Molecular Structure of 1,3-Disubstituted π-Allyl Palladium(II) Complexes with a Chiral Diphosphine: The Intermediate of Palladium-catalyzed Asymmetric Allylic Alkylation

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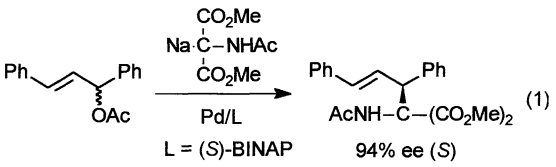
Structural studies by X-ray analysis and NMR spectroscopy of the π-allyl complex, [Pd(η³-1,3-diphenylallyl)((*S*)-BINAP)]-PF_6·AcOEt, have been carried out, and revealed the stereochemical feature for the intermediate of palladium-catalyzed asymmetric allylic alkylation. The dissimilarity of the two phenyl groups attached to the π-allyl moiety is assumed to be one of the origin of the selectivity. In solution two configurational isomers, (syn, syn) and (syn, anti), exist.

Asymmetric allylic alkylation catalyzed by π-allylpalladium complex is a useful reaction as the asymmetric carbon-carbon bond formation, and high enantioselectivity has been achieved by utilizing chiral bidentate ligand containing phosphorous and/or nitrogen atoms as chiral auxiliaries.[1,2] The structure of the π–allylpalladium(II) complexes with a chiral ligand, which is the intermediate of the catalytic reaction, has drawn much attention and been studied intensively by both X-ray analysis[3,4] and NMR spectroscopy.[3-5] We have reported the successful allylic alkylation reaction with 1,3-diphenylallyl acetate and acetamidomalonate (formula (1)),[2b,2c] however, the structure of 1,3-diphenylallylpalladium(II) complexes with a chiral diphosphine ligand has rarely been reported, so far.[6,7] Since 1,3-diphenylallyl acetate is most widely employed in asymmetric allylic alkylation reaction,[2] it is of much importance to get a better knowledge of the structure of the intermediate for the elucidation of the asymmetric allylic alkylation. Here we report the structural studies of the (η³-1,3-diphenylallyl)palladium(II) complexes with (*S*)-BINAP, [Pd(η³-1,3-diphenylallyl)((*S*)-BINAP)]PF_6·AcOEt, by NMR spectroscopy and X-ray analysis, which is the key intermediate of the successful asymmetric allylic alkylation.[2b,2c]



The π-allylpalladium(II) complex was prepared from the corresponding π-allylpalladium chloride dimer, $[(\eta^3\text{-PhCHCHCHPh})PdCl]_2$, and (*S*)-BINAP.[8] The $^{31}P\{^1H\}$ NMR spectrum of the η³-1,3-diphenylallyl complex reveals that two species are present in solution, which is in contrast with the fact that a single isomer was observed for the corresponding complex with (*S,S*)-chiraphos.[9] Inspecting the ^3J(HH) values of the π-allyl protons, the configurations of the two phenyl groups attached to the π-allyl moiety of the major isomer are both assigned to be syn. On the other hand, one phenyl group of the minor one is assigned to be anti.[8] These two isomer are in equilibrium, and the ratio is dependent on the solvent used: 93/7(MeCN), 87/13(THF), 86/14 ($CDCl_3$), and 84/16(CD_2Cl_2), respectively, at 25 °C. Further, the isomer ratio varies with temperature: 92/8(40 °C), 93/7(25 °C), 95/5(0 °C), and 96/4(-20 °C), respectively, in MeCN. The highest enantioselectivity was obtained at -20 °C in MeCN.[10] The differences of the chemical shifts between two phosphorous atoms and allylic terminal carbon atoms of the BINAP complex are larger than those of the chiraphos complex: 3.4 and 1.0 ppm (^{31}P); 17.2 and 3.0 ppm (^{13}C), respectively.[9] It suggests that BINAP affords an effective electronic differentiation of the two allylic termini.

From these results, it is likely that the (syn, syn) isomer is the key intermediate in the asymmetric allylic alkylation, although it is not certain that the configuration of the complex in the crystal is the same as that of the major isomer in solution. To get further insight into the reason why high selectivity is realized in this catalytic system, the X-ray analysis of the π-allyl complex, [Pd(η³-1,3-diphenylallyl)-((*S*)-BINAP)]PF_6·AcOEt, has been carried out.[11] As shown in Figure 1, the configurations of the two phenyl groups attached to the π-allyl moiety are both syn to the central

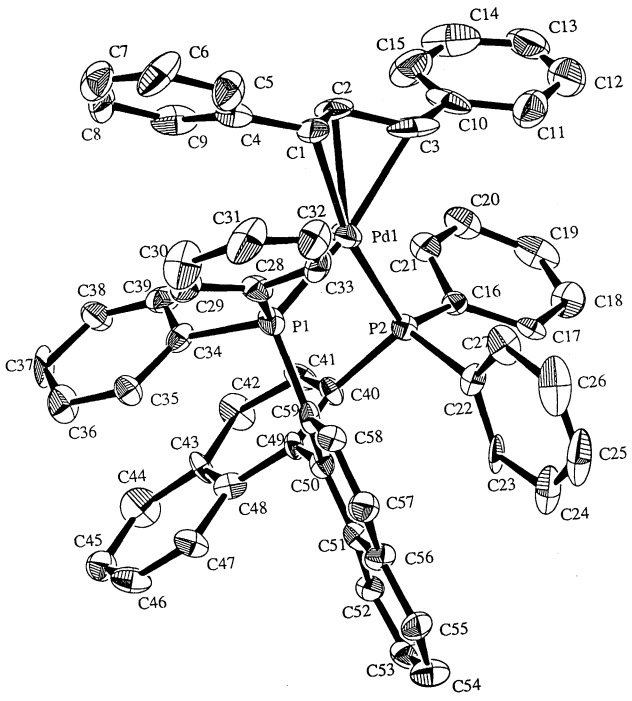


Figure 1. Perspective drawing of [Pd(η³-1,3-diphenylallyl)-((*S*)-BINAP)]⁺. Selected interatomic distances (Å): Pd1-P1, 2.324(5); Pd1-P2, 2.309(4); Pd1-C1, 2.29(2); Pd1-C2, 2.23(2); Pd1-C3, 2.28(2); P1-C1, 3.44(2); P2-C3, 3.63(2). Selected bond angles (deg): P1-Pd1-P2, 93.1(2); C1-Pd1-C3, 64.8(7); P1-Pd1-C1, 96.6(5); P2-Pd1-C3, 104.7(5).

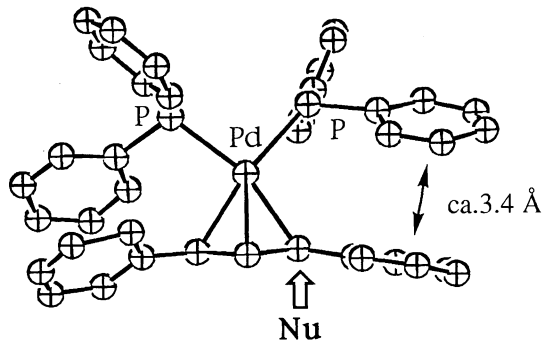


Figure 2. Top view of [Pd(η^3-1,3-diphenylallyl)-((*S*)-BINAP)]$^+$ ion. Binaphthyl group is omitted for clarity.

π-allyl proton. The chiral diphosphine ligand, (*S*)-BINAP, has quasi-C_2 symmetry. The phenyl groups on phosphorous atoms in equatorial position are closer to the π-allyl moiety than those in axial position, and the equatorial phenyl group on P2 atom and the allylic phenyl group on C3 atom of the π-allyl moiety stack together. This stacking keeps the allylic phenyl group on C3 atom co-planar to the π-allyl plane. On the other hand, the allylic phenyl group on C1 atom is twisted so that C1 atom is rather protected from the nucleophilic attack than C3 atom, as shown in Figure 2.[12] This intramolecular interaction causes the distortion of the square-planar coordination plane. P2 atom is more distant from the π-allyl moiety than P1 atom, and P-Pd-C bond angles are significantly different: 97° and 105°. The dissimilarity of the two allylic phenyl groups on the π-allyl moiety is assumed to be the origin of (*S*)-selectivity on asymmetric allylic alkylation: C3 atom is preferentially attacked by a nucleophile (Figure 2).

It is noteworthy that we found no difference in the bond lengths of two Pd-C bonds to allylic termini, although several X-ray studies on (η^3-1,3-diphenylallyl)palladium(II) complexes with a chiral bidentate ligand were reported that there is a significant difference in them.[7]

References and Notes

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7 X-ray studies of the (η^3-1,3-diphenylallyl)Pd(II) complexes with a P-N or N-N ligand: a) Ref. 4b. b) J. Sprinz, M. Kiefer, G. Helmchen, M. Reggelin, G. Huttner, O. Walter, and L. Zsolnai, *Tetrahedron Lett.*, **35**, 1523 (1994). c) P. von Matt, G. C. Lloyd-Jones, A. B. E. Minidis, A. Pfaltz, L. Macko, M. Neuburger, M. Zehnder, H. Rüegger, and P. S. Pregosin, *Helv. Chim. Acta* **78**, 265 (1995).

8 [(η^3-1,3-diphenylallyl)Pd((*S*)-BINAP)]PF_6. Found: C, 66.08; H, 4.18%. Calcd for $C_{59}H_{45}F_6P_3Pd$: C, 66.39; H, 4.25%. $(M\text{-}PF_6)^+$ 921. δ_H($CDCl_3$, 270MHz) 4.5(1H, t, $^3J_{HH} = {}^3J_{HP} = 11.2$ Hz, C*H*-Ph, major), 5.2(1H, t, $^3J_{HH} = {}^3J_{HP} = 13.4$ Hz, C*H*-Ph, minor), 5.5(1H, t, $^3J_{HH} = {}^3J_{HP} = 8.6$ Hz, C*H*-Ph, minor), 6.5*(2H, C*H*-Ph, and CHC*H*CH major), 6.7*(1H, CHC*H*CH, minor), 6.2-8.0(42 H, aromatic protons); Selected δ_C($CDCl_3$, 67.5 MHz) 85.2(dd, $^2J_{CP}$, 28.7, 6.7 Hz, *C*H-Ph, major), 102.4(dd, 21.3, 5.5 Hz, *C*H-Ph, major), 109.4(t, 7.3 Hz, CHCHCH, major), 90.5(dd, 25.1, 6.1 Hz, *C*H-Ph, minor), 97.8(dd, 25.1, 5.0 Hz, *C*H-Ph, minor), 108.1(t, 7.3 Hz, CHCHCH, minor); δ_P($CDCl_3$, 162 MHz) 20.2(d, $^2J_{PP}$, 74.4 Hz, minor) 23.4(d, 74.4, major), 23.8(d, 74.4, minor), 26.8(d, 74.4, major). The data indicated by asterisk were overlapped with the signals of aromatic protons but were assigned by C-H COSY spectrum.

9 M. Yamaguchi, M. Yabuki, and T. Yamagishi, unpublished results: Selected δ_C (acetone-d_6, 67.5 MHz) 89.2(dd, $^2J_{CP}$, 22.0, 8.5 Hz, *C*H-Ph), 92.2(dd, 23.8, 9.1 Hz, *C*H-Ph), 114.5(t, 8.0 Hz, CHCHCH); δ_P ($CDCl_3$, 162 MHz) 49.8(d, $^2J_{PP}$, 68 Hz) and 50.8(d, $^2J_{PP}$, 68 Hz).

10 The catalytic asymmetric allylic alkylation reaction with $NaCH(NHAc)(CO_2Me)_2$: 98% ee at -20 °C in MeCN.

11 The crystal suitable for an X-ray analysis was obtained by recrystallization from ethyl acetate and dichloromethane. Crystallographic data: $C_{63}H_{53}F_6O_2P_3Pd$, FW = 1155.42, monoclinic, space group $P2_1$; a = 11.264(6), b = 22.911(4), c = 11.219(6) Å, β = 111.73(4)°, V = 2689(2) Å^3, F(000) = 1184, Z = 2, Dc = 1.427 g/cm^3, Do = 1.410 g/cm^3, Cu Kα radiation, λ = 1.54178 Å, μ(Cu Kα) = 41.72 cm^{-1}. Data collection was done on a Rigaku AFC5S diffractometer at room temperature. 3216 reflections with $F > 3\sigma(F)$ were used in the structure refinement. The final R value was 0.081 (R_w= 0.056).

12 Selected torsional angles (deg): C2-C3-C10-C15, -7; C2-C1-C4-C9, 36.