chloride (0.04 g, 1.0 mmol) in methanol (5 ml) was boiled in a water bath with a reflux condenser for one hour. The resulting solution of lithium tetrachloropalladate (dark-red color) added to a solution of imine HL^1 (0.13 g, 0.5 mmol) and sodium acetate (0.04 g, 0.5 mmol) in methanol (5 ml). After stirring at room temperature for 1 hour the solvent was removed from the reaction mixture, the complex 1 was extracted with benzene (3×20 mL). The crude product was purified using column chromatography on silica gel with benzene and benzene/acetone 10:1 mixture as eluents. After precipitation from benzene by hexane and drying in vacuum, complex 1 was obtained in the yield of 40% (0.080 g, mmol) as a yellow amorphous powder: mp (dec) 166-167 °C, R_f 0.71 (5:1 benzene/acetone), $[\alpha]_D^{25}$ = -415.9 (*c* 0.06, $CHCl_3$).

IR, ν, cm^{-1}: 3441 (OH), 1618 (C = N). ^1H NMR ($CDCl_3$, δ / ppm., *J* / Hz): 0.73 (s, 3H, H^9, Me), 0.98 (d, 1H, 7-H_α, $J^{7\alpha,7\beta}$ 11.0), 1.10 (s, 3H, H^8, Me), 2.12 (ddd, 1H, 7-H_β, *J* 2.0, *J* 5.8, $J^{7\beta,7\alpha}$ 11.0), 2.26 (d, 1H, $H^{4\alpha}$, $J^{4\alpha,4\beta}$ 18,3), 2.56 (dd, 1H, $H^{4\beta}$, *J* 4.1, $J^{4\beta,4\alpha}$ 18.3), 2.94 (s, 3H, H^{10}, Me), 4.22 (d, 1H, $H^{11\alpha}$, $J^{11\alpha,11\beta}$ 14.5), 4.47 (d, 1H, $H^{11\beta}$, $J^{11\beta,11\alpha}$ 14.5), 7.15-7.45 m (4H, arom.). ^{13}C NMR ($CDCl_3$, δ, ppm): 23.27 (C^9), 26.88 (C^8), 28.18 (C^7), 32.10 (C^{10}), 32.94 (C^4), 39.17 (C^5), 40.13 (C^6), 51.41 (C^1), 55.06 (C^{11}), 92.46 (C^2), 127.27 (C^{18}), 127.55 (C^{17}), 128.33 (C^{16}), 128.57 (C^{14}), 128.85 (C^{15}), 135.24 (C^{13}), 197.63 (C^3).

2.4 Dichloro{(1R,2R,5R)-3-(Benzylimino)-2,6,6-Trimethylbicyclo [3.1.1]Heptane-2-ol-N,N}Palladium(II), 2

A suspension of palladium chloride(II) (0.04 g, 0.2 mmol) and lithium chloride (0.02 g, 0.4 mmol) in methanol (5 ml) was boiled in a water bath with a reflux condenser for one hour. The resulting solution of lithium tetrachloropalladate (dark-red) color was added to a solution of imine HL^1 (0.1 g, 0.4 mmol) in methanol (2 ml). After stirring at room temperature for 1 h the solvent was removed from the reaction mixture, the coordinated complex 2 was extracted with benzene (3×20 mL). The crude product was purified using column chromatography on silica gel with benzene and benzene/acetone 10:1 mixture as eluents. After precipitation from benzene by hexane and drying in vacuum, complex 2 was obtained in the yield of 50% (0.070 g, mmol) as a yellow amorphous powder: mp (dec) 153-154 °C, R_f 0.8 (5:1 benzene/acetone), $[\alpha]_D^{25}$ = +113.5 (*c* 0.07, $CHCl_3$).

IR, ν, cm^{-1}: 3410 (OH), 1612 (C = N). ^1H NMR ($CDCl_3$, δ / ppm., *J* / Hz): 0.75 (s, 3H, H^9, Me), 1.22 (s, 3H, H^8, Me), 1.5 (d, 1H, $H^{7\alpha}$, $J^{7\alpha,7\beta}$ 9.0), 1.8 (m, 1H, $H^{7\beta}$), 2.1 (m, 1H, H^1), 2.2 (m, 2H, H^4), 2.5 (m, 1H, H^5), 2.8 (s, 3H, H^{10}, Me), 5.1 (d, 1H, $H^{11\alpha}$, $J^{11\alpha,11\beta}$ 16.0), 5.9 (d, 1H, $H^{11\beta}$, $J^{11\beta,11\alpha}$ 16.0), 7.4 (m, 5H, arom.). ^{13}C NMR ($CDCl_3$, δ, ppm): 22.97 (C^9), 26.71 (C^8), 27.61 (C^7), 31.06 (C^{10}), 37.97 (C^4), 38.13 (C^5), 38.54 (C^6), 52.87 (C^1), 63.00 (C^{11}), 76.61 (C^2), 127.21 (C^{15}), 127.55 (C^{16}), 128.83 (C^{14}), 133.81 (C^{13}), 192.35 (C^3).

2.5. Dichloro{(1S,2S,3S,5S)-3-(Benzylamino)-2,6,6-Trimethylbicyclo [3.1.1]Heptane-2-ol-N,N} Palladium(II), 3

A suspension of palladium chloride(II) (0.04 g, 0.2 mmol) and lithium chloride (0.02 g, 0.4 mmol) in methanol (5 ml) was boiled in a water bath with a reflux condenser for one hour. The resulting solution of lithium tetrachloropalladate (dark-red color) was added to a solution of imine HL2 (0.12 g, 0.4 mmol) in methanol (2 ml). After stirring at room temperature for 1 h the solvent was removed from the reaction mixture, the coordinated complex 3 was extracted with benzene (3×20 mL).The crude product was purified using column chromatography on silica gel with benzene and benzene/acetone 10:1 mixture as eluents. After precipitation from benzene by hexane and drying in vacuum, complex 3 was obtained in the yield of 60% (0.085 g, mmol) as a yellow amorphous powder: mp (dec) 167-168 °C, R_f 0.85 (5:1 benzene/acetone), $[\alpha]_D^{25}$ = -62.6 (*c* 0.09, $CHCl_3$).

IR, ν, cm^{-1}: 3479 (OH), 3253 (NH). ^1H NMR ($CDCl_3$, δ / ppm., *J* / Hz): 0.75 (s, 3H, H^9,Me), 1.24 (s, 3H, H^8, Me), 1.43 (s, 3H, H^{10}, Me), 1.46 (d, 1H, $H^{7\alpha}$, $J^{7\alpha,7\beta}$ 11.0), 1.73-1.81 (m, 2H, H^1, H^5), 1.88 (dd, 1H, $H^{4\alpha}$, $J^{4\alpha,3}$ 10.0, $J^{4\alpha,4\beta}$ 14.1), 2.10 ddd (1H, $H^{7\beta}$, *J* 5.7, *J* 6.1, $J^{7\beta,7\alpha}$ 11.0), 2.61 (ddd, 1H, $H^{4\beta}$, *J* 4.9, $J^{4\beta,3}$ 9.8, $J^{4\beta,4\alpha}$ 14.1), 3.08 (dd, 1H, H^3, $J^{3,4\beta}$ 9.8, $J^{3,4\alpha}$ 10.0), 4.04 m (2H, H (11)), 7.33 (d, 1H, H^{16}, $J^{16,15}$ 7.0), 7.40 (dd, 2H, H^{15}, $J^{15,16}$ 7.0 , $J^{15,14}$ 7.6), 7.50 (d, 2H, H^{14}, $J^{14,15}$ 7.6). ^{13}C NMR ($CDCl_3$, δ / ppm.): 23.22 (C^9), 23.39 (C^{10}), 24.05 (C^7), 27.54 (C^8), 32.14 (C^4), 39.48 (C^6), 40.58 (C^5), 57.13 (C^1), 57.55 (C^{11}), 65.18 (C^3), 76.60 (C^2), 127.74 (C^{16}), 128.38 (C^{15}), 129.90 (C^{14}), 135.53 (C^{13}).

2.6. Di-μ-Chlorobis{(1R,2R,5R)-3-((1S)-α-Methylbenzylimino)-2,6,6-Trimethylbicyclo[3.1.1] Heptane-2-ol-C,N}Dipalladium(II), 4

Synthesis is carried out similarly to that described for (1). Dimer 4 as a yellow amorphous powder, yield 50% (0.103 g, mmol), mp (dec) 145-146 °C, Rf 0.4 (5:1 benzene/acetone), $[\alpha]_D^{25}$ = -32.0 (c 0.08, aceton).

IR, ν, cm-1: 3337 (OH), 1631 (C = N). 1H NMR (CDCl3, δ / ppm., J / Hz): 0.99 (s, 3H, H9, Me), 1.29 (d, 3H, H12, Me, J 12,11 6.8), 1.39 (s, 3H, H8, Me), 1.91 (d, 1H, H7α, J 7α,7β 11.8), 1.95 (s, 3H, H10, Me), 2.12 (m, 1H, H5, J 5,1 5.5), 2.27 (m, 1H, H1, J 1,5 5.5, J 5.5), 2.59 (m, 2H, H4α, H7β), J 3.9, J 4β,4α 18.3), 2.73 (dd, 1H, H4β, J 3.9, J 4β,4α 18.3), 4.05 (sq, 1H, H11, J 11,12 6.8), 6.57 (d, 1H, H18, J 18,17 7.6), 6.84 (dd, 1H, H17, J 17,18 7.6, J 17,16 8.0), 7.04 (dd, 1H, H16, J 16,17 8.0, J 16,15 8.0), 7.44 (d, 1H, H15, J 15,16 8.0). 13C NMR ($CDCl_3$, δ, ppm): 22.43 (C^{12}), 23.18 (C^9), 27.23 (C^8), 27.90 (C^{10}), 28.87 (C^7), 33.90 (C^4), 38.41 (C^5), 40.52 (C^6), 51.78 (C^1), 67.00 (C^{11}), 88.64 (C^2)), 122.33 (C^{18}), 124.61 (C^{16}), 124.75 (C^{17}), 135.51 (C^{15}), 138.84 (C^{13}), 156.52 (C^{14}), 185.10 (C^3).

2.7. Di-μ-Chlorobis{(1R,2R,3R,5R)-3-((S)-α-Methylbenzylamino)-2,6,6-Trimethylbicyclo[3.1.1] Heptane-2-ol-C,N}Dipalladium(II), 5

Synthesis is carried out similarly to that described for (1). Dimer 5 as a yellow amorphous powder, yield 55% (0.114 g, mmol), mp (dec) 169-170 °C, Rf 0.3 (5:1 benzene/acetone), $[\alpha]_D^{25}$ = +19.7 (c 0.04, CHCl3).

IR, ν, cm-1: 3421 (OH), 3217 (NH). 1H NMR (CDCl3, δ / ppm., J / Hz): 0.96 (s, 3H, H9, Me), 1.29 (s, 3H, H8, Me), 1.56 (s, 3H, H10, Me), 1.66 (dd, 1H, H4α, J 4α,3 11.3, J 4α,4β 13.9), 1.75 (d, 1H, H7α, J 7α,7β 10.9), 1.81 (d, 3H, H12, J 12,11 6.4), 1.95 (m, 1H, H1, J 1,7β 5.6), 2.01 (m, 1H, H5), 2.17 (dd, 1H, H7β, J 7β,1 5.6, J 7β,7α 10.9), 2.46 (s, OH), 2.56 (ddd, 1H, H4β, J 5.6, J 4β,3 9.0, J 4β,4α 13.9), 4.14 (sq, 1H, H11, J 11,12 6.4), 4.18 (dd, 1H, H3, J 3,4β 9.0, J 3,4α 11.3), 4.40 (s, NH)), 6.74 (dd, 1H, H18, J 18,16 1.3, J 18,17 7.2), 6.87 (ddd, 1H, H16, J 16,181.3, J 16,17 7.3, J 16,15 8.5), 6.96 (dd, 1H, H17, J 17,18 7.2, J 17,16 7.3), 7.24 (d, 1H, H15, J 15,16 8.5). 13C NMR (CDCl3, δ, ppm): 22.89 (C9), 24.02 (C7), 24.24 (C10), 25.88 (C^{12}), 28.05 (C^8), 28.48 (C^4), 40.16 (C^6), 40.62 (C^5), 55.47 (C^1), 64.39 (C^{11}), 67.51 (C^3), 77.55 (C^2), 119.89 (C^{18}), 124.79 (C^{17}), 125.10 (C^{16}), 134.01 (C^{15}), 141.92 (C^{13}), 156.95 (C^{14}).

3. RESULTS AND DISCUSSION

Earlier, we reported on the synthesis of chiral imines and amines on the basis of 2α-hydroxypinan-3-one [19]. These ligands, containing in its composition benzylamine fragment, are of interest from the standpoint of the possibility of obtaining ortho-palladated complexes. In the present work we investigated the interaction of the obtained ligands **HL[1]**, **HL[2]**, **HL[3]**, **HL[4]** with lithium tetrachloropalladate (Li_2PdCl_4) in the method of Cope [20]. Reaction of cyclopalladation is accompanied by the release of hydrogen chloride. An insertion of an additional base is necessary for the neutralization of the hydrogen chloride.

The structure of obtained complex compounds is confirmed by NMR, IR spectroscopy and elemental analysis data, last are given in **Table 1** .

On the basis of imine **HL[1]** we managed to get binuclear palladacycle **1** with the yield of 40% in the presence of sodium acetate as base at a molar ratio of reagents 1:1. In the absence of the base at a molar ratio of reagents 1:2 mononuclear coordinated complex **2** was obtained in 50% yield (**Scheme 1**). Complex compounds **1** and **2** were isolated from the reaction mixture by column chromatography and further purified by crystallization from a mixture of benzene-hexane.

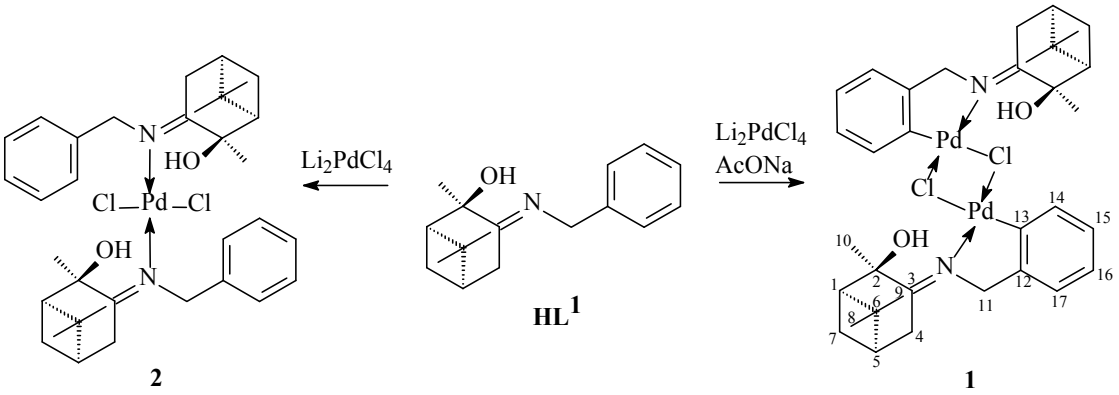
The signals of protons of methylene group -CH_2N = were observed in the ^{1}H NMR spectrum of compound **1** in the form of two doublets with geminal constant of 14.5 Hz (two-proton singlet was observed in the spectrum of the initial ligand), which confirms the formation of the cycle. The change of the multiplicity and the integrated intensity of signals of protons of benzene ring corresponds to the ortho-disubstituted ring. The preservation of the multiplicity and the integral intensity of proton signals of the monosubstituted benzene ring in the ^{1}H NMR spectrum of compound **2** excludes ortho-palladation.

In contrast to the corresponding imine **HL[1]** amine **HL[2]** forms only mononuclear coordinated complex **3** even in the presence of a base (AcONa) (**Scheme 2**). This result can be explained by the fact that the secondary amino group exhibits stronger electron donor properties than the imine, and reduces the electrophilic activity of palladium, preventing the ortho-palladation.

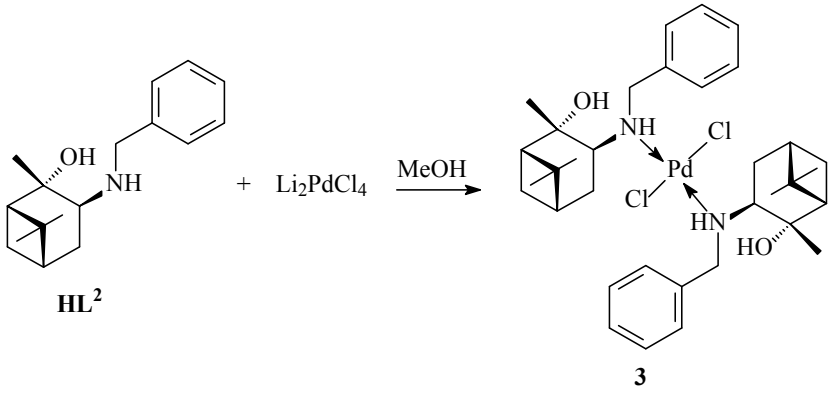
The interaction of amine **HL[2]** with Li_2PdCl_4 may form a mixture of diastereomeric complexes in which the configuration of tetragonal nitrogen atom consolidates with the metal and the nitrogen becomes an additional center of chirality. There is only one set of signals in the ^{1}H NMR spectrum of compound **3** that indicates the forma-

Table 1. The analytical data for the complexes.

№.	Complex	Color [Empirical formula] (Formula weight)	Analytical Data % Found (Calculated) C	H	N
1	C34H44N2O2Pd2Cl2	yellow (795.75)	51.8 (51.3)	5.67 (5.53)	3.2 (3.5)
2	C34H46N2O2PdCl2	yellow (691.37)	57.2 (59.1)	6.62 (6.65)	3.9 (4.0)
3	C34H50N2O2PdCl2	yellow (695.36)	58.7 (58.7)	7.31 (7.20)	3.90 (4.03)
4	C36H48N2O2Pd2Cl2	yellow (823.77)	52.6 (52.4)	5.93 (5.93)	3.3 (3.3)
5	C36H52N2O2Pd2Cl2	yellow (827.76)	52.4 (52.2)	6.21 (6.28)	3.21 (3.30)



Scheme 1

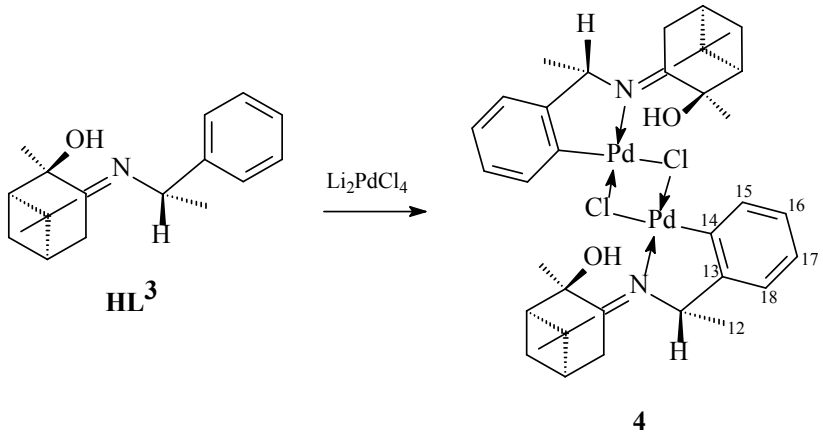


Scheme 2

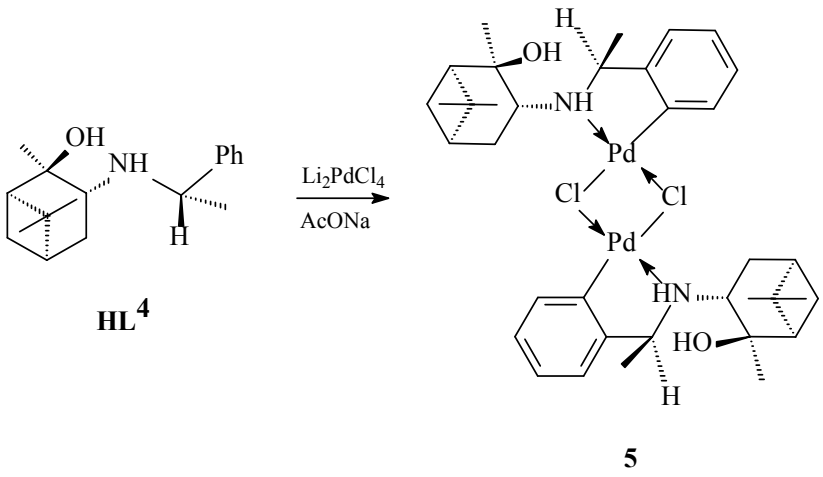
tion of one of the possible diastereomers. Multiplicity and integral intensity of proton signals corresponds to the monosubstituted benzene ring.

The interaction of imine **HL**[3] and amine **HL**[4], containing α-methylbenzylamine fragment with lithium tetrachloropalladate was investigated under the specified above conditions. It was found that the imine **HL**[3] exposed cyclopalladation even in the absence of a base. Binuclear palladacycle **4** was obtained in the presence of sodium acetate at a molar ratio of reagents 1:1 and in the absence of sodium acetate at a molar ratio of reagents 1:2 (**Scheme 3**). This result is quite understandable given the fact that the second molecule of imine can serve as a base, binding hydrogen chloride, thereby stimulating cyclometallation.

Unlike amine **HL**[2], that forms only the coordinated complex in the investigated conditions, amine **HL**[4], that contains a methyl group in α-position, reacts with lithium tetrachloropalladate in the presence of sodium acetate at a molar ratio of reagents 1:1 to form a binuclear palladacycle **5** with yield 55% (**Scheme 4**). A mixture of two complex compounds - coordinated and palladacycle are formed in the absence of sodium acetate at a molar ratio of reagents 1:2, which was is confirmed by ^{1}H



Scheme 3



Scheme 4

NMR and ^{13}C spectroscopy.

The formation of ortho-palladated complexes **4** and **5** is confirmed by NMR spectra: there are four nonequivalent signals of aromatic protons in the ^{1}H spectra with a particular splitting (two doublets and two doublets of doublets) and four aromatic methine groups in the ^{13}C spectra. All set of signals of terpene fragments remains in the spectra. A slight shift is reported (compared to the ligands) for nucleis located close to palladium. One set of signals in the spectra of the complexes 4 and 5 is observed which indicates the symmetry of the complexes.

The ease of the cyclopalladation of the α-methylbenzilamine derivatives **HL^3** and **HL^4** once again underlines the role of spatial factors in reactions of the metallocycles formation.

4. CONCLUSIONS

Mononuclear coordination complexes - (HL1)2PdCl2 (2), (HL2)2 PdCl2 (3) and palladacycle dimers PdL1Cl (1), PdL3Cl (4), PdL4Cl (5) have been isolated separately, the structure of which was studied and confirmed by spectral methods and by elemental analysis

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