Synthesis and Structural Studies of (1R,2R,5R)-Chloro{o-[β-(2-hydroxy-2,6,6-trimethylbicyclo[3.1.1]hept-3-ylideno)ethyliminomethyl]phenoxy-O,N,N}palladium(II)


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Abstract—The reaction of (1R,2R,5R)-3-[2-[(2-hydroxybenzylidene)amino]ethyl]imino]-2,6,6-trimethylbicyclo[3.1.1]heptan-2-ol with lithium tetrachloropalladate was studied. A chiral palladium(II) complex was thus obtained and its structure was confirmed by NMR spectroscopy and X-ray diffraction analysis.

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The widely known catalytic activity of palladium complexes and attractive prospects of the use of their chiral forms in asymmetric catalysis stimulate the works on the synthesis of new complex compounds.

Previously we performed and described the synthesis of derivatives of ethylenediamine and enantiomerically pure (1S,2S,5S)-hydroxypran-3-one [1]. Using the described procedure, (1R,2R,5R)-2-hydroxypran-3-one was converted to unsymmetrical diimine, (1R,2R,5R)-3-[2-[(2-hydroxybenzylidene)amino]ethyl]imino]-2,6,6-trimethylbicyclo[3.1.1]heptan-2-ol (I), yield 82%. [α]D^20 +76.2 (c 1.1, EtOH). In this work we used diimine I as a ligand to prepare chiral palladium complexes.

EXPERIMENTAL

As the starting compounds, high-purity grade palladium chloride with 98% purity and high-purity lithium chloride were used as purified. Reagent grade methanol, chloroform, and high-purity grade hexane were used as solvents.

Synthesis of C_{19}H_{25}N_{2}O_{2}PdCl (II). A suspension of PdCl₂ (35 mg, 0.2 mmol) and LiCl (18 mg, 0.4 mmol) in methanol (5 mL) was refluxed for 1 h. This gave a dark red solution of Li₂PdCl₄, which was cooled to room temperature, and a solution of diimine I (63 mg, 0.2 mmol) in methanol (5 mL) was added. The reaction mixture was stirred at room temperature for 1 h. The solvent was removed in vacuum, the product was extracted from the residue with chloroform and precipitated with hexane to give compound II as yellow-colored prismatic crystals. Yield 36 mg (40%).

1H NMR (δ, ppm, J, Hz): 0.81 (s, 3H, CH₃), 1.33 (s, 3H, CH₃), 1.70 (d, 1H, H₆β, J = 11.0), 2.04 (m, 1H, H₉, J = 5.9), 2.10 (dd, 1H, H₇, J = 5.9, 6.0), 2.30 (m, 1H, H₆δ, J = 6.0, 11.0), 2.53 (s, 3H, CH₃), 2.87 (m, 2H, CH₂), 3.51, 3.68, 4.19, 4.52 (all m, 4H, H¹¹, H¹²), 5.98 (s, OH), 6.55 (dd, 1H, Ar, J = 7.0, 7.1), 7.07 (dd, 1H, Ar, J = 7.9), 7.10 (d, 1H, Ar, J = 7.1), 7.29 (dd, 1H, Ar, J = 7.0, 7.9), 7.46 (s, 1H, H¹³), 13C (δ, ppm): 22.92 (C⁶), 26.57 (C⁷), 27.02 (C⁸), 28.76 (C⁹), 37.51 (C₁₀), 37.96 (C₁₁), 38.11 (C₁₂), 52.82 (C₁₃), 58.68 (C₁₄), 59.31 (C₁₅), 75.94 (C₂), 115.8, 121.1, 133.9, 135.7 (C–H, Ar), 119.3 (Ar), 163.6 (Ar), 190.2 (C₃). IR (KBr, ν, cm⁻¹): 3328 v(OH), 1636 ν(C=O).
EA 1110 elemental analyzer (CHNSO). The reactions were monitored and the product purity was verified by TLC on Sorbil plates.

**X-Ray diffraction analysis** of compound II was carried out at 20°C on a Bruker Smart APEX2 automated diffractometer (MoKα-radiation, graphite monochromator, θ scan mode). The absorption corrections were applied by the SADABS program [2]. The structure was solved by the direct method by the SIR program package [3] and refined first in the isotropic and then anisotropic approximation using the SHELXL-97 program package [4]. Most of hydrogen atoms were placed in the calculated positions and refined by the riding model. The hydrogen atoms at oxygen atoms were revealed from difference Fourier series and refined isotropically. All calculations were carried out by the WinGX [5] and APEX [6] programs. The Figures and hydrogen bond analysis were performed by the PLATON program [7]. The crystal data and structure refinement details for II are summarized in Table 1. The atom coordinates and other parameters of structure II were deposited with the Cambridge Crystallographic Data Centre (no. 793745; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

**RESULTS AND DISCUSSION**

Diimine I can be assigned to salen type polydentate ligands. We found that the reaction of I with lithium tetrachloropalladate affords complex II in 40% yield. Note that the outcome of the reaction does not depend on the presence of a base, only the phenolic hydroxy group taking part in the complexation, while less acidic alcohol OH group is not deprotonated even in the presence of sodium acetate or methoxide.

The \( ^1\text{H} \) and \( ^{13}\text{C} \) NMR spectra of complex II correspond to the presented structure. The proton signals of the ethylenediamine bridge are differentiated, and each proton is manifested as a separate multiplet. This