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Axially Dissymmetric Bis(aminophosphine)s Derived from 2,2′-Diamino-1,1′-binaphthyl. Synthesis and Application to Rhodium(I)-Catalyzed Asymmetric Hydrogenations[1)]

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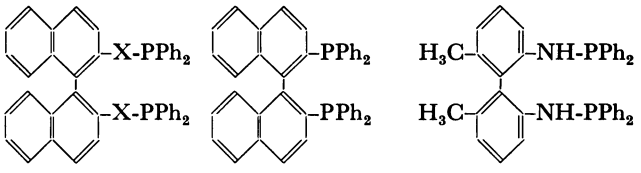
Axially dissymmetric bisphosphine ligands, (*R*)- and (*S*)-2,2′-bis(diphenylphosphinoamino)-1,1′-binaphthyl (BDPAB) and (*R*)-2,2′-bis[*N*-(diphenylphosphino)methylamino]-1,1′-binaphthyl (Me-BDPAB) were conveniently prepared from 2,2′-diamino-1,1′-binaphthyl. The rhodium(I)-catalyzed asymmetric hydrogenation of α-acylamidoacrylic acids and esters gave the corresponding amino acids of up to 95% optical purity. The sign of the centro-chirality of the product amino acids was always the same to that of the axial chirality of the ligand in both cases of BDPAB and Me-BDPAB.

Asymmetric hydrogenation of prochiral olefins catalyzed by rhodium(I)-chiral phosphine complexes has been widely studied.[2)] Although the mechanism of the hydrogenation has recently been greatly clarified,[3)] there has still been continuing interest in the synthesis of novel chiral phosphine ligands,[4)] as subtle variations in ligand structure not only greatly affect the optical yields but sometimes alter even the absolute configuration of the preferential products. Some of these ligands have shown enantioselectivity which rivals that of enzymic reactions. However, the synthesis and isolation of many of chiral phosphines require tedious manipulations, imposing some restrictions to their wide use. In this regard, aminophosphines have recently attracting much interest because they can be readily prepared and show high stereoselectivity in the rhodium-catalyzed asymmetric hydrogenation.[5)]

Axially dissymmetric 1,1′-binaphthyl moiety has proved to be highly desirable asymmetry-inducing unit because of its structural rigidity and simplicity, resistance to racemization, and above all, effectiveness of chiral recognition.[6)] Three research groups have reported chiral bisphosphine ligands, **1a** (NAPHOS),[7)] **1b**,[8)] and **2** (BINAP),[9)] which contain the atropisomeric 1,1′-binaphthyl residue as the chiral element for use in the rhodium-catalyzed asymmetric hydrogenation of prochiral olefins. Recently a biphenyl phosphine **3** (MABP) has appeared.[10)]



1 a -X- = $-CH_2-$ (NAPHOS)
b -X- = -O-
c -X- = -NH- (BDPAB)
d -X- = $-N(CH_3)-$ (Me-BDPAB)

2 (BINAP)

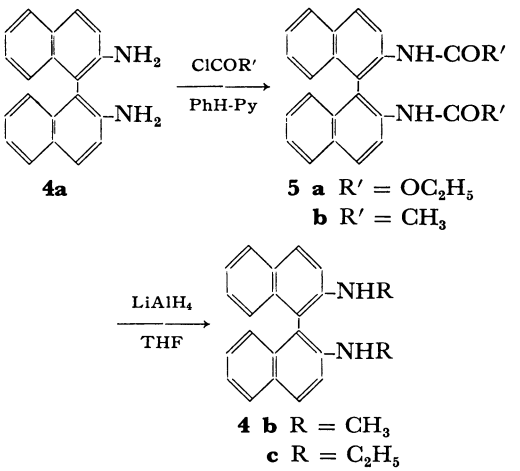
3 (MABP)

We ourselves have reported briefly a facile synthesis of (*R*)- and (*S*)-2,2′-bis(diphenylphosphinoamino)-1,1′-binaphthyl (**1c**, hereafter abbreviated as BDPAB) and asymmetric hydrogenation of α-acylamidoacrylic acids and esters by use of Rh(I)–BDPAB complexes.[1)] In this paper, we wish to report the results we have obtained in the course of this investigation including the synthesis of 2,2′-bis[*N*-(diphenylphosphino)methylamino]-1,1′-binaphthyl (**1d**, Me-BDPAB).

Results and Discussion

Synthesis of 2,2′-Diamino-1,1′-binaphthyls. According to the method reported briefly by Clemo and Dawson,[11)] 2-naphthol was converted to 2,2′-diamino-1,1′-binaphthyl (**4a**) by heating with hydrazine hydrate to 170—180 °C in a sealed vessel, and then treating with hot aq HCl. Although the yield of the diamine was not so much good (less than 40% at our hand) and the formation of carcinogenic 2-naphthylamine as a by-product requires careful handling of the reaction mixture, the procedure seems to be the one of choice because of operational simplicity and inexpensive starting materials.[12)] Both enantiomers of the diamine (**4a**) were readily obtained by the method of Kuhn and Goldfinger using *d*-camphorsulfonic acid as the resolving agent.[12)]

Preparation of 2,2′-bis(methylamino)- and 2,2′-bis(ethylamino)-1,1′-binaphthyl (**4b** and **4c**) is summarized in Eq. 1. Treatment of parent diamine **4a** with



4a

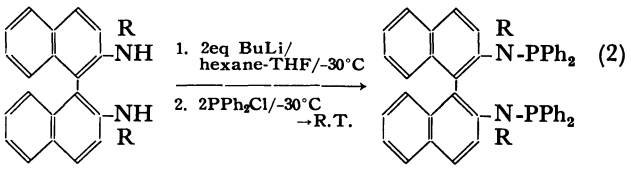
5 a R′ = OC_2H_5
b R′ = CH_3

4 b R = CH_3
c R = C_2H_5

(1)

ethyl chloroformate in benzene-pyridine gave 2,2′-bis(ethoxycarbonylamino)-1,1′-binaphthyl (**5a**), which was then boiled with lithium aluminium hydride (LAH) in THF to give **4b**. By using (*R*)- or (*S*)-**4a**, the corresponding atropisomeric **4b** was obtained. Similar treatment of diamine **4a** with acetyl chloride and then reduction with LAH gave *N*-ethyl analogue, **4c**.

Synthesis of 2,2'-Bis(diphenylphosphinoamino)-1,1'-binaphthyls. At first, diamine **4a** was treated with diphenylphosphinous chloride in THF in the presence of triethylamine or pyridine according to the conventional procedure,[5] but no detectable amount of phosphinated amine was resulted. Then, racemic **4a** was *N,N'*-dilithiated with stoichiometric amount of butyllithium in THF–hexane at −30 °C followed by treatment with diphenylphosphinous chloride; BDPAB **1c** was obtained as white crystals in a 75% yield (Eq. 2). Similar treatment of (*R*)- and (*S*)-**4a** gave the corresponding (*R*)- and (*S*)-BDPAB, respectively. The (*R*)-BDPAB was recrystallized twice from ethanol–benzene to show $[\alpha]_D^{23}$+27.2° in benzene. Significant racemization of the axial dissymmetry is ruled out considering the high asymmetric induction in the Rh(I)-catalyzed hydrogenation of (*Z*)-α-benzamidocinnamic acid (*vide infra*).



(2)

4 a R = H
b R = CH_3

1 c R = H (BDPAB)
d R = CH_3 (Me-BDPAB)

N-Methyl analogue of BDPAB, 2,2'-bis[*N*-(diphenylphosphino)methylamino]-1, 1'-binaphthyl (**1d**, Me-BDPAB), was prepared from **4b** by the similar procedure. (*R*)-Me-BDPAB was obtainable by use of (*R*)-**4b**. *N*-Ethylamine **4c**, however, did not afford the (ethylamino)phosphine (Et-BDPAB) even under somewhat forcing conditions. This was unexpected result at first, but inspection of CPK molecular models suggests that replacement of *N*-ethyl for *N*-methyl substituent imposes rather severe steric bulk on the amide anion due to the steric repulsion against naphthalene nucleus, and thus inhibits the nucleophilic attack to phosphorous center.

Asymmetric Hydrogenation. Generally, chiral catalysts were prepared just prior to the hydrogenation by mixing $[Rh(olefin)_2Cl]_2$ with 2.2 molar amount of one of the chiral bis(aminophosphine)s in the presence or absence of sodium tetraphenylborate under an inert atmosphere. Hydrogenation of several olefinic substrates was carried out in a glass tube placed in an autoclave. After the reaction, products were recovered according to the literature.[13] The optical yields were determined by comparing the rotations of the isolated products with those of the reported values for the pure enantiomers.

Table 1 shows the effects of reaction variables on the hydrogenation of (*Z*)-α-acetamidocinnamic acid using (*R*)- or (*S*)-BDPAB as the ligand. Reaction medium significantly affected the catalyst activity and optical yield. Solvent comprised of a 1:2 mixture of benzene and methanol or ethanol gave good results; the hydrogenation proceeded almost quantitatively at initial hydrogen pressure of 30 kg/cm² at ambient temperature with high optical yield. In such solvent system, the active catalyst seemed to be a cationic rhodium(I) species,[14] as was demonstrated from the fact that comparable result was obtained by using [Rh(COD)(*R*)-BDPAB]$^+BF_4^-$ as the catalyst. The optical yield was rather insensitive to the hydrogenation pressure, while addition of triethylamine was harmful to chiral recognition.[15]

Table 2 summarizes the results of the hydrogenation of several olefinic substrates. High optical yields (80—95%) were obtained with (*R*)- and (*S*)-BDPAB ligand in the hydrogenation of α-acetamidoacrylic acids **6a**—**6c**, ester **6e**, and itaconic acid **6g**. Comparison of these results with those reported by Tamao *et al.*[7] and by Grubbs and DeVries[8] shows that among bisphosphine ligands **1** which apparently form a nine-membered chelate ring, BDPAB (**1c**) is superior to NAPHOS (**1a**) or phosphite **1b** in chiral recognition in the hydrogenation of dehydroamino acids. Although the conversion was low, an appreciable optical yields were obtained with (*E*)-α-methylcinnamic acid. Simple olefin **6h** reacted completely but gave poor optical yields.

Recent studies on the mechanism of asymmetric hydrogenation of dehydroamino acids have demonstrated that thermodynamic and kinetic profiles of the process must be clarified before correlating catalyst structure to the product conformation.[3] It is widely accepted, however, that a chiral ligand which can fix rigid complex catalyst is essential for effective

Table 1. Asymmetric hydrogenation of (z)-α-acetamidocinnamic acid catalyzed by Rh(I)-BDPAB[a]

Catalyst[b]	Config. of BDPAB	Solvent /ml	Initial H_2 pres. /kg/cm²	Opt. yield[c] /%	Config. of product
A	R	EtOH(8)–PhH(4)	30	85	R
A	R	MeOH(8)–PhH(4)	30	89	R
A	R	EtOH(8)–PhH(4)	30	29[d]	R
A	R	*i*-PrOH(10)–PhH(5)	30	15	R
A	R	$PhCH_3$(12)–Me_2CO(12)	30	7[e]	R
A	S	THF(12)	80	9.5[f]	S
B	R	MeOH(8)–PhH(4)	5	87	R
B	R	MeOH(8)–PhH(4)	10	85	R
B	R	MeOH(8)–PhH(4)	30	90	R
B	R	MeOH(8)–PhH(4)	80	68	R
C	R	MeOH(6)–PhH(6)	30	91	R

a) Reaction conditions: Substrate **6b**, 0.45—0.50 g; [**6b**]/[Rh] (mol/mol)=50; 24—25 °C, 24 h. Conversion was 100% unless otherwise noted. b) A: 1/2[Rh(cycooctene)$_2$Cl]$_2$+1.1(p*—p) or 1/2[Rh(COD)Cl]$_2$+1.1(p*—p). B: 1/2[Rh(COD)Cl]$_2$+1.1(p*—p)+3$NaBPh_4$. C: [Rh(COD)(*R*)-BDPAB]$^+BF_4^-$. c) See footnote e) in Table 2. d) Et_3N was added ([Et_3N]/[Rh] (mol/mol)=4.7). e) Conversion, 20%. f) Conversion, 32%.

Table 2. Asymmetric hydrogenation of olefinic substrates[a]

Substrate	Catalyst[b]	Ligand[c]	Solvent[d]	Opt. yield/%[e]	Config. of product
$CH_2=C(NHCOCH_3)(COOH)$ (6a)	A	(*R*)	EtOH-PhH	86	*R*
	A	(*S*)	EtOH-PhH	88	*S*
	A	(*R*)-Me	EtOH-PhH	90	*R*
$Ph(H)C=C(NHCOCH_3)(COOH)$ (6b)	A	(*R*)	MeOH-PhH	89	*R*
	A	(*R*)-Me	EtOH-PhH	36	*R*
$Ph(H)C=C(NHCOPh)(COOH)$ (6c)	A	(*R*)	EtOH-PhH	95	*R*
	A	(*R*)-Me	EtOH-PhH	61	*R*
$Ph(H)C=C(NHCOCH_3)(COOCH_3)$ (6d)	A	(*R*)	MeOH-PhH	69	*R*
$Ph(H)C=C(NHCOPh)(COOCH_3)$ (6e)	A	(*R*)	MeOH-PhH	89	*R*
$Ph(H)C=C(CH_3)(COOH)$ (6f)	A	(*S*)	EtOH-PhH	47[f]	*S*
	B	(*R*)	MeOH-PhH	49[g]	*R*
$CH_2=C(CH_2COOH)(COOH)$ (6g)	B	(*R*)	MeOH-PhH	80	*S*
	B	(*S*)	MeOH-PhH	77	*R*
	B	(*R*)-Me	MeOH-PhH	40	*S*
$CH_2=C(Ph)(C_2H_5)$ (6h)	B	(*R*)	MeOH-PhH	2.4[h]	*S*
	B	(*R*)-Me	MeOH-PhH	1.3[h]	*S*

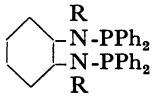
a) See footnote a) in Table 1; initial H_2 pressure, 30 kg/cm^2. b) See footnote b) in Table 1. c) (*R*): (*R*)-BDPAB. (*S*): (*S*)-BDPAB. (*R*)-Me: (*R*)-Me-BDPAB. d) ROH(8—10 ml)-PhH(4—5 ml). e) Optical yields were determined on the basis of the reported rotation for the optically pure enantiomers: (*R*)-*N*-acetylalanine,[25] $[\alpha]_D^{26}$+66.3°(*c* 2.0, H_2O); (*S*)-*N*-acetylphenylalanine,[25] $[\alpha]_D^{26}$+46.0°(*c* 1.0, EtOH); (*S*)-*N*-benzoylphenylalanine,[25] $[\alpha]_D^{27}$—40.3° (*c* 1.0, MeOH); (*S*)-2-methyl-3-phenylpropionic acid,[26] $[\alpha]_D^{25}$+27.06° (PhH); (*R*)-methylsuccinic acid,[25] $[\alpha]_D^{20}$+16.88° (*c* 2.16, EtOH); (*R*)-2-phenylbutane,[27] $[\alpha]_D^{20}$—27.31°(neat); (*S*)-*N*-acetylphenylalanine methyl ester,[14] $[\alpha]_D^{25}$+21.4° (*c* 1.9, MeOH); (*S*)-*N*-benzoylphenylalanine methyl ester,[14] $[\alpha]_D^{25}$—45.3° (*c* 1.3, EtOH). Values for the (*S*)-BDPAB were corrected for the 95% optical purity of the ligand. f) Conversion, 38%. g) Conversion, 54%. h) [Substrate]/[Rh] (mol/mol)=160.

dissymmetric discrimination, and here we would like to point out some structural features of the BDPAB ligand.

It is noted that the hydrogenation of (*Z*)-dehydroamino acids **6a—6e** using (*R*)-BDPAB ligand always gave (*R*)-α-amino acids preferentially, and (*S*)-BDPAB preferred (*S*)-counterparts. Similar ligand-product relationship in chirality is reported in the hydrogenation of **6b** with (*S*)-NAPHOS.[7] Examination of CPK molecular models suggests that (*R*)-BDPAB confines rigid nine-membered chelate ring with square planar Rh(I) containing hardly flexible 1,1′-binaphthyl skeleton, arraying four phenyl rings in an alternating edge-face manner as is observed in the seven-membered (*R*,*R*)-DIOP-Rh(I) complex of nearly δ-conformation.

On the other hand, Miyashita *et al.* have shown that BINAP ligand (**2**) fixes seven-membered chelate ring of λ-skew-boat conformation, and that (*R*)- and (*S*)-BINAP induce (*S*)- and (*R*)-chirality, respectively, in the Rh(I)-catalyzed hydrogenation of (*Z*)-α-acylamidoacrylic acids. That is, the sense of asymmetric induction is quite opposite between BDPAB and BINAP. It is surprising that MABP (**3**),[10] which seems to form closely related Rh(I)-complex to BDPAB, also gave opposite enantioselection in the hydrogenation of (*Z*)-α-acetamidoacrylic acid to *N*-acetylalanine, and at present we have no idea to explain these results.

It has been reported that *N*-methylation of 1,2-bis(diphenylphosphinoamino)ethane-type ligand such as **7a** to **7b** causes inversion of the chiral stereoselectivity on the Rh(I)-catalyzed hydrogenation of α-acetamidoacrylic acids.[5d,5e] This drastic change in stereoselectivity has been explained from the structural studies of the complexes including X-ray analysis that the helical orientation of the phenyl rings of the ligand would be inverted by *N*-methyl groups in the aminophosphine when coordinated to rhodium.[16]



7 a R = H
b R = CH_3

In all cases examined, however, hydrogenation with (*R*)-Me-BDPAB ligand gave reduction products of the same chirality to those obtained with (*R*)-BDPAB ligand, although the effects of *N*-methylation on optical yields were different from substrate to substrate (Table 2). It seems that the rigid 1,1′-binaphthyl skeleton is mostly responsible for the overall structure

of BDPAB-type ligand regardless of the presence or absence of *N*-methyl substituents.

Experimental

Measurements. IR spectra were obtained on a Shimadzu IR 430 spectrophotometer. NMR spectra were determined on a Hitachi R-24A instrument using hexamethyldisiloxane as an internal standard. Mass spectra were recorded on a JEOR-D 300 double focussing mass spectrometer with direct sample injection. Optical rotations were recorded on a Union PM-101 automatic digital polarimeter. Melting points were corrected.

Materials. Following commercial materials were recrystallized or distilled before use; α-acetamidoacrylic acid (**6a**) (mp 185—186 °C), (*Z*)-α-acetamidocinnamic acid (**6b**) (mp 185—187 °C (H_2O)), and itaconic acid (**6g**) (mp 169.5—171.5 °C (EtOH)). (*Z*)-α-Benzamidocinnamic acid (**6c**) (mp 229—231 °C),[17] (*E*)-α-methylcinnamic acid (**6f**) (mp 81—81.5 °C),[18] 2-phenyl-1-butene (**6h**) (bp 66—67 °C/20 mmHg†)[19] were prepared by standard methods. Methyl (*Z*)-α-acetamidocinnamate (**6d**) (mp 122.5—124 °C (MeOH)) and methyl (*Z*)-α-benzamidocinnamate (**6e**) (mp 140—141 °C (MeOH)) were obtained by the reaction of diazomethane with **6b** and **6c**, respectively. $[Rh(cyclooctene)_2Cl]_2$[20] and $[Rh(COD)Cl]_2$[21] were prepared according to the literature. Commercial BuLi in hexane (*ca.* 15% solution) was titrated before use.[22] Solvents were purified as usual under nitrogen. All reactions involving phosphines were routinely performed under an inert atmosphere of nitrogen or argon.

*2,2'-Diamino-1,1'-binaphthyl (**4a**).* Clemo and Dawson's procedure[11] was utilized as follows: 2-Naphthol (40.0 g, 0.278 mol) and 8.8 ml of hydrazine hydrate (80% solution, *ca.* 0.14 mol) were heated in a *ca.* 90 ml inner-volume stainless steel autoclave at 170—180 °C for 48 h. After the vessel was cooled, it was opened and the contents were remelted by heating. The yellowish viscous material was poured into a 2-necked round-bottom flask containing 600 ml of 1:1 HCl. To the flask were attached mechanical stirrer and a reflux condenser. The stirred mixture was heated at reflux, during which time brown tarry matter appeared. After standing for a while, supernatant liquid was siphoned off. Similar hot extraction was repeated 3 times by using 300 ml of 1:1 HCl each time. The combined HCl extracts were made alkaline by cautious addition of NaOH pellets with ice-cooling. The mixture was boiled and filtered while hot. Then, the precipitate was boiled in 500 ml of water and filtered hot; the procedure was repeated several times to thoroughly remove 2-naphthylamine. The precipitate was dissolved in a 400 ml of 2 M†† HCl, filtered hot from activated charcoal. The filtrate was made alkaline with 10% NaOH; formed precipitate was filtered off and dried *in vacuo*, 14.4 g (36.6%), mp 187—188 °C. Recrystallization from ethanol–acetone gave a pure sample of mp 193.2—194.3 °C (lit,[23] mp 193 °C); IR (KBr): 3450, 3300, 3100, 1610, 1500, 1430, 1380, 1350, 1280, 810, and 750 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.5 (4H, br), 6.9—7.3 (8H, m), and 7.5—7.8 (4H, m). Found: C, 84.41; H, 5.67; N, 9.72%. Calcd for $C_{20}H_{16}N_2$: C, 84.48; H, 5.67; N, 9.85%.

*Resolution of **4a**.* The method was Kuhn and Goldfinger's,[12] while control of temperature seemed important to obtain fine precipitate of the less soluble diastereomer salt. (±)-Diamine (**4a**) (10.5 g, 36.9 mmol) was dissolved in 300 ml of chlorobenzene with warming up to 70 °C. To the stirred solution kept at *ca.* 50 °C was added slowly a solution of *d*-camphorsulfonic acid monohydrate (8.4 g, 34 mmol) in ethanol (60 ml). By the end of the addition, fine white crystals began to deposit. The mixture was stirred till it reached to room temperature, and then allowed to stand overnight. The precipitate was filtered off, washed with chlorobenzene (50 ml×3), and dried *in vacuo* to give (*d*)-(*d*)-salt, $[\alpha]_D^{23}$+101° (*c* 0.86, py) (lit,[23] $[\alpha]_D^{19}$+103.6° (*c* 1.05, py)); IR (KBr): 3450, 3300, 1740, 1130, and 1030 cm^{-1}. The salt was dissolved in 60 ml of pyridine, and poured into 500 ml of water to give white suspension. Solid was collected by filtration, dissolved in 200 ml of 2 M HCl, decolorized with activated charcoal, and filtered. The filtrate was made alkaline with aq NH_3 to give white precipitate, which was recovered by filtration, dried, and recrystallized from ethanol–benzene to give 4.50 g (86%) of (*R*)-(+)-**4a**; mp 245—246 °C (lit,[24] mp 245 °C); $[\alpha]_D^{22}$+157.4° (*c* 0.712, py) (lit,[23] $[\alpha]_D^{21-22}$ +151.7° (*c* 0.5-1, py)). A weak, but somewhat broad IR absorption at 1105 cm^{-1} of (±)-**4a** was missing in (*R*)-**4a**. Found: C, 84.29; H, 5.63; N, 9.45%.

The above chlorobenzene–ethanol filtrate which contained more soluble (*d*)-(*l*)-salt was evaporated *in vacuo* to leave brown residue, which was treated as above to liberate free (*S*)-(−)-base. The crude material was recrystallized twice from ethanol–benzene, 2.5 g (48%), mp 244—246 °C, $[\alpha]_D^{23}$−153.0° (*c* 0.758, py). Found: C, 84.50; H, 5.77; N, 9.53%.

*2,2'-Bis(ethoxycarbonylamino)-1,1'-binaphthyl (**5a**).* To a stirred, water-chilled solution of racemic **4a** (3.95 g, 13.9 mmol) in benzene (80 ml) and pyridine (10 ml) was added dropwise a solution of ethyl chloroformate (3.75 g, 34.6 mmol) in benzene (20 ml). After the addition was complete, the mixture was stirred for 2 h at ambient temperature. The reaction was quenched by adding 100 ml of 10% NaOH. The resulting organic layer and benzene extracts (50 ml×2) from the aqueous layer were combined, washed with water and dried over $MgSO_4$. The solvents were evaporated *in vacuo*, and resulting residue was recrystallized from ethanol–acetone to give 3.77 g of diester **5a** (63.3%); mp 155—156 °C; IR (KBr): 3400, 3300, 2900, 1720, 1600, 1490, 1210, 1090, 820, and 740 cm^{-1}cm ; ^1H NMR (acetone-d_6) δ=1.0 (6H, t, *J*=6.8 Hz), 2.7 (2H, s), 3.9 (4H, q, *J*=6.8 Hz), 6.8—7.5 (8H, m), and 7.6—8.3 (4H, m). Found: C, 72.95; H, 5.71; N, 6.20%. Calcd for $C_{26}H_{24}O_4N_2$: C, 72.88; H, 5.65; N, 6.54%.

*(R)-(+)-**5a***: Similar treatment of (*R*)-(+)-**4a** (2.2 g, 7.7 mmol) gave (*R*)-(+)-**5a**, 2.2 g (67%), mp 70—72 °C, $[\alpha]_D^{23}$+68.5° (*c* 1.23, THF).

*2,2'-Bis(methylamino)-1,1'-binaphthyl (**4b**).* To a stirred suspension of LAH (4 g) in 100 ml of THF was added dropwise a solution of **5a** (7.6 g, 17.7 mmol) in 50 ml of THF. The mixture was heated at reflux for 3 h. The reaction mixture was cooled in an ice-bath and the remaining hydride was carefully quenched by dropwise addition of water (5 ml) and then 15% NaOH (5 ml). A white precipitate was filtered off and thoroughly washed with ether. The combined filtrate and ether washings were washed with water, dried over Na_2SO_4 overnight. After the solvents were evaporated under reduced pressure, the residue was recrystallized from ethanol–benzene, 4.5 g (81%); mp 149—151 °C; IR (KBr): 3400, 1620, 1600, 1500, 1420, 1340, 1300, 1170, 1150, 810, and 750 cm^{-1}. ^1H NMR (acetone-d_6) δ=2.7 (6H, d, *J*=6.0 Hz), 3.9 (2H, br), 6.5—7.3 (8H, m), and 7.3—8.0 (4H, m). Found: C, 84.37; H, 6.40; N, 8.96%. Calcd for $C_{22}H_{20}N_2$: C, 84.58; H, 6.45; N, 8.97%.

*(R)-(+)-**4b***: The (*R*)-(+)−**5a** (1.53 g, 3.56 mmol) was treated with LAH (0.9 g) in 50 ml of THF and worked up as above. After removal of volatiles *in vacuo*, the residue was recrystallized from ethanol to give (*R*)-(+)-**4b**, 0.73 g (66%), mp 143—144 °C, $[\alpha]_D^{23}$+182° (*c* 1.09, PhH). Found: C, 84.21; H, 6.59; N, 8.82%.

*2,2'-Bis(ethylamino)-1,1'-binaphthyl (**4c**).* A mixture of diamine **4a** (1.2 g, 4.2 mmol) and acetyl chloride (1.1 g,

† 1 mmHg≈133.322 Pa.

†† 1 M=1 mol dm^{-3}

14 mmol) in benzene (40 ml) and pyridine (8 ml) was stirred overnight at ambient temperature. Organic residue obtained after usual workup was recrystallized from ethanol to give a 1.22 g sample (79% yield) of 2,2′-bis(acetamido)-1,1′-binaphthyl **5b**, mp 235—235.5 °C; IR (KBr): 3300, 1670, 1600, 1490, 1420, 1270, 820, and 740 cm^{-1}. ^1H NMR ($CDCl_3$+DMSO-d_6) δ=1.7 (6H, s) and 6.5—8.3 (14H, m); MS (70 eV), *m/z* (%) 369 (M+1, 3.0) and 368 (M^+, 10.5). Found: C, 78.13; H, 5.60; N, 7.65%. Calcd for $C_{24}H_{20}N_2O_2$: C, 78.24; H, 5.47; N, 7.60%.

A mixture of **5b** (0.50 g, 1.4 mmol) and LAH (0.3 g) was boiled in 35 ml of THF for 3 h. The mixture was worked up as was stated in the synthesis of **4b**. Recrystallization from ethanol gave 0.25 g of **4c** (54%), mp 127.5—128 °C; IR (KBr): 3400, 2900, 1610, 1600, 1480, 1410, 1320, 1290, 1140, 800, and 740 cm^{-1}: ^1H NMR ($CDCl_3$) δ=0.95 (6H, t, *J*=7.0 Hz), 3.1 (4H, q, *J*=7.0 Hz), 3.9 (2H, br), and 6.5—8.0 (12H, m); MS (70 eV), *m/z* (%), 341 (M+1, 8.8) and 340 (M^+, 29.8). Found: C, 84.21; H, 6.88; N, 8.03%. Calcd for $C_{24}H_{24}N_2$: C, 84.67; H, 7.11; N, 8.23%.

*2,2′-Bis(diphenylphosphinoamino)-1,1′-binaphthyl (**1c**, BDPAB).* In a 100 ml, three-necked round-bottom flask equipped with a magnetic stirrer, a thermometer, a pressure equilibrating dropping funnel, and a reflux condenser topped with nitrogen inlet was placed racemic **4a** (1.55 g, 5.45 mmol). The whole system was purged with nitrogen. After the amine had been dissolved in 50 ml of THF, the solution was cooled to −30—−32 °C in a methanol-Dry Ice bath. To the cooled solution was added dropwise a hexane solution (8.8 ml) of 1.30 M BuLi (11.4 mmol) over 40 min. After the addition, the mixture was stirred at −30 °C for 20 min. To the stirred mixture kept at −28—−30 °C was added dropwise a solution of diphenylphosphinous chloride (2.46 g, 11.2 mmol) dissolved in 10 ml of THF over 40 min. Stirring was continued for another 1 h. Then the cooling bath was removed, and the mixture was stirred overnight at ambient temperature. Lithium chloride precipitated was filtered off under nitrogen, and then volatiles were evaporated *in vacuo* to leave yellowish resinous residue. This was digested with portions of warm ethanol (*ca.* 30 ml×3) to give white solid. Recrystallization from ethanol-benzene gave white crystals, 2.58 g (72.6%); mp 164—165 °C; IR (KBr): 3330, 3030, 1610, 1590, 1500, 1460, 1430, 1390, 1340, 1270, 1240, 980, 810, 740, 730, and 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ=4.4 and 4.6 (2H, br), and 6.6—7.4 and 6.5—7.9 (32H, m); MS (70 eV), *m/z* (%), 654 (M+2, 6.3), 653 (M+1, 26.5), and 652 (M^+, 52.2). Found: C, 80.48; H, 5.12; N, 4.33%. Calcd for $C_{44}H_{34}N_2P_2$: C, 80.97; H, 5.25; N, 4.29; P, 9.49%.

(R)-(+)-BDPAB: The diamine (*R*)-**4a** (2.16 g, 7.59 mmol) was treated as above to give (*R*)-(+)-BDPAB, 3.3 g (67%), mp 153—155 °C (PhH-EtOH); $[\alpha]_D^{23}$+26.1° (*c* 1.14, PhH). The product was again recrystallized from ethanol-benzene to increase the rotation to $[\alpha]_D^{23}$+27.2° (*c* 1.14, PhH), mp 154—155 °C. Subsequent recrystallization did not change the rotation. Found: C, 80.66; H, 5.19; N, 4.42%.

(S)-(−)-BDPAB: A sample of (*S*)-(−)-**4a** of $[\alpha]_D$ −153.0° gave diphosphine (*S*)-(−)-BDPAB of $[\alpha]_D^{23}$−25.8° (*c* 0.776, PhH) after two recrystallization from ethanol-benzene, mp 152—153 °C, the optical purity of which was estimated to be 95% on the basis of the maximum rotation of (*R*)-(+)-BDPAB of $[\alpha]_D$ +27.2°. Found: C, 80.93; H, 5.38; N, 4.59%.

2,2′-Bis[N-(diphenylphosphino)methylamino]-1,1′-binaphthyl (Me-BDPAB). According to the procedure used for the synthesis of BDPAB, **4b** (0.50 g, 1.6 mmol) was treated with BuLi (3.36 mmol), and then with diphenylphosphinous chloride (0.74 g, 3.3 mmol). Recrystallization from ethanol-benzene gave fine crystals, 0.60 g (56.2%), mp 159—161 °C; IR (KBr): 3050, 2800, 1615, 1590, 1500, 1470, 1430, 1350, 1325, 1270, 1240, 1090, 960, 930, 740, 695, and 495 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.5 (6H, s) and 6.6—8.0 (32H, m); MS (70 eV), *m/z* (%), 682 (M+2, 2.9), 681 (M+1, 9.7), and 680 (M^+, 33.8). Found: C, 81.05; H, 5.68; N, 3.99%. Calcd for $C_{46}H_{38}N_2P_2$: C, 81.16; H, 5.63; N, 4.12; P, 9.10%.

(R)-(−)-Me-BDPAB: A sample of (*R*)-(+)-**4b** of $[\alpha]_D$+182° (0.63 g, 2.0 mmol) was treated with BuLi (4.2 mmol) and then with diphenylphosphinous chloride (0.93 g, 4.2 mmol) as above. After the reaction, the filtrate was evaporated *in vacuo*; the residue was freed from LiCl by dissolution in benzene and filtration. The benzene filtrate was evaporated *in vacuo* to give yellowish powder, 0.65 g (48%), mp 68—71 °C, $[\alpha]_D^{23}$ −20.7° (*c* 1.26, PhH). IR and ^1H NMR spectra were identical to those of the racemic phosphine. Found: C, 80.62; H, 5.96; N, 3.51%. Attempts to recrystallize the optically active phosphine by varying solvents were unsuccesful.

Attempted Preparation of 2,2′-Bis[N-(diphenylphosphino)-ethylamino]-1,1′-binaphthyl (Et-BDPAB). Diamine **4c** (0.23 g, 0.68 mmol) was treated with BuLi (1.4 mmol), and then with diphenylphosphinous chloride (0.35 g, 1.6 mmol) as above. After usual workup, almost all of the diamine was recovered unchanged. In an another attempt, after the reaction mixture had been stirred overnight at ambient temperature, it was finally refluxed for 2 h, while no appreciable aminophosphine was obtained.

Preparation of Hydrogenation Catalysts. Catalyst A, (1/2 [Rh(olefin)$_2$Cl]$_2$+1.1BDPAB): The catalyst was prepared just prior to the hydrogenation by the reaction of [Rh(COD)Cl]$_2$ or [Rh(cyclooctene)$_2$Cl]$_2$ with a chiral diphosphine in benzene ([diphosphine]/[Rh] (mol/mol)=1.1). Typically, 17 mg (2.4×10^{-2} mmol) of [Rh(cyclooctene)$_2$Cl]$_2$ and 35 mg (5.4×10^{-2} mmol) of (*R*)-BDPAB in 4 ml of benzene was stirred at room temperature for 20 min under argon. The clear wine-red catalyst solution was transferred under rigorous exclusion of air to a reaction vessel, which contained an olefinic substrate (*vide infra*), by a hypodermic syringe.

Catalyst B, (1/2[Rh(COD)Cl]$_2$+1.1BDPAB+3NaBPh$_4$): Typically, (*R*)-BDPAB (35 mg, 5.4×10^{-2} mmol) in benzene (2 ml) was added to a methanol solution (2 ml) of [Rh(COD)Cl]$_2$ (12 mg, 2.4×10^{-2} mmol). The solution was stirred for 15 min, to which was added $NaBPh_4$ (48 mg, 14×10^{-2} mmol) in 2 ml of MeOH. The mixture was stirred for 10 min before it was transferred to a hydrogenation vessel.

Catalyst C, ([Rh(COD)(R)-BDPAB]$^+$BF$_4^-$): To a warm benzene solution (2 ml) of (*R*)-BDPAB (0.79 g, 1.2 mmol) was added [Rh(COD)Cl]$_2$ (0.28 g, 0.57 mmol) in MeOH (5 ml). After the mixture was stirred at 30—35 °C for 2 h, $NaBF_4$ (0.43 g, 3.9 mmol) in H_2O (4 ml) was added over 2 h period. The two-layer mixture was allowed to stand for 5 days at room temperature. Precipitated [Rh(COD)(*R*)-BDPAB]$^+$BF$_4^-$ was collected, 0.99 g (89%).

Hydrogenation Procedure. A reaction in a benzene-methanol solution is representative. The hydrogenation was carried out in a glass tube (*ca.* 30 ml volume) placed in a 100 ml inner-volume autoclave. After the glass tube was charged with an olefinic substrate (0.45—0.50 g), the whole system was evacuated and refilled with argon several times. The substrate was dissolved in 4 ml of methanol, and to the stirred solution was added a catalyst solution. If necessary, another benzene and/or methanol were added to adjust the solvent volume. The whole system was purged thoroughly with hydrogen, and it was charged to initial hydrogen pressure of 30 kg/cm^2. After the reaction mixture had been stirred at room temperature for 24 h, whole contents in the glass tube was transferred to a flask and solvents were removed *in vacuo*.

N-Acyl amino acids were recovered by the literature procedure.[13] 2-Methyl-3-phenylpropionic acid was isolated by preparative TLC (silica gel, ethyl acetate–aq NH_3 (trace)). *N*-Acyl amino acid esters were recovered by TLC (silica gel,

ethyl acetate–hexane (1.5/1). Hydrogenation products were characterized by IR and NMR spectra.[13]

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