New chiral cyclopalladated complexes based on the pinane and bornane imines*

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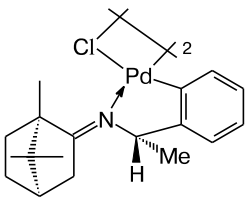
2α-Hydroxypinan-3-one imino derivatives react with lithium tetrachloropalladate to form palladacycles, while similar bornane derivative undergo cyclopalladation only when treated with palladium acetate.

Key words: palladium complexes, palladacycles, imines, bicyclic monoterpenoids.

Chiral palladacycles, possessing high thermal, oxidation, and hydrolytic stability, are known[1,2] to be successfully used in asymmetric synthesis and catalysis. Earlier,[3,4] we have studied the cyclopalladation of 2α-hydroxypinan-3-one and camphor benzylimines and found that the direction of cyclometallation depended on the structural specificity of the ligand: camphor α-methylbenzylimine formed the *ortho*-palladated complex **1**, whereas in the case of camphor benzylimine, the cyclometallation of the bornane fragment for the first time was accomplished at the methyl group at position 1 (complex **2**).



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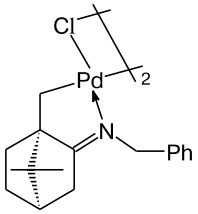

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In the present work, we report the synthesis of new cyclopalladated complexes based on the enantiomerically pure pinane and bornane derivatives containing vicinal imino- and hydroxy groups and some other types of functionalization.

Results and Discussion

Enantiopure natural bicyclic monoterpenoids (−)-α-pinene (**3**) and (−)-camphor (**4**) were used as the starting chiral compounds for the synthesis of imines. They were converted to the corresponding α-hydroxy ketones in order to further develop the vicinal imino- and hydroxy groups in them (Scheme 1). The oxidation of α-pinene **3** with potassium permanganate in aqueous acetone led[5] to 2α-hydroxypinan-3-one (**5**) in 50% yield.

Camphorquinone **6** was obtained according to the described procedure[6] by the oxidation of bromocamphor with atmospheric oxygen in DMSO in 84% yield (see Scheme 1). The ketalization of camphorquinone with ethylene glycol took place only at one keto group, and the reduction of the other group with sodium borohydride with subsequent hydrolysis of the intermediate hydroxy ketal led to 2β-hydroxybornan-3-one (**7**) in 75% yield.[7] The new ligands, *viz.*, imines **8**—**11**, were synthesized by the condensation of the corresponding oxo derivatives with diphenylmethylamine, benzylamine, and (*S*)-α-methylbenzylamine in 49—56% yields (see Scheme 1). The data on the studies of imines **12**—**16** as the ligands for the preparation of chiral palladium complexes were reported earlier.[3,4,8,9]

The formation of the imines proceeded stereoselectively: their NMR spectra exhibited one set of signals, that indicated the formation of one geometrical isomer. The studies of the NOE interactions showed that imines **8** and **9** have *E*-configuration, whereas imines **10** and **11** have *Z*-configuration. Thus, the NOESY spectra of imines **8** and **9** demonstrated the interaction of the benzyl protons with the protons of the terpene fragment at positions 4 and 3, respectively, that confirmed the *E*-configuration of the imines obtained. The *Z*-configuration of imines **10** and **11** was confirmed by the NOE interaction of their protons at position 11 with the proton of the terpene fragment at position 2 and the proton of the hydroxy group.

The synthesized imines **8**—**11** and **16** were studied in the cyclopalladation reaction. Benzylamine derivatives are known to readily undergo the palladation at the aromatic

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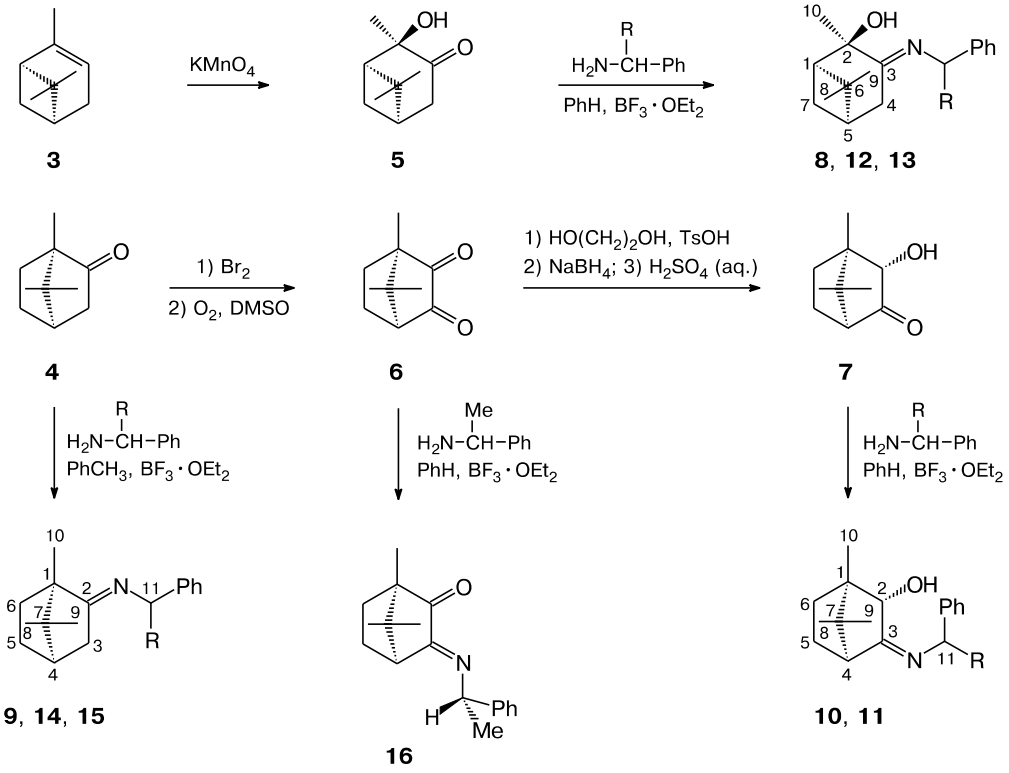
Scheme 1



R = Ph (**8**, **9**), H (**10**, **12**, **14**), Me (**11**, **13**, **15**)

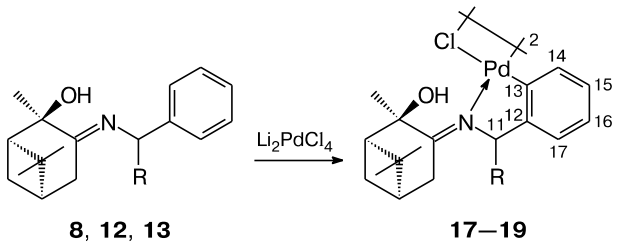
ring. We found that imine **8** under the Cope reaction conditions, which suggested that the ligand reacted with lithium tetrachloropalladate (Li_2PdCl_4) in the presence of sodium acetate as a base (see the data in Ref. 3), formed *ortho*-palladated dimer **17** in 58% yield (Scheme 2).

The formation of the *ortho*-palladated complex **17** was unambiguously confirmed by the ^1H and ^{13}C NMR spectra, in which only one set of signals was observed, that indicated the formation of one individual isomer. The *ortho*-disubstituted aromatic ring was identified by the signals in the region of aromatic protons, which contained the signals for four nonequivalent protons with the indicative splitting. The ^1H NMR spectrum still retained the splitting and the integral intensity of the signals for the protons of the second monosubstituted benzene ring.

Comparing the reactivity of imines **8**, **12**, and **13**, one can note that the presence of a substituent at α-position of the benzyl fragment facilitates the *ortho*-palladation: the phenyl- and methyl-substituted benzylimines **8** and **13** form the binuclear cyclopalladated complexes **17** and **19** (see Ref. 3) in close yields (58 and 53%, respectively) even in the absence of AcONa as a base.

Earlier,[4] we have studied the cyclometallation of camphor benzyl- and α-methylbenzylimines **14** and **15** and have shown that no cyclopalladation of these compound

Scheme 2

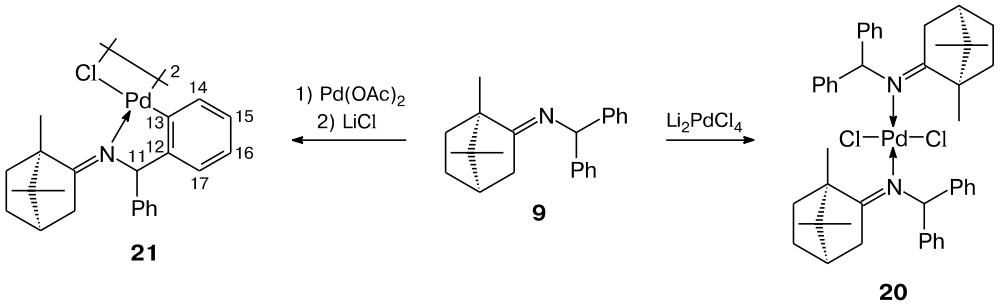


R = Ph (**8**, **17**), H (**12**, **18**), Me (**13**, **19**)

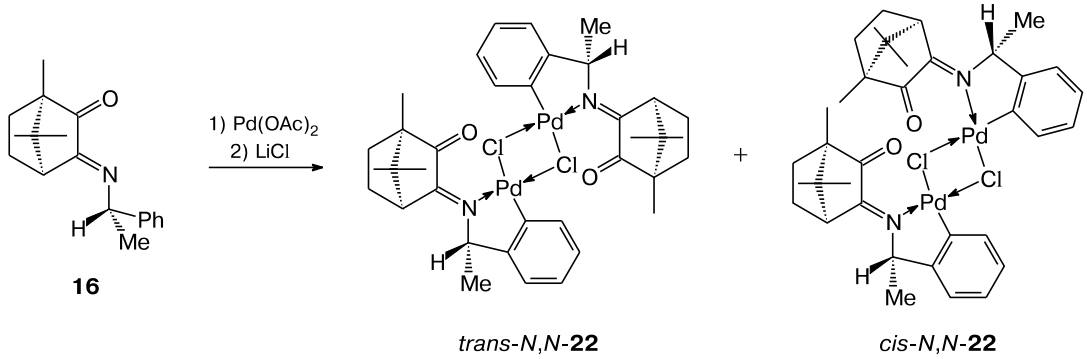
took place under the Cope reaction conditions. When lithium tetrachloropalladate was replaced with stronger electrophile palladium acetate, the reaction gave cyclometallated complexes **1** and **2**. Therefore, we used similar conditions for the studies of the ligand properties of camphor diphenylmethylimine **9**. The results were not unexpected: the reaction of imine **9** with lithium tetrachloropalladate gave the coordination palladium compound **20**, whereas treatment with palladium acetate led to the *ortho*-palladation of the aromatic ring (Scheme 3).

The formation of *ortho*-disubstituted aromatic ring in complex **21** was confirmed by the NMR spectra. Thus, the ^1H NMR spectra exhibit the signals for the four non-

Scheme 3



Scheme 4



equivalent aromatic protons as separate multiplets, whereas the ^{13}C NMR spectra have of the signals the methine aromatic groups.

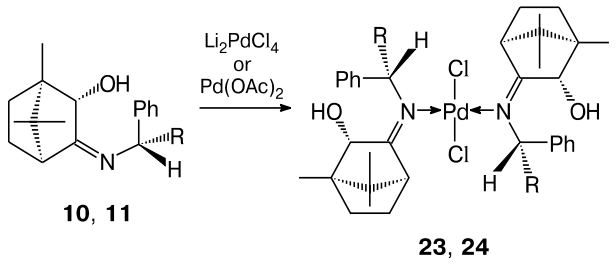
It should be noted that an additional chiral center emerges at position 11 upon the *ortho*-palladation of diphenylmethylimine derivatives **8** and **9**. The presence of only one set of signals in the NMR spectra of the corresponding palladacycles **17** and **21** indicates that *ortho*-palladation is a diastereoselective process.

Unlike imines **9**, **14**, and **15** forming individual cyclometallated complexes **21**, **1**, and **2**, respectively, the *ortho*-palladation of camphorquinone α-methylbenzylimine **16** leads to a mixture of geometrical isomers (Scheme 4). The ^1H NMR spectrum of complex **22** exhibits two sets of signals with the 5 : 1 ratio of intensities.

The studies of the reaction of 2β-hydroxybornan-3-one imines **10** and **11** with lithium tetrachloropalladate and palladium acetate showed that no cyclopalladation of these compounds occured: the complexes **23** and **24** were formed instead in 58 and 64% yields, respectively (Scheme 5).

The NMR spectra of complexes **23** and **24** with the monodentate coordinated ligands still have all the signals corresponding to the starting imines with their slight low-field shift for the nuclei arranged close to palladium. The splitting and the integral intensity of the signals for the protons of the benzene ring correspond to the monosubstitution. The absence of the double signals indicate the formation of individual isomers.

Scheme 5



R = H (**10**, **23**), Me (**11**, **24**)

In conclusion, we for the first time studied the cyclopalladation reaction of a number of imines of the pinane and bornane structures and found that the 2α-hydroxypinan-3-one derivatives readily enough underwent cyclopalladation in the reaction with lithium tetrachloropalladate. Unlike the pinane structures, the bornane derivatives underwent cyclometallation only when treated with palladium acetate.

Experimental

IR spectra (neat or in KBr pellets) were recorded on a Shimadzu IR Prestige 21 spectrometer. ^1H and ^{13}C NMR spectra were recorded on a Bruker AVANCE-II-300 spectrometer (300 (^1H) and 75 MHz (^{13}C)) in $CDCl_3$, using residual signals of

chloroform (δ_H 7.27, δ_C 77.00) and DMSO (δ_H 2.50) as references. The signal were assigned using the ^{13}C NMR spectra recorded in the J-modulation mode and the 2D correlation spectra $^1H—^1H$ (COSY, NOESY) and $^1H—^{13}C$ (HSQC, HMBC). Optical rotation was measured on a Kruss P3002RS automatic polarimeter (Germany). Elemental analysis was performed on an EA 1110 elemental analyzer.

The reaction progress was monitored by TLC on Sorbfil plates, using the hexane—Et_2O and the benzene—acetone solvent systems as eluents. To visualize compounds, the plates were treated with the iodine vapors. Alfa-Aesar silica gel (70—230 μ) was used for column chromatography. (*S*)-α-Methylbenzylamine (*ee* 99.5%), (1*S*)-α-pinene (**3**) (Acros Organics), camphor **4** recrystallized from ethanol ($[\alpha]_D$ −40.9 (*c* 1.0, $CHCl_3$)), and palladium chloride and acetate were used without additional purification.

(1*R*,2*R*,5*R*)-2-Hydroxypinan-3-one (**5**) ($[\alpha]_D^{20}$ +39 (*c* 0.9, $CHCl_3$), m.p. 39—40 °C), (1*R*,4*S*)-camphorquinone (**6**) ($[\alpha]_D^{20}$ −97.8 (*c* 1.5, toluene)), and (1*R*,2*S*,4*S*)-2-hydroxybornan-3-one (**7**) ($[\alpha]_D^{20}$ −132.7 (*c* 0.1, EtOH)) were synthesized according to the known procedures.[5—7]

Preparation of imines (general procedure). The corresponding keto derivative (7 mmol) and primary amine (8 mmol) were dissolved in anhydrous benzene (20 mL) or toluene (20 mL). Then, boron trifluoride etherate (3 mmol) was added, and the mixture was refluxed for 4—15 h. The reaction progress was monitored by TLC (eluent a mixture of hexane—diethyl ether, visualization by iodine). The compounds were isolated by column chromatography on SiO_2 (eluent a mixture of light petroleum—diethyl ether). All the compounds were obtained as oils.

(1*R*,2*R*,5*R*)-3-Diphenylmethylimino-2,6,6-trimethylbicyclo-[3.1.1]heptan-2-ol (8). The yield was 0.9 g (49%), $[\alpha]_D^{21}$ −32.2 (*c* 0.2, $CHCl_3$), bright yellow oil soluble in diethyl ether, chloroform, acetone, benzene, and DMSO, R_f 0.5 (hexane—diethyl ether, 3 : 1). IR, ν/cm^{-1}: 3435 (OH), 1647 (C=N). ^1H NMR ($CDCl_3$), δ: 0.78 (s, 3 H, C(9)H_3); 1.34 (s, 3 H, C(8)H_3); 1.57 (d, 1 H, H(7)$_\alpha$, *J* = 10.6 Hz); 1.64 (s, 3 H, C(10)H_3); 2.05 (m, 1 H, H(5), *J* = 5.9 Hz); 2.15 (dd, 1 H, H(1), *J* = 5.9 Hz, *J* = 6.0 Hz); 2.36 (dddd, 1 H, H(7)$_\beta$, *J* = 2.5 Hz, *J* = 5.9 Hz, *J* = 6.0 Hz, *J* = 10.6 Hz); 2.58 (ddd, 1 H, H(4)$_\beta$, *J* = 2.5 Hz, *J* = 5.8 Hz, *J* = 18 Hz); 2.62 (s, 1 H, OH); 2.73 (dd, 1 H, H(4)$_\beta$, *J* = 3.0 Hz, *J* = 18 Hz); 5.73 (s, 1 H, H(11)); 7.22—7.46 (m, 10 H, H arom.). ^{13}C NMR ($CDCl_3$), δ: 22.88 (C(9)), 27.39 (C(8)), 28.14 (C(7)), 28.60 (C(10)), 33.68 (C(4)), 38.44 (C(5)), 38.49 (C(6)), 50.06 (C(1)), 66.60 (C(11)), 76.90 (C(2)), 126.77 (C(15)), 126.88 (C(15′)), 127.31 (C(13)), 127.50 (C(13′)), 128.43 (C(14)), 128.50 (C(14′)), 144.13 (C(12), C(12′)), 175.77 (C(3)).

(1*S*,4*S*)-2-Diphenylmethylimino-1,7,7-trimethylbicyclo[2.2.1]-heptane (9). The yield was 1.3 g (51%), $[\alpha]_D^{23}$ +19.2 (*c* 0.3, $CHCl_3$), colorless oily liquid soluble in diethyl ether, chloroform, acetone, benzene, and DMSO, R_f 0.6 (hexane—diethyl ether, 3 : 1). IR, ν/cm^{-1}: 1682 (C=N). ^1H NMR ($CDCl_3$), δ: 0.70 (s, 3 H, C(9)H_3); 0.97 (s, 3 H, C(8)H_3); 1.14 (s, 3 H, C(10)H_3); 1.18 (m, 1 H, H(5)$_\alpha$, *J* = 10 Hz); 1.42 (m, 1 H, H(6)$_\alpha$, *J* = 13 Hz); 1.72 (m, 1 H, H(6)$_\beta$, *J* = 13 Hz); 1.85 (m, 1 H, H(5)$_\beta$, *J* = 10 Hz); 1.94 (dd, 1 H, H(4), *J* = 4.3 Hz, *J* = 4.7 Hz); 1.96 (d, 1 H, H(3)$_\alpha$, *J* = 17 Hz); 2.40 (ddd, 1 H, H(3)$_\beta$, *J* = 4.0 Hz, *J* = 7.5 Hz, *J* = 17 Hz); 5.51 (s, 1 H, H(11)); 7.19—7.48 (m, 10 H, H arom.). ^{13}C NMR ($CDCl_3$), δ: 11.58 (C(10)), 19.08 (C(8)), 19.56 (C(9)), 27.49 (C(5)), 32.04 (C(6)), 35.94 (C(3)), 44.02 (C(4)), 47.15 (C(7)), 54.05 (C(1)), 68.25 (C(11)), 126.44 (C(15)), 126.46 (C(15′)), 127.50 (C(13)), 127.56 (C(13′)), 128.18 (C(14)), 128.25 (C(14′)), 145.00 (C(12)), 145.09 (C(12′)), 181.56 (C(2)).

(1*R*,2*S*,4*S*)-3-Benzylimino-1,7,7-trimethylbicyclo[2.2.1]-heptan-2-ol (10). The yield was 0.68 g (53%), $[\alpha]_D^{21}$ +24.1 (*c* 0.5, $CHCl_3$), bright yellow oil soluble in diethyl ether, chloroform, acetone, benzene, and DMSO, R_f 0.5 (hexane—diethyl ether, 3 : 1). IR, ν/cm^{-1}: 3319 (OH), 1644 (C=N). ^1H NMR ($CDCl_3$), δ: 0.90 (s, 3 H, C(9)H_3); 0.96 (s, 3 H, C(10)H_3); 1.04 (s, 3 H, C(8)H_3); 1.38 (m, 1 H, H(6)$_\alpha$); 1.66 (m, 1 H, H(5)$_\alpha$); 1.72 (m, 1 H, H(6)$_\beta$); 1.91 (br.s, 1 H, OH); 2.04 (m, 1 H, H(5)$_\beta$); 2.16 (dd, 1 H, H(4), *J* = 4.1 Hz, *J* = 4.3 Hz); 3.37 (d, 1 H, H(2), *J* = 4.5 Hz); 3.78 (d, 1 H, H(11)$_\alpha$, *J* = 15 Hz); 3.82 (d, 1 H, H(11)$_\beta$, *J* = 15 Hz); 7.25—7.37 (m, 5 H, H arom.). ^{13}C NMR ($CDCl_3$), δ: 9.40 (C(10)), 18.83 (C(5)), 19.42 (C(8)), 19.73 (C(9)), 32.10 (C(6)), 44.17 (C(1)), 47.22 (C(4)), 52.78 (C(11)), 58.40 (C(7)), 64.68 (C(2)), 127.02 (C(15)), 128.18 (C(14)), 128.35 (C(13)), 140.01 (C(12)), 219.30 (C(3)).

(1*R*,2*S*,4*S*)-3-[(1*S*)-α-Methylbenzylimino]-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol (11). The yield was 83 mg (51%), $[\alpha]_D^{21}$ −26.0 (*c* 0.5, $CHCl_3$), bright yellow oil soluble in diethyl ether, chloroform, acetone, benzene, and DMSO, R_f 0.6 (hexane—diethyl ether, 3 : 1). IR, ν/cm^{-1}: 3175 (OH), 1686 (C=N). ^1H NMR ($CDCl_3$), δ: 0.80 (s, 3 H, C(9)H_3); 0.90 (s, 3 H, C(8)H_3); 0.92 (s, 3 H, C(10)H_3); 1.29 (m, 1 H, H(6)$_\alpha$); 1.41 (d, 3 H, C(12)H_3, *J* = 6.5 Hz); 1.45 (m, 1 H, H(5)$_\alpha$); 1.51 (m, 1 H, H(4)); 1.62 (m, 1 H, H(6)$_\beta$); 1.89 (m, 1 H, H(5)$_\beta$); 1.90 (br.s, OH); 3.30 (d, 1 H, H(2), *J* = 4.5 Hz); 3.93 (q, 1 H, H(11), *J* = 6.5 Hz); 7.20—7.40 (m, 5 H, H arom.). ^{13}C NMR ($CDCl_3$), δ: 9.43 (C(10)), 19.14 (C(5)), 19.20 (C(8)), 19.68 (C(9)), 24.36 (C(12)), 32.25 (C(6)), 43.89 (C(1)), 48.34 (C(4)), 58.34 (C(7)), 59.35 (C(11)), 65.64 (C(2)), 126.97 (C(16)), 127.04 (C(15)), 128.17 (C(14)), 145.78 (C(13)), 220.83 (C(3)).

Synthesis of cyclopalladated complexes. ***A.*** A suspension of palladium(II) chloride (0.2 mmol) and lithium chloride (0.5 mmol) in methanol (5 mL) was boiled with a reflux condenser in a water bath for 1 h. A dark red solution of lithium tetrachloropalladate was poured to a solution of imine (0.2 mmol) and sodium acetate (0.2 mmol) in methanol (5 mL), and the reaction mixture was stirred at room temperature for 5—7 h. The solvent was evaporated from the reaction mixture *in vacuo*, the residue was dissolved in benzene and purified by chromatography (SiO_2, eluent a mixture of benzene—acetone). The oil left after evaporation of the solvents was recrystallized from the system benzene—hexane to obtain the complex compound as powders.

B. A suspension of imine (0.4 mmol) and palladium acetate (0.4 mmol) in toluene (15 mL) was heated for 3—6 h at 60 °C. The solvent was evaporated from the reaction mixture *in vacuo*, then a solution of lithium chloride (2 mmol) in methanol (5 mL) was added to the residue. The reaction mixture was stirred for 3—5 h at room temperature. The solvent was evaporated from the reaction mixture *in vacuo*, the residue was dissolved in benzene and purified by chromatography (SiO_2, eluent a mixture of benzene—acetone). The oil left after evaporation of the solvents was recrystallized from the system benzene—hexane to obtain the complex compound as powders.

Di-μ-chlorobis{2-[((1*R*,2*R*,5*R*)-2-hydroxy-2,6,6-trimethylbicyclo[3.1.1]hept-3-ylideneamino)(phenyl)methyl]phenyl-*C*,*N*}-dipalladium(II) (17). The yield was 133 mg (58%), m.p. 159—160 °C

(with decomp.), $[\alpha]_D^{20}$ +115.4 (*c* 0.4, $CHCl_3$), yellow powder soluble in chloroform, acetone, benzene, and DMSO, R_f 0.4 (benzene—acetone, 10 : 1). Found (%): C, 57.80; H, 5.64; N, 2.66. $C_{46}H_{52}Cl_2N_2O_2Pd_2$. Calculated (%): C, 58.20; H, 5.49; N, 2.95. IR, ν/cm^{-1}: 3204 (OH), 1632 (C=N). ^{1}H NMR ($CDCl_3$), δ: 0.62 (s, 3 H, C(9)H_3); 1.30 (s, 3 H, C(8)H_3); 1.36 (d, 1 H, H(4)$_\alpha$, *J* = 20 Hz); 1.88 (m, 1 H, H(5)); 2.06 (s, 3 H, C(10)H_3); 2.15—2.30 (m, 3 H, H(1), H(4)$_\beta$, H(7)$_\alpha$); 2.58 (m, 1 H, H(7)$_b$); 3.95 (s, 1 H, H(11)); 6.20 (d, 1 H, H(17), *J* = 7.6 Hz); 6.55 (s, 1 H, OH); 6.91 (dd, 1 H, H(15), *J* = 7.4 Hz, *J* = 7.8 Hz); 6.98 (d, 2 H, H arom., *J* = 7 Hz); 7.10 (dd, 1 H, H(16), *J* = 7.4 Hz, *J* = 7.6 Hz); 7.22—7.35 (m, 3 H, H arom.); 7.60 (d, 1 H, H(14), *J* = 7.8 Hz). ^{13}C NMR ($CDCl_3$), δ: 22.92 (C(9)), 27.13 (C(8)), 27.73 (C(10)), 28.86 (C(7)), 36.30 (C(4)), 38.00 (C(5)), 40.57 (C(6)), 51.65 (C(1)), 75.32 (C(11)), 88.39 (C(2)), 124.71 (C(15)), 124.83 (C(16)), 124.93 (C(17)), 127.68 (*p*-C_{Ph}), 127.82 (*o*-C_{Ph}), 128.93 (*m*-C_{Ph}), 135.85 (C(14)), 140.51 (C_{Ar}), 142.48 (C(12)), 157.49 (C(13)), 187.77 (C(3)).

***trans*-Dichlorobis{(1*S*,4*S*)-2-diphenylmethylimino-1,7,7-trimethylbicyclo[2.2.1]heptane-*N*}palladium(II) (20).** The yield was 100 mg (82%), m.p. 169—170 °C (with decomp.), $[\alpha]_D^{20}$ +200 (*c* 0.03, $CHCl_3$), orange powder soluble in acetone, benzene, and DMSO, R_f 0.7 (benzene—acetone, 10 : 1). Found (%): C, 67.80; H, 6.69; N, 3.37. $C_{46}H_{54}Cl_2N_2Pd$. Calculated (%): C, 68.10; H, 6.65; N, 3.45. IR, ν/cm^{-1}: 1622 (C=N). ^{1}H NMR (DMSO-d_6), δ: 0.57 (s, 3 H, C(9)H_3); 0.90 (s, 3 H, C(8)H_3); 1.01 (s, 3 H, C(10)H_3); 1.15 (m, 1 H, H(5)$_\alpha$); 1.24 (m, 1 H, H(6)$_\alpha$); 1.67 (m, 1 H, H(6)$_\beta$); 1.75 (m, 1 H, H(5)$_\beta$); 1.80 (m, 1 H, H(4)); 1.94 (d, 1 H, H(3)$_\alpha$, *J* = 17 Hz); 2.29 (m, 1 H, H(3)$_\beta$, *J* = 17 Hz); 5.52 (s, 1 H, H(11)); 7.15—7.45 (m, 10 H, H arom.). ^{13}C NMR (DMSO-d_6), δ: 12.02 (C(10)), 19.28 (C(8)), 19.62 (C(9)), 27.42 (C(5)), 32.12 (C(6)), 35.95 (C(3)), 43.73 (C(4)), 47.24 (C(7)), 54.00 (C(1)), 67.85 (C(11)), 126.80 (C(15)), 126.81 (C(15′)), 127.55 (C(13)), 127.60 (C(13′)), 128.60 (C(14)), 128.64 (C(14′)), 145.56 (C(12)), 145.68 (C(12′)), 197.26 (C(2)).

Di-μ-chlorobis{2-[((1*S*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-ylideneamino)(phenyl)methyl]phenyl-*C*,*N*}dipalladium(II) (21). The yield was 90 mg (45%), m.p. 161—162 °C (with decomp.), $[\alpha]_D^{20}$ +114.5 (*c* 0.2, $CHCl_3$), yellow powder soluble in chloroform, acetone, benzene, and DMSO, R_f 0.7 (benzene—acetone, 10 : 1). Found (%): C, 59.80; H, 5.75; N, 3.39. $C_{46}H_{52}Cl_2N_2Pd_2$. Calculated (%): C, 60.20; H, 5.68; N, 3.06. IR, ν/cm^{-1}: 1625 (C=N). ^{1}H NMR ($CDCl_3$), δ: 0.80 (s, 3 H, C(9)H_3); 0.99 (s, 3 H, C(8)H_3); 1.07 (m, 1 H, H(5)$_\alpha$); 1.73—2.00 (m, 5 H, H(6)$_\alpha$, H(5)$_\beta$, H(3)$_\alpha$, H(4), H(6)$_\beta$); 2.04 (s, 3 H, C(10)H_3); 2.89 (dd, 1 H, H(3)$_\beta$, *J* = 3.6 Hz, *J* = 17 Hz); 5.67 (s, 1 H, H(11)); 6.55 (br, 1 H, H(14)); 6.79 (br, 1 H, H(15)); 6.92 (m, 1 H, *p*-H_{Ph}); 7.04 (m, 2 H, H(16), H(17)); 7.27 (m, 2 H, *m*-H_{Ph}); 8.02 (d, 2 H, *o*-H_{Ph}, *J* = 7 Hz). ^{13}C NMR ($CDCl_3$), δ: 13.16 (C(10)), 19.01 (C(8)), 20.17 (C(9)), 26.71 (C(5)), 31.35 (C(6)), 39.61 (C(3)), 43.14 (C(4)), 49.98 (C(7)), 55.80 (C(1)), 80.06 (C(11)), 121.06 (C(17)), 124.53 (C(16)), 125.23 (*p*-C_{Ph}), 126.68 (*o*-C_{Ph}), 126.95 (C(15)), 128.36 (C(14)), 134.54 (*m*-C_{Ph}), 140.13 (C(12), C(12′)), 151.11 (C(13)), 193.07 (C(2)).

Di-μ-chlorobis{2-[((1*S*,4*S*)-1,7,7-trimethyl-2-oxobicyclo-[2.2.1]hept-3-ylideneamino)(phenyl)methyl]phenyl-*C*,*N*}dipalladium(II) (22). The yield was 89 mg (54%), m.p. 167—168 °C (with decomp.), $[\alpha]_D^{20}$ +28.7 (*c* 0.2, $CHCl_3$), yellow powder soluble in chloroform, acetone, benzene, and DMSO, R_f 0.7 (benzene—acetone, 10 : 1). Found (%): C, 53.10; H, 5.72; N, 3.16. $C_{36}H_{44}Cl_2N_2O_2Pd_2$. Calculated (%): C, 52.70; H, 5.37; N, 3.41. IR, ν/cm^{-1}: 1745 (C=O), 1651 (C=N). ^{1}H NMR ($CDCl_3$), δ: 0.92 (s, 3 H, C(9)H_3); 1.06 (s, 3 H, C(10)H_3); 1.09 (s, 3 H, C(8)H_3); 1.57 (m, 1 H, H(6)$_\alpha$); 1.80 (d, 3 H, C(12)H_3, *J* = 6.4 Hz); 1.87 (m, 1 H, H(5)$_\alpha$); 1.88 (m, 1 H, H(6)$_\beta$); 2.26 (m, 1 H, H(5)$_\beta$); 3.62 (d, 1 H, H(4), *J* = 4.1 Hz); 6.30 (q, 1 H, H(11), *J* = 6.4 Hz); 6.84 (d, 1 H, H(18), *J* = 7.2 Hz); 6.92 (dd, 1 H, H(16), *J* = 7.1 Hz, *J* = 7.7 Hz); 6.98 (dd, 1 H, H(17), *J* = 7.1 Hz, *J* = 7.2 Hz); 7.15 (d, 1 H, H(15), *J* = 7.7 Hz). ^{13}C NMR ($CDCl_3$), δ: 9.32 (C(10)), 17.72 (C(8)), 21.11 (C(9)), 24.87 (C(5)), 26.60 (C(12)), 30.27 (C(6)), 44.39 (C(7)), 57.71 (C(4)), 60.25 (C(1)), 72.16 (C(11)), 120.16 (C(18)), 125.24 (C(17)), 125.39 (C(16)), 132.99 (C(15)), 140.84 (C(13)), 152.55 (C(14)), 175.12 (C(3)), 201.51 (C(2)).

***trans*-Dichlorobis[(1*R*,2*S*,4*S*)-3-benzylimino-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol-*N*]palladium(II) (23).** The yield was 80 mg (58%), m.p. 159—160 °C (with decomp.), $[\alpha]_D^{20}$ +138.9 (*c* 0.2, acetone), yellow powder soluble in acetone, benzene, and DMSO, R_f 0.7 (benzene—acetone, 5 : 1). Found (%): C, 58.50; H, 6.70; N, 3.55. $C_{34}H_{46}Cl_2N_2O_2Pd$. Calculated (%): C, 59.00; H, 6.60; N, 3.81. IR, ν/cm^{-1}: 3456 (OH), 1638 (C=N). ^{1}H NMR (DMSO-d_6), δ: 0.73 (s, 3 H, C(10)H_3); 0.74 (s, 3 H, C(9)H_3); 0.92 (s, 3 H, C(8)H_3); 1.20 (m, 1 H, H(5)$_\alpha$); 1.26 (m, 1 H, H(6)$_\alpha$); 1.47 (m, 1 H, H(6)$_\beta$); 1.78 (m, 1 H, H(5)$_\beta$); 2.09 (m, 1 H, H(4)); 3.43 (d, 1 H, H(2), *J* = 7 Hz); 3.81 (d, 1 H, H(11′), *J* = 12 Hz); 4.36 (d, 1 H, H(11″), *J* = 12 Hz); 4.78 (br.d, 1 H, OH, *J* = 7 Hz); 7.30—7.65 (m, 5 H, H arom.). ^{13}C NMR (DMSO-d_6), δ: 10.06 (C(10)), 18.82 (C(8)), 19.87 (C(9)), 19.95 (C(5)), 30.37 (C(6)), 43.43 (C(1)), 47.82 (C(4)), 56.52 (C(11)), 59.74 (C(7)), 68.44 (C(2)), 127.92 (C(15)), 128.27 (C(14)), 130.76 (C(13)), 137.21 (C(12)), 214.88 (C(3)).

***trans*-Dichlorobis{(1*R*,2*S*,4*S*)-3-[(1*S*)-α-methylbenzylimino]-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol-*N*}palladium (II) (24).** The yield was 92 mg (64%), m.p. 162—163 °C (with decomp.), $[\alpha]_D^{20}$ +94.4 (*c* 0.3, $CHCl_3$), yellow powder soluble in chloroform, acetone, benzene, and DMSO, R_f 0.8 (benzene—acetone, 5 : 1). Found (%): C, 60.60; H, 7.40; N, 4.61. $C_{36}H_{50}Cl_2N_2O_2Pd$. Calculated (%): C, 60.55; H, 6.99; N, 4.36. IR, ν/cm^{-1}: 3192 (OH), 1643 (C=N). ^{1}H NMR ($CDCl_3$), δ: 0.89 (s, 3 H, C(9)H_3); 0.91 (s, 3 H, C(10)H_3); 1.07 (s, 3 H, C(8)H_3); 1.39 (m, 1 H, H(6)$_\alpha$); 1.70 (d, 3 H, C(12)H_3, *J* = 7 Hz); 1.79 (m, 1 H, H(6)$_\beta$); 2.02 (m, 1 H, H(5)$_\alpha$); 2.55 (m, 1 H, H(5)$_\beta$); 3.37 (dd, 1 H, H(4), *J* = 4.0 Hz, *J* = 4.2 Hz); 3.70 (d, 1 H, H(2), *J* = 4 Hz); 3.80 (br.s, 1 H, OH); 4.69 (q, 1 H, H(11), *J* = 7 Hz); 7.20—7.70 (m, 5 H, H arom.). ^{13}C NMR ($CDCl_3$), δ: 9.67 (C(10)), 18.78 (C(8)), 19.69 (C(9)), 20.37 (C(5)), 21.41 (C(12)), 31.91 (C(6)), 43.62 (C(1)), 50.49 (C(4)), 60.34 (C(7)), 60.99 (C(11)), 65.66 (C(2)), 128.02 (C(15)), 128.35 (C(16)), 129.90 (C(14)), 139.14 (C(13)), 216.15 (C(3)).

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