ISSN 1070-3632, Russian Journal of General Chemistry, 2014, Vol. 84, No. 1, pp. 137–142. © Pleiades Publishing, Ltd., 2014.
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Chiral Palladium Complexes with Monoterpenoids Oximes

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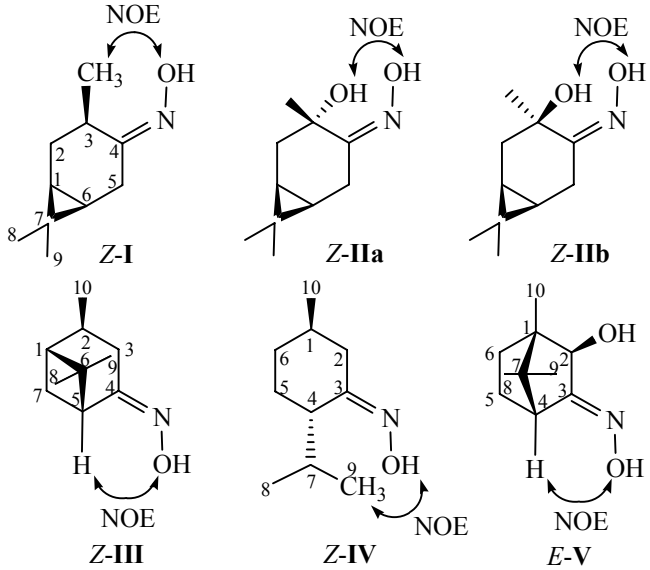
Received January 14, 2013

Abstract—Oximes of *cis*-caran-4-one, 3α- and 3β-hydroxycaran-4-ones, *cis*-verbanone, menthone, and 2β- hydroxybornan-3-one have been synthesized. The obtained oximes react with lithium tetrachloropalladate to give new chiral palladium complexes containing mono- or bidentate oxime ligands.

DOI: 10.1134/S1070363214010216

Oximes are known to readily form complexes with many transition metal ions, including palladium. Therefore, they are widely used in quantitative palladium determination [1, 2] and extractive isolation of palladium compounds from the mixtures [3, 4]. Oxime-based palladium complexes are applied as catalysts in asymmetric synthesis [5, 6].

We prepared the oximes of (–)-*cis*-caran-4-one (**I**), (+)-3α-hydroxycaran-4-one (**IIa**) and 3β-hydroxycaran-4-one (**IIb**), (+)-*cis*-verbanone (**III**), (–)-menthone (**IV**), and (+)-2β-hydroxybornan-3-one (**V**), and applied them as ligands to form palladium complexes.

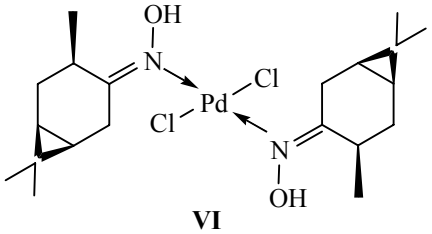


The oximes were synthesized via condensation of the initial oxo derivatives with hydroxylamine hydrochloride according to the standard procedure [7] to yield 70–94% of the products.

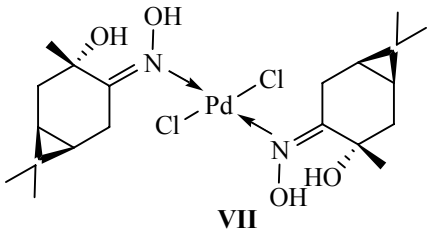
Oximes **I**, **IV**, **V** were obtained in the form of *Z*- and *E*-isomers mixtures, and the major isomers were isolated by column chromatography; whereas the individual isomers were obtained in the cases of **IIa**, **IIb,** and **III**.

In the ^{1}H and ^{13}C NMR spectra of all the oximes obtained, the signals were not duplicated thus proving the presence of a single isomer. According to NOE analysis, oximes **I**–**IV** were *Z*-isomers, and oxime **V** was of *E*-configuration. In particular, the NOESY spectra of oximes **IIa** and **IIb** revealed the interaction of protons of two hydroxyl groups; that indicated the formation of intramolecular hydrogen bond stabilizing the *Z*-isomers. In the NOESY spectra of oximes **I**, **III**, and **IV**, the interactions of the hydroxyl proton and the protons of terpene moiety at position 10 (**I**), 5 (**III**) or 9 (**IV**) were revealed; that confirmed the *Z*-configuration of the oximes. *E*-Configuration of oxime **V** was elucidated from the NOE interaction between the NOH group proton and H^4 of terpene moiety.

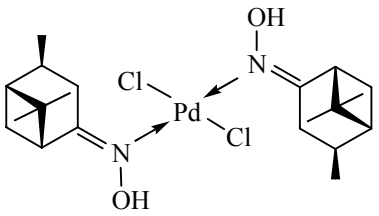
The prepared oximes **I**, **IIa**, **III**, and **IV** were found to interact with lithium tetrachloropalladate in methanol to give the stable complexes **VI**–**IX,** respectively**,** with 53–83% yield.



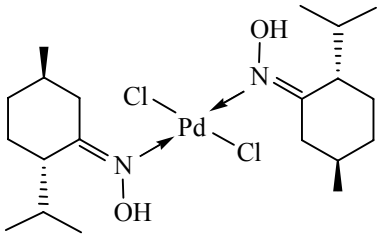
VI



VII



VIII

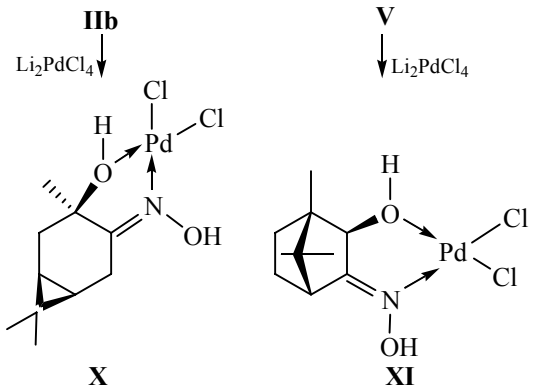


IX

In the IR spectra of the **VI**–**IX** complexes, absorption bands of C=N stretching were shifted to lower frequencies as compared with those in the spectra of initial oximes, indicating that imino group participated in coordination. The NMR data confirmed the monodentate nature of the oxime ligands.

^{1}H and ^{13}C NMR spectra of all the complexes **VI**–**IX** did not contain the duplicated signals, thus indicating formation of the only isomer; in particular, formation of the thermodynamically more stable *trans*-isomer could be assumed. In NOESY correlation spectra of **VI**–**IX**, the same protons NOE interactions were observed that were previously used to identify the initial oximes. Therefore, the oximes configuration was retained in the course of the complexes formation.

Oximes **IIa**, **IIb**, and **V** were *N*,*O*-bidentate ligands capable of formation the chelate complexes. Indeed, reactions of oximes **IIb** and **V** with lithium tetrachloropalladate resulted in chelate complexes **X** (80%) and **XI** (90%), respectively.



X **XI**

^{1}H NMR and ^{13}C NMR spectra of the complexes **X** and **XI** confirmed their suggested structure. In particular, the ^{1}H NMR spectra contained all the signals assigned to the starting oximes, the signals of the hydroxyl protons in positions 3 and 2 were shifted downfield by 1.8 ppm (**X**) and 0.8 ppm (**XI**), confirming their participation in coordination to palladium.

The structure of **X** was elucidated from X-ray diffraction data as well; the spacial structure of the molecule is shown in the Figure. The crystals of **X** were assigned to the $P2_12_12_1$ chiral space group of orthorhombic crystal system. In the molecule of **X**, the chlorine atoms were *cis*-positioned in the distorted square-planar surrounding of the palladium atom. The organic part acted as neutral bidentate chelating ligand, forming the five-membered ring. Cyclohexyl moiety existed in the *half-chair* conformation (*envelope*) with five ring atoms situated in the same plane (the deviation being of <0.04 Å), and the C^2 atom was out-of-plane by 0.664 Å.

Noteworthily, chelation of **IIb** changed the configuration of the C=N bond of the oxime. That was likely caused by additional stabilization of the formed complex operative only in the case of the *E*-isomer. Such configuration change was only possible in the case of the β-isomer (**IIb**); under the same conditions, the corresponding α-isomer (**IIa**) formed the **VII** complex containing monodentate ligand.

To conclude, palladium coordination compounds with monodentate oximes **VI**–**IX** as well as chelates **X** and **XI** were obtained. The complexes structure was confirmed by IR and NMR spectroscopy and elemental

analysis as well as by X-ray diffraction analysis (in the case of **X**).

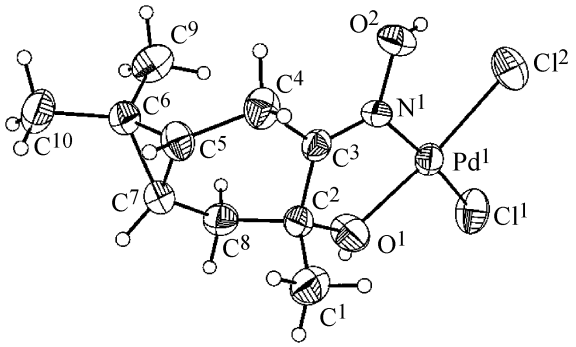
EXPERIMENTAL

IR spectra of thin films or KBr pellets were registered with IR Prestige 21 Shimadzu spectrometer. ^{1}H and ^{13}C NMR spectra of solutions in $CDCl_3$ were recorded with Bruker AVANCE-II-300 spectrometer at 300 MHz (^{1}H) or 75 MHz (^{13}C). The signals assignment was confirmed using two-dimensional ^{1}H–^{1}H and ^{1}H–^{13}C correlation spectra (COSY, NOESY, HSQC, and HMBC). Optical rotation was measured with automatic P3002RS Kruss polarimeter (Germany). Elemental analysis was performed with EA 1110 (CHNSO) elemental analyzer.

The reaction progress was monitored by TLC using Sorbfil plates, eluting with C_6H_{14}–Et_2O or benzene–acetone (5 : 1) mixtures and detecting with iodine vapor or with 10% solution of phosphomolybdic acid in ethanol followed by heating to 100–120°C. Silica gel (Alfa Aesar, 70–230 μ) was used for column chromatography purification. Palladium chloride was used as received.

The following initial monoterpenoids were used: 3α-hydroxycaran-4-one {$[\alpha]_D^{20}$ +35° (*c* 0.6, EtOH), the spectral data were consistent with [8]}, 3β-hydroxylcaran-4-one {$[\alpha]_D^{20}$ +25° (*c* 0.4, EtOH), the spectral data were consistent with [9]}, *cis*-verbanone {$[\alpha]_D^{20}$ –29.5° (*c* 1.0, EtOH), the spectral data were consistent with [10]}, menthone {$[\alpha]_D^{20}$ –25° (*c* 0.5, EtOH), prepared by oxidation of commercial (–)-menthol with potassium dichromate in acidic medium [11]}, 2-hydroxybornan-3-one {$[\alpha]_D^{20}$ +114° (*c* 0.2, EtOH)}, *cis*-caran-4-one {$[\alpha]_D^{20}$ –134° (*c* 1.5, EtOH), obtained as described in [12, 13]}.

Single crystal X-ray diffraction analysis of the compound **X** was performed with automatic four-circle Xcalibur 3 diffractometer equipped with CCD-detector [λ(MoK_α) 0.71073 Å]. Data were collected and processed following the standard procedures [14]. Absorption was accounted for analytically (polyhedral crystal model [15]). The structure was solved and refined using the SHELX software package [16]. Refinement was performed with a full-matrix least square of F^2 using anisotropic approximation for all the non-hydrogen atoms. The hydrogen atoms were placed into geometrically calculated positions and included into the refinement with isotropic approximation and dependent thermal parameters



General view of **X** molecule.

(*rider* model). The unit cell parameters at 295(2) K for the red rhombic crystal (0.23 × 0.16 × 0.11 mm) were as follows: space group $P2_12_12_1$, a = 7.1140(5), b = 12.1058(9), c = 15.4189(11) Å, V = 1327.89(17) Å^3, Z = 4, $C_{10}H_{17}Cl_2NO_2Pd$; d_{calc} = 1.803 g cm^{-3}, μ = 1.785 mm^{-1}. In the range of 3.13 < θ < 33.51, 10964 reflections were collected, including 4726 independent ones (R_{int} 0.0258), and 2767 ones with $I > 2\sigma(I)$. Completeness at θ 30.00° was of 99.7%. Final refinement parameters: R_1 = 0.0272, wR_2 = 0.0410 [reflections with $I > 2\sigma(I)$], R_1 = 0.0538, wR_2 = 0.0420 (all reflections) at S factor of 1.002. The absolute structure parameter was of 0.02 (2), the highest and the lowest residual electron density being of 0.583 and –1.534 $\bar{e}$Å^{-3}, respectively.

***cis*-Caran-4-one oxime (I).** Yield 70%, mp 42°C, white crystals, soluble in chloroform, acetone, benzene, and DMSO; R_f 0.5 [hexane–diethyl ether (3 : 1), detection with a solution of phosphomolybdic acid], $[\alpha]_D^{20}$ –15.6° (*c* 0.2, EtOH). IR spectrum, ν, cm^{-1}: 3285 (OH), 1649 (C=N). ^{1}H NMR spectrum (300 MHz, $CDCl_3$), δ, ppm (J, Hz): 0.82 m (1H, H^1, $J_{1,6}$ 5.4), 0.85 s (3H, CH_3^9), 0.91 d. d (1H, H^6, $J_{6,1}$ 5.4, $J_{6,5}$ 8.6), 1.04 s (3H, CH_3^8), 1.08 d (3H, CH_3^{10}, $J_{10,3}$ 6.5), 1.12 d. d (1H, H_α^2, J 5.0, $J_{2\alpha,2\beta}$ 13.2), 2.15 m (1H, H_β^2), 2.25 m (1H, H^3), 2.40 d. d (1H, H_α^5, $J_{5\alpha,6}$ 8.6, $J_{5\alpha,5\beta}$ 18.6), 2.93 d (1H, H_β^5, $J_{5\beta,5\alpha}$ 18.6), 9.35 br. s (1H, NOH). ^{13}C NMR spectrum (75 MHz, $CDCl_3$), δ_C, ppm: 14.76 (C^9), 16.20 (C^{10}), 18.48 (C^7), 19.30 (C^1), 20.19 (C^5), 20.53 (C^6), 28.13 (C^8), 29.39 (C^2), 34.53 (C^3), 163.78 (C^4). Found, %: C 72.6; H 10.4; N 8.5. $C_{10}H_{17}NO$. Calculated, %: C 71.9; H 10.2; N 8.4.

3α-Hydroxycaran-4-one oxime (IIa). Yield 70%, mp 101–102°C, white crystals, soluble in chloroform, acetone, benzene, and DMSO; R_f 0.4 [hexane–diethyl ether (2 : 1), detection with solution of phosphormolybdic acid], $[\alpha]_D^{20}$ +155.5° (*c* 0.2, EtOH). IR

spectrum, ν, cm^{-1}: 3377 (OH), 3183 (OH), 1653 (C=N). ^1H NMR spectrum (300 MHz, $CDCl_3$), δ, ppm (*J*, Hz): 0.83 s (3H, CH_3^9), 0.85 d. d. d (1H, H^1, $J_{1,2\alpha}$ 5.0, $J_{1,2\beta}$ 9.4, $J_{1,6}$ 10.5), 1.00 d. d. d (1H, H^6, $J_{6,5\beta}$ 1.8, $J_{6,5\alpha}$ 8.7, $J_{6,1}$ 10.5), 1.07 s (3H, CH_3^8), 1.38 s (3H, CH_3^{10}), 1.44 d. d (1H, H_α^2, $J_{2\alpha,1}$ 5.0, $J_{2\alpha,2\beta}$ 15.3), 2.25 d. d (1H, H_β^2, $J_{2\beta,1}$ 9.4, $J_{2\beta,2\alpha}$ 15.3), 2.41 br. s (1H, OH), 2.62 d. d (1H, H_α^5, $J_{5\alpha,6}$ 8.7, $J_{5\alpha,5\beta}$ 18.7), 2.89 d. d (1H, H_β^5, $J_{5\beta,6}$ 1.8, $J_{5\beta,5\alpha}$ 18.7), 9.03 br. s (1H, NOH). ^{13}C NMR spectrum (75 MHz, $CDCl_3$), δ_C, ppm: 14.43 (C^9), 16.74 (C^1), 17.71 (C^5), 18.65 (C^7), 19.06 (C^6), 24.87 (C^{10}), 28.01 (C^8), 34.78 (C^2), 69.84 (C^3), 162.46 (C^4). Found, %: C 66.2; H 9.42; N 7.6. $C_{10}H_{17}NO_2$. Calculated, %: C 65.6; H 9.28; N 7.6.

3β-Hydroxycaran-4-one oxime (IIb). Yield 91%, yellow oil, soluble in chloroform, acetone, benzene, and DMSO; R_f 0.5 [hexane–diethyl ether (1 : 2), detection with solution of phosphomolybdic acid], $[\alpha]_D^{20}$ +54.4° (*c* 0.2, EtOH). IR spectrum, ν, cm^{-1}: 3331 (OH), 1653 (C=N). ^1H NMR spectrum (300 MHz, $CDCl_3$), δ, ppm (*J*, Hz): 0.83 s (3H, CH_3^9), 0.84 m (2H, H^1, H^6), 1.05 s (3H, CH_3^8), 1.44 s (3H, CH_3^{10}), 1.45 m (1H, H_α^2), 2.21 m (1H, H_β^2), 2.43 m (1H, H_α^5), 2.98 m (1H, H_β^5), 3.90 br. s (1H, OH), 8.25 br. s (1H, NOH). ^{13}C NMR spectrum (75 MHz, $CDCl_3$), δ_C, ppm: 14.58 (C^9), 15.13 (C^7), 18.73 (C^1), 18.93 (C^6), 19.12 (C^5), 26.92 (C^{10}), 27.95 (C^8), 35.03 (C^2), 71.14 (C^3), 163.74 (C^4).

***cis*-Verbanone oxime (III).** Yield 71%, mp 64–65°C, white crystals, soluble in chloroform, acetone, benzene, and DMSO; R_f 0.3 [hexane–diethyl ether (3 : 1), detection with solution of phosphomolybdic acid], $[\alpha]_D^{20}$ +12.4° (*c* 0.2, EtOH IR spectrum, ν, cm^{-1}: 3215 (OH), 1674 (C=N). ^1H NMR spectrum (300 MHz, $CDCl_3$), δ, ppm (*J*, Hz): 0.95 s (3H, CH_3^8), 1.15 d (3H, CH_3^{10}, $J_{10,2}$ 7.3), 1.21 d (1H, H_α^7, $J_{7\alpha,7\beta}$ 9.9), 1.33 s (3H, CH_3^9), 1.98 m (1H, H^1), 2.27 m (1H, H^2), 2.39 d (1H, H_α^3, $J_{3\alpha,3\beta}$ 20.0), 2.55 d. d (1H, H_β^7, $J_{7\beta,5}$ 5.9, $J_{7\beta,7\alpha}$ 9.9), 2.62 d. d (1H, H^5, $J_{5,7\beta}$ 5.9, $J_{5,3\beta}$ 10.4), 3.02 d. d (1H, H_β^3, $J_{3\beta,5}$ 10.4, $J_{3\beta,3\alpha}$ 20.0), 8.98 br. s (1H, NOH). ^{13}C NMR spectrum (75 MHz, $CDCl_3$), δ_C, ppm: 21.66 (C^{10}), 24.44 (C^8), 26.84 (C^9), 27.39 (C^3), 30.78 (C^7), 31.82 (C^2), 40.35 (C^6), 47.67 (C^1), 48.33 (C^5), 164.85 (C^4). Found, %: C 72.8; H 10.9; N 8.2. $C_{10}H_{17}NO$. Calculated, %: C 71.9; H 10.2; N 8.4.

Menthone oxime (IV). Yield 70%, mp 51–52°C, white crystals, soluble in chloroform, acetone, benzene, and DMSO; R_f 0.8 [hexane–diethyl ether (3 : 1), detection with solution of phosphomolybdic acid], $[\alpha]_D^{20}$ –48.8° (*c* 0.3, EtOH). IR spectrum, ν, cm^{-1}: 3285 (OH), 1664 (C=N). ^1H NMR spectrum (300 MHz, $CDCl_3$), δ, ppm (*J*, Hz): 0.94 d (3H, CH_3^9, $J_{9,7}$ 6.8), 0.97 d (3H, CH_3^8, $J_{8,7}$ 6.8), 1.01 d (3H, CH_3^{10}, $J_{10,1}$ 6.2), 1.18 m (1H, H_α^6), 1.40 m (1H, H_α^5), 1.69 m (1H, H_α^2), 1.75 m (1H, H^1), 1.86 m (1H, H_β^6), 1.91 m (1H, H_β^5), 1.92 m (1H, H^4), 2.16 septet (1H, H^7, $J_{7,8,9}$ 6.8), 3.08 m (1H, H_β^2), 9.15 br. s (1H, NOH). ^{13}C NMR spectrum (75 MHz, $CDCl_3$), δ_C, ppm: 19.05 (C^9), 21.46 (C^8), 21.75 (C^{10}), 26.34 (C^7), 26.81 (C^5), 31.90 (C^2), 32.39 (C^1), 32.81 (C^6), 48.76 (C^4), 161.44 (C^3). Found, %: C 71.2; H 11.6; N 8.3. $C_{10}H_{19}NO$. Calculated, %: C 71.0; H 11.2; N 8.3.

2β-Hydroxybornan-3-one oxime (V). Yield 75%, mp 128–129°C, white crystals, soluble in chloroform, acetone, benzene, and DMSO; R_f 0.3 [hexane–diethyl ether (1 : 2), detection with solution of phosphormolybdic acid], $[\alpha]_D^{20}$ –91.7° (*c* 0.1, EtOH). IR spectrum, ν, cm^{-1}: 3537 (OH), 3395 (OH), 1688 (C=N). ^1H NMR spectrum (300 MHz, $CDCl_3$), δ, ppm (*J*, Hz): 0.91 s (3H, CH_3^9), 0.99 s (3H, CH_3^{10}), 1.05 s (3H, CH_3^8), 1.24 m (1H, H_α^5), 1.32 m (1H, H_α^6), 1.67 m (1H, H_β^5), 1.86 m (1H, H_β^6), 3.08 d (1H, H^4, $J_{4,6\beta}$ 4.3), 3.98 s (1H, H^2), 4.45 br. s (1H, OH), 9.45 br. s (1H, NOH). ^{13}C NMR spectrum (75 MHz, $CDCl_3$), δ_C, ppm: 10.79 (C^{10}), 19.03 (C^9), 21.33 (C^8), 22.89 (C^6), 33.72 (C^5), 47.08 (C^1), 47.67 (C^4), 49.54 (C^7), 77.73 (C^2), 170.45 (C^3). Found, %: C 66.2; H 9.8; N 7.4. $C_{10}H_{17}NO_2$. Calculated, %: C 65.6; H 9.3; N 7.6.

General procedure of the palladium complexes preparation. Suspension of palladium(II) chloride (0.2 mmol) and lithium chloride (0.5 mmol) in methanol (5 mL) was refluxed during 1 h (water bath). The so obtained dark-red solution of lithium tetrachloropalladate was added to solution of an oxime (0.2 mmol) in methanol (3 mL). The reaction mixture was stirred at room temperature during 1–8 h. After that, the solvent was evaporated in vacuum, and the residue was extracted with chloroform and precipitated with hexane. The resulting products were in the form of powder or crystalline.

Complex VI. Yield 188 mg (61%), mp 121–122°C (decomp.), yellow powder, soluble in chloroform, acetone, benzene, and DMSO; R_f 0.7 [benzene–acetone (5 : 1), detection with iodine vapor], $[\alpha]_D^{20}$ –262.5° (*c* 0.2, $CHCl_3$). IR spectrum, ν, cm^{-1}: 3304 (OH), 1643 (C=N). ^1H NMR spectrum (300 MHz, $CDCl_3$), δ, ppm (*J*, Hz): 0.76 m (1H, H^1), 0.85 m (1H, H^6), 0.98 m (1H, H_α^2), 1.05 s (3H, CH_3^8), 1.07 s (3H, CH_3^9), 1.55 d. d (1H,

H_{α}^{5}, *J* 8.0, $J_{5\alpha,5\beta}$ 15.2), 1.80 d (3H, CH_3^{10}, $J_{10,3}$ 7.3), 2.15 m (1H, H_{β}^{2}), 3.40 d. d (1H, H_{β}^{5}, *J* 7.3, $J_{5\beta,5\alpha}$ 15.2), 3.37 m (1H, H^3), 8.72 br. s (1H, NOH). ^{13}C NMR spectrum (75 MHz, $CDCl_3$), δ_C, ppm: 14.59 (C^9), 19.92 (C^7), 20.09 (C^{10}), 20.75 (C^1), 20.80 (C^6), 22.23 (C^5), 27.75 (C^8), 27.91 (C^2), 35.09 (C^3), 177.02 (C^4). Found, %: C 47.8; H 6.87; N 3.8. $C_{20}H_{34}N_2O_2PdCl_2$. Calculated, %: C 46.9; H 6.65; N 5.2.

Complex VII. Yield 170 mg (53%), mp 127–128°C (decomp.), yellow powder, soluble in acetone, benzene, and DMSO; R_f 0.2 [benzene–acetone (5 : 1), detection with iodine vapor], $[\alpha]_D^{20}$ +59.4° (*c* 0.2, acetone). IR spectrum, ν, cm^{-1}: 3375 (OH), 3184 (OH), 1643 (C=N). ^{1}H NMR spectrum (300 MHz, DMSO-d_6), δ, ppm (*J*, Hz): 0.70 d. d. d (1H, H^1, $J_{1,2\alpha}$ 4.5, $J_{1,6}$ 8.4, $J_{1,2\beta}$ 9.5), 0.71 s (3H, CH_3^9), 0.85 d. d (1H, H^6, $J_{6,1}$ 8.4, $J_{6,5\alpha}$ 8.5), 0.99 s (3H, CH_3^8), 1.20 s (3H, CH_3^{10}), 1.25 d. d (1H, H_{α}^{2}, $J_{2\alpha,1}$ 4.5, $J_{2\alpha,2\beta}$ 14.9), 2.09 d. d (1H, H_{β}^{2}, $J_{2\beta,1}$ 9.5, $J_{2\beta,2\alpha}$ 14.9), 2.31 d. d (1H, H_{α}^{5}, $J_{5\alpha,6}$ 8.5, $J_{5\alpha,5\beta}$ 17.6), 2.82 d (1H, H_{β}^{5}, $J_{5\beta,5\alpha}$ 17.6), 3.37 br. s (1H, OH), 10.45 br. s (1H, NOH). ^{13}C NMR spectrum (75 MHz, DMSO-d_6), δ_C, ppm: 14.69 (C^9), 17.53 (C^1), 17.80 (C^7), 17.83 (C^5), 20.40 (C^6), 26.50 (C^{10}), 28.54 (C^8), 35.71 (C^2), 68.43 (C^3), 161.09 (C^4). Found, %: C 48.8; H 6.70; N 5.3. $C_{20}H_{34}N_2O_4PdCl_2$. Calculated, %: C 47.9; H 6.30; N 5.2.

Complex VIII. Yield 170 mg (55%), mp 155–156°C (decomp.), yellow powder, soluble in chloroform, acetone, benzene, and DMSO; R_f 0.8 [benzene–acetone (5 : 1), detection with iodine vapor], $[\alpha]_D^{20}$ –5.5° (*c* 0.2, $CHCl_3$). IR spectrum, ν, cm^{-1}: 3292 (OH), 1661 (C=N). ^{1}H NMR spectrum (300 MHz, $CDCl_3$), δ, ppm (*J*, Hz): 1.04 s (3H, CH_3^8), 1.12 d (3H, CH_3^{10}, $J_{10,2}$ 7.3), 1.30 d (1H, H_{α}^{7}, $J_{7\alpha,7\beta}$ 10.4), 1.43 s (3H, CH_3^9), 2.04 m (1H, H^1), 2.27 m (1H, H^2), 2.49 d (1H, H_{α}^{3}, $J_{3\alpha,3\beta}$ 20.9), 2.71 m (1H, H_{β}^{7}), 3.13 d. d (1H, H_{β}^{3}, $J_{3\beta,5}$ 10.4, $J_{3\beta,3\alpha}$ 20.9), 3.87 d. d (1H, H^5, $J_{5,7\beta}$ 5.3, $J_{5,3\beta}$ 10.4), 8.08 br. s (1H, NOH). ^{13}C NMR spectrum (75 MHz, $CDCl_3$), δ_C, ppm: 21.30 (C^{10}), 24.69 (C^8), 26.55 (C^9), 30.58 (C^7), 30.80 (C^3), 31.63 (C^2), 40.73 (C^6), 47.07 (C^1), 51.02 (C^5), 176.79 (C^4). Found, %: C 47.1; H 6.86; N 5.1. $C_{20}H_{34}N_2O_2PdCl_2$. Calculated, %: C 47.0; H 6.65; N 5.4.

Complex IX. Yield 257 mg (83%), mp 141–142°C (decomp.), yellow powder, soluble in acetone, benzene, and DMSO; R_f 0.7 [benzene–acetone (5 : 1), detection with iodine vapor], $[\alpha]_D^{20}$ –15.8° (*c* 0.3, acetone). IR spectrum, ν, cm^{-1}: 3393 (OH), 1645 (C=N). ^{1}H NMR spectrum (300 MHz, DMSO-d_6), δ, ppm (*J*, Hz): 0.88 d (3H, CH_3^9, $J_{9,7}$ 6.8), 0.91 d (3H, CH_3^8, $J_{8,7}$ 6.8), 1.11 d (3H, CH_3^{10}, $J_{10,1}$ 6.4), 1.53 m (1H, H_{α}^{6}), 1.78 m (1H, H_{α}^{5}), 2.05 m (1H, H_{β}^{5}), 2.07 m (1H, H^1), 2.08 m (1H, H_{α}^{2}), 2.18 m (1H, H^7), 2.91 m (1H, H_{β}^{6}), 2.92 m (1H, H_{β}^{2}), 3.81 m (1H, H^4), 11.08 br. s (1H, NOH). ^{13}C NMR spectrum (75 MHz, DMSO-d_6), δ_C, ppm: 18.16 (C^9), 21.17 (C^{10}), 22.10 (C^8), 24.29 (C^5), 27.39 (C^1), 30.56 (C^2), 31.82 (C^6), 32.09 (C^7), 50.87 (C^4), 172.11 (C^3). Found, %: C 46.7; H 7.44; N 5.3. $C_{20}H_{38}N_2 \cdot O_2PdCl_2$. Calculated, %: C 46.6; H 7.40; N 5.4.

Complex X. Yield 168 mg (80%), mp 139–140°C (decomp.), red crystals, soluble in chloroform, acetone, and benzene; R_f 0.4 [benzene–acetone (5 : 1), detection with iodine vapor], $[\alpha]_D^{20}$ –117.8° (*c* 0.2, $CHCl_3$). IR spectrum, ν, cm^{-1}: 3227 (OH), 1618 (C=N). ^{1}H NMR spectrum (300 MHz, $CDCl_3$), δ, ppm (*J*, Hz): 0.85 m (1H, H^6), 0.98 s (3H, CH_3^9), 1.02 m (1H, H^1), 1.04 s (3H, CH_3^8), 1.82 s (3H, CH_3^{10}), 1.95 m (1H, H_{α}^{2}), 2.31 m (1H, H_{β}^{2}), 2.74–2.95 m (2H, H_{α}^{5}, H_{β}^{5}), 5.70 br. s (1H, OH), 9.20 br. s (1H, NOH). ^{13}C NMR spectrum (75 MHz, $CDCl_3$), δ_C, ppm: 15.08 (C^9), 18.17 (C^6), 21.68 (C^7), 21.92 (C^1), 24.08 (C^5), 25.89 (C^{10}), 27.73 (C^8), 33.50 (C^2), 88.42 (C^3), 171.97 (C^4). Found, %: C 34.3; H 5.2; N 3.81. $C_{10}H_{17}NO_2PdCl_2$. Calculated, %: C 33.2; H 4.7; N 3.88.

Complex XI. Yield 195 mg (90%), mp 163–164°C (decomp.), yellow powder, soluble in acetone and benzene; R_f 0.7 [benzene–acetone (5 : 1), detection with iodine vapor], $[\alpha]_D^{20}$ –21.4° (*c* 0.2, acetone). IR spectrum, ν, cm^{-1}: 3415 (OH), 1632 (C=N). ^{1}H NMR spectrum (300 MHz, $CDCl_3$), δ, ppm (*J*, Hz): 0.71 s (3H, CH_3^9), 0.88 s (3H, CH_3^{10}), 0.95 s (3H, CH_3^8), 1.07 m (1H, H_{α}^{5}), 1.13 m (1H, H_{α}^{6}), 1.56 m (1H, H_{β}^{6}), 1.67 m (1H, H_{β}^{5}), 2.81 d (1H, H^4, $J_{4,6\beta}$ 4.1), 3.69 d (1H, H^2, $J_{2,OH}$ 4.8), 5.22 d (1H, OH, $J_{OH,2}$ 4.8), 10.21 br. s (1H, NOH). ^{13}C NMR spectrum (75 MHz, $CDCl_3$), δ_C, ppm: 11.55 (C^{10}), 19.48 (C^9), 21.70 (C^8), 23.46 (C^5), 33.52 (C^6), 46.49 (C^1), 47.10 (C^4), 49.59 (C^7), 77.57 (C^2), 167.39 (C^3). Found, %: C 34.3; H 5.2; N 3.7. $C_{10}H_{17}NO_2PdCl_2$. Calculated, %: C 33.2; H 4.7; N 3.9.

ACKNOWLEDGMENTS

This work was financially supported by the Russian Foundation for Basic Research (project No. 13-03-98805).

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