# *trans*-Dichlorobis{(1*R*,4*S*)-1,7,7-Trimethyl-3-[(*S*)-α-Methylbenzylimino]bicyclo[2.2.1]heptan-2-one-*N*}Palladium(II): Synthesis and Structural Examination

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**Abstract**—A reaction of (1R,4S)-1,7,7-trimethyl-3-[(*S*)- $\alpha$ -methylbenzylimino]bicyclo[2.2.1]heptan-2-one with lithium tetrachloropalladate gave a chiral palladium(II) complex with monodentate coordination of the organic ligand. The structure of the complex was confirmed by NMR spectra and X-ray diffraction data. **DOI:** 10.1134/S1070328413010107

Chiral palladium complexes are known to be widely used as catalysts in modern asymmetric synthesis [1, 2]. In connection with this, the preparation and structural studies of new palladium complexes are of current interest. Derivatives of naturally occurring monoterpenoids can serve as starting materials for the synthesis of enantiomerically pure ligands. Here, we used (1R, 4S)-camphor quinone (special purity grade 98%) for the synthesis of imine I.

#### **EXPERIMENTAL**

(1R, 4S)-Camphor quinone  $([\alpha]_D^{20} - 97.8 (c 1.5, tol$ uene) was prepared as described in [3]. (*S* $)-<math>\alpha$ -Methylbenzylamine (ee 99.5%, Lancaster), palladium chloride (high-purity grade, 98%), and lithium chloride (reagent grade) were employed as purchased. Methanol, chloroform, hexane, benzene, and diethyl ether (analytical grade all) were used as solvents. Silica gel (70–230 mesh, Lancaster) was used for column chromatography.

Synthesis of  $C_{18}H_{23}NO$  (I). Camphor quinone (566 mg, 3 mmol) and (*S*)- $\alpha$ -methylbenzylamine (410 mg, 3 mmol) were dissolved in dry benzene (20 mL) and then BF<sub>3</sub> · Et<sub>2</sub>O (141 mg, 1 mmol) was added. The resulting solution was refluxed for 12 h and concentrated in vacuo. The product was isolated by column chromatography on SiO<sub>2</sub> with hexane–diethyl ether as an eluent. The yield of compound I was 600 mg (75%), yellow crystals,  $[\alpha]_D^{20}$  +30.3 (*c* 0.6, EtOH).

<sup>1</sup>H NMR ( $\delta$ , ppm): 0.92 (s, 3H, CH<sub>3</sub>), 1.03 (s, 3H, CH<sub>3</sub>), 1.05 (s, 3H, CH<sub>3</sub>), 1.12 (m, 1H, H<sup>6</sup><sub> $\alpha$ </sub>), 1.48 (m, 1H, H<sup>5</sup><sub> $\alpha$ </sub>), 1.58 (d, 3H, CH<sub>3</sub>, *J* = 6.6 Hz), 1.77 (m, 1H,

 $H_{\beta}^{5}$ ), 1.91 (m, 1H,  $H_{\beta}^{6}$ ), 3.05 (d, 1H, H<sup>4</sup>, *J* = 4.7 Hz), 4.64 (q, 1H, H<sup>11</sup>, *J* = 6.6 Hz), 7.27 (d, 1H, Ar, *J* = 7.1 Hz), 7.34 (dd, 2H, Ar, *J* = 7.1 Hz, *J* = 7.3 Hz), 7.43 (d, 2H, Ar, *J* = 7.3 Hz).

<sup>13</sup>C NMR (δ, ppm): 9.12 (C<sup>10</sup>), 17.73 (C<sup>8</sup>), 20.86 (C<sup>9</sup>), 23.39 (C<sup>6</sup>), 24.41 (C<sup>12</sup>), 29.94 (C<sup>5</sup>), 44.18 (C<sup>7</sup>), 49.04 (C<sup>4</sup>), 57.87 (C<sup>1</sup>), 62.47 (C<sup>11</sup>), 126.88, 127.10, 128.51 (C-H<sub>Ar</sub>), 144.27 (Ar), 169.98 (C<sup>3</sup>), 206.40 (C<sup>2</sup>).

IR (KBr, v, cm<sup>-1</sup>): 1751 (v(C=O)), 1672 (v(C=N)).

For C<sub>18</sub>H<sub>23</sub>NO

anal. calcd. (%):	C, 80.3;	Н, 8.55;	N, 5.2.
Found (%):	C, 79.2;	H, 8.76;	N, 4.8.

Synthesis of  $C_{36}H_{46}N_2O_2Cl_2Pd$  (II). A suspension of PdCl<sub>2</sub> (74 mg, 0.4 mmol) and LiCl (35 mg, 0.8 mmol) in methanol (5 mL) was refluxed for 1 h. The resulting dark red solution of Li<sub>2</sub>PdCl<sub>4</sub> was cooled to room temperature and a solution of imine I (112 mg, 0.4 mmol) in methanol (5 mL) was added. The reaction mixture was stirred at room temperature for 1 h and concentrated in vacuo. The product was extracted from the residue with chloroform and precipitated with hexane. The yield of complex II was 171 mg (60%), yellow crystals.

<sup>1</sup>H NMR ( $\delta$ , ppm, *J*, Hz): 0.62 (s, 3H, CH<sub>3</sub>), 0.73 (s, 3H, CH<sub>3</sub>), 1.05 (s, 3H, CH<sub>3</sub>), 1.06 (m, 1H, H<sup>6</sup><sub> $\alpha$ </sub>), 1.6 (m, 3H, H<sup>5</sup><sub> $\alpha$ </sub>), H<sup>5</sup><sub> $\beta$ </sub>, H<sup>6</sup><sub> $\beta$ </sub>), 2.31 (d, 3H, CH<sub>3</sub>, *J* = 7.0 Hz), 2.59 (d, 1H, H<sup>4</sup>, *J* = 3.5 Hz), 6.05 (q, 1H, H<sup>11</sup>, *J* = 7.0 Hz), 7.26 (d, 1H, Ar, *J* = 7.1 Hz), 7.33 (dd, 2H, Ar, *J* = 7.1 Hz, *J* = 7.4 Hz), 7.70 (d, 2H, Ar, *J* = 7.4 Hz).

Table 1. Crystallographic parameters and the data of	collec-
tion and refinement statistics for structure II	

## For C<sub>36</sub>H<sub>46</sub>N<sub>2</sub>O<sub>2</sub>Cl<sub>2</sub>Pd

anal. calcd. (%):	C, 60.3;	Н, 6.41;	N, 3.92.
Found (%):	C, 60.3;	Н, 6.53;	N, 3.84.

The <sup>1</sup>H and <sup>13</sup>C NMR spectra of imine I and complex II were recorded on a Bruker AVANCE-II 300 spectrometer (300.17 and 75.49 MHz, respectively) in CDCl<sub>3</sub> with the signals of chloroform ( $\delta_{\rm H}$  7.27,  $\delta_{\rm C}$  77.00) as the internal standards. The IR spectra of compounds I and II were recorded on an IR Prestige 21 spectrometer (KBr pellets, diffuse reflection mode). Elemental analysis was carried out using gas chromatography on an EA 1110 CHNSO analyzer. The course of the reactions was monitored, and the purity of the reaction products was checked, by TLC on Sorbfil plates.

**X-ray diffraction study** of complex **II** was carried out at 22°C on an Xcalibur S automated diffractometer equipped with the CCD detector according to a standard procedure (Mo $K_{\alpha}$  radiation,  $\lambda = 0.71073$  Å, graphite monochromator,  $\omega$  scan mode, scan step 1°). An absorption correction was applied analytically using a multifaceted crystal model [4]. The structure was solved by direct methods and refined anisotropically (for all non-hydrogen atoms) on  $F^2$  by the fullmatrix least-squares method with the SHELXTL-97 program package [5]. All hydrogen atoms were located from the difference electron-density map and refined isotropically. Crystallographic parameters and the data collection and refinement statistics for structure **II** are given in Table 1.

The atomic coordinates and other parameters of structure **II** have been deposited with the Cambridge Crystallographic Data Centre (no. 875043; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac. uk/data\_request/cif).

#### **RESULTS AND DISCUSSION**

Imine I was obtained in 75% yield by condensation of (*1R*, *4S*)-camphor quinone with (*S*)- $\alpha$ -methylbenzylamine. The condensation may produce two geometric isomers with *Z*- and *E*-configurations of the C=N bond. The NMR spectra of imine I contain one set of signals, which suggests the formation of only one geometric isomer. Using 2D correlation spectroscopy (NOESY), we found that imine I has *E*-configuration: the NOESY experiment revealed a coupling between the benzylic proton and the H(4) proton of the terpene fragment.

Ligand I was obtained for use in the synthesis of cyclopalladated complexes. Benzylamine derivatives are known to readily undergo *ortho*-palladation at the aromatic ring [6]. For this purpose, we carried out a complexation reaction as described by Cope in [7]. However, it turned out that no cyclopalladation occurs

Parameter	Value	
Crystal system	Monoclinic	
Μ	716.05	
Space group	<i>P</i> 2 <sub>1</sub>	
Unit cell parameters		
a, Å	9.8336(8)	
b, Å	14.0082(11)	
c, Å	13.0059(9)	
β, deg	105.336(7)	
<i>V</i> , Å <sup>3</sup>	1727.8(2)	
Ζ	2	
$\rho_{calcd}, g/cm^3$	1.376	
$\mu$ , mm <sup>-1</sup>	0.725	
$\theta$ scan range, deg	28.29-2.59	
Number of measured reflections	11068	
Number of independent reflec- tions ( $R_{int}$ )	6984 (0.0229)	
Number of reflections with $I > 2\sigma(I)$	4784	
Completeness, % (for $\theta$ , deg)	99.9 (26.00)	
S	1.025	
Number of parameters refined	388	
<i>R</i> factor for $I > 2\sigma(I)$	$R_1 = 0.0292, wR_2 = 0.0505$	
<i>R</i> factor for all reflections	$R_1 = 0.0495, wR_2 = 0.0519$	
$\Delta \rho_{\rm max} / \Delta \rho_{\rm min}$ , $e  {\rm \AA}^{-3}$	1.081/-0.411	
Flack parameter	-0.023(18)	

<sup>13</sup>C NMR (δ, ppm): 9.36 (C<sup>10</sup>), 17.60 (C<sup>8</sup>), 20.57 (C<sup>9</sup>), 21.20 (C<sup>12</sup>), 23.21 (C<sup>6</sup>), 29.47 (C<sup>5</sup>), 44.53 (C<sup>7</sup>), 54.25 (C<sup>4</sup>), 57.31 (C<sup>1</sup>), 67.07 (C<sup>11</sup>), 127.46, 128.20, 128.48 (C-H<sub>Ar</sub>), 141.49 (Ar), 181.11 (C<sup>3</sup>), 201.74 (C<sup>2</sup>).

IR (KBr, v, cm<sup>-1</sup>): 1757 (v(C=O)), 1662 (v(C=N)).

under these conditions; in the resulting complex **II**, the imine functions as a monodentate ligand.



The <sup>1</sup>H and <sup>13</sup>C NMR spectra of complex **II** agree with the structure shown above. The spectra retain all the signals of the starting imine, with their small downfield shifts for the nuclei in close vicinity of palladium. The fact that the benzene ring is monosubstituted is evident from the multiplicity and integrated intensity of the signals for its protons. The absence of doubled signals suggests the formation of an individual isomer.

Structure **II** determined from X-ray diffraction data is shown in figure; the bond lengths and bond angles are listed in Table 2.

In structure II, the Pd atom has a square planar environment with *trans* arrangement of the Cl



Structure II in the crystal (the H atoms are omitted).

atoms. The carbon atoms at the N atoms are virtually coplanar (deviations are < 0.017 Å); their plane makes an angle of 82.3° with the plane of the coordination environment of the Pd atom. Structure II does not have symmetry  $C_2$  because the other phenyl substituent changes from the (–)-anticlinal to (+)-anticlinal conformation relative to the Pd atom. The corresponding torsion angles C(18)–

Bond	d, Å	Bond	d, Å
Pd(1)–N(2)	2.025(3)	O(2)-C(5)	1.189(4)
Pd(1)–N(1)	2.039(2)	N(1)-C(8)	1.278(3)
Pd(1)–Cl(2)	2.3017(11)	N(1)–C(11)	1.504(4)
Pd(1)-Cl(4)	2.3106(11)	N(2)–C(12)	1.270(3)
O(1)-C(28)	1.190(4)	N(2)–C(17)	1.489(4)
Angle	ω, deg	Angle	ω, deg
N(2)Pd(1)N(1)	175.44(12)	O(2)C(5)C(8)	127.4(2)
N(2)Pd(1)Cl(2)	91.53(8)	N(1)C(8)C(31)	131.2(3)
N(1)Pd(1)Cl(2)	89.57(7)	N(1)C(8)C(5)	124.0(3)
N(2)Pd(1)Cl(4)	88.00(8)	C(9)C(11)N(1)	113.3(3)
N(1)Pd(1)Cl(4)	90.75(7)	N(1)C(11)C(4)	111.1(3)
Cl(2)Pd(1)Cl(4)	178.08(5)	N(1)C(11)H(11A)	107.4
C(8)N(1)C(11)	117.6(3)	N(2)C(12)C(20)	132.9(3)
C(8)N(1)Pd(1)	120.3(2)	N(2)C(12)C(28)	122.4(3)
C(11)N(1)Pd(1)	122.1(2)	N(2)C(17)C(34)	111.4(3)
C(12)N(2)C(17)	120.8(3)	N(2)C(17)C(18)	112.7(3)
C(12)N(2)Pd(1)	126.7(2)	N(2)C(17)H(17A)	106.1
C(17)N(2)Pd(1)	112.27(19)	O(1)C(28)C(3)	128.4(4)
O(2)C(5)C(24)	129.2(3)	O(1)C(28)C(12)	127.4(4)

**Table 2.** Selected bond lengths d and bond angles  $\omega$  in structure II

C(17)-N(2)-Pd(1) and C(9)-C(11)-N(1)-Pd(1)are 120.6(3)° and 111.5(3)°, respectively.

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