Modification of (*S*)-*N*,*N*-Dimethyl-1-[(*R*)-1′,2-bis(diphenylphosphino)-ferrocenyl]ethylamine (BPPFA) as a Ligand for Asymmetric Hydrogenation of Olefins Catalyzed by a Chiral Rhodium(I) Complex†

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Asymmetric homogeneous hydrogenation of prochiral olefins catalyzed by chiral rhodium(I) complexes was carried out by using several ferrocenylphosphines as ligands which play a key role of the chiral recognition. Modifications of BPPFA were made in order to examine a steric effect of the given substutient at the asymmetric center on the efficiency of the chiral ligands, indicating the parent BPPFA to be superior to the others examined for the asymmetric hydrogenation of highly functionalized olefins.

Rapid development in asymmetric homogeneous hydrogenation of olefins catalyzed by chiral rhodium(I) complexes has encouraged significant efforts in the preparation of chiral phosphines for some years.

Although the choice of the chiral ligand for this purpose is still empirical at the present time, there are several efficient bisphosphine ligands which enable the catalyst for hydrogenation of certain functionalized prochiral olefins, *e.g.* α-(acylamino)acrylic acid, to attain 80—100% in enantioselectivity.[1] Among such ligands, (2*R*, 3*R*)-2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane(DIOP),[2] (1*R*,2*R*)-bis[(*o*-methoxyphenyl)phenylphosphino]ethane (DIPAMP),[3] and (2*S*,3*S*)-2,3-bis(diphenylphosphino)-butane (CHIRAPHOS)[4] have equivalent diarylphosphino groups in the molecule, forming more or less rigid chelates with the metal atom. (2*R*)-1,2-Bis(diphenylphosphino)propane(PROPHOS)[5] and (1*S*)-1,2-bis(diphenylphosphino)-1-phenylethane[6] may also be included in this class of ligands.

The most convincing explanation for the existing effective chiral recognition by these chelate ligands is that the four phenyl (aryl) groups on the phosphorus atoms are arranged around the rhodium metal in an alternating 'edge-face' manner, which is dictated by the chiral centers present in the ligand molecule.[3,4]

On the other hand, (2*S*,4*S*)-*N*-*t*-butoxycarbonyl-2-[(diphenylphosphino)methyl]-4-(diphenylphosphino)-pyrrolidine (BPPM),[7] and (*S*)-*N*,*N*-dimethyl-1-[(*R*)-1′,2-bis(diphenylphosphino)ferrocenyl]ethylamine (BPPFA)[8] contain sterically non-equivalent phsophorus atoms and clear modelling of the 'edge-face' conformation is rather difficult. However, (*S*)-(*R*)-BPPFA is unique in that it has planar element of chirality which arises from introducing the phosphino groups into the optically pure *N*,*N*-dimethyl-1-ferrocenylethylamine.[9]

We describe here some modifications of BPPFA by changing a methyl group bound to the asymmetric carbon atom with an isopropyl or a phenyl group in order to examine a steric effect of the asymmetric center on the conformation of the chelate and thus the efficiency of the chiral ligands: They were used for the rhodium(I) complex-catalyzed hydrogenation of a variety of olefinic substrates.

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There has been another approach to the modification of BPPFA, which involves retentive substitution of a dimethylamino group with higher dialkylamino groups or a hydroxyl group, indicating a remarkable participation of these functional groups to the asymmetrically catalyzed reactions.[10,11]

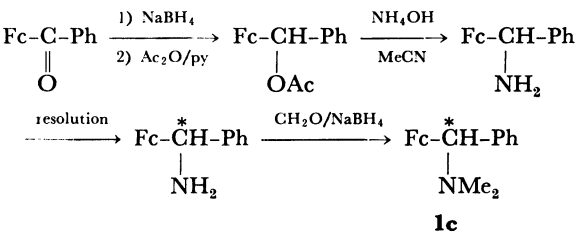
Results and Discussion

Preparation of Analogs of BPPFA. *N*,*N*-Dimethyl-1-ferrocenyl-2-methylpropylamine (**1b**) was obtained by a similar procedure to the preparation of *N*,*N*-dimethyl-1-ferrocenylethylamine (**1a**)[9] (Eq. 1), and was resolved by crystallization of the tartrates from aqueous acetone.

$$\underset{\text{(Fc=ferrocenyl)}}{\text{Fc-CH(CN)NMe}_2} + \text{RMgX} \rightarrow \underset{\begin{matrix}\mathbf{1a},\ \text{R=Me}\\ \mathbf{1b},\ \text{R=}i\text{-Pr}\end{matrix}}{\text{Fc-CHRNMe}_2} \qquad (1)$$

It was noted that the reaction with isopropylmagnesium chloride gave not only **1b**, but a ketone which came from an attack of the Grignard reagent on the nitrile group. Ugi *et al.*[12] have recently reported the preparation of optically active **1b**.

Optically pure *N*,*N*-dimethyl-α-ferrocenylbenzylamine (**1c**) (absolute configuration unknown) was prepared according to Scheme 1. Resolution of the



Scheme 1.

primary amine[13] was carried out by crystallization of the hydrogen dibenzoyltartrate from ethanol by a reported procedure.[14] The absolute configuration of (−)-**1c** was most likely estimated to be *S* by correlating CD spectra of BPPFA analogs (*vide infra*).

Chiral ferrocenylphosphines were prepared by way of stereoselective lithiation[9] of optically active ferrocenyl-substituted amines (**1a**—**c**). Thus, stepwise lithiation of **1a**—**c** with butyllithium in ether and with butyllithium/*N*, *N*, *N*′, *N*′-tetramethylethylenediamine

Table 1. Physical and analytical data of BPPFA (2) and PPFA (3) analogs

		Mp/°C	$[\alpha]_D^{25}$ (deg) (*c*, $CHCl_3$)	Found (Calcd)(%) C	H	N
(*S*)-(*R*)-BPPFA	(**2a**)	136	+349 (0.604)[a]		——	
(*R*)-(*S*)-BPPFA-IP	(**2b**)	85	−350 (0.496)	73.83(73.50)	6.41(6.34)	2.13(2.14)
(*S*)-(*R*)-BPPFA-Ph	(**2c**)	70	+260 (0.520)	74.36(75.11)	5.87(5.72)	2.11(2.04)
(*S*)-(*R*)-PPFA	(**3a**)	139	+343 (0.600)[b]		——	
(*R*)-(*S*)-PPFA-IP	(**3b**)	116	−396 (0.208)	70.82(71.65)	6.75(6.87)	2.70(2.98)
(*S*)-(*R*)-PPFA-Ph	(**3c**)	96	+238 (0.246)[c]	73.68(73.96)	6.07(6.01)	2.71(2.78)

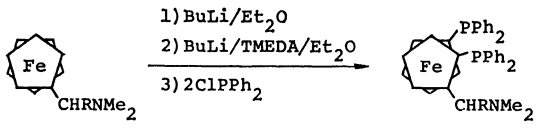
a) Lit,[11] (*R*)-(*S*)-**2a**, $[\alpha]_D^{25}$ −349° (*c* 0.5, $CHCl_3$). b) Lit,[8a] (*S*)-(*R*)-**3a**, $[\alpha]_D^{25}$ +361° (*c* 0.6, EtOH). $[\alpha]_D^{25}$ +361° (*c* 0.50, EtOH) was observed. c) Optical purity 95%.

Table 2. IR and NMR spectral data of BPPFA (2) and PPFA (3) analogs

	IR (KBr) $\tilde{\nu}/cm^{-1}$	NMR ($CDCl_3$, TMS) (δ/ppm)
2b	2920, 1485, 1435, 745, and 700	1.03 and 1.39 (dd, J=6.8 Hz, CMe_2), 1.84 (s, NMe_2), 1.9—2.5 (m, $CHMe_2$), 3.25—4.49 (m, Cyclopentadienyl ring protons, Fc-CH[a]), and 7.05—7.75 (m, phenyls).
2c	1435, 740, and 700	1.74 (s, NMe_2), 3.04—3.40, 3.56—3.82 (m, C_5H_4, Fc-CH) 4.00—4.58 (m, C_5H_3), and 6.86—7.80 (m, phenyls).
3b	2920, 1475, 1435, 1025, 820,[b] 740, and 700	1.04 and 1.35 (dd, J=6.8 Hz, CMe_2), 1.86 (s, NMe_2), 1.9—2.65 (m, $CHMe_2$), 3.91 (s, C_5H_5), 3.65—4.03 and 4.42—4.47 (m, FcCH, C_5H_3), and 7.02—7.82 (m, phenyls).
3c	1435, 1110, 820,[b] 750, and 700	1.79 (s, NMe_2), 3.42 (s, C_5H_5), 3.99 (bm, Fc-CH), 4.23—4.27 (m, C_5H_3), and 7.10—7.85 (m, phenyls).

a) Fc=Ferrocenyl. b) Characteristic 9, 10 μ rule.

(TMEDA)[8a] led to the introduction of two diphenylphosphino groups into each of the cyclopentadienyl rings to give the corresponding BPPFA (**2a**) and its analogs (**2b** and **c**) in moderate yields (Eq. 2).

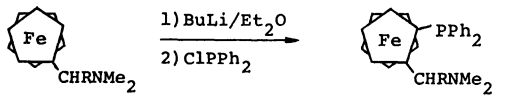


(2)

1a, R=Me
b, R=*i*-Pr
c, R=Ph

2a, BPPFA
b, BPPFA-IP (antipode)
c, BPPFA-Ph

Analogs of (*S*)-*N*,*N*-dimethyl-1-[(*R*)-2-(diphenylphosphino)ferrocenyl]ethylamine (PPFA) (**3a**) were also prepared from **1a**—**c** by single lithiation, followed by treatment with diphenylphosphinous chloride[8a] (Eq. 3).



(3)

1a—c

3a, PPFA
b, PPFA-IP (antipode)
c, PPFA-Ph

Physical properties of ferrocenylphosphines (**2** and **3**) were given in Table 1 and NMR and IR spectral data of **2** and **3** were summarized in Table 2. The circular dichroism (CD) spectra of **2a**—**c** were shown in Fig. 1. Since the enantiomeric property of (*R*)-(*S*)-**2b** as compared with (*S*)-(*R*)-**2a** is obvious from the CD spectra, it is most probable that the absolute configuration of (−)-**2c** with a positive Cotton effect is (*S*)-(*R*), and in turn that of (−)-**1c** is *S*.

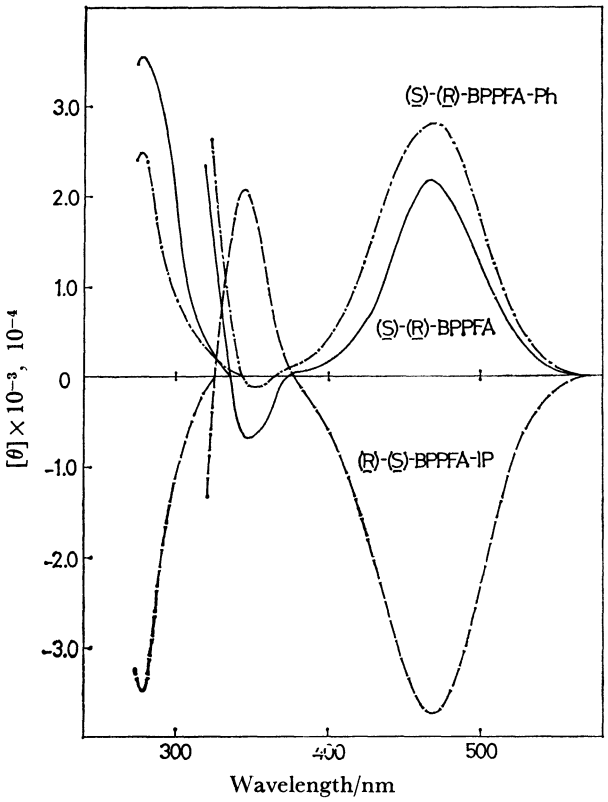


Fig. 1. Circular dichroism (CD) spectra of BPPFA (**2a—c**).

Asymmetric Hydrogenation of α-(Acylamino)acrylic Acids Using BPPFA Rhodium(I) Catalyst. We are primarily concerned with the modification of (*S*)-(*R*)-BPPFA (**2a**) which has been found to exert an effective chiral influence in the rhodium(I) complex-catalyzed hydrogenation of α-acetamidocinnamic acid.[8b] Kagan, *et al.*[15] have previously reported that the geometry of the olefinic acids and esters has a marked effect on the optical yield of phenylalanine derivatives obtained by asymmetric hydrogenation catalyzed by Rh(I)–DIOP system. Therefore, we have also carried out the hydrogenation of (*Z*)-α-acetamido- and (*Z*)- and (*E*)- α-benzamidocinnamic acid and their methyl esters using Rh(I)–BPPFA as catalyst under the standard conditions where complete hydrogenation of each substrate is confirmed. (details in Experimental)

TABLE 3. DEPENDENCE OF THE OPTICAL YIELDS ON THE GEOMETRY OF SUBSTRATES IN THE ASYMMETRIC HYDROGENATION CATALYZED BY Rh(I)-BPPFA

Substrate	Optical yield (% e.e.)[a]	
	(*S*)-(*R*)-BPPFA	(+)-DIOP[b]
Ph, H, NHAc, CO_2H	86	82
Ph, H, NHAc, CO_2Me	69	74
Ph, H, NHBz, CO_2H	37	70
Ph, H, NHBz, CO_2Me	35	38
Ph, H, CO_2H, NHBz	4	25
Ph, H, CO_2Me, NHBz	*nil*	5

a) (*S*)-Phenylalanine derivatives obtained. Optical yields are calculated with respect to the following values of the optically pure compounds: *N*-Acetylphenylalanine, $[\alpha]_D^{25}$ +46.8° (*c* 1.06, 95% EtOH).[15] Methyl ester, $[\alpha]_D^{25}$ +15.9° (*c* 2.0, MeOH): R. Glazer, *J. Organomet. Chem.*, **121**, 249 (1976). *N*-Benzoylphenylalanine, $[\alpha]_D^{25}$ −19.8° (*c* 8.8, 0.4 M NaOH).[2] Methyl ester, $[\alpha]_D^{25}$ −45.3° (*c* 1.325, 95% EtOH).[15] b) Lit.[15]

Table 3 shows the results together with the corresponding data reported by Kagan *et al.*[15] Dependence of the optical yield on the geometry of substrates is evident, deficiency of the optical yields starting from (*E*)-α-benzamidocinnamic acid and its ester being stronger in BPPFA than in DIOP. The results show that the same basis of the chiral recognition as mentioned above can be applied for these chelate ligands. Intrinsic low enantioselectivity with (*E*)-α-benzamidocinnamic acid has recently been discussed in terms of an inferior matching of the substrate with the catalyst in addition to a partial isomerization into the (*Z*)-isomer.[16,17]

BPPFA (**2a**—**c**) were examined as ligands in Rh(I) complex-catalyzed hydrogenation of (*Z*)-α-acetamidocinnamic acid and α-acetamidoacrylic acid, respectively. Results obtained were given in Table 4.

As is seen in Table 4, the parent BPPFA (**2a**) is much superior in asymmetric hydrogenation of these two amino acid precursors to the analogs **2b** and **2c**. Also PPFA–Ph (**3c**) is not effective as compared with **3a**, preferred configuration being inverted from *S* with bisphosphines **2** to *R* with monophosphines **3**. The fact that inverse enantioselectivity was observed between **2c** and **3c** as well as **2a** and **3a** despite the identical absolute configuration of these chiral ligands may well be explained by the different conformation of bisphosphine chelate of **2c** and **2a** from that of P–N chelate of **3c** and **3a**, respectively.

Although change in the structure at asymmetric carbon atom of BPPFA (**2a**) or PPFA (**3a**) so far deteriorated the enantioselective hydrogenation of the amino acid precursors, it does not appear to be true that the parent BPPFA (**2a**) is of sole choice of these chiral ferrocenylphosphines for the catalyzed asymmetric hydrogenation of various olefin substrates.

Asymmetric Hydrogenation of Itaconic Acid, Atropic Acid, and α-Ethylstyrene. These substrate were chosen

TABLE 4. ASYMMETRIC HYDROGENATION OF (*Z*)-α-ACETAMIDOCINNAMIC ACID AND α-ACETAMIDOACRYLIC ACID CATALYZED BY Rh(I)-BPPFAs

Substrate	Ligand	Optical yield %	Configuration
Ph, H, NHAc, CO_2H	(*S*)-(*R*)-BPPFA (**2a**)	86[a]	*S*
	(*R*)-(*S*)-BPPFA-IP (**2b**)	52	*R*
	(*S*)-(*R*)-BPPFA-Ph (**2c**)	52	*S*
	(*S*)-(*R*)-PPFA (**3a**)	67[b]	*R*
	(*S*)-(*R*)-PPFA-Ph (**3c**)	34	*R*
H_2C, NHAc, CO_2H	**2a**	55[c,d]	*S*
	2b	42	*R*
	2c	45	*S*

a) In ethanol, 93% e.e.[8b] b) W. R. Cullen and E. S. Yeh, *J. Organomet. Chem.*, **139**, C 13 (1977), 73—84% e.e. c) In ethanol, 69% e.e.[18] d) Based on the values of the optically pure compound: *N*-Acetyl-(*R*)-alanine, $[\alpha]_D$ +66.5° (*c* 2, H_2O): S. M. Birbaum, L. Levintov, R. B. Kingsley, and J. P. Greenstein, *J. Biol. Chem.*, **194**, 455 (1952).

Table 5. Asymmetric hydrogenation of itaconic acid, atropic acid, and α-ethylstyrene catalyzed by Rh(I)-BPPFAs

Substrate	Ligand	Optical yield[a] %	Configuration
CH_2=C-CO_2H | CH_2CO_2H	BPPFA (**2a**)	32	*R*
	BPPFA-IP (**2b**)	21	*S*
	BPPFA-Ph (**2c**)	34	*R*
CH_2=C-CO_2H | Ph	**2a**	8	*S*
	2b	3	*S*
	2c	9	*R*
CH_2=C-Et | Ph	**2a**	6	*R*
	2b	3	*S*
	2c	34	*R*

a) Optical yields are calculated with respect to the following maximum rotations: (*R*)-α-Methylsuccinic acid, $[\alpha]_D^{20}$ +17.09° (*c* 4.41, abs. EtOH): R. Rossi, P. Diversi, and G. Ingrosso, *Gazz. Chim. Ital.* **38**, 1391 (1968). (*S*)-Hydratropic acid, $[\alpha]_D^{25}$ +76.3° (*c* 1.6, $CHCl_3$): S. P. Bakshi and E. E. Turner, *J. Chem. Soc.*, 171 (1961). (*R*)-2-Phenylbutane, $[\alpha]_D^{25}$ −27.3° (neat): W. A. Bonner and T. W. Greenlee, *J. Am. Chem. Soc.*, **81**, 3336 (1959).

because they lack any attractive interaction as is expected for α-(acylamino)acrylic acids which coordinate with both the olefin bond and the amido carbonyl group to the rhodium. We have reported the preparation of (*S*)-*N*,*N*-dimethyl-1-[2-(diphenylphosphino)-1-naphthyl]ethylamine (1,2-DPNEA),[19] which was used as ligand in the rhodium complex-catalyzed asymmetric hydrogenation of itaconic acid. The optical yield of α-methylsuccinic acid obtained was up to 54% e.e. with added triethylamine. Lately, rhodium(I)–BPPM system has been found to give rise to an exceedingly high optical yield in the hydrogenation of itaconic acid.[20,20a]

As simple olefinic acids, itaconic acid and atropic acid were readily hydrogenated under standard conditions employed with Rh(I)–BPPFA catalyst system, but only moderate to low optical yields for these substrates were observed (Table 5).

It is of interest, however, to note that three BPPFAs exert no significant difference in the extent of enantioselective hydrogenation of itaconic acid, whereas a marked dependence on these ligands was observed for α-acetamidocinnamic acid. Furthermore, atropic acid undergoes hydrogenation with no coincidence between the observed configuration of product and absolute configuration of BPPFAs used.

Finally, asymmetric hydrogenation of α-ethylstyrene, one of the simplest hydrocarbon prochiral olefins, was examined using Rh(I)–BPPFAs as catalyst. Results are given in Table 5. Although the low enantioselection by Rh(I)–BPPFAs is again due to the simple structure of nonfunctionalized olefin substrate, BPPFA–Ph (**2c**) gave much higher optical yield of *s*-butylbenzene than the other two. Thus, it is encouraging to find that the simpler the structure of substrate olefin is, the more efficient would be the steric effect at the asymmetric carbon in BPPFAs. On the other hand, the uniformyl low ability of BPPFA–IP (**2b**) in the present asymmetric hydrogenation is presumably explained by the fact that an isopropyl group is of the same steric bulk as the dimethylamino group, and rather interferes in the proper conformation of the chelate present in the parent BPPFA (**2a**).

Experimental

Preparation of N,N-*Dimethyl-1-ferrocenyl-2-methylpropylamine (**1b**).* To an ether solution of isopropylmagnesium chloride, prepared from isopropyl chloride (14.5 g, 0.185 mol) and magnesium turnings (4.5 g) in anhydrous ether (80 ml), was added α-ferrocenyl-α-dimethylaminoacetonitrile[9] (24.8 g, 0.092 mol) dissolved in ether (150 ml) at room temperature. The mixture was stirred for 4.5 h, and hydrolyzed with 10% aqueous ammonium chloride solution. The organic layer was separated and the aqueous layer was extracted with three 50 ml portions of ether. The combined organic layer and extracts were washed with brine and the solvent was removed by evaporation to give 28.8 g of crude product. This was taken up in benzene, extracted with aqueous phosphoric acid (30 g in 400 ml water). The extract was washed with benzene and neutralized with 10% sodium carbonate solution. The organic layer separated was extracted with benzene, and the benzene solution was dried ($MgSO_4$) and evaporated to give 21.1 g, of a mixture of **1b** and a ketone which was separated by distillation.

1b (17.5 g, 65% yield): bp 106—109 °C/0.05 Torr; mp 20—21 °C; NMR ($CDCl_3$, TMS): δ 1.10, 1.24 (dd, *J*= 6.8 Hz, CHMe), 1.81—2.48 (m, CHMe), 2.11 (s, NMe_2), 3.20 (d, *J*=6.0 Hz, Fc-CH), and 4.14 ppm (s, $C_5H_5FcC_5H_4$); IR: 3050 (m), 2900(s), 2800(m), 1448(m), 1100(s), 1020 (m), 1009(s), 1000(m), 810(s), and 730(m) cm^{-1}. The ketone (4.3 g, 15% yield, mp 81—82 °C) was found by its NMR and IR spectrum to be 1-ferrocenyl-1-dimethylamino-3-methyl-2-butanone. NMR ($CDCl_3$): δ 1.17 (d, *J*=7.2 Hz, $CHMe_2$), 2.10 (s, NMe_2), 3.15 (m, *J*=3.3 Hz, CHMe), 4.06 (s, C_5H_5), 4.15 (C_5H_4), and 4.45 ppm (m, CHN); IR (KBr): 1705 cm^{-1} (C=O).

*Resolution of **1b**.* Crude **1b** (23.75 g, 83 mmol) dissolved in acetone (30 ml) was added to a solution of (*R*,*R*)-tartaric acid (12.4 g, 83 mmol) in 85% aqueous acetone (35 ml). Crystals of the hydrogen tartrate formed (28.3 g, 65 mmol) were extracted with hot acetone to leave yellow crystals (11.4 g), while the acetone extract gave orange crystals (10.7 g) after evaporation. From these salts (+)-**1b** (7.79 g, 27.3 mmol, 42%), $[\alpha]_D^{20}$ +135.8° ($CHCl_3$), and (−)-**1b** (7.44 g, 26.0 mmol, 40%), $[\alpha]_D^{20}$ −125.3° ($CHCl_3$), were recovered, respectively. The procedure was repeated five times for further resolution to the highest and constant rotation:

(*S*)-**1b** (4.30 g, 24%), $[\alpha]_D^{20}$ +158.9° (*c* 1.00, $CHCl_3$)
$[\alpha]_D^{20}$ +190.0° (*c* 1.00, benzene)

(*R*)-**1b** (4.00 g, 21%), $[\alpha]_D^{20}$ −160.6° (*c* 1.00, $CHCl_3$)
$[\alpha]_D^{20}$ −192.0° (*c* 1.00, benzene)

The reported maximum rotation is $[\alpha]_D^{20}$ +192.8° (*c* 1, benzene).[12] It should be noted that (−)-**1b**-tartrate as orange crystals is more soluble in hot acetone than the (+)-**1b** salt, though the rate of formation of the latter is faster than that of the former. In addition, (−)-**1b**-tartrate was better purified at the later stage of resolution by washing with diethyl ether.

Preparation of N,N-*Dimethyl-α-ferrocenylbenzylamine (**1c**).*
α-Ferrocenylbenzylamine. To a stirred solution of α-fer-

TABLE 6. THE MOLECULAR ELLIPTICITY [θ] OF FERROCENYLPHOSPHINES

	[θ] (nm)
(*R*)-(*S*)-BPPFA-IP (**2b**)	-3.77×10^3 (469), 2.09×10^3 (345), -3.52×10^4 (279).
(*S*)-(*R*)-BPPFA-Ph (**2c**)	2.82×10^3 (469), -1.47×10^2 (351), 2.53×10^4 (279).
(*S*)-(*R*)-PPFA (**3a**)	2.07×10^3 (459), -1.42×10^3 (342), ——
(*S*)-(*R*)-PPFA-IP (**3b**)	1.30×10^3 (470), 14.0 (365), 5.52×10^3 (280).
(*S*)-*N*,*N*-Dimethyl-1-ferrocenylethylamine (**1a**)	3.91×10^2 (455), -72.0 (338), 3.86×10^3 (257)

rocenylbenzyl acetate[21] (8.0 g, 24 mmol) in acetonitrile (150 ml) was added 38% ammonia solution (35 ml), and the mixture was allowed to stand overnight at room temperature. (Methanol cannot be used as a solvent contrary to the reaction of 1-ferrocenylethyl acetate.[13])

The reaction mixture was evaporated to the minimum volume, and the residue was dissolved in ether (50 ml). The resulting solution was extracted with 8.5% phosphoric acid. The extract was washed with ether and an amine was set free by adding excess 20% sodium hydroxide solution. After usual work up, there obtained α-ferrocenylbenzylamine (4.35 g, 62%): mp 47—49 °C; NMR ($CDCl_3$): δ 1.87 (br.s, $-NH_2$), 4.00—4.32 (m, C_5H_4); 4.12 (s, C_5H_5), 4.81 (s, Fc–CH), and 7.10—7.40 ppm (m, C_6H_5); IR (KBr): 3080, 1600, 1490, 1100, 1000, 810, 720, 700 cm^{-1}.

Resolution of α-Ferrocenylbenzylamine. According to the procedure by Allenmark,[14] a hot solution of (*R*,*R*)-*O*,*O*′-dibenzoyltartaric acid monohydrate (6.48 g, 17.2 mmol) in ethanol (69.5 ml) was added to a hot solution of the racemic amine (5.01 g, 17.2 mmol). After the solution was cooled, an yellow salt precipitated was collected (6.88 g, 59.9%), $[\alpha]_D^{25}$ −87.6° (*c*, 0.502, MeOH). The mother liquor was evaporated to dryness to leave another salt (4.31 g, 37.5%), $[\alpha]_D^{25}$ −41.2° (*c* 0.712, MeOH). Further resolution of the yellow salt was carried out by successive extraction with hot ethanol (180 ml and 85 ml) to give 3.25 g (29.1%) of the purified salt, $[\alpha]_D^{20}$ −107.6° (*c* 0.392, MeOH) (lit,[14] $[\alpha]_D^{25}$ −107°). From this salt the pure (−)-amine was obtained (1.40 g, 96% recovery), mp 80—83 °C, $[\alpha]^{25}$ −27.3° (*c* 0.504, MeOH) (lit,[14] $[\alpha]_D^{25}$ −26.1°).

*(−)-N,N-Dimethyl-α-ferrocenylbenzylamine (**1c**).* To a solution of (−)-amine (1.87 g, 6.42 mmol, 94% optical purity) in methanol (80 ml) was added 37% aqueous formaldehyde (21 ml) in an ice-water bath. To the cooled solution was added sodium borohydride (4.01 g) portionwise, and the mixture was stirred at room temperature overnight. After usual work up and purification, there obtained pure dimethylated amine (1.51 g, 74%), mp 62—64 °C, $[\alpha]_D^{25}$ −106.9° (*c*, 0.350, MeOH). (lit,[14] $[\alpha]_D^{25}$ −109°).

NMR ($CDCl_3$): δ 2.03 (s, NMe_2), 3.68 (s, C_5H_5), 3.73 (s, Fc–CH), 3.98—4.20 (m, C_5H_4), and 7.13—7.50 ppm (m, C_6H_5). IR (KBr): 1450, 1110, 1005, 820, 740, 705 cm^{-1}. In the same procedure as above, optically pure (−)-amine was dimethylated, $[\alpha]_D^{25}$ −112° (MeOH).

*Preparation of BPPFA-IP (**2b**), PPFA-IP (**3b**), BPPFA-Ph (**2c**), and PPFA-Ph (**3c**).* The procedures were the same as those reported by Kumada and coworkers,[8] the following is typical: To a stirred solution of (*R*)-**1b** (2.02 g, 7.1 mmol), $[\alpha]_D^{20}$ −192° (benzene), in anhydrous ether (2 ml) cooled in an ice-water bath was added dropwise butyllithium (2.32 M in hexane, 3.3 ml, 7.7 mmol) under a nitrogen atmosphere. Stirring was continued for 1.5 h at room temperature. To the mixture was added dropwise a mixture of butyllithium (3.3 ml) and TMEDA (0.945 g, 8.1 mmol) with cooling. The resulting mixture was stirred for 4.5 h at room temperature, followed by addition of diphenylphosphinous chloride (4.65 g, 21.0 mmol) in ether. After the reaction mixture was stirred overnight, 5% sodium hydrogencarbonate solution (50 ml) was added. Usual work up and column chromatographic purification (silica gel, hexane–benzene–ethyl acetate) to give (*R*)-(*S*)-**2b** (1.53 g, 33% yield): mp 80—82 °C (ethanol). Similarly, using (−)-**1c** (0.874 g, 2.65 mmol) was obtained (*S*)-(*R*)-**2c** (0.564 g, 30%).

In the same manner as above but with single lithiation, (*R*)-(*S*)-**3b** (38%) and (*S*)-(*R*)-**3c** (35%; 95% optical purity) were prepared. Physical, analytical, and spectral data for these ferrocenylphosphines are given in Tables 1 and 2, respectively. CD spectra of BPPFAs (**2a**—**c**) were shown in Fig. 1. The molecular ellipticity [θ] of ferrocenylphosphines newly prepared were given in Table 6.

Assymmetric Hydrogenation of Olefins Using BPPFAs-Rh(I) Catalyst. Materials: (*Z*)-α-Acetamidocinnamic acid, its methyl ester,[15] (*E*)- and (*Z*)-α-benzamidocinnamic acid,[22] and their methyl esters were prepared by the known procedures. Atropic acid and α-ethylstyrene were also prepared from hydrolysis of ethyl atropate[23] and thermolysis of 2-phenylbutyl acetate,[24] respectively. Commercially available itaconic acid was used as received.

All solvents used were dried and distilled.

General Procedure of Hydrogenation. The following is chosen as standard conditions.

In a 50 ml microautoclave fitted with a glass tube were placed $[RhCl(C_6H_{10})]_2$ (5.5 mg, 1.25×10^{-2} mmol), BPPFA (**2**) (2.50×10^{-2} mmol), and a substrate olefin (5.00 mmol) under a nitrogen atmosphere. Benzene–methanol (10 ml, 1:3 v/v) previously deoxygenated was added to the mixture and hydrogen was then introduced after three successive substitution of nitrogen with hydrogen (20 atm). Reactions were carried out at 20 atm of initial hydrogen pressure and at room temperature with magnetical stirring for an appropriate period of time to ensure 100% conversion. The extent of reaction was monitored by approximately 3 atm of hydrogen uptake and was checked by NMR spectrum of the final products which were purified by a known procedure.

When a cationic rhodium(I) catalyst, $[Rh(COD)BPPFA]^+ClO_4^-$ or $[Rh(COD)PPFA]^+ClO_4^-$, was used, the concentration of the catalyst was also 2.5 mM and that of the substrate 0.50 M.

Tables 3—5 show all results obtained for the catalyzed asymmetric hydrogenation of a variety of olefins examined.

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References

1) For a review, see H. B. Kagan and J. C. Fiaud, "Topics in Stereochemistry," ed by E. L. Eliel and N. L.

Allinger, Interscience (1978), Vol. 10, p. 175.
2) H. B. Kagan and T. P. Dang, *J. Am. Chem. Soc.*, **94**, 6429 (1972).
3) W. S. Knowles, M. J. Sabacky, B. D. Vineyard, and D. J. Weinkauff, *J. Am. Chem. Soc.*, **97**, 2567 (1975).
4) M. D. Fryzuk and B. Bosnich, *J. Am. Chem. Soc.*, **99**, 6262 (1977).
5) M. D. Fryzuk and B. Bosnich, *J. Am. Chem. Soc.*, **100**, 5491 (1978).
6) R. B. King, J. Bakos, C. D. Hoff, and L. Markó, *J. Org. Chem.*, **44**, 1729 (1979).
7) K. Achiwa, *J. Am. Chem. Soc.*, **98**, 8265 (1976).
8) a) T. Hayashi, K. Yamamoto, and M. Kumada, *Tetrahedron Lett.*, **1974**, 4405; b) T. Hayashi, T. Mise, S. Mitachi, K. Yamamoto, and M. Kumada, *ibid.*, **1976**, 1133.
9) D. Marquarding, H. Klusacek, G. Gokel, P. Hoffmann, and I. Ugi, *J. Am. Chem. Soc.*, **92**, 5389 (1970).
10) T. Hayashi, M. Tajika, K. Tamao, and M. Kumada, *J. Am. Chem. Soc.*, **78**, 3718 (1976).
11) T. Hayashi, T. Mise, and M. Kumada, *Tetrahedron Lett.*, **1976**, 4351.
12) a) D. Marquarding, H. Burghard, I. Ugi, R. Urban, and H. Klusacek, *J. Chem. Res. (M)*, **1977**, 915; b) G. Eberle, I. Lagerlund, I. Ugi, and R. Urban, *Tetrahedron*, **34**, 977 (1978). We are indebted to Prof. Ugi for informing us of their results prior to publication.
13) G. W. Gokel, D. Marquarding, and I. Ugi, *J. Org. Chem.*, **37**, 3052 (1972).
14) S. Allenmark, K. Kalen, and A. Sandblom, *Chem. Scr.*, **7**, 97 (1975).
15) G. Gelbard, H. B. Kagan, and R. Stern, *Tetrahedron*, **32**, 233 (1976).
16) C. Detellin, G. Gelbard, and H. B. Kagan, *J. Am. Chem. Soc.*, **100**, 7556 (1978).
17) K. E. Koenig and W. S. Knowles, *J. Am. Chem. Soc.*, **100**, 7561 (1978).
18) T. Hayashi and M. Kumada, "Fundamental Research in Homogeneous Catalysis," ed by Y. Ishii and M. Tsutsui, Plenum (1978), Vol. 2, p. 159.
19) K. Yamamoto, A. Tomita, and J. Tsuji, *Chem. Lett.*, **1978**, 3.
20) I. Ojima, T. Kogure, and K. Achiwa, *Chem. Lett.*, **1978**, 567.
20a) Note added. It is recently reported that an intramolecular hydrogen bonding of itaconic acid remarkably interferes with the enantioselectivity. W. C. Christopfel and B. D. Vineyard, *J. Am. Chem. Soc.*, **101**, 4406 (1979).
21) M. D. Rausch, M. Vogel, and H. Rosenberg, *J. Org. Chem.*, **22**, 903 (1957).
22) Y. S. Rao and R. Filler, *Synthesis*, **1975**, 749.
23) G. R. Ames and W. Davey, *J. Chem. Soc.*, **1958**, 1794.
24) C. G. Overberger and D. Tanner, *J. Org. Chem.*, **20**, 369 (1955).