# Chiral Recognition in Catalytic Hydrogenation of α-Acylaminoacrylic Acids by Cationic Rhodium(I) Complexes of Chiral Aminophosphines Derived from (*R,R*)-1,2-Cyclohexanediamine or (*R*)-1,2-Propanediamine[1]

Kazuo KASHIWABARA, Kazuhiro HANAKI, and Junnosuke FUJITA*

*Department of Chemistry, Faculty of Science, Nagoya University, Chikusa-ku, Nagoya 464*

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Four chiral diphosphines, (*R,R*)-1,2-bis[*N*-methyl(diphenylphosphino)amino]cyclohexane, (*R,R*)-1,2-bis[(diphenylphosphino)amino]cyclohexane, (*R*)-1,2-bis[*N*-methyl(diphenylphosphino)amino]propane, and (*R*)-1,2-bis[(diphenylphosphino)amino]propane have been prepared from the corresponding optically active diamines. The cationic 1,5-cyclooctadiene rhodium(I) complexes with these diphosphines act as effective homogeneous catalysts for the stereoselective hydrogenation of α-acylaminoacrylic acids. The optical yields and the absolute configurations of the products depend on the kind of diphosphine ligands. The (*R,R*)-1,2-bis[*N*-methyl(diphenylphosphino)amino]cyclohexane complex catalyst yields *N*-benzoyl-(*S*)-leucine, *N*-benzoyl-(*S*)-phenylalanine, and *N*-acetyl-(*S*)-phenylalanine in 94, 92, and 89% e.e., respectivcly. The other three catalysts are less effective (6—74% e.e.). The aminophosphine complexes with methyl groups on the nitrogen atoms always give (*S*)-amino acids, those with no methyl group (*R*)-amino acids. Such a difference in the chiral recognition has been discussed on the basis of circular dichroism spectra and Dreiding molecular models of the rhodium(I) complexes.

Reports have been given on the surprisingly high stereoselectivity for asymmetric hydrogenation of α-acylaminoacrylic acids catalyzed by chiral rhodium(I) diphosphine complexes.[2-4] The mechanism of the hydrogenation reactions has been found to involve oxidative addition of molecular hydrogen which takes place after the coordination of a substrate molecule to a catalyst.[5] Brown and Chaloner[6] confirmed the formation of a diastereomeric intermediate complex coordinated with a substrate molecule by $^{31}P$ NMR spectroscopy in solution. However, it is still not clear as to how chiral recognition operates in such asymmetric hydrogenation reactions.

Recently, three research groups reported that rhodium(I) complex catalysts of aminophosphines derived from (*R,R*)-1,2-diamines always give (*R*)-amino acid derivatives, and those from *N,N'*-dimethyl derivatives of these diamines (*S*)-amino acid derivatives.[1,7,8] The results seem to be useful for elucidating the mechanism of chiral recognition in catalytic hydrogenation reactions by rhodium(I) complexes, since a simple modification of a ligand affords an enantiomeric product. In this paper, we wish to report the results of catalytic hydrogenation reactions by rhodium(I) complexes with aminophosphines derived from chiral 1,2-diamines and to discuss factors of the chiral recognition in these reactions on the basis of circular dichroism spectra and Dreiding molecular models of the catalysts.

## Experimental

NMR, absorption, and circular dichroism spectra were recorded on a JEOL JNM-PMX 60 spectrometer, a Hitachi 323 spectrophotometer, and a JASCO J-40 spectropolarimeter, respectively. Optical rotations were determined with a JASCO DIP-4 polarimeter. (*Z*)-α-Acetamidocinnamic acid,[9] (*Z*)-α-benzamidocinnamic acid,[10] and (*Z*)-β-isopropyl-α-benzamidoacrylic acid[11] were prepared according to the procedures reported.

*Preparation of Ligands.* *(R,R)-1,2-Bis[N-methyl(diphenylphosphino)amino]cyclohexane (1)*: To a vigorously stirred aqueous solution (40 cm$^3$) of sodium hydroxide (8.0 g, 0.2 mol) was added 5.0 g (0.044 mol) of (*R,R*)-1,2-cyclohexanediamine[12] ($[\alpha]_D^{22}=-36.0°$ (*c* 2.8, $H_2O$)) under cooling in an ice-cold bath. A solution of ethyl chloroformate (7.6 cm$^3$, 0.095 mol) in 40 cm$^3$ of benzene was then added dropwise over 30 min. The reaction mixture was allowed to stand at room temperature for 3 h. The resulting precipitate, (*R,R*)-1,2-bis(ethoxycarbonylamino)cyclohexane was filtered, washed with cold water, and dried *in vacuo*. The product was recrystallized from ethanol. Yield: 9.0 g (80%). 10 g (0.26 mol) of lithium tetrahydridoaluminate(III) and 150 cm$^3$ of dry tetrahydrofuran (THF) were placed in a 500-cm$^3$ three-necked, round-bottomed flask equipped with a mechanical stirrer and a reflux condenser with a soda lime tube. To this vigorously stirred mixture was added 9.0 g (0.035 mol) of (*R,R*)-1,2-bis(ethoxycarbonylamino)cyclohexane in small portions, the vessel being kept in an ice-cold bath. After the addition was completed, the mixture was allowed to stand at room temperature for 30 min and then refluxed overnight. The reaction mixture was cooled in an ice-bath and the unreacted hydride was carefully quenched by dropwise addition of water (30 cm$^3$). A white precipitate was filtered and washed three times with boiling THF (300 cm$^3$). The combined filtrate and washings were evaporated under reduced pressure to give an oily residue. This was neutralized with concd hydrochloric acid, mixed with acetone, and cooled in an ice bath. The resulting crystalline product, (*R,R*)-1,2-bis(methylamino)cyclohexane dihydrochloride was filtered and dried in a vacuum desiccator over diphosphorus pentaoxide. Yield: 5.0 g (67%). The product (6.6 g, 0.031 mol) and ethanol-free chloroform (200 cm$^3$) were placed in a 500-cm$^3$ three-necked, round-bottomed flask equipped with a serum cap and a nitrogen inlet. The flask was successively evacuated and filled with nitrogen while the contents were stirred. 12.5 g (0.124 mol) of triethylamine and 13.0 g (0.059 mol) of chlorodiphenylphosphine were then injected through the serum cap with syringes. The resulting solution was stirred overnight at room temperature. Chloroform was removed under reduced pressure and ether (300 cm$^3$) was added. The mixture was refluxed for 1 h and filtered in order to remove triethylamine hydrochloride. All the precedures were carried out under nitrogen atmosphere. The filtrate was evaporated under reduced pressure to yield

a pale yellow solid, which was recrystallized from acetone and water. Yield: 8.0 g (50%) (overall yield from the starting amine, 27%). Mp 137—139 °C, $[\alpha]_D^{22}=-7.3°$ (*c* 1.1, $CHCl_3$). Found: C, 75.09; H, 6.92; N, 5.33%. Calcd for $C_{32}H_{36}N_2P_2$: C, 75.26; H, 7.12; N, 5.49%. NMR ($CDCl_3$, TMS): $\delta$(ppm)=1.0—2.1 (8p, $CH_2$), 2.63 (d, 6p, $CH_3$, $J_{H-P}=3.5$ Hz), 3.47 (m, 2p, CH), 7.4 (m, 20p, $C_6H_5$).

*(R,R)-1,2-Bis[(diphenylphosphino)amino]cyclohexane (2)*: This ligand was prepared from (*R,R*)-1,2-cyclohexanediamine (4.0 g, 0.035 mol), triethylamine (7.1 g, 0.070 mol), and chlorodiphenylphosphine (15.4 g, 0.070 mol) by a method similar to that for aminophosphine **1**, dry benzene (100 $cm^3$) being used as solvent instead of chloroform. A white solid obtained was recrystallized from acetone and water. Yield: 4.25 g (25%). Mp 119—120 °C, $[\alpha]_D^{22}=-69.0°$ (*c* 1.3, $CHCl_3$). Found: C, 74.30; H, 6.92; N, 5.57%. Calcd for $C_{30}H_{32}N_2P_2$: C, 74.64; H, 6.70; N, 5.80%. NMR ($CDCl_3$, TMS): $\delta$(ppm) =0.9—2.5 (m, 8p, $CH_2$), 2.7 (m, 2p, CH), 7.4 (m, 20p, $C_6H_5$).

*(R)-1,2-Bis[N-methyl(diphenylphosphino)amino]propane (3)*: (*R*)-1,2-Bis(methylamino)propane dihydrochloride was prepared from (*R*)-1,2-propanediamine[13] ($[\alpha]_D^{22}=-33.8°$ (*c* 1.56, $C_6H_6$)) by a procedure similar to that for aminophosphine **1**. Yield: 79%. A solution of (*R*)-1,2-bis(methylamino)-propane dihydrochloride (4.0 g, 0.023 mol), triethylamine (9.3 g, 0.092 mol), and chlorodiphenylphosphine (10.1 g, 0.046 mol) in 100 $cm^3$ of ethanol-free chloroform was stirred overnight at room temperature under nitrogen atmosphere. Chloroform was evaporated under reduced pressure and the resulting residue was extracted with benzene (100 $cm^3$). The benzene solution was filtered in order to remove triethylamine hydrochloride, the filtrate being evaporated under reduced pressure to give an oily product. Yield: 7.4 g (69%) (overall yield from the starting amine, 54%). NMR ($CDCl_3$, TMS): $\delta$(ppm)=1.18 (d, 3p, $CH_3$, $J_{H-H}=6.0$ Hz), 2.4 (d, 3p, $NCH_3$, $J_{P-H}=4.0$ Hz), 2.5 (d, 3p, $NCH_3$, $J_{P-H}=5.0$ Hz), 3.2 (m, 2p, $CH_2$), 3.8 (m, 1p, CH), 7.4 (s, 20p, $C_6H_5$).

*(R)-1,2-Bis[(diphenylphosphino)amino]propane (4)*: (*R*)-1,2-propanediamine dihydrochloride (2.4 g, 0.016 mol) was added to an aqueous solution (20 $cm^3$) of sodium hydroxide (12.0 g). The amine was extracted with boiling benzene (100 $cm^3$) and the extract was dried over potassium hydroxide overnight. To the benzene solution were added triethylamine (2.3 g, 0.023 mol) and chlorodiphenylphosphine (5.1 g, 0.023 mol) with stirring under nitrogen atmosphere over a period of 30 min. The mixture was stirred at room temperature for 1 h and the triethylamine hydrochloride precipitated was removed by filtration. The filtrate was evaporated under reduced pressure to give an oily product. Yield: 3.0 g (60%). NMR ($CDCl_3$, TMS): $\delta$(ppm)=1.11 (d, 3p, $CH_3$, $J_{H-H}$= 6.0 Hz), 2.7—3.5 (m, 3p, CH and $CH_2$), 7.45 (s, 20p, $C_6H_5$).

Aminophosphines **3** and **4** were used for preparing rhodium (I) complexes without further purification.

*Preparation of Rhodium(I) Complexes.* *[Rh(cod)(1)]$PF_6$ (I)*: A dichloromethane solution (10 $cm^3$) of [Rh(cod)-Cl]$_2$[14] (0.5 g, 1 mmol, cod=1,5-cyclooctadiene) was mixed with an aqueous solution (10 $cm^3$) of sodium hexafluorophosphate (0.5 g, 3 mmol) with stirring under nitrogen atmosphere. To the mixture was added aminophosphine **1** (1.1 g, 2.2 mmol) and the solution was stirred vigorously for 20 min. The dichloromethane layer was washed three times with water (10 $cm^3$), its volume being reduced to *ca.* 5 $cm^3$ by passing nitrogen. On addition of ethanol (10 $cm^3$) and then diethyl ether (25 $cm^3$), the solution gave fine orange crystals which were filtered, washed with diethyl ether, and recrystallized from chloroform and diethyl ether. Yield: 1.14 g (66%). $[\alpha]_D^{25}=-79.1°$ (*c* 0.18, $CHCl_3$). Found: C, 54.78; H, 5.60; N, 3.19%. Calcd for $RhC_{40}H_{48}N_2P_3F_6$: C, 55.41; H, 5.59; N, 3.23%. NMR ($CDCl_3$, TMS): $\delta$(ppm)= 0.8—1.9 (m, 8p, $CH_2$), 2.1 (m, 8p, $CH_2$ of cod), 2.48 (d, 6p, $NCH_3$, $J_{P-H}=8.0$ Hz), 4.0 and 4.6 (m, 4p, -CH=CH-), 5.0 (m, 2p, CH), 6.4—8.3 (m, 20p, $C_6H_5$).

The other aminophosphine complexes were prepared similarly.

*[Rh(cod)(2)]$PF_6\cdot CHCl_3$ (II)*: Yield: 77%, orange blocks from chloroform/diethyl ether. $[\alpha]_D^{25}=-94.8°$ (*c* 0.13, $CHCl_3$). Found: C, 48.96; H, 4.68; N, 3.07%. Calcd for $RhC_{39}H_{45}N_2P_3F_6Cl_3$: C, 48.89; H, 4.74; N, 2.92%. NMR ($CDCl_3$, TMS): $\delta$(ppm)=0.5—2.0 (m, 8p, $CH_2$), 2.3 (m, 8p, $CH_2$ of cod), 3.4 (m, 2p, CH), 4.4 and 4.9 (m, 4p, -CH=CH-), 6.9—8.2 (m, 20p, $C_6H_5$),

*[Rh(cod)(3)]$PF_6$ (III)*: Yield: 35%, orange crystalline needles from chloroform/diethyl ether. $[\alpha]_D^{25}=-97.6°$ (*c* 0.17, $CHCl_3$). Found: C, 53.43; H, 5.66; N, 2.99%. Calcd for $RhC_{37}H_{44}N_2P_3F_6$: C, 53.74; H, 5.38; N, 3.39%. NMR ($CDCl_3$, TMS): $\delta$(ppm)=1.24 (d, 3p, $CH_3$, $J_{H-H}=7.0$ Hz), 2.2 (m, 8p, $CH_2$ of cod), 2.34 (d, 3p, $NCH_3$, $J_{P-H}=9.0$ Hz), 2.51 (d, 3p, $NCH_3$, $J_{P-H}=7.0$ Hz), 4.4 and 5.0 (m, 4p, -CH=CH-), 7.2—8.0 (m, 20p, $C_6H_5$).

*[Rh(cod)(4)]$PF_6\cdot CHCl_3$ (IV)*: Yield: 44%, orange blocks from chloroform/diethyl ether. $[\alpha]_D^{25}=-0.5°$ (*c* 0.20, $CHCl_3$). Found: C, 46.99; H, 4.29; N, 3.14%. Calcd for $RhC_{36}H_{41}N_2P_3F_6Cl_3$: C, 47.10; H, 4.51; N, 3.05%. NMR ($CDCl_3$, TMS): $\delta$(ppm)=1.17 (d, 3p, $CH_3$, $J_{H-H}=7.0$ Hz), 2.3 (m, 8p, $CH_2$ of cod), 2.7 (m, 2p, $CH_2$), 2.9—3.5 (m, 1p, CH), 4.55 and 4.80 (m, 4p, -CH=CH-), 7.4—7.8 (m, 20p, $C_6H_5$).

*Hydrogenation Procedures.* Ethanol was dried overnight over molecular sieves 3A and purged with a stream of nitrogen for at least 30 min before use. In a Schlenk tube equipped with a serum cap were placed 6 mmol of a substrate and 0.03 mmol of a rhodium (I) complex. The tube was successively evacuated and filled with nitrogen. Ethanol (20—60 $cm^3$) was then injected. The mixture was stirred vigorously and the reaction vessel was connected to an atmospheric pressure hydrogenation apparatus. After hydrogen uptake ceased, reaction work-up and isolation of the products were carried out according to reported methods[2,15] in order to avoid undue optical enrichment. NMR spectra of all the products were measured to check the chemical conversions. Optical purities were determined by optical rotations of the products at 589 nm.

## Results and Discussion

*Catalysts and Hydrogenation.* The optically pure aminophosphines **1**—**4** (Fig. 1) are easily obtained in a large scale since the parent 1,2-diamines can be resolved by a simple procedure with *d*-tartaric acid and the reactions proceed with full configurational retention. Aminophosphines **1** and **2** form stable white block and needle crystals, respectively, while **3** and **4** are viscous oily substances. These aminophosphines would form chelate rings with similar skeletal structures upon coordination. The absolute configurations of aminophosphines **1**—**4** are shown together with those prepared by Onuma *et al.*[7] and Fiorini and Giongo[8] (**5**—**7**), which were derived from (*S,S*)-2,3-butanediamine or (*S,S*)-1,2-diphenyl-1,2-ethanediamine (Fig. 1).

Hydrogenation was carried out with (*Z*)-α-acylamino-acrylic acid derivatives.

Table 1. Optical purity/%, and absolute configuration of products

| Substrate | Catalyst (I) | (II) | (III) | (IV) | (V)[a] | (VI)[b] | (VII)[c] |
|---|---|---|---|---|---|---|---|
| (a) $R^1=C_6H_5$, $R^2=CH_3$ | 89(*S*) | 49(*R*) | 70(*S*) | 28(*R*) | 68(*R*) | 93(*S*) | 45(*S*) |
| (b) $R^1=C_6H_5$, $R^2=C_6H_5$ | 92(*S*) | 41(*R*) | 48(*S*) | 21(*R*) | — | — | 32(*S*) |
| (c) $R^1=(CH_3)_2CH$, $R^2=C_6H_5$ | 94(*S*) | 9(*R*) | 74(*S*) | 6(*R*) | — | — | — |
| (d) $R^1=H$, $R^2=CH_3$ | 91(*S*)[d] | 24(*R*)[d] | — | — | 86(*R*) | 89(*S*) | — |

Solvent: Ethanol. $P_{H_2}$: 1.0 atm. Room temperature. Substrate/Rh=200. [Rh]: 0.5—1.5 mmol/dm³. Hydrogenation time: 15—50 min. Chemical yield: 90—98%. Optical purity was determined based on the values given in Ref. 2. a) Rhodium (I) catalyst with aminophosphine **5** (Fig. 1) derived from (*S,S*)-1,2-diphenyl-1,2-ethanediamine, see Ref. 8. b) Rhodium(I) catalyst with aminophosphine **6** derived from (*S,S*)-1,2-diphenyl-1,2-ethane diamine, see Ref. 8. c) Rhodium(I) catalyst with aminophosphine **7** derived from (*S,S*)-2,3-butanediamine, see Ref. 7. d) Ref. 8.

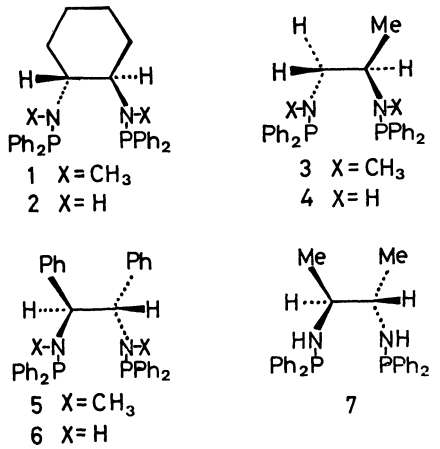
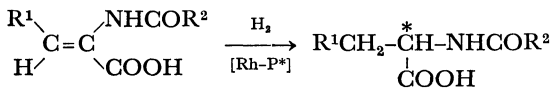



Fig. 1. Absolute configurations of chiral aminophosphines.



The optical purity and absolute configuration of the reaction products are summarized in Table 1 together with those reported by Onuma *et al.*[7] and Fiorini and Giongo.[8] The values were reproducible within ±2%. The addition of triethylamine did not improve the optical purity. The results can be summarized as follows, (1) The catalysts of (*R,R*)-aminophosphines with secondary amino groups, (II) *etc.*, show selectivity giving (*R*)-amino acid derivatives. Several rhodium(I) catalysts with other (*R,R*)-diphosphines[16] or -phosphites[17] whose skeletal structures are similar to those of catalysts (II) *etc.* also give the same (*R*)-amino acid derivatives. The *N*-methylation of the aminophosphines reverses the selectivity to afford (*S*)-amino acid derivatives. (2) The optical purity of the products depends on the bulkiness of substituents in a chelate ring, (I), (VI)>(V)>(III)>(II)>(VII)>(IV). (3) The products from substrate (c) show a big difference in optical purity between catalysts (I) and (II), and (III) and (IV), indicating the importance of fitness of the substrate to the catalysts. (4) The cationic catalyst (I) gives a product of higher optical purity than that obtained *in situ*,[18] suggesting that chloride ions have strong coordinating ability to the rhodium(I) ion to reduce the stereoselectivity in the hydrogenation. The cationic complexes work more effectively in asymmetric hydrogenation reactions.[19,20]

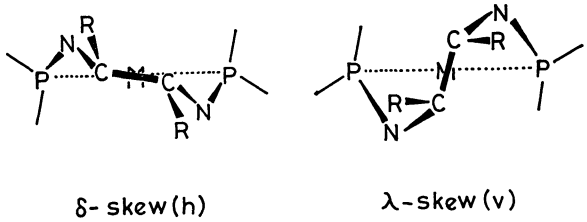



Fig. 2. Two skew conformations of a (1*R*, 2*R*)-aminophosphine chelate ring.

*Chiral Recognition.* Each of the aminophosphines (Fig. 1) coordinates to a rhodium(I) ion to form a seven-membered chelate ring. It will be more flexible than a five- and probably a six-membered one and can form a variety of conformations. Among the conformations, two skew forms, skew(h) and skew(v) appear to be stable (Fig. 2), since the forms would involve less intra- and inter-ligand steric interactions. The skew(h) and skew(v) imply "horizontal" and "vertical," respectively, named with reference to the direction of the central C–C bonds of the chelate rings. The skew(h) conformation was confirmed by X-ray analysis of $[Co(1,4\text{-butanediamine})_3]^{3+}$.[21] In *trans*-$[CoCl_2(1,4\text{-butanediamine})_2]^+$, one chelate ring is the skew(h), and the other the skew(v).[22] Thus, the two skew forms of a seven-membered chelate ring with no substituent group appear to have similar conformational stability.

Similar skew conformations of seven-membered chelate rings can be assumed for the aminophosphines in the rhodium(I) complexes. Aminophosphine **1** can form stereoselectively two types of chiral chelate rings, δ-skew(h) and λ-skew(v), owing to the chirality of the (*R,R*)-1,2-cyclohexanediamine moiety. However, molecular models show that the δ-skew(h) form is a less crowded

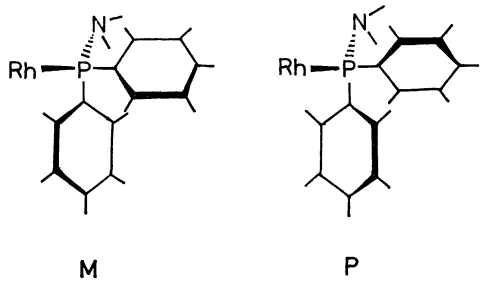



Fig. 3. Two helical orientations of two phenyl groups.

and a less strained structure than the other form. When the $\delta$-skew(h) conformation is assumed for aminophosphine **1**, the two nitrogen atoms are forced to take (*S*)-configuration stereoselectively in order to reduce steric interactions with the phenyl groups. Furthermore the two phenyl groups on each phosphorus atom are prohibited to rotate freely around the phosphorus–carbon bonds and would be disposed in particular orientations to afford, in most cases, new helical chirality, left-handed helicity(*M*) or right-handed helicity(*P*)[23] such as seen in biaryls (Fig. 3). It is not clear from studies of molecular models which helicity is preferred for the $\delta$-skew(h) conformation of aminophosphine **1**. However, according to X-ray analysis, the 1,2-bis-[(*R*)-(*o*-methoxyphenyl)phenylphosphino]ethane[3] and (+)-isopropylidene-2,3-dihydroxy-1,4-(diphenylphosphino)butane (diop)[24] complexes have *P* helicity and give products of (*S*)-amino acids, while the (*S*,*S*)-2,3-bis(diphenylphosphino)butane complex[25] with *M* helicity produces (*R*)-amino acids. Thus aminophosphine **1** is tentatively assumed to have *P* helicity.

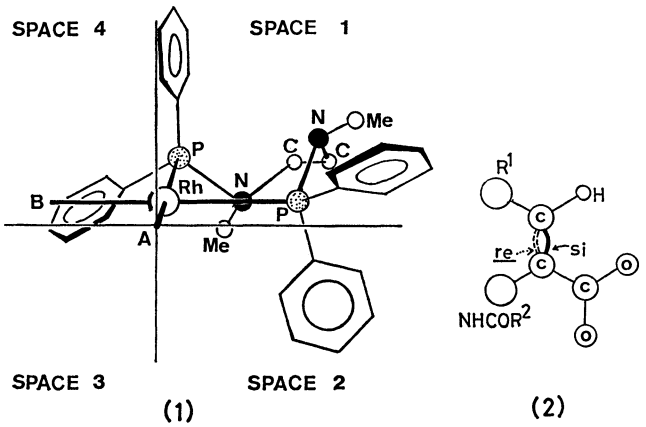



Fig. 4. (1): A schematic drawing of aminophosphine **1** coordinated to a rhodium(I) ion with the $\delta$-skew conformation and the *P* helicity. (2): A substrate.

Figure 4 shows a schematic drawing of aminophosphine **1** coordinated to the rhodium(I) ion with the $\delta$-skew form, viewed from the site (A) where a substrate would enter. The space 1 viewed from site (A) is occupied by the edge of one phenyl group and would be the most crowed. A substrate (Fig. 4(2)) would therefore preferentially coordinate to the rhodium(I) ion *via* the $\alpha$-*re* face so that the most crowded site 1 is occupied by the small hydrogen atom on the olefinic carbon atom. The coordination through the $\alpha$-*re* face of a substrate can lead to the formation of a bond between the rhodium(I) ion (site B) and the oxygen atom of the amido carbonyl of the substrate as shown by X-ray analysis on [Rh{1,2-bis(diphenylphosphino)ethane}-{methyl(*Z*)-$\alpha$-acetamidocinnamate}]$^+$.[26] An (*S*)-*N*-acylamino acid is derived, when the substrate thus coordinated is hydrogenated stereoselectively from the olefinic face coordinated to the rhodium(I) ion. $CH_2$=C-($NHCOCH_3$)COOH (substrate (d), Table 1) has two hydrogen atoms on one olefinic carbon atom, and hence the two coordination modes of this prochiral olefin may not be discriminated by the $CH_2$ group. However, the coordination through the same $\alpha$-*re* face as the other olefins can similarly induce the coordination of the oxygen atom of the amido group, while that through the opposite $\alpha$-*si* face introduces the bulky carboxyl group instead of the hydrogen to the most crowded space 1. Thus, substrate (d) would coordinate preferentially to the rhodium(I) ion through its $\alpha$-*re* face to give (*S*)-*N*-acylalanine.

In contrast to catalyst (I), catalyst (II) gives products of (*R*)-*N*-acylamino acids, although the difference in the structure of these catalysts seems to be small. For such reverse chiral recognition, two explanations can be given. (a) The seven-membered chelate ring of aminophosphine **2** which would be less crowded and more flexible than aminophosphine **1** is in the $\lambda$-skew(v) conformation opposite to the $\delta$-skew(h) conformation of aminophosphine **1**. (b) The stable orientation of the two phenyl groups has *M* helicity opposite to that for aminophosphine **1**, although the seven-membered chelate ring is fixed in the same $\delta$-skew(h) form as aminophosphine **1**. Explanation (b) is more likely since molecular models indicate that the $\delta$-skew(h) form of aminophosphine **2** is also less crowded than $\lambda$-skew(v) form, but the phenyl groups in the less crowded complex (II) can rotate more freely than those in the more crowded complex (I) and it is possible to form *M* helicity as the stable orientation. The circular dichroism (CD) spectra of the catalysts seem to support this explanation.

Figure 5 shows absorption and CD spectra of catalysts (I) and (II) in chloroform. Both catalysts exhibit similar absorption spectra over the whole region. On the other hand, the CD curves are nearly the same in the small wave number region to *ca.* 31000 $cm^{-1}$, but

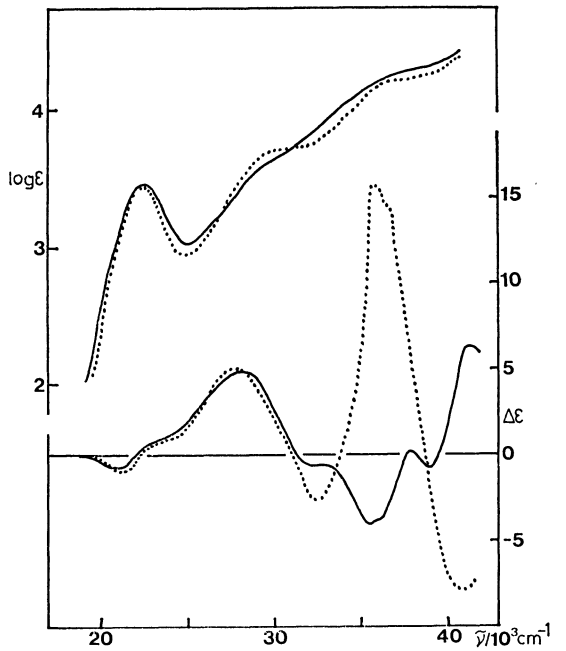



Fig. 5. Absorption and circular dichroism spectra of rhodium(I) complexes in chloroform.
——: [I], ·····: [II].

appreciably differ in the ultraviolet region. The absorption bands in the small wave number region might comprise d-d transitions in the rhodium(I) ion and charge transfer transitions from the metal ion to the ligands.[27] The CD spectra corresponding to these transitions should be affected by chiral conformation of the seven-membered aminophosphine chelate rings as observed in many cobalt(III) complexes with chiral chelate ligands.[28] The similarity in the CD spectra of catalysts (I) and (II) in this transition region suggests that the chiral aminophosphine ligands in both catalysts are in the same conformation, $\delta$-skew(h). The CD spectra of the catalysts in the ultraviolet region differ considerably from each other. The CD bands may correspond to the intra-ligand transitions. In fact, the signs or patterns resemble those of the free ligands (Fig. 6). No definite information seems to be provided on the conformation of the chelate ligands.

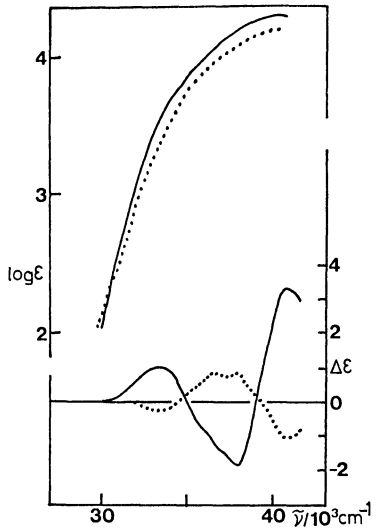



Fig. 6. Absorption and circular dichroism spectra of free aminophosphines in chloroform.
——: (**1**), ……: (**2**).

When catalyst (II) in the $\delta$-skew(h) conformation has the phenyl groups of *M* helicity, the edge phenyl group occupies site 2. Thus site 2 is more crowded than site 1 and the substrate given in Fig. 4(2) would coordinate to the rhodium(I) ion *via* the $\alpha$-*si* face to produce an (*R*)-amino acid by the same hydrogenation mechanism as that given for catalyst (I), although the optical yields are rather low. The low optical yields might be attributed to the instability of a conformer with the phenyl groups in a particular helicity resulting from the less crowded structure of catalyst (II) as compared with that of catalyst (I).

A similar chiral recognition would operate on the hydrogenation reactions with catalysts (III) and (IV) and their analogues (Table 1), since these catalysts give the same selectivity as that of catalysts (I) and (II) depending on the presence or absence of the methyl groups on the nitrogen atoms. The optical yields of catalysts (III) and (IV) are considerably lower than those of the corresponding catalysts (I) and (II), respectively, probably because of more flexible skeletones

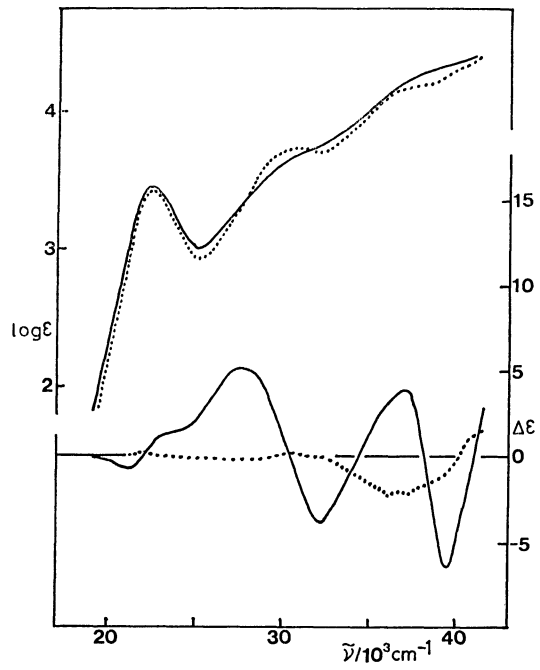



Fig. 7. Absorption and circular dichroism spectra of rhodium(I) complexes in chloroform.
——: [III], ……: [IV].

of the seven-membered chelate rings in the former catalysts. The absorption and CD spectra of catalysts (III) are similar to those of catalysts (I) and (II) in the small wave number region. On the other hand, catalyst (IV) shows very weak CD in this region, although the absorption spectrum is nearly the same as those of the other catalysts (Fig. 7). The very weak CD of catalyst (IV) suggests that the seven-membered aminophosphine **4** chelate ring is extremely flexible, existing in the two conformers of opposite chirality, $\delta$-skew(h) and $\lambda$-skew(v), the amounts of which are almost equal at equilibrium. The conformational flexibility of catalyst (IV) is also suggested from $^1$H NMR spectrum. The coordinated 1,5-cyclooctadiene ligand in each catalyst (I—IV) shows two kinds of vinyl proton signals probably because of the two nonequivalent phenyl groups disposed in different orientations on each phosphorus atom. The difference in chemical shift of such two vinyl proton signals would decrease with an increase in the flexibility of a diphosphine ligand.[2] The differences are 0.5—0.6 ppm for catalysts (I), (II), and (III), and only 0.25 ppm for catalyst (IV). The phenyl groups in such a flexible catalyst would hardly form a stable helical configuration, and thus the chiral recognition would not operate effectively on the hydrogenation if we assume the same mechanism as that given for catalyst (I). It seems that selectivity in the hydrogenation reactions catalyzed by rhodium(I) complexes with aminophosphines derived from chiral 1,2-diamines is most closely related with the helicity and stability of orientations of the phenyl groups on phosphorus atoms of the diphosphine ligands.

The discussion has been made on the basis of the mechanism proposed by Halpern *et al.*[5] and Brown and Chaloner[6] that a substrate coordinates to a catalyst

prior to the hydrogenation. It has also been made by assuming that the stereoselective coordination of a prochiral substrate to a vacant coordination site of a catalyst is controlled thermodynamically. In order to elucidate the selectivity of a complex catalyst, detailed kinetic studies will also be needed.[29]

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