Asymmetric Hydrogenation of Dehydroamino Acids and Dehydrodipeptides with Rhodium(I)-modified DIOP Catalysts

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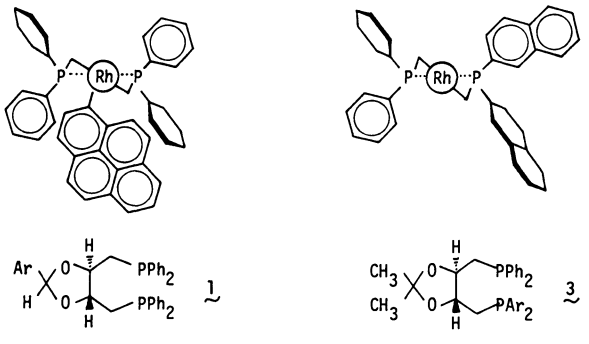
(Received November 9, 1983)

(−)-DIOP was modified in two ways: i), Introduction of a large aromatic substituent at the dioxolane ring of (-)-DIOP and ii), replacement of one diphenylphosphino group by diarylphosphino group to give unsymmetrical DIOPs. Modification at the dioxolane ring had a small effect on the asymmetric induction by DIOP in the hydrogenation. Modification at the phosphino group affected the stereocontrol by the ligand and the unsymmetrical DIOP with di-2-naphthylphosphino group gave higher optical yields than (−)-DIOP for the hydrogenation of α-acetamidocinnamic acid and dehydrodipeptides.

Asymmetric hydrogenation of dehydroamino acid derivatives has been intensively studied using many chiral diphosphine or diphosphinite ligands. DIOP, the first chiral diphosphine reported in the literature,[1] has been widely used because of its ease of preparation and its effectiveness for asymmetric hydrogenation of various substrates, but the optical yields of hydrogenation reported are about 80% e.e. at most.[1,2] Many modifications of DIOP have been reported;[2a,3] only a few ligands could give a little higher stereoselectivity than the DIOP in the hydrogenation of α-acetamidocinnamic acid.

The authors have modified (−)-DIOP in two ways (Scheme 1):
i) Introduction of a large aromatic substituent on the dioxolane ring of (−)-DIOP (compound **1**).
ii) Modification at the phosphino group of (−)-DIOP (compound **3**). The former would cause a change in face and edge conformation of the phenyl groups on phosphorus atoms of the ligand by steric repulsion between the aromatic substituent and the methylene unit adjacent to the phosphino group. The latter affords unsymmetrical DIOPs with a diphenylphosphino group at one side and a diarylphosphino group at the other side. This modification would provide a significant change in the steric and electronic factors of the bidentate ligand. The unsymmetrical DIOP coordinated onto Rh(I) would provide different degrees of congestion at two apical sites of the complex,[4] while prochiral substrates will generally coordinate unsymmetrically onto rhodium. Therefore, the unsymmetrical DIOP may allow more preferable fitting of the prochiral substrate than symmetrical DIOP[5] at the step of face-selection of the substrate.

Using two types of modifiefd DIOPs, the asymmetric hydrogenation of dehydroamino acid derivatives and dehydrodipeptides was studied. The effect of modification was large in the case of unsymmetrical DIOP with 2-naphthyl substituent.



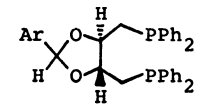
Scheme 1.

Results and Discussion

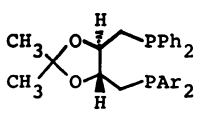
The modified DIOPs examined in this paper are listed in Table 1. As DIOP derivatives modified at the dioxolane ring, two derivatives (**1a** and **1b**) were prepared by the phosphination of acetals derived from corresponding aromatic aldehydes and 1,4-di-*O*-tosyl-L-threitol. In the hydrogenation, cationic rhodium(I) complexes, [Rh(diphosphine)(nbd)]$^+BF_4^-$ (nbd: norbornadiene), were used as catalysts.

Unsymmetrical DIOPs (**3a—3d**) were prepared by two-step phosphination of 2,3-*O*-isopropylidene-1,4-di-*O*-tosyl-L-threitol (ditosylate) using $LiPPh_2$ and $LiPAr_2$ successively (Scheme 2). For the monophosphination of ditosylate, lithium diphenylphosphide was

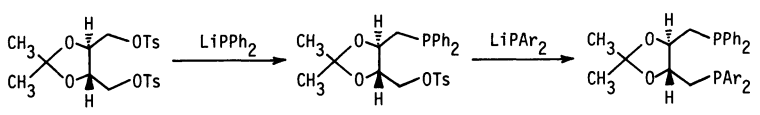
Table 1. Modified DIOPs



1
1a: Ar=2-naphthyl
1b: Ar=1-pyrenyl



3
3a: Ar=*p*-tolyl
3b: Ar=*p*-methoxyphenyl
3c: Ar=1-naphthyl
3d: Ar=2-naphthyl



Scheme 2.

used in 0.5 molar excess to ditosylate in order to consume ditosylate completely. Extraction of by-products such as (−)-DIOP or tetraphenyldiphosphane (Ph_2P–PPh_2) from the reaction products with hot hexane left monophosphine **2** as a viscous oil. Monophosphine **2** was phosphinated by lithium diarylphosphide to give unsymmetrical DIOPs. As these DIOPs were viscous oil, they were converted to cationic rhodium(I) complexes and purified by recrystallization.

Circular Dichroism Spectra. The circular dichroism (CD) spectra for [Rh(diphosphine)(nbd)]$^+BF_4^-$ complexes are shown in Figs. 1 and 2. Though modification at the dioxolane ring of (−)-DIOP gave a relatively small change in the CD spectra (Fig. 1), CD spectra of unsymmetrical DIOP complexes were strongly dependent on the aryl substituent in the phosphino group. The intensity of CD spectra near 350 nm

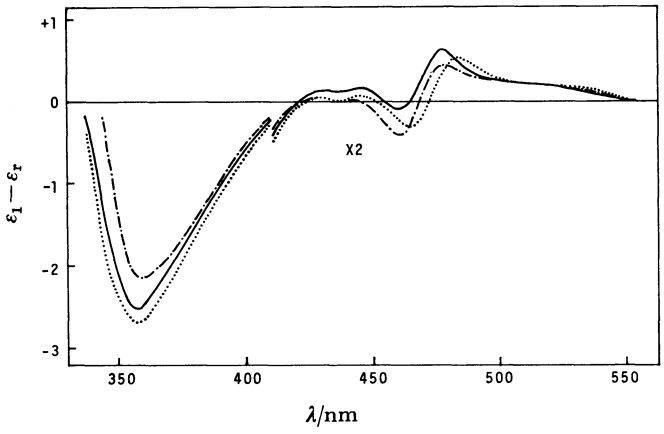


Fig. 1. CD spectra of cationic Rh(I) complexes of DIOP derivatives modified at the dioxolane ring in methanol solution.
——: [Rh((−)-DIOP)(nbd)]$^+BF_4^-$; ·····: [Rh(**1a**)(nbd)]$^+BF_4^-$; —·—: [Rh(**1b**)(nbd)]$^+BF_4^-$.

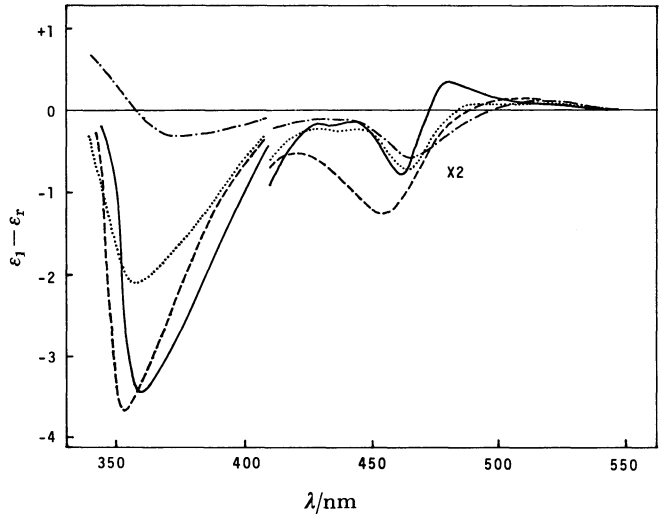


Fig. 2. CD spectra of cationic Rh(I) complexes of unsymmetrical DIOPs in methanol solution.
——: [Rh(**3a**)(nbd)]$^+BF_4^-$; ·····: [Rh(**3b**)(nbd)]$^+BF_4^-$; ----: [Rh(**3c**)(nbd)]$^+BF_4^-$; —·—: [Rh(**3d**)(nbd)]$^+BF_4^-$.

of the complexes of **3a**—**3d** was strongest for the complex of **3c** and least strong for the complex of **3d**, thus suggesting a different stereoelectronic effect of the aryl substituent in the ligands.

Hydrogenation with Modified DIOPs. Asymmetric hydrogenations of dehydroamino acid derivatives using cationic complex of **1a** or **1b** were compared with those by (−)-DIOP complex. As for the reaction rate, no apparent difference was observed between (−)-DIOP and **1a** or **1b**. The optical yields were decreased slightly in the order of (−)-DIOP, **1a** and **1b** (for example, optical yields for the reaction of α-acetamidocinnamic acid were 79, 79, and 70% e.e., respectively). A CPK model of the cationic complex coordinated by **1a** or **1b** suggested a steric repulsion between the aromatic substituent and the methylene unit adjacent to the phosphino group. It will cause a change of the face and edge conformation of phenyl groups of the ligand to alter the steric control, but the obtained results would indicate that the change in the face and edge conformation was not so large even in the case of **1b** with a pyrene ring. In the reactions of methyl esters of α-acetamidocinnamic acid and α-benzamidocinnamic acid, however, **1a** gave higher optical yields than those by DIOP.

In the case of cationic rhodium complexes, modification at the dioxolane ring of DIOP gave generally a small negative effect on the stereoselection. On the other hand, neutral rhodium(I) complexes prepared from $[Rh(cod)Cl]_2$ and modified DIOPs (**1a** and **1b**) *in situ* gave higher optical yields in the reaction of α-acetamidocinnamic acid than the catalyst from $[Rh(cod)Cl]_2$ and (−)-DIOP (Optical yields were 77, 77 and 72% e.e., respectively). This result would indicate that the structures of neutral chlororhodium–diphosphine complexes are different from the square planar cationic complexes.[6] Cationic rhodium(I)-**1a**-α-acetamidocinnamic acid and neutral chlororhodium(I)-**1a**-α-acetamidocinnamic acid systems showed different absorption maxima corresponding to d-d transition in ethanol–benzene(2:1) solution (Fig. 3).

The introduction of aromatic substituent on the dioxolane ring of DIOP had a small effect on the steric control by DIOP in the hydrogenation of dehydroamino

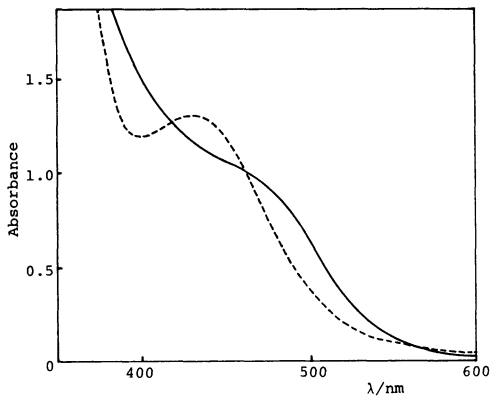
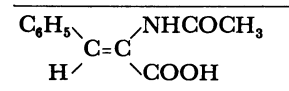
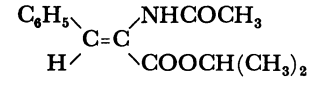
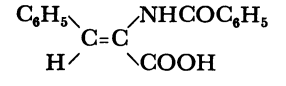
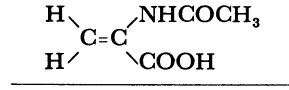


Fig. 3. Absorption spectra of Rh(I)-**1a**-α-acetamidocinnamic acid in ethanol–benzene(2/1).
——: cationic Rh(I)-**1a**-α-acetamidocinnamic acid; ----: neutral Rh(I)Cl-**1a**-α-acetamidocinnamic acid.

acid derivatives. Therefore, it will be necessary to introduce larger ring systems to cause a significant change in the face and edge conformation of the phenyl groups of the ligand.[7]

Results of hydrogenation of dehydroamino acids using unsymmetrical DIOPs (**3a—3d**) are summarized in Table 2. As shown in the Table, modification at the phosphino group influenced the optical yields depending on the combination of the ligand and substrate, though the (*R*)-selectivity held for all ligands. As for α-acetamidocinnamic acid, **3a** and **3d** afforded higher optical yields than DIOP did; **3d** gave an especially high yield about 90% e.e., suggesting the increased stereocontrol by the 2-naphthyl group. For isopropyl α-acetamidocinnamate, however, **3d** was less effective than (−)-DIOP. It is likely that the less electron-donating di-2-naphthylphosphino group favors the coordination of carbonyl oxygen in amido group of the substrate in the trans position on the rhodium complex, thus olefinic double bond occupying the cis position to the di-2-naphthylphosphino group.[4] So, bulky isopropyl group of ester would lower the stereoselectivity by the steric repulsion between naphthyl substituent of **3d** and isopropyl group of ester. For α-acetamidoacrylic acid **3d** gave only low optical yield. **3b** with *p*-methoxyphenyl group gave generally low optical yields, though the hydrogenation itself proceeded faster than the reaction with DIOP or **3a**. Using Rh(I)-DIOP catalysts, α-benzamidocinnamic acid was reduced with much lower optical yields than α-acetamidocinnamic acid, and the decrease in optical yields was large with **3a** or **3b** catalysts. In the case of **3a** or **3b** with an electron-donating substituent carbonyl oxygen in amido group of the substrate would occupy the cis position to the diarylphosphino group of **3a** or **3b**. Thus, substituent on the phenyl group of **3a** or **3b** would increase the steric repulsion with benzoyl group of the substrate. In the case of α-acetamidoacrylic acid, the difference between the steric factors by **3a** and **3b** seems to be not so large. Therefore, the large difference in optical yields between **3a** and **3b** for α-acetamidoacrylic acid would suggest that not only the steric effect but also the electronic effect by electron-donating substituent on the phenyl group played a role in the stereoselection.

Table 2. Asymmetric hydrogenation of dehydroamino acid derivatives with Rh(I)-unsymmetrical DIOP catalysts[a]

Substrate[b]	% e.e.[c]				
	(−)-DIOP	**3a**	**3b**	**3c**	**3d**
	79	83	68	63	88
	85	84	71	59	78
	62	55	40	—	—
	77	64	55	—	47

a) Hydrogenations were performed with cationic Rh(I) complexes in ethanol-benzene (2/1) under atmospheric hydrogen pressure at 20 °C. b) Substrate/Rh=200. c) Optical yields (% e.e.) were determined from the specific rotation of the product and that of optically pure substance.[2e,9] Absolute configuration of the products was (*R*) in every case.

In the CD spectra of the Rh(I)-unsymmetrical DIOP complexes, **3c** with 1-naphthyl groups showed the strongest CD spectra, suggesting a large stereoelectronic effect by 1-naphthyl substituent on the rhodium complex, but the rate of hydrogenation using **3c** was slow and the stereoselectivity was poor, presumably because of a very crowded structure around the phosphorus atom of the ligand.

The results of dehydrodipeptide reductions using modified DIOPs (**1a**, **1b**, and **3a—3d**) are shown in Table 3. In the reaction of Ac-ΔPhe-(*S*)-Phe-OH, which has a large steric factor, **1b** with a pyrene ring at the dioxolane ring gave a higher optical yield (64% d.e.) than DIOP (58% d.e.) and the reaction with **1b** pro-

Table 3. Asymmetric hydrogenation of dehydrodipeptides with Rh(I)-modified DIOP catalysts[a]

Dehydrodipeptide[b]	Diphosphine	Time / min	Conv. / %	(*S,S*)/(*R,S*) or (*S,R*)/(*R,R*)	% d.e.
Ac-ΔPhe-(*S*)-Phe-OH	(−)-DIOP	10	100	21/79	58
	1a	10	100	24/76	52
	1b	8	100	18/82	64
	3a	10	100	22/78	56
	3b	8	100	23/77	54
	3d	5	100	14/86	72
Ac-ΔPhe-(*S*)-Ala-OMe	(−)-DIOP	3	100	3/97	94
	3d	5	100	3/97	94
Ac-ΔPhe-(*R*)-Phe-OMe	(−)-DIOP	5	100	6/94	88
	3d	5	100	3/97	94

a) Hydrogenations were performed with cationic Rh(I) complexes in ethanol under atmospheric hydrogen pressure at 20 °C. b) Dehydrodipeptide/Rh=50.

ceeded faster than that with DIOP or **1a**, though **1b** was less effective than DIOP or **1a** for the reactions of dehydroamino acid derivatives. In the case of dehydrodipeptides, carboxyl group in the substrate would weakly occupy the apical site of the complex, and this will favor the stereoselection.[8] For Ac-ΔPhe-(*R*)-Phe-OH, DIOP and **1b** gave almost the same optical yields (92 and 90% d.e., respectively). Unsymmetrical **3a** and **3b** showed similar stereoselectivities to that by DIOP. It is noted that **3d** with 2-naphthyl groups afforded a higher optical yield (72% d.e.). We think that the di-2-naphthylphosphino group caused different congestions at two apical sites of the complex and had a different electronic effect on rhodium from that caused by the diphenylphosphino group. This would affect the fitting of dehydrodipeptide onto rhodium and the succeeding reactions on the complex. The effectiveness of **3d** was observed also in the cases of Ac-ΔPhe-(*S*)-Ala-OMe and Ac-ΔPhe-(*R*)-Phe-OMe to give high optical yields, more than 90% d.e..

Among the modified DIOPs, unsymmetrical DIOPs affected the stereocontrol in the asymmetric hydrogenation and the unsymmetrical DIOP with 2-naphthyl groups was effective for the hydrogenation of α-acetamidocinnamic acid and dehydrodipeptides. It will be possible to widen the applicability of the unsymmetrical ligands for other catalytic asymmetric reactions by selecting the diarylphosphino group.

Experimental

General Procedures. ^{1}H NMR spectra were recorded on a HITACHI R-24 spectrometer. Absorption spectra and CD spectra were recorded on a HITACHI 220A spectrophotometer and on a JASCO J-40A spectropolarimeter, respectively. Optical rotations were measured with a UNION P 101 automatic digital polarimeter.

Materials. α-Acetamidoacrylic and α-acetamidocinnamic acids were commercial products. α-Acylaminocinnamic acid derivatives and *N*-acetyldehydrodipeptides were prepared according to the literature.[2e,11-13] Chlorodiarylphosphines (aryl=*p*-tolyl, *p*-methoxyphenyl, 1-naphthyl, and 2-naphthyl) were prepared by the reaction of sodium diethyl phosphonite with corresponding Grignard reagent[14] followed by the reaction with PCl_3.[15] 2,3-*O*-Isopropylidene-1,4-di-*O*-tosyl-L-threitol,[16] 1,4-di-*O*-tosyl-L-threitol,[17] and (−)-DIOP[1b] were prepared by the methods reported. [Rh(nbd)(acac)] was prepared according to the literature.[18]

*Preparation of DIOP Derivatives Modified at the Dioxolane Ring (**1a** and **1b**).* 1,4-Di-*O*-tosyl-L-threitol was reacted with aromatic aldehyde (2-formylnaphthalene or 1-formylpyrene) in the presence of *p*-toluenesulfonic acid in dry benzene under reflux using a Dean-Stark trap.[17] Recrystallization of the product gave the acetal as white crystals. Phosphination of the acetal was performed in a THF solution using lithium diphenylphosphide. Solvent was evaporated and the residue was recrystallized from THF-ethanol after washing with ethanol to give white needles.

2,3-O-(2-Naphthylmethylene)-1,4-di-O-tosyl-L-thretiol: White crystals from THF-ethanol (42% yield). Mp 120.0—120.8 °C (corr.). ^{1}H NMR($CDCl_3$) δ=7.1—7.9 (15H, m, aromatic H), 5.1 (1H, s, CH), 4.3 (6H, bs, CH and CH_2), 2.36 (3H, s, CH_3), 2.31 (3H, s, CH_3).

2,3-O-(1-Pyrenylmethylene)-1,4-di-O-tosyl-L-threitol: White crystals from benzene-ethanol (55% yield). Mp 54.2—55.0 °C (corr.). ^{1}H NMR($CDCl_3$) δ=6.7—8.1 (22H, m, aromatic H and CH), 4.3 (6H, m, CH and CH_2), 2.3 (3H, s, CH_3), 2.2 (3H, s, CH_3).

*(−)-2,3-O-(2-Naphthylmethylene)-1,4-bis(diphenylphosphino)-2,3-butanediol (**1a**)*: White needles (66% yield). Mp 122—123 °C (corr., sealed tube). $[\alpha]_D^{25}$ −48.8° (*c* 0.48, C_6H_6). ^{1}H NMR($CDCl_3$) δ=7.2—7.9 (27H, m, aromatic H), 6.0 (1H, s, CH), 4.0—4.4 (2H, m, CH), 2.55 (4H, d, CH_2).

*(−)-2,3-O-(1-Pyrenylmethylene)-1,4-bis(diphenylphosphino)-2,3-butanediol (**1b**)*: White needles (66% yield). Mp 158.5—159.1 °C (corr., sealed tube). $[\alpha]_D^{25}$ −70.0° (*c* 0.55, C_6H_6). ^{1}H NMR($CDCl_3$) δ=7.8—8.3 (9H, m, aromatic H), 7.1—7.6 (20H, m, aromatic H), 6.8 (1H, s, CH), 4.1—4.6 (2H, m, CH), 2.5—2.7 (4H, q, CH_2).

*Preparation of Unsymmetrical DIOPs (**3a**—**3d**).* *(−)-2,3-O-Isopropylidene-4-diphenylphosphino-1-O-tosyl-1,2,3-butanetriol (**2**)*: To a THF solution of 2,3-*O*-isopropylidene-1,4-di-*O*-tosyl-L-threitol (ditosylate), 0.5 molar excess of lithium diphenylphosphide in THF was added slowly over 8 h and the mixture was stirred for another 12 h. Evaporation of solvent and extraction of the residue with dry benzene gave an oily crude product. Extraction of by-products (DIOP and tetraphenyldiphosphane) from the oily product with hot hexane gave monophosphine **2** as a very viscous oil containing a small amount of ditosylate (less than 5 mol%). 49% yield. ^{1}H NMR($CDCl_3$) δ=7.2—7.9 (14H, m, aromatic H), 3.6—4.2 (4H, m, CH and CH_2), 2.3—2.5 (5H, d, CH_2 and CH_3), 1.4 (3H, s, CH_3), 1.2 (3H, s, CH_3).

Phosphination of **2** was performed by adding a THF solution of **2** slowly to 0.2—0.4 molar excess of lithium diarylphosphide in THF. Solvent was evaporated and the residue was extracted with ether. The ether extract was concentrated. After removing tetraaryldiphosphane (Ar_2P-PAr_2) and unreacted **2** by cooling at −20 °C, unsymmetrical DIOP was precipitated by adding hexane to the ethereal mother liquor and cooling at −20 °C.

*(−)-2,3-O-Isopropylidene-1-diphenylphosphino-4-(di-p-tolylphosphino)-2,3-butanediol (**3a**)*: Viscous oil (68% yield). $[\alpha]_D^{25}$ −6.6° (*c* 0.7, C_6H_6). ^{1}H NMR($CDCl_3$) δ=6.9—7.6(18H, m, aromatic H), 3.7—4.2 (2H, m, CH), 2.2—2.5 (10H, m, CH_2 and CH_3), 1.3 (6H, s, CH_3).

*(−)-2,3-O-Isopropylidene-1-diphenylphosphino-4-[bis(p-methoxyphenyl)phosphino]-2,3-butanediol (**3b**)*: Viscous oil (*ca.* 40% yield). ^{1}H NMR ($CDCl_3$) δ=6.8—7.7 (18H, m, aromatic H), 3.7—4.0 (2H, m, CH), 3.8 (6H, s, OCH_3), 2.9 (4H, m, CH_2), 1.35 (3H, s, CH_3), 1.25 (3H, s, CH_3).

*(−)-2,3-O-Isopropylidene-1-diphenylphosphino-4-(di-1-naphthylphosphino)-2,3-butanediol (**3c**)*: Pale yellow solid (*ca.* 25% yield). ^{1}H NMR($CDCl_3$) δ=7.0—8.8 (25H, m, aromatic H), 4.0—4.3 (2H, m, CH), 2.4—2.6 (4H, m, CH_2), 1.35 (6H, bs, CH_3).

*(−)-2,3-O-Isopropylidene-1-diphenylphosphino-4-(di-2-naphthylphosphino)-2,3-butanediol (**3d**)*: Viscous oil (*ca.* 25% yield). ^{1}H NMR($CDCl_3$) δ=7.0—8.2 (25H, m, aromatic H), 4.0—4.3 (2H, m, CH), 2.4—2.5 (4H, m, CH_2), 1.4 (3H, s, CH_3), 1.3 (3H, s, CH_3).

TLC analysis and NMR spectra showed that **3c** and **3d** contained corresponding tetranaphthyldiphosphane (about 10%).

Preparation of Cationic Rhodium(I) Complexes. Cationic Rh(I) complexes [Rh(diphosphine)(nbd)]$^+BF_4^-$ were prepared from [Rh(nbd)(acac)], modified DIOP and $NaBF_4$ in CH_2Cl_2-H_2O two phase system,[19] and the complexes were recrystallized from methanol-ether.

*[Rh(**1a**)(nbd)]$^+BF_4^-$*: Orange-red crystals (60% yield). ^{1}H NMR($CDCl_3$) δ=7.3—7.8 (27H, m, aromatic H), 5.9 (1H, s, CH), 4.5 (4H, m, olefinic H), 3.9—4.1 (4H, m, CH), 2.8—3.1 (4H, m, CH_2), 1.5 (2H, m, CH_2).

*[Rh(**1b**)(nbd)]$^+BF_4^-$*: Bright red crystals (82% yield). ^{1}H NMR($CDCl_3$) δ=7.2—8.0 (29H, m, aromtic H), 6.8 (1H,

s, CH), 4.4—4.6 (4H, m, olefinic H), 3.8—4.1 (4H, m, CH), 2.9—3.2 (4H, m, CH_2), 1.4 (2H, m, CH_2).

[Rh(3a)(nbd)]$^+BF_4^-$: Orange-red crystals (60% yield). ^1H NMR($CDCl_3$) δ=7.2—7.8 (18H, m, aromatic H), 4.4—4.7 (4H, m, olefinic H), 3.5—4.2 (4H, m, CH), 2.4—3.0 (4H, m, CH_2), 2.45 (3H, s, CH_3), 2.50 (3H, s, CH_3), 1.55 (2H, m, CH_2), 1.2 (6H, s, CH_3).

[Rh(3b)(nbd)]$^+BF_4^-$: Orange crystals (69% yield). ^1H NMR($CDCl_3$) δ=7.0—7.8 (18H, m, aromatic H), 4.3—4.6 (4H, m, olefinic H), 3.7—4.0 (4H, m, CH), 3.85 (3H, s, OCH_3), 3.90 (3H, s, OCH_3), 2.2—2.8 (4H, m, CH_2), 1.5 (2H, m, CH_2), 1.2 (6H, s, CH_3).

[Rh(3c)(nbd)]$^+BF_4^-$: Orange crystals (39% yield). ^1H NMR($CDCl_3$) δ=7.0—8.5 (24H, m, aromatic H), 4.3—4.8 (4H, m, olefinic H), 3.8—4.2 (4H, m, CH), 2.5 (4H, m, CH_2), 1.4 (2H, m, CH_2), 1.2 (3H, s, CH_3), 1.1 (3H, s, CH_3).

[Rh(3d)(nbd)]$^+BF_4^-$: Orange crystals (32% yield). ^1H NMR($CDCl_3$) δ=7.2—8.2 (24H, m, aromatic H), 4.5—4.9 (4H, m, olefinic H), 3.8—4.2 (4H, m, CH), 2.3—2.4 (4H, m, CH_2), 1.6 (2H, m, CH_2), 1.3 (3H, s, CH_3), 1.2 (3H, s, CH_3).

Hydrogenations. Typically, dehydroamino acid derivatives (2 mmol) was hydrogenated using 0.01 mmol of cationic Rh(I) catalyst in 10 cm^3 benzene-ethanol(2/1). Optical yields were determined polarimetrically. In the case of dehydrodipeptides, 1 mmol of dehydrodipeptide was hydrogenated with 0.02 mmol of Rh(I) catalyst in 3 cm^3 ethanol. Diastereomeric excess and the chirality, newly formed, were determined by ^1H NMR with shift reagent.

Absorption Spectra Measurements. Hydrogen was introduced to a 10 mm cell containing [Rh(**1a**)(nbd)]$^+BF_4^-$ or neutral chlororhodium complex from $[Rh(nbd)Cl]_2$ and **1a** (**1a**/Rh=1.1) in ethanol-benzene. The cell was shaken until the absorption of coordinated olefin disappeared. Then the cell was evacuated and α-acetamidocinnamic acid solution was added under nitrogen (Rh: 0.5 mmol/dm^3).

CD Spectra Measurements. CD spectra of cationic Rh(I) complexes [Rh(diphosphine)(nbd)]$^+BF_4^-$ were recorded in methanol solution (0.5 mmol/dm^3) using a 10 mm cell under nitrogen.

The authors express their gratitude to Professor M. Kobayashi and Dr. N. Kamigata, Tokyo Metropolitan University, for CD spectroscopy.

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