Optical Resolution of (2-Aminoethyl)butylphenylphosphine and the Absolute Configuration Assigned on the Basis of Circular Dichroism Spectra of Its Palladium(II) Complexes

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Synopsis. (2-Aminoethyl)butylphenylphosphine was resolved with (+)$_D$-di-μ-chlorobis[(*S*)-*N*,*N*-dimethyl-α-methylbenzylamine-2*C*,*N*]dipalladium(II), and the absolute configuration of the chiral phosphorus atom was assigned on the basis of the circular dichroism spectra of dichloro palladium(II) complexes with the resolved aminophosphine.

In recent years, chiral metal phosphine complexes have been widely utilized in various asymmetric syntheses for organic compounds.[1] While a tertiary aminoalkylphosphine also would be an effective ligand for such purposes, one with a chiral phosphorus atom has little been reported. We have succeeded in resolving (2-aminoethyl)butylphenylphosphine with a chiral palladium(II) complex which was developed for the optical resolution of monodentate[2] and bidentate[3] tertiary phosphines.

There has been no convenient way to assign the absolute configuration of a chiral phosphorus atom. In a previous paper,[4] we found a correlation between the absolute configuration of a pair of diastereomers of (*S*(C))-2-(butylphenylphosphinomethyl)pyrrolidine and the circular dichroism (CD) spectra of their palladium(II) complexes. In this note, we have assigned the absolute configuration of (2-aminoethyl)butylphenylphosphine by applying the correlation to the CD spectra of dichloro palladium(II) complexes with the resolved aminophosphine.

Experimental

Free aminophosphines were handled under nitrogen atmosphere until they formed palladium(II) complexes which were stable to air. Solvents were dried in the usual way and degassed by distillation in a stream of pure nitrogen. Absorption, CD, and ^{1}H and ^{13}C NMR spectra were recorded on a Hitachi 323 spectrophotometer, a JASCO J-40 spectropolarimeter, and JEOL PMX-60 and FX-60 spectrometers, respectively.

(2-Aminoethyl)butylphenylphosphine. Preparation: To liquid ammonia (250 cm^3) was added small pieces of sodium (2.3 g, 0.1 mol) and then (2-aminoethyl)diphenylphosphine (11.5 g, 0.05 mol)[5] with vigorous stirring. After 2 h, butyl bromide (14 cm^3, 0.11 mol) was added to the resulting deep red solution, the color of the solution turning gradually orange yellow. Liquid ammonia was evaporated off and the aminophosphine formed was extracted with diethyl ether. The extract was evaporated and distilled under reduced pressure to give colorless liquid, bp *ca.* 115°C/*ca.* 80 Pa. Yield: *ca.* 4.5 g (40%). Issleib and Oehme[6] prepared this aminophosphine from phenylphosphine.

Optical Resolution: To a benzene solution (15 cm^3) of (+)$_D$-di-μ-chlorobis[(*S*)-*N*,*N*-dimethyl-α-methylbenzylamine-2*C*,*N*]-dipalladium(II) (2.06 g)[2] was added a benzene solution (3 cm^3) of *rac*-(2-aminoethyl)butylphenylphosphine (1.49 g) with stirring. After a while, acetone was added to the solution to yield white precipitate which was filtered and washed with acetone. The precipitate was found from the ^{1}H NMR spectrum to be a pure diastereomer of [(*S*)-*N*,*N*-dimethyl-α-methylbenzylamine-2*C*,*N*][(2-aminoethyl)butylphenylphosphine]plladium(II) chloride, (**1a**). Yield: 1.26 g. Found: C, 52.97; H, 6.82; N, 5.58%. Calcd for $PdC_{22}H_{34}N_2PCl$: C, 52.91; H, 6.87; N, 5.61%. The filtrate was evaporated to dryness. The residue was mixed with boiling water (300 cm^3) and filtered. To the filtrate was added an aqueous solution (200 cm^3) of sodium hexafluorophosphate (1.8 g). This was stirred at 40 °C for 4 h and then at room temperature for 18 h. The resulting white precipitate was found from the ^{1}H NMR spectrum to be another optically pure diastereomer of the palladium(II) hexafluorophosphate, (**1b**). Yield: 2.0 g. Found: C, 43.42; H, 5.92; N, 4.54%. Calcd for $PdC_{22}H_{34}P_2F_6$: C, 43.39; H, 5.64; N, 4.60%.

The optically active free aminophosphines were obtained from **1a** and **1b** by adding excess sodium cyanide to the aqueous solutions and by extracting with diethyl ether.

Dichloro[(2-aminoethyl)butylphenylphosphine]palladium(II). Sodium cyanide (100 mg) was added to an aqueous solution (3 cm^3) of the less soluble diastereomer, **1a** (87 mg). The liberated aminophosphine was extracted with diethyl ether (3 cm^3) three times. The extract was mixed with an acetonitrile solution (30 cm^3) of $PdCl_2$ (30 mg) and filtered. The filtrate was evaporated to dryness and the residue was dissolved in a small amount of acetonitrile. The solution was chromatographed with an acidic alumina column and a mixture of acetonitrile and ethanol (4 : 1) for an eluent. The main yellow eluate was evaporated to dryness to give yellow residue which was recrystallized from a mixture of acetonitrile, diethyl ether, and petroleum ether. Yield: 29 mg. Found: C, 36.18; H, 5.20; N, 3.90%. Calcd for $PdC_{12}H_{20}NPCl_2 \cdot 1/2H_2O$: C, 36.43; H, 5.35; N, 3.54%.

[(S)-N,N-dimethyl-α-methylbenzylamine-2C,N][(2-aminoethyl)-diphenylphosphine]palladium(II) Chloride. This complex was prepared by the same method as that for the corresponding (2-aminoethyl)butylphenylphosphine complex. Found: C, 55.11; H, 5.79; N, 5.33%. Calcd for $PdC_{20}H_{38}N_2PCl$: C, 55.50; H, 5.83; N, 5.39%.

Results and Discussion

(2-Aminoethyl)butylphenylphosphine was resolved by forming a pair of diastereomers, **1a** and **1b**. The (+)$_D$-di-μ-chlorobis[(*S*)-*N*,*N*-dimethyl-α-methylbenzylamine-2*C*,*N*]dipalladium(II) complex is known to be a useful resolving reagent for various tertiary phosphines.[2,3] The separation of **1a** and **1b** was complete as evidenced by ^{1}H NMR spectra and both diastereomers were obtained in good chemical yields. For the planar [(*S*)-*N*,*N*-dimethyl-α-methylbenzylamine-2*C*,*N*][(2-aminoethyl)butylphenylphosphine]palladium(II) ion, there are two possible geometrical isomers; one has two

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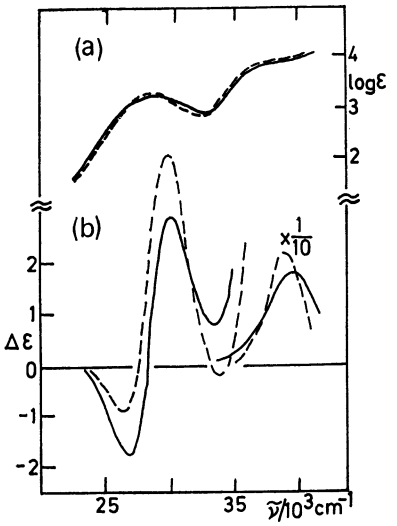

Fig. 1. (a) Absorption spectra of [$PdCl_2$-{(2-aminoethyl)-butylphenylphosphine}] (——) and [$PdCl_2$-{(*S*)-2-(butylphenylphosphinomethyl)pyrolidine}] (---). (b) CD spectrum of [$PdCl_2$-{(2-aminoethyl)butylphenylphosphine}] derived from diastereomer **1a** (——) and calculated vicinal CD curve due to the (*S*)-phosphorus atom in [$PdCl_2$-{(*S*)-2-(butylphenylphosphinomethyl)-pyrrolidine}] (----).[4]

nitrogen donor atoms in the trans positions, and the other those atoms in the cis positions. The **1a** and **1b** isomers show a similar pattern in the ^1H or ^{13}C NMR spectra, in which the long-range couplings between the phosphorus atom and the *N*-methyl protons or the *N*-methyl carbons are observed, respectively. Thus both isomers would have the phosphorus atom trans to the *N*-methyl nitrogen donor atom, the cis(*N*,*N*) configuration. The optically active free aminophosphine can be obtained from **1a** and **1b** by treating with sodium cyanide in water. The aminophosphines obtained from **1a** and **1b** form a pair of enantiomers of the dichloro palladium(II) complex.

In order to assign the absolute configuration of the chiral phosphorus atom, the CD spectrum of the dichloro palladium(II) complex of the aminophosphine obtained from the less soluble chloride, **1a** was compared with the vicinal CD curve for the (*S*)-phosphorus atom calculated from a pair of diastereomers of [$PdCl_2$-{(*S*(C)-2-(butylphenylphosphinomethyl)pyrrolidine}][4] (Fig. 1). The absolute configuration of the *R*(P)-isomer of the latter complex has been determined by the X-ray analysis.[4] Both curves in Fig. 1 are very similar and the absolute configuration of the phosphorus atom in the (2-aminoethyl)butylphenylphosphine complex given can

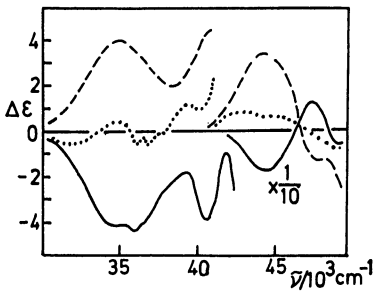

Fig. 2. CD spectra of diastereomers **1a** (——) and **1b** (------) of [Pd{(*S*)-*N*,*N*-dimethyl-α-methylbenzylamine-2*C*,*N*}-{(2-aminoethyl)butylphenylphosphine}] and [Pd{(*S*)-*N*,*N*-dimethyl-α-methylbenzylamine-2*C*,*N*}-{(2-aminoethyl)diphenylphosphine}] (·····).

be assigned to the (*S*)-configuration. This assignment coincides with the previous one based on the ^1H NMR and CD spectra of the bis(acetylacetonato)cobalt(III) complex of (2-aminoethyl)butylphenylphosphine obtained from the same **1a** isomer.[7]

The CD spectra of diastereomers, **1a** and **1b** are nearly enantiomeric to each other over the whole region (Fig. 2). This indicates that the CD depends largely on the donating chiral phosphorus atom and little on the chiral cyclometallated amine ligand. In fact, the corresponding (2-aminoethyl)diphenylphosphine complex whose phosphorus atom is achiral shows very weak CD. Thus the absolute configuration of chiral phosphorus atoms of aminoalkylphosphines could be assigned from CD spectra of their dichloro- or more conveniently [(*S*)-*N*,*N*-dimethyl-α-methylbenzylamine-2*C*,*N*]palladium(II) complexes.

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