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Molecular structure of π-allyl palladium(II) complex, [Pd(η^3-PhCHCHCHPh)-((*S,S*)-chiraphos)]PF_6: a novel envelope conformation of chiral C_2-symmetric diphosphine

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Abstract

The X-ray structure analysis of [Pd(η^3-1,3-diphenylallyl)((*S,S*)-chiraphos)]PF_6 shows that the conformation of the five-membered chelate ring of chiraphos is an envelope form, and the whole complex has quasi-C_s-symmetry in the crystal, while the circular dichroism spectrum of the complex suggests that the chelate ring takes the gauche conformation in solution.

Keywords: Palladium; Allyl complex; Chiral diphosphine; Chiraphos; Crystal structure; Asymmetric allylic alkylation

1. Introduction

Catalytic asymmetric synthesis utilizing transition metal complex is a focus of a number of studies for its significance in modern organic syntheses. A variety of chiral C_2-symmetric bidentate ligands, such as chiral diphosphines, have been developed for asymmetric catalysts and shown high enantioselectivity in many reactions (for recent reviews, see Ref. [1]). These ligands coordinate to a metal ion in a C_2-symmetrical fashion, which is considered to be a key feature of these ligands. A chiral 'edge-face' array of four phenyl groups attaching to two phosphorus atoms provides repulsive interactions between the chiral ligand and the substrate in the intermediate, and has a significant role to attain high enantioselectivity [2]. Palladium-catalyzed asymmetric allylic alkylation using allyl acetate derivatives as a substrate is one of the useful reaction for the asymmetric carbon–carbon bond formation and has been studied extensively in this decade [1,3]. Especially, 1,3-diphenylallyl acetate, which forms η^3-1,3-diphenylallyl Pd(II) intermediate by the oxidative addition to Pd(0)-diphosphine catalyst, is considered to be the 'standard' substrate to testify the ability of chiral ligands [4], and high enantioselectivity has been achieved by using a variety of chiral ligands. It is important to get insight into the structural knowledge of the intermediate of the asym-

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2. Results and discussion

The complex [Pd(η^3-1,3-diphenylallyl)((*S*,*S*)-chiraphos)]PF$_6$ (**1**) was readily prepared [2] and recrystallization from dichloromethane–ethyl acetate gave good crystals suitable for X-ray analysis. [3] Fig. 1 shows the structure of **1**. Two phosphine atoms and π-allyl moiety coordinate to a Pd(II) ion in square planar configuration, and the two phenyl groups of π-allyl moiety are in syn configuration. Both of the two phenyl groups attaching to the π-allyl moiety are almost coplanar to the π-allyl plane. On the other hand, conformation of the five-membered chelate ring of chiraphos is a novel envelope form as shown in Fig. 1(b), and the whole complex ion has quasi-C_s-symmetry. This structure is in contrast with those of other complexes containing chiraphos ligand, in which the ligand has quasi-C_2-symmetry in the solid state [7]. The two axial phenyl groups on the same side of the coordination plane turn their edges to π-allyl moiety, while the two equatorial phenyl groups on the other side turn their faces, resulting in the C_s-symmetric array of the four phenyl groups attaching to the phosphorus atoms.

Usually, (*S*,*S*)-chiraphos chelate ring is in δ gauche conformation [6]; however, the chiraphos chelate ring of **1** is an envelope form: the C4–C5–P2–Pd1 torsional angle is −4.4(5)°. Consequently, Pd1, P2, C4, and C5 are in a plane, and P1 is out of the plane. [4] The P–Pd–P angle of 83.43(5)° is slightly smaller than that of 85.8(2)° in [Pd(η^3-C(Xyl)$_2$CHCHPh)((*S*,*S*)-chiraphos)]$^+$ complex [9]. The two Pd–P distances are 2.280(2) and 2.299(2) Å, and the distances between the Pd atom and the two terminal allylic carbon atoms are 2.21(1) and 2.24(1) Å.

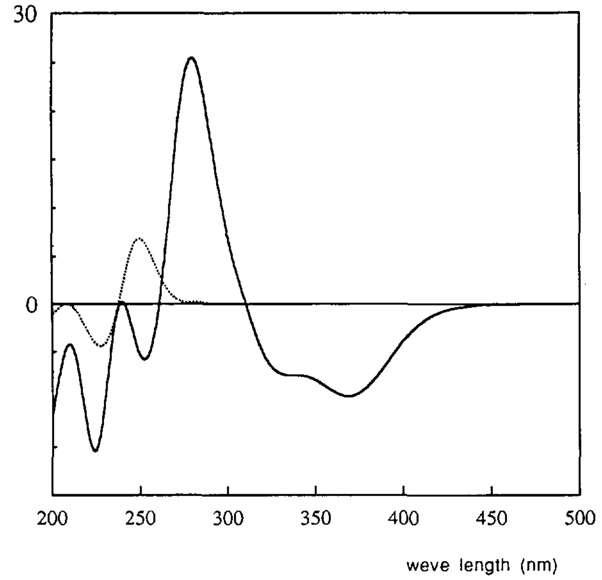

Fig. 2. CD spectra of the complex **1** (solid line) and (*S*,*S*)-chiraphos (dotted line) in THF.

Thus, it has been revealed that the chiraphos complex **1** has quasi-C_s-symmetry in the crystal. [5] Recently, Seebach and his coworkers reported the extensive search for the structure of complexes containing C_2-symmetric bidentate bis(diphenylphosphino)-type ligands found in the Cambridge Crystallographic Data Base, and they classified them into two classes of structure: one has approximate C_2-symmetry, and the other one has only C_1-symmetry [10]. In the latter case, lower selectivity is expected. In the asymmetric allylic alkylation using chiraphos as a chiral auxiliary, however, high selectivity was achieved in the reaction between 1,3-diphenylallyl acetate and sodium dimethyl malonate catalyzed by Pd complex up to 90% *ee*, in which **1** is assumed as the intermediate [11]. Therefore, if the structure of this complex in solution is the same as that in the crystal, it is difficult to explain such a high enantioselectivity.

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[2] Complex **1** was prepared as follows. The dimer complex [8] [Pd$_2$(η^3-1,3-diphenylallyl)$_2$Cl$_2$] (0.134 g, 0.2 mmol) and diphosphine (0.171 g, 0.4 mmol) were stirred for 3 h in dichloromethane (5 cm^3) under nitrogen in the dark. To a resulting solution was added ammonium hexafluorophosphate (0.32 g, 2.0 mmol) in methanol (1.5 cm^3). The mixture was stirred at room temperature overnight. After addition of ether the product was filtered and dried in vacuo. The pale yellow solid was obtained, which was recrystallized from dichloromethane–ethyl acetate. Yield: 296 mg (85%); m/z 725 (M $-$PF$_6$)$^+$. Found: C, 59.12; H, 4.68%. Calcd for C$_{43}$H$_{41}$F$_6$P$_3$Pd: C, 59.29; H, 4.74%. Selected ^{1}H NMR (CDCl$_3$, 270 MHz): 4.91 (1H, m, C*H*Ph), 5.15 (1H, m, C*H*Ph), 6.49 (1H, t, ^3J(H,H) = 13.0 Hz, CHC*H*CH); selected ^{13}C NMR (acetone-d_6, 67.5 MHz): 89.2 (dd, ^3J(C,P) = 23.8, 9.1 Hz, *C*HPh), 92.2 (dd, ^3J(C,P) = 22.0, 8.5 Hz, *C*HPh), and 114.5 (t, ^4J(C,P) = 7.95 Hz, CH*C*HCH); ^{31}P NMR (CDCl$_3$, 162 MHz) 49.8 (d, ^2J(P,P) = 68 Hz) and 50.8 (d, 68 Hz). CD (THF) λ_{max}/nm ($\Delta\varepsilon$/dm^3 mol^{-1} cm^{-1}) 368.5 (−9.7), 335sh (−7.5), 280 (25.5), 252.5 (−5.8).

[3] Crystal data for **1**: monoclinic, $P2_1$, with $a = 10.005(1)$ Å, $b = 22.130(1)$ Å, $c = 10.1023(9)$ Å, $\beta = 117.609(7)°$, $V = 1982.0(3)$ Å^3, $D_c = 1.460$ g cm^{-3}, $D_o = 1.459$ g cm^{-3}, $F(000) = 888$, $Z = 2$, μ(Cu Kα) = 54.18 cm^{-1}. Data collection was done on a Rigaku AFC7R diffractometer at room temperature. 2974 reflections with $F > 3\sigma(F)$ were used in the structure refinement. The structure was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. $R = 0.026$ and $Rw = 0.034$ ($w = 1/\sigma^2(F_o^2)$).

Tables of atom coordinates and thermal parameters, bond lengths and angles, and least-squares planes have been deposited at the Cambridge Crystallographie Data Centre.

[4] Distances (Å) from the least-squares plane through Pd1, P2, C4, and C5: Pd1, 0.001(4); P2, 0.007(3); C4, 0.034(9); C5, −0.044(8); P1, −0.898.

[5] X-ray analysis has been repeated three times using three independent crystals, and given similar results.

To elucidate the structure of the complex in solution, circular dichroism (CD) spectra of the complex **1** and (*S,S*)-chiraphos were measured (Fig. 2). The complex **1** shows a negative Cotton effect at 368.5 nm and a positive one at 280 nm, [6] where the ligand itself shows no Cotton effect. [7] The CD pattern of the complex is similar to those of [Pd(η^3-allyl)((*S,S*)-chiraphos)]PF_6 [8] and [Rh$(MeOH)_2$((*S,S*)-chiraphos)] [12], in which chiraphos is considered to have δ gauche conformation. Further, molecular mechanics calculation has been applied to the conformational isomers of **1** and shown that the C_2-symmetric isomer is 1.7 kcal mol^{-1} more stable than the symmetric one. [9] Consequently, these results suggest that the chiraphos chelate ring of the complex **1** has C_2-symmetry in solution, being able to give high enantioselectivity in catalytic asymmetric allylic alkylation, and that care must be taken in interpreting crystal-structure data.

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[6] See footnote 2.

[7] CD data. (*S,S*)-chiraphos in THF: λ_{max}/nm ($\Delta\varepsilon$/dm^3 mol^{-1} cm^{-1}) 250 (6.9), 227.5 (−4,4); [Pd(η^3-allyl)((*S,S*)-chiraphos)]PF_6 in THF: 302.5 (−6.2), 270 (24.4), 250 (−16.1).

[8] See footnote 7.

[9] The MM2 calculations have been done by the CAChe system using the force field developed by Åkermark and coworkers [13] with slight modifications. We assume that the energy difference between the conformational isomers may be underestimated, because the NMR spectrum of **1** shows a single species even at low temperature.

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