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cis-Di-μ-Chlorobis{(1*S*,4*S*)-2-[Benzylimino]-7,7-Dimethylbicyclo[2.2.1]heptylmethyl-C,N}dipalladium(II) and *trans*-Dichlorobis{(1*S*,4*S*)-2-[Benzylimino]-1,7,7-Trimethylbicyclo[2.2.1]heptane-N}palladium(II): Syntheses and Structural Studies

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Abstract—Enantiomerically pure palladium complexes of different compositions, binuclear palladacycle containing the (sp^3)C–Pd bond (**I**) and mononuclear coordination palladium compound (**II**), are synthesized and studied by X-ray diffraction analysis. In complex **I**, the cyclopalladated ligands are in the *cis* position (CIF file CCDC no. 1049805 (**I**)). In compound **II**, the ligands coordinated through the monodentate mode occupy the *trans* position (CIF file CCDC no. 1049806 (**II**)).

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INTRODUCTION

Chiral cyclopalladated complexes find wide use in modern asymmetrical synthesis aimed at preparing enantiomerically pure compounds [1, 2]. They are very successfully applied as initial matrices [2, 3] and catalysts [4–7]. Chiral cyclopalladated complexes found use as efficient splitting agents for the separation of racemic mixtures to individual enantiomers [8–10] and as shifting agents in NMR studies [11–13].

EXPERIMENTAL

(1*S*,4*S*)-Camphor ($[\alpha]_D^{20}$ −40.9 (c = 1.0 mol/L; $CHCl_3$), benzylamine (Acros Organics), palladium acetate without additional purification, and lithium chloride (reagent grade) were used as the starting compounds. Methanol, chloroform, hexane, and benzene (analytical grade) served as solvents. Silica gel (70–230 μ, Alfa Aesar) was used.

Camphor benzylimine ($C_{17}H_{23}N$) was synthesized according to a described procedure [14] as a colorless liquid in a yield of 63% ($[\alpha]_D^{21}$ = +23.8 (c = 0.8 mol/L; $CHCl_3$).

Syntheses of $C_{34}H_{44}Cl_2N_2Pd_2$ (I) and $C_{34}H_{46}Cl_2N_2Pd$ (II). A suspension of camphor benzylimine (0.17 g, 0.7 mmol) and palladium acetate (0.16 g, 0.7 mmol) in benzene (25 mL) was heated at 60°C for 3 h. The solvent was removed from the reaction mixture in vacuo, and a methanol solution of lithium chloride (0.15 g, 3.5 mmol) was added to the residue. The reaction mixture was stirred at room temperature for 2 h. The formation of two products in the reaction was monitored by TLC. The solvent was removed in vacuo from the dark red reaction mixture, the residue was dissolved in benzene, and the products were isolated by chromatography (SiO_2, benzene–acetone (50 : 1) as an eluent). Complexes **I** and **II** were obtained after recrystallization from a chloroform–hexane (1 : 10) mixture in yields of 0.16 g (61%) and 0.07 g (15%), respectively, as yellow crystals.

Compound **I** was obtained as yellow crystals, $[\alpha]_D^{20}$ +116.1 (c = 0.1 mol/L; acetone). The spectral data of compound **I** correspond to literature data [14].

Compound **II** was obtained as yellow crystals, $[\alpha]_D^{20}$ +73.4 (c = 0.2 mol/L; $CHCl_3$). The spectral data of complex **II** coincide with the data for the binuclear coordination palladium compound based on camphor benzylimine [14].

For $C_{34}H_{46}N_2Cl_2Pd$

anal. calcd., %:	C, 61.8;	H, 6.97;	N, 4.24.
Found, %:	C, 61.8;	H, 6.95;	N, 4.16.

The X-ray diffraction analyses of compounds **I** and **II** were carried out on an Xcalibur S automated four-circle diffractometer using a standard procedure

Table 1. Crystallographic parameters and refinement details for structures **I** and **II**

Parameter	Value	
	I	**II**
Crystal system	Orthorhombic	Monoclinic
FW	764.41	660.03
Space group	$P2_12_12_1$	$P2_1$
Unit cell parameters:		
a, Å	8.0608(10)	11.5085(18)
b, Å	12.9148(14)	7.7191(10)
c, Å	30.918(3)	18.571
β, deg		93.725(19)
V, Å^3	3218.6(6)	1646.3(3)
Z	4	2
ρ_{calcd}, g/cm^3	1.577	1.331
μ, mm^{-1}	1.309	0.750
Scan range θ, deg	2.61–28.31	2.73–26.39
Measured reflections	22908	10941
Independent reflections (R_{int})	7978 (0.0526)	3626 (0.0443)
Number of reflections with $I > 2\sigma(I)$	4349	1956
S	1.004	1.002
R_1, wR_2 ($I > 2\sigma(I)$)	0.0364, 0.0567	0.0350, 0.0432
R_1, wR_2 (for all reflections)	0.0747, 0.0583	0.0666, 0.0445
$\Delta\rho_{max}/\Delta\rho_{min}$, e Å^{-3}	0.908/–0.511	0.740/–0.501

(MoK_α radiation, graphite monochromator, ω scan mode with an increment of 1°, $T = 295(2)$ K). An empirical absorption correction was applied. The structures were solved by a direct method and refined by the full-matrix least-squares method for F^2 (SHELX-97) [15]. Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed in the calculated positions and refined in the riding model with dependent isotropic thermal parameters. The crystallographic parameters and refinement details for structures **I** and **II** are presented in Table 1.

The coordinates of atoms and other parameters for structures **I** and **II** were deposited with the Cambridge Crystallographic Data Centre (CIF files CCDC nos. 1049805 (**I**) and 1049806 (**II**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

RESULTS AND DISCUSSION

Chiral cyclopalladated complexes with different types of chirality were obtained to date [1, 2]. Compounds of diverse classes were studied as ligands for their synthesis. However, synthetic accessibility of enantiometrically pure ligands remains to be an important problem. The objects of our studies are benzylimine derivatives of bicyclic monoterpenoid (–)-camphor. Two directions of cyclometallation are possible for these ligands. It is known that the benzylimine derivatives easily undergo *ortho*-palladation at the aromatic ring. The bornane derivatives are of special interest, because cyclopallada-

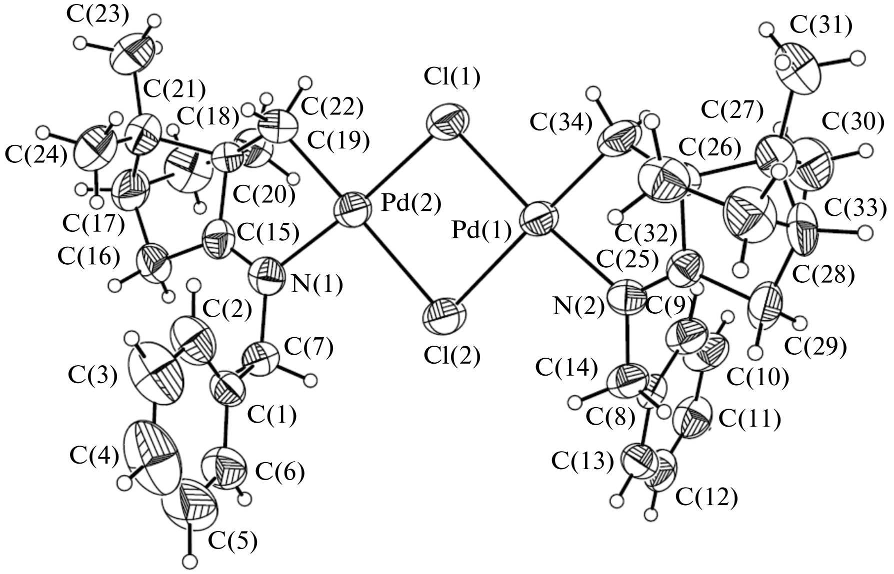
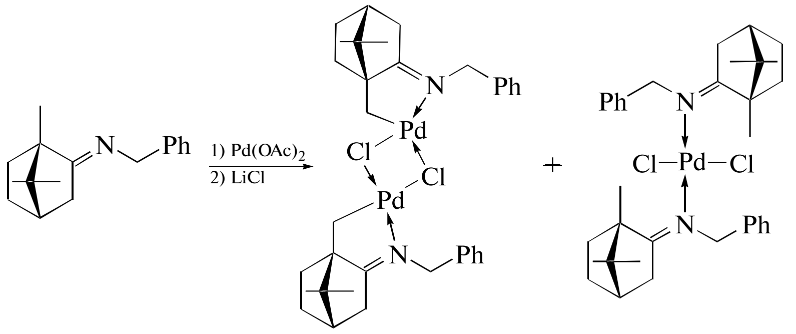


Fig. 1. Compound **I** in 50% probability ellipsoids according to the X-ray diffraction analysis data.

tion at the methyl group of the terpene fragment is possible for them. It should be mentioned that only a small group of enantiomerically pure palladacycles containing the (sp^3)C–Pd bond is known among numerous chiral cyclopalladated complexes [16–18].

We studied the reactions of camphor benzylimine with various palladating agents giving palladacycles. Camphor benzylimine is cyclopalladated on heating an equimolar mixture of the latter with palladium acetate in benzene at 60°C for 3 h



(I) **(II)** **(III)**

The acetate derivative formed was not isolated. After benzene was removed, the reaction mixture was treated with a solution of lithium chloride in methanol and stirred at room temperature for 2 h to replace the acetate bridge by the chloride one. After methanol was removed, the reaction products were extracted from the residue with benzene and separated by column chromatography. As a result, the palladium complexes of different types were obtained: C-metallated palladacycle **I** and palladium complex **II** with imine coordinated through the monodentate mode (61 and 15% yields, respectively).

The structures of the obtained palladium complexes were determined by X-ray diffraction analyses. The *cis*-N,N geometry of the arrangement of two cyclopalladated ligands in binuclear complex **I** is unexpected. An analysis of literature data indicates that the *trans* isomers are formed as a rule [18–20].

According to the X-ray diffraction analysis data, complex **I** is an organometallic binuclear chiral structure with the bridging chlorine atoms (Fig. 1). The bridged moiety is symmetrical relatively to the 2-fold axis passing through the Cl(1)Cl(2) atoms (Table 2). Due to the symmetrical arrangement of heavy atoms, the anomalous scattering effect turns out to be low and

Table 2. Selected bond lengths (Å) and angles (deg) in molecules of compounds **I** and **II**

Bond	*d*, Å	Bond	*d*, Å
		I	
Pd(1)–C(34)	1.994(4)	Pd(2)–C(22)	2.014(4)
Pd(1)–N(2)	2.033(3)	Pd(2)–N(1)	2.038(4)
Pd(1)–Cl(1)	2.3286(12)	Pd(2)–Cl(1)	2.3298(12)
Pd(1)–Cl(2)	2.4727(12)	Pd(2)–Cl(2)	2.4698(11)
		II	
Pd(1)–Cl(2)	2.302(3)	Pd(1)–N(2)	2.032(7)
Pd(1)–N(1)	2.011(8)	Pd(1)–Cl(1)	2.306(3)
Angle	**ω, deg**	**Angle**	**ω, deg**
		I	
Pd(1)Cl(1)Pd(2)	94.25(4)	Pd(2)Cl(2)Pd(1)	87.38(4)
		II	
N(1)Pd(1)Cl(2)	91.86(19)	N(1)Pd(1)Cl(1)	87.8(2)
N(2)Pd(1)Cl(2)	88.7(2)	N(2)Pd(1)Cl(1)	91.66(17)

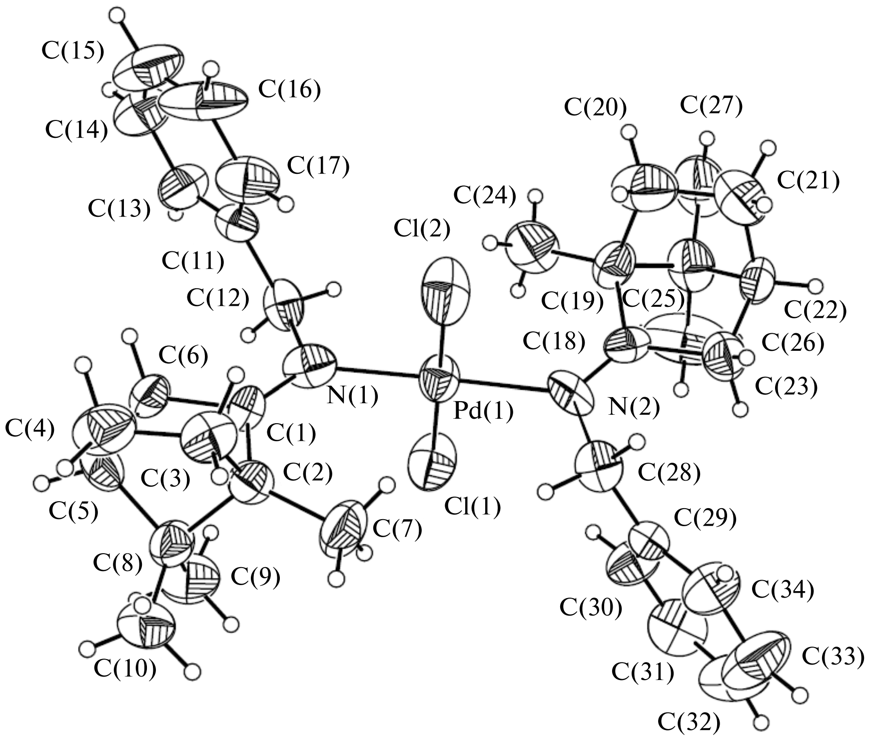


Fig. 2. Compound **II** in 50% probability ellipsoids according to the X-ray diffraction analysis data.

does not allow one to establish the absolute configuration of this compound.

Complex **II** is a classical structure with a distorted square configuration of the ligands and the *trans* arrangement of the chlorine atoms at the Pd atom (Fig. 2). The structure is centrosymmetrical except for the monoterpenoid fragment, which aligns the anomalous scattering effect as for the previous structure.

REFERENCES

1. Dupont, J., Consorti, C.S., and Spencer, J., *Chem. Rev.*, 2005, no. 105, p. 2527.
2. Dunina, V.V. and Zykov, P., *Russ. Chem. Rev.*, 2011, no. 80, p. 51.
3. Troitskaya, L.L., Starikova, Z.A., Demeshchik, T.V., and Sokolov, V.I., *Russ. Chem. Bull.*, 1999, vol. 48, p. 1738.
4. Dunina, V.V., Razmyslova, E.D., Gorunova, O.N., et al., *Tetrahedron: Asymmetry*, 2003, vol. 14, p. 2331.
5. Chew, R.J., Huang, Y., Li, Y., et al, *Adv. Synth. Catal.*, 2013, vol. 355, p. 1403.
6. Lu, J., Ye, J., and Duan, W.-L., *Org. Lett.*, 2013, vol. 15, p. 5016.
7. Hyodo, K., Nakamura, S., and Shibata, N., *Angew. Chem., Int. Ed. Engl.,* 2012, vol. 51, p. 10337.
8. Weber, V.M., Jautze, S., Frey, W., and Peters, R., *Chem.-Eur. J.*, 2012, vol. 18, p. 14792.
9. Chooi, S.Y.M., Leung, P.H., Lim, C.C., et al., *Tetrahedron: Asymmetry*, 1992, vol. 3, p. 529.
10. Bohm, A. and Seebach, D., *Helv. Chim. Acta*, 2000, vol. 83, p. 3262.
11. Dunina, V.V., Gorunova, O.N., Livantsov, M.V., and Grishin, Y.K., *Tetrahedron: Asymmetry*, 2000, vol. 11, p. 2907.
12. Figge, A., Altenbach, H.J., Brauer, D.J., and Tielmann, P., *Tetrahedron: Asymmetry*, 2002, vol. 13, p. 137.
13. Duran, E., Gordo, E., Granell, J., et al., *Tetrahedron: Asymmetry*, 2001, vol. 12, p. 1987.
14. Gur'eva, Ya. Frolova, L.L., et al., *Russ. J. Gen. Chem.*, 2012, vol. 82, p. 1117.
15. Sheldrick, G.M., *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, vol. 64, p. 112.
16. Malik, K.M.A. and Newman, P.D., *Dalton Trans.*, 2003, p. 3516.
17. Watson, A.A., House, D.A., and Steel, P.J., *J. Organomet. Chem.*, 1986, vol. 311, p. 387.
18. Dickmu, G.C., Stahl, L., Smoliakova, I.P., *J. Organomet. Chem.*, 2014, vol. 756, p. 27.
19. Gorunova, O.N., Keuseman, K.J., Goebel, B.M., et al., *J. Organomet. Chem.*, 2004, vol. 689, p. 2382.
20. Schildbach, D., Arroyo, M., and Lehmen, K., *Organometallics*, 2004, vol. 23, p. 3228.

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