Asymmetric Synthesis Catalyzed by Chiral Ferrocenylphosphine–Transition Metal Complexes. I. Preparation of Chiral Ferrocenylphosphines

Tamio HAYASHI, Takaya MISE, Motoo FUKUSHIMA, Masahiro KAGOTANI, Nobuo NAGASHIMA, Yuji HAMADA, Akira MATSUMOTO, Sota KAWAKAMI, Mitsuo KONISHI, Keiji YAMAMOTO,† and Makoto KUMADA*

Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Yoshida, Kyoto 606

(Received October 22, 1979)

As chiral ligands for transition metal complex catalyzed asymmetric reactions, various kinds of chiral ferrocenylphosphines, which have planar chirality due to 1,2-unsymmetrically substituted ferrocene structure and also have a functional group on the side chain of the ferrocene nucleus, were prepared. (*S*)-*N*,*N*-dimethyl-1-[(*R*)-2-(diphenylphosphino)ferrocenyl]ethylamine [(*S*)-(*R*)-PPFA], (*S*)-*N*,*N*-dimethyl-1-[(*R*)-1′,2-bis(diphenylphosphino)ferrocenyl]ethylamine [(*S*)-(*R*)-BPPFA], and their dimethylphosphino derivatives were prepared by way of lithiation of optically resolved *N*,*N*-dimethyl-1-ferrocenylethylamine. The 1-(dimethylamino)ethyl group on the ferrocenylphosphines was converted stereospecifically by nucleophilic substitution reactions into 1-methoxy-, 1-hydroxy-, 1-diphenylphosphino-, and several 1-(dialkylamino)ethyl groups. 1-Diphenylphosphino-2-(dimethylaminomethyl)ferrocene (FcPN) was optically resolved *via* its phosphine sulfide dibenzoyltartaric acid salt. The relationship between CD spectra of the chrial ferrocenylphosphines and the configuration of their planar chirality is discussed.

There has been intense interest and activity recently in asymmetric synthesis catalyzed by transition metal complexes with chiral ligands.[1,2] This has resulted in so great a success in asymmetric homogeneous hydrogenation by chiral phosphine rhodium complexes as to produce α-amino acids with over 90% optical purity.[3] One of the most significant problems in studies on the catalytic asymmetric synthesis is how to develop a chiral ligand which will enable the catalyst for a given reaction to be as efficient in stereoselectivity as possible, and considerable efforts have been devoted to searching for new chiral phosphine ligands. These chiral phosphines may be classified into two classes: (A) phosphines bearing an asymmetric center at the phosphorus atom and (B) phosphines whose chirality is due to asymmetric carbons in groups bonded to phosphorus.

Methylphenylpropylphosphine[4] was used by Horner *et al.*[5] and Knowles *et al.*[6] in their early studies on catalytic asymmetric hydrogenation. Many optically active tertiary phosphines have been prepared since Mislow *et al.* developed a new synthetic method for the chiral phosphines in 1967,[7] and some of them have been reported to be effective ligands for catalytic asymmetric reactions. (*o*-Methoxyphenyl)cyclohexylmethylphosphine (CAMP)[8] and 1,2-bis[(*o*-methoxyphenyl)phenylphosphino]ethane (diPAMP)[9] by Knowles *et al.* gave, when complexed with rhodium, optical yields of over 90% in the hydrogenation of α-(acylamino)acrylic acids.

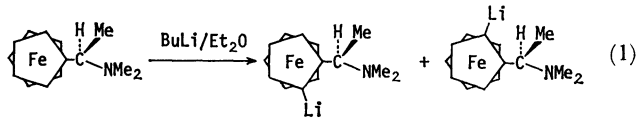
Phosphines containing asymmetric alkyl groups were usually derived from optically active natural compounds. Kagan *et al.* have achieved a great success with 2,3-*O*-isopropylidene-1,4-bis(diphenylphosphino)-2,3-butanediol (DIOP),[10] prepared relatively easily from tartaric acid. The DIOP has been successfully applied in various kinds of catalytic asymmetric synthesis, *e.g.*, hydrogenation of olefins[11–15] and ketones,[16,17] hydrosilylation of ketones[18–21] and imines,[11a] hydroformylation,[22–24] Grignard cross-coupling,[25,26] and allylic alkylation.[27] Neomenthyldiphenylphosphine (NMDPP)[28,29] and its diastereomeric isomer (MDPP),[29] prepared by Morrison *et al.*, have been used for the hydrogenation of acrylic acids to give up to 62% optical yield.[3,28] They have also studied a bisphosphine ligand (CAMPHOS) derived from camphoric acid.[3] Dimenthylphosphines have been synthesized and used as chiral ligands for a nickel catalyzed cooligomerization of olefins.[30] Optically active amino acids, proline and hydroxyproline, have been employed as chiral sources of phosphine ligands. They are (*S*)-2-(diphenylphosphinomethyl)pyrrolidines[31] and (2*S*, 4*S*)-4-diphenylphosphino-2-(diphenylphosphinomethyl)pyrrolidines,[32] respectively, the latter affording enantiomeric excess of 83—91% in the hydrogenation of α-(acylamino)cinnamic acids. Mono- and diphosphines derived from sugars have been reported to be effective for the asymmetric hydrogenation.[33] (*S*,*S*)-2,3-bis(diphenylphosphino)butane (chiraphos) and (*R*)-1,2-bis(diphenylphosphino)propane (prophos) developed by Fryzuk and Bosnich[34] are among the best ligands for the synthesis of optically active amino acids by the rhodium complex catalyzed hydrogenation. 2,2′-Bis(diphenylphosphinomethyl)-1,1′-binaphthyl (NAPHOS),[35] whose chirality is due to binaphthyl axial chirality, has been prepared and used as a ligand in several catalytic asymmetric reactions.

Chiral ferrocenylphosphines, which have planar chirality due to 1,2-unsymmetrically substituted ferrocene structure[36] and also have various functional groups such as an amino or a hydroxyl group, have been found to give rise to a high asymmetric induction in several transition metal catalyzed asymmetric reactions, *viz.*, hydrogenation of olefins,[37,38] ketones,[39] and imines[40] catalyzed by rhodium complexes, hydrosilylation of ketones by rhodium complexes[41] and of olefins by palladium complexes,[42] Grignard cross-coupling by nickel[43] and palladium[44] complexes, and isomerization of allylamines to enamines by cobalt complexes.[45] In this paper, we wish to describe in detail the preparation of the chiral ferrocenylphosphines.

† Present address: Department of Chemical Engineering, Tokyo Institute of Technology, Meguro-ku, Tokyo 152.

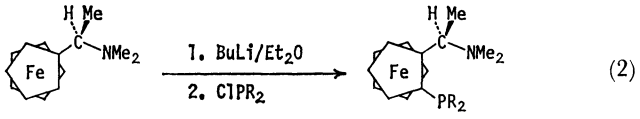
Results and Discussion

Introduction of Phosphino Groups into N,N-*Dimethyl-1-ferrocenylethylamine.* Chiral ferrocenylphosphines are readily prepared by way of lithiation of optically resolved *N,N*-dimethyl-1-ferrocenylethylamine (**1**). The lithiation of (*R*)-**1** with butyllithium was previously reported by Ugi and coworkers[36] to proceed with high stereoselectivity to give preferentially (*R*)-*N,N*-dimethyl-1-[(*R*)-2-lithioferrocenyl]ethylamine[(*R*)-(*R*)-**2**] (Eq. 1).



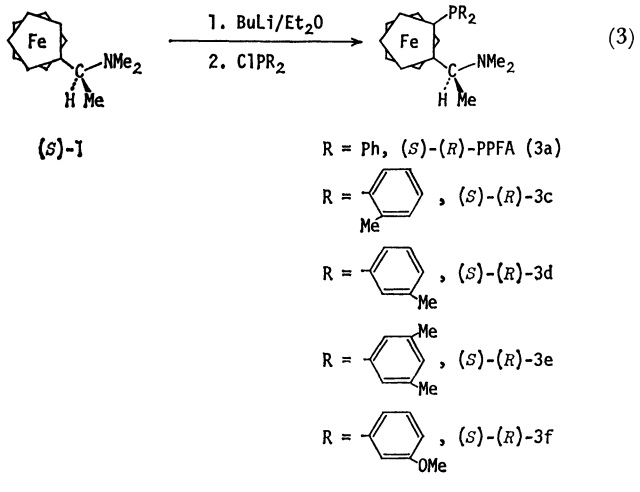
(1)

In our studies, (*R*)-**1** was lithiated, after the Ugi's procedures, with a slight excess of butyllithium in ether, and the lithiated ferrocene was then treated with chlorodiphenylphosphine. (*R*)-*N,N*-dimethyl-1-[(*S*)-2-(diphenylphosphino)ferrocenyl]ethylamine [(*R*)-(*S*)-PPFA] (**3a**), formed *via* (*R*)-(*R*)-**2**, was obtained in 55% isolated yield (Eq. 2). A small amount of



(2)

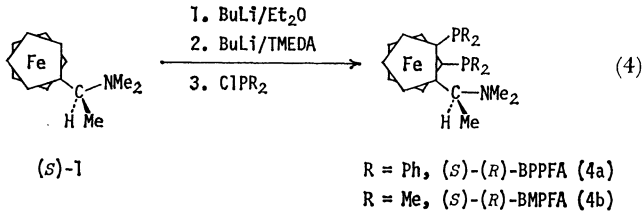
diastereomeric by-product (*R*)-(*R*)-PPFA (**3a**), formed *via* (*R*)-(*S*)-**2**, was readily removed by recrystallization. (*S*)-(*R*)-PPFA, which is an enantiomer of (*R*)-(*S*)-PPFA, was also prepared from (*S*)-**1** (Eq. 3). Simi-



(3)

larly, (*R*)-*N,N*-dimethyl-1-[(*S*)-2-(dimethylphosphino)-ferrocenyl]ethylamine [(*R*)-(*S*)-MPFA] (**3b**) was prepared in 31% yield starting with (*R*)-**1** and with chlorodimethylphosphine. Several bis(substituted phenyl)phosphino groups, such as bis(2-methylphenyl)phosphino, bis(3-methylphenyl)phosphino, bis(3,5-dimethylphenyl)phosphino, and bis(3-methoxyphenyl)phosphino groups, were introduced into (*S*)-**1** in a similar manner using the corresponding chlorodiarylphosphines (Eq. 3).

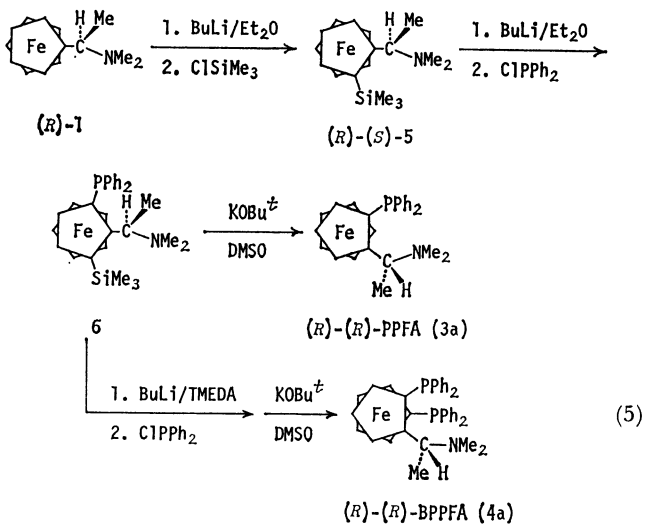
Lithiation of ferrocene in the presence of *N,N,N',N'*-tetramethylethylenediamine (TMEDA) is known[46] to produce 1,1'-dilithioferrocene, and it was expected that chiral ferrocenylphosphines bearing two phosphino groups could be prepared by the dilithiation of **1**; indeed, the stepwise lithiation of (*S*)-**1** with butyllithium in ether and then with butyllithium/TMEDA in the same solvent followed by diphenylphosphination with chlorodiphenylphosphine led to the introduction of two diphenylphosphino groups, one onto each of the cyclopentadienyl rings to give (*S*)-*N,N*-dimethyl-1-[(*R*)-1',2-bis(diphenylphosphino)ferrocenyl]ethylamine [(*S*)-(*R*)-BPPFA] (**4a**) in 58% yield (Eq. 4). The analogous bis(dimethylphosphino) derivative [(*S*)-(*R*)-BMPFA] (**4b**) was also prepared. The lithiation of PPFA (**3a**) with butyllithium followed by phosphination with chlorodiphenylphosphine resulted in the formation of *N,N*-dimethyl-1-[2,5-bis(diphenylphosphino)ferrocenyl]ethylamine, and BPPFA (**4a**) was not formed in any noticeable amounts.



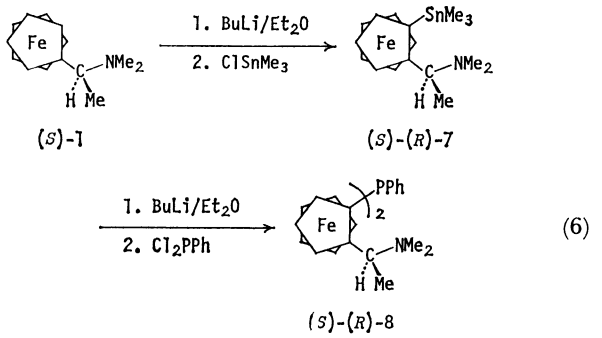
(4)

Although the ferrocenylphosphines with (*S*)-(*R*) or (*R*)-(*S*) configuration were readily obtained in good yields as shown in Eqs. 2—4, it was difficult to obtain pure (*R*)-(*R*) or (*S*)-(*S*) isomers in quantity by the lithiation-phosphination of **1**, since the lithioferrocene **2** which leads to (*R*)-(*R*) or (*S*)-(*S*) ferrocenylphosphine is produced only in small quantities from the highly stereoselective lithiation of **1** (see Eq. 1). This difficulty was solved by first protecting the ring hydrogen liable to lithiation with a trimethylsilyl group, then metalating the other lower reactive hydrogen, vicinal to the 1-(dimethylamino)ethyl group, followed by treating with chlorodiphenylphosphine, and finally desilylating. Thus, (*R*)-*N,N*-dimethyl-1-[(*S*)-2-(trimethylsilyl)ferrocenyl]ethylamine (**5**)[36] obtained by trimethylsilylation of (*R*)-**1** with butyllithium and chlorotrimethylsilane, was diphenylphosphinated with butyllithium and chlorodiphenylphosphine to give regioselectively (*R*)-*N,N*-dimethyl-[2-trimethylsilyl-5-(diphenylphosphino)ferrocenyl]ethylamine (**6**). Desilylation of **6** to (*R*)-(*R*)-PPFA was effected by treatment with potassium *t*-butoxide in dimethyl sulfoxide after Price's techniques.[47] Usual protodesilylation methods were not successful in this special case. Desilylation after introduction of the second diphenylphosphino group into **6** gave (*R*)-(*R*)-BPPFA.

Attempts to prepare bis[2-[1-(dimethylamino)ethyl]-ferrocenyl]phenylphosphine (**8**) by the lithiation of **1** with butyllithium and then addition of dichlorophenylphosphine failed, probably due to the low conversion (≈60%) of **1** into the lithioferrocene **2**. Main products were dibutylphenylphosphine and a phenyl-

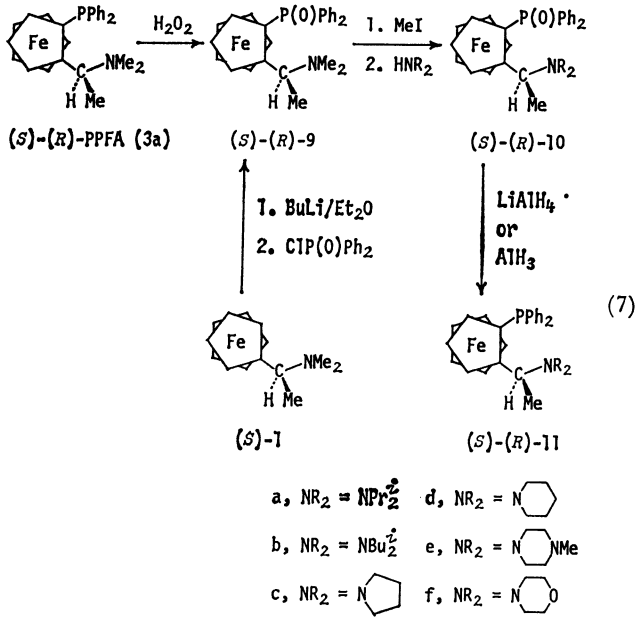


butylphosphinoferrocene derivative, formed by the reaction of chlorophosphines with unreacted butyllithium. The preparation of (*S*)-(*R*)-**8** was achieved *via* transmetalation of (*S*)-*N*,*N*-dimethyl-1-[(*R*)-2-(trimethylstannyl)ferrocenyl]ethylamine (**7**) which had been once isolated as a precursor of lithioferrocene (*S*)-(*S*)-**2** (Eq. 6).[48]

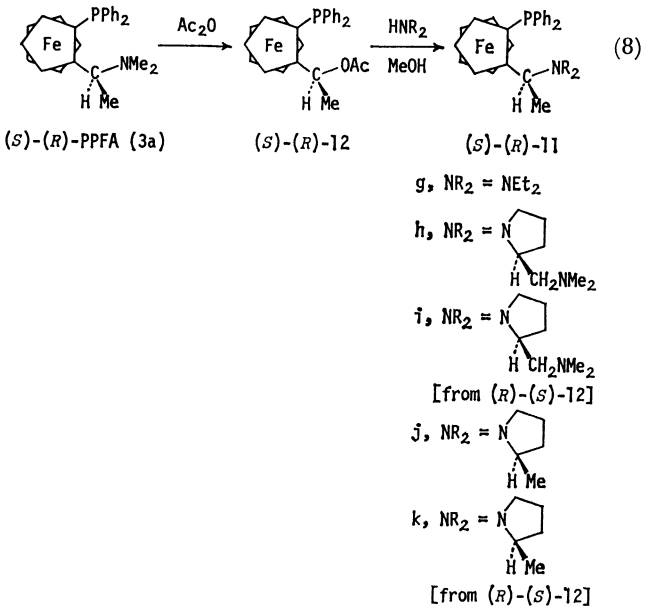


Modification of the Side Chain of Chiral Ferrocenylphosphines. Ferrocenylethane derivatives with a suitable leaving group such as trimethylammonium or acetate in the α-position have been reported[36,49] to undergo nucleophilic substitutions generally with complete retention of configuration.

Attempts to replace the dimethylamino group in (*S*)-(*R*)-PPFA (**3a**) by other dialkylamino groups by treating **3a** with methyl iodide and then with dialkylamines were not successful. The reaction of **3a** with methyl iodide formed preferentially the phosphonium salt rather than the desired ammonium salt. Protection of the diphenylphosphino group against the formation of phosphonium salt enabled the nucleophilic substitution to occur on the side chain. Thus, the preparation of several (*R*)-[(*S*)-1-(diaklylamino)-ethyl]ferrocenylphosphines (**11**) could be achieved first by converting (*S*)-(*R*)-**3a** into the phosphine oxide (**9**), then quaternization of the dimethylamino group, treatment with a dialkylamine and finally by reduction with lithium aluminum hydride or alane (Eq. 7). The diisopropylamino (**11a**), diisobutylamino (**11b**), 1-pyrrolidinyl (**11c**), piperidino (**11d**), 4-methyl-1-piperazinyl (**11e**), and morpholino (**11f**) derivatives were obtained in 30—60% overall yields. The phosphine oxide (*S*)-(*R*)-**9** could also be obtained by the reaction of lithioferrocene **2** with diphenylphosphinyl chloride in a similar way to the preparation of (*S*)-(*R*)-**3a**.

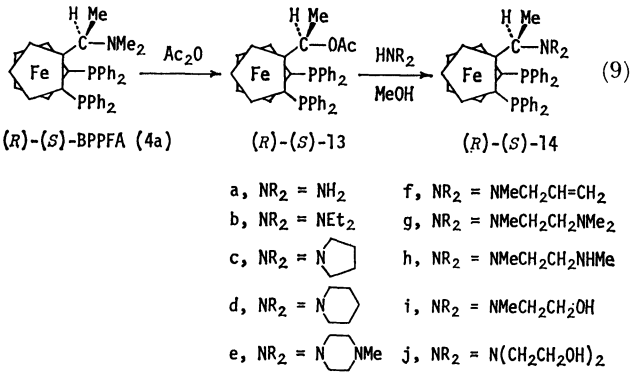


The dimethylamino group in (*S*)-(*R*)-PPFA (**3a**) was found to be substituted by other amino groups more conveniently by way of (*S*)-1-[(*R*)-2-(diphenylphosphino)ferrocenyl]ethyl acetate (**12**) (Eq. 8). (*S*)-(*R*)-PPFA (**3a**) was treated with an excess of acetic anhydride at 100 °C employing a modification of Nesmeyanov's procedure[50] to give the acetate (*S*)-(*R*)-**12** in the epimeric pure form in almost quantitative yield. The configuration *S* of the carbon central chirality of **12** was inferred from the result that the same substitution reaction on [1-(dimethylamino)-ethyl]ferrocene proceeded with nearly complete retention of configuration. (*S*)-(*R*)-**12** was then allowed to react with a dialkylamine in refluxing methanol to give (*S*)-(*R*)-**11f—k** in a high yield.



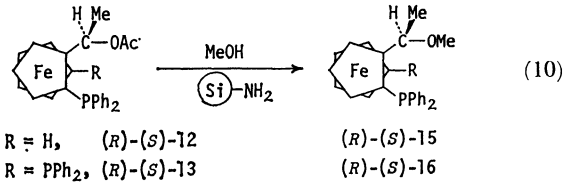
Replacement of the dimethylamino group in (*R*)-(*S*)-

BPPFA (**4a**) by other amino groups was also carried out *via* its acetate derivative (**13**) in a similar manner to the preparation of **11** (Eq. 9).



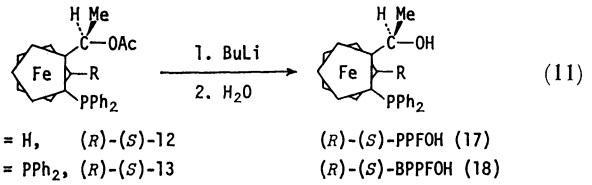
(9)

A methoxyl group also was introduced into the side chain of the chiral ferrocenylphosphines by treatment of the acetate (*R*)-(*S*)-**12** or (*R*)-(*S*)-**13** with refluxing methanol in the presence of 3-aminopropylated silica gel[51] (Eq. 10). (*R*)-(*S*)-**16** was also found to be formed by the reaction of (*R*)-(*S*)-**13** with sodium methoxide in methanol.



(10)

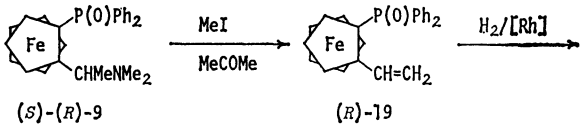
The acetate (*R*)-(*S*)-**13** was converted quantitatively into a ferrocenylphosphine with the hydroxyl group, (*R*)-1-[(*S*)-1′,2-bis(diphenylphosphino)ferrocenyl]ethanol (BPPFOH) (**18**) by treatment with an excess of butyllithium in ether followed by hydrolysis (Eq. 11). Direct acid or base hydrolysis of the acetate in the usual way gave only lower yields.

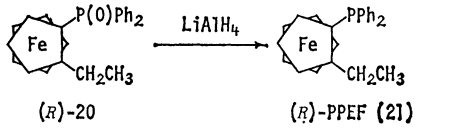


(11)

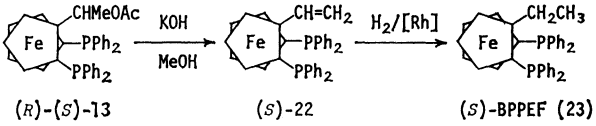
The chiral ferrocenylphosphines mentioned above all contain both planar and central elements of chirality and also a functional group such as the amino, hydroxyl, or methoxyl. Ferrocenylphosphines, (*R*)-1-diphenylphosphino-2-ethylferrocene (PPEF) (**21**) and (*S*)-1′,2-bis(diphenylphosphino)-2-ethylferrocene (BPPEF) (**23**), having only a planar element of chirality, were prepared by a sequence of reactions as shown in Eqs. 12 and 13. (*S*)-(*R*)-**9** was subjected to Hofmann elimination to give a vinylferrocene (*R*)-**19**. Hydrogenation of (*R*)-**19** in the presence of chlorotris(triphenylphosphine)rhodium(I) to (*R*)-**20** followed by reduction with lithium aluminum hydride gave (*R*)-PPEF (**21**).

Treatment of (*R*)-(*S*)-**13** with potassium hydroxide in methanol gave elimination product (*S*)-**22** in 34% yield together with substitution product (*R*)-(*S*)-**18** (39%). (*S*)-**22** was then converted into (*S*)-BPPEF (**23**) by the rhodium catalyzed hydrogenation.



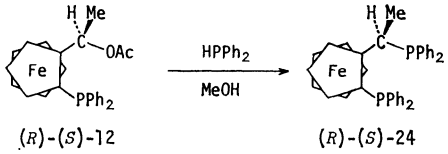


(12)



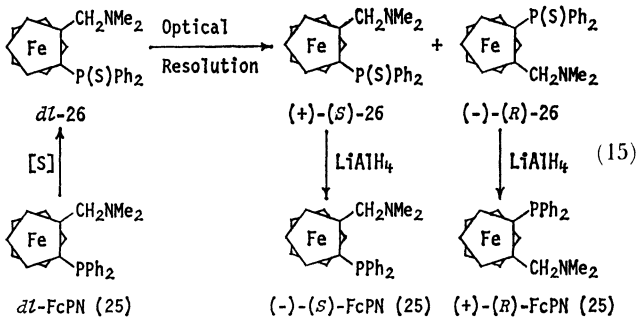
(13)

Finally, a new type of bisphosphine [(*R*)-1-[(*S*)-2-(diphenylphosphino)ferrocenyl]ethyl]diphenylphosphine (**24**) was prepared from (*R*)-(*S*)-**12** by substitution reaction with diphenylphosphine in methanol (Eq. 14).



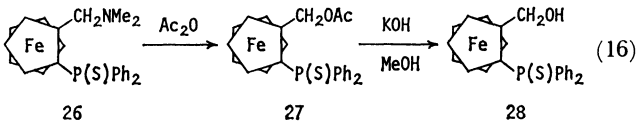
(14)

Preparation of Optically Active 1-Dimethylaminomethyl-2-(diphenylphosphino)ferrocene (FcPN). 1-Dimethylaminomethyl-2-(diphenylphosphino)ferrocene (FcPN)[52] (**25**), which is analogous to **3a** but lacks carbon central chirality, was optically resolved *via* its phosphine sulfide dibenzoyltartaric acid salt (Eq. 15). Attempted resolution of *dl*-**25** directly *via* its ammonium salts with optically active acids, such as tartaric acid, dibenzoyltartaric acid, or camphor-10-sulfonic acid, was not successful. Alkaline hydrolysis of one of the diastereoisomers, which were separated as crystals in the fractional recrystallization of the ammonium salts consisting of the *dl*-phosphine sulfide **26** and dibenzoyl-*d*-tartaric acid in methanol, gave (+)-isomer of **26**,



(15)

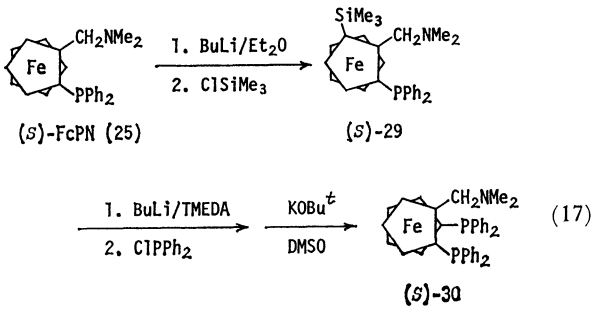
which was converted into (−)-**25** by reduction with lithium aluminum hydride in dioxane. The configuration of (−)-**25** was inferred to be *S* by comparison of its CD spectrum with that of other ferrocenylphosphines of definite configuration (*vide infra*). The phosphine sulfide **26** was converted into the hydroxy derivative **28** (Eq. 16), and the enantiomeric purity



(16)

was determined by NMR spectroscopy using a chiral lanthanoid shift reagent,[53] tris(3-trifluoroacetyl-*d*-camphorato)europium(III) [Eu(facam)$_3$]. **26** of $[\alpha]_{545}^{25}$ ±50.5° (chloroform) turned out to be optically pure.

The bisphosphine (*S*)-**30** analogous to FcPN (**25**) was also prepared from the optically active **25** using the protecting method with the trimethylsilyl group (Eq. 17).



(17)

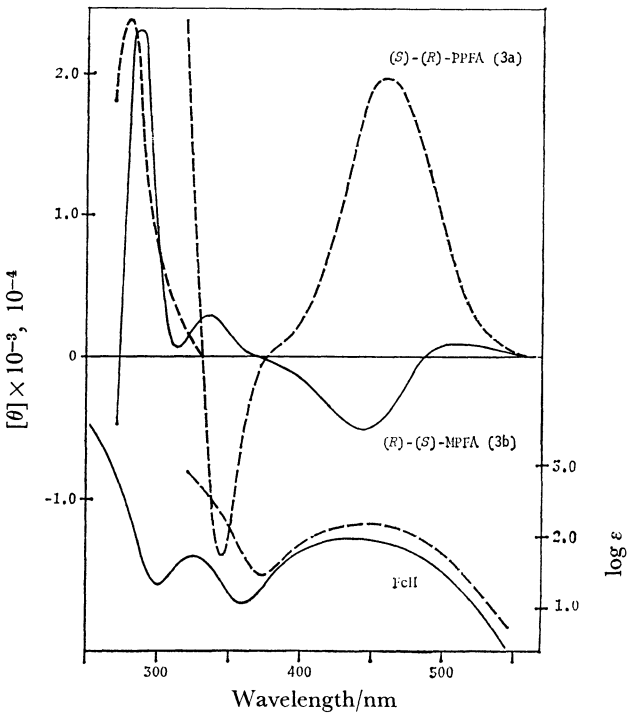


Fig. 1. CD and UV spectra of (*S*)-(*R*)-PPFA (**3a**) and (*R*)-(*S*)-MPFA (**3b**) in chloroform.

Physical Properties of Chiral Ferrocenylphosphines. Melting points, specific rotations, and analytical data for the chiral ferrocenylphosphines are summarized in Table 1. The absorption and CD spectra of PPFA (**3a**), MPFA (**3b**), BPPFA (**4a**), PPEF (**21**), and FcPN (**25**) are shown in Figs. 1, 2, and 3. The absorption spectrum of ferrocene has two long wavelength bands at 440 and 325 nm assignable to d-d type transition.[54] The CD spectra of chiral ferrocenylphosphines reveal optical activity arising from

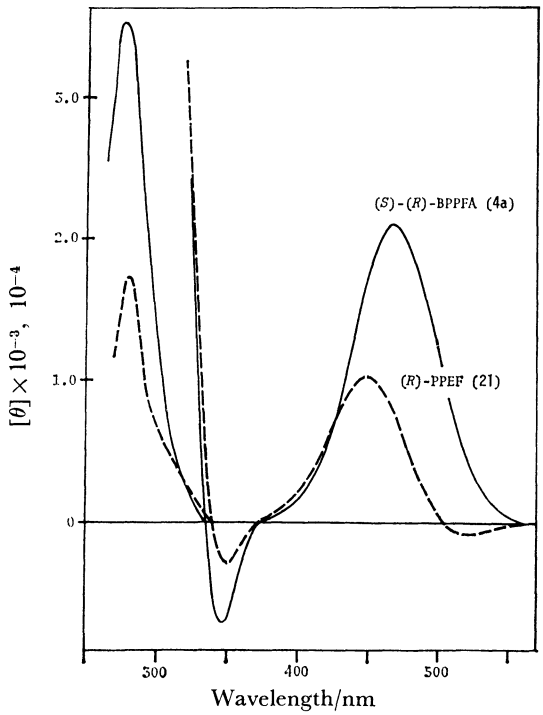


Fig. 2. CD spectra of (*S*)-(*R*)-BPPFA (**4a**) and (*R*)-PPEF (**21**) in chloroform.

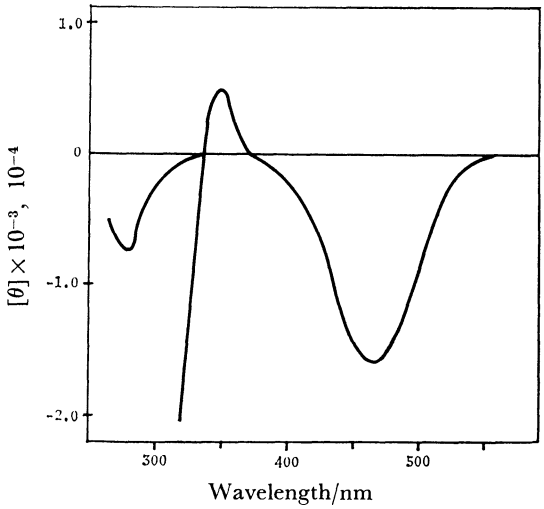


Fig. 3. CD spectrum of (*S*)-FcPN (**25**) in chloroform.

the planar chirality around these two absorption bands. The ferrocenylphosphines with planar chirality of *R* configuration, (*S*)-(*R*)-PPFA (**3a**), (*S*)-(*R*)-BPPFA (**4a**), and (*R*)-PPEF (**21**), all have positive Cotton effects around 450—470 and negative ones around 340—350 nm, whereas opposite Cotton effects are observed in the case of (*R*)-(*S*)-MPFA (**3b**) whose planar chirality is *S*. The negative and positive Cotton effects around 450—470 and 340—350 nm respectively observed in the CD spectrum of (−)-FcPN (**25**) shows that the absolute configuration of (−)-FcPN is *S*.

Conclusions. In conclusion we summarize some unique and significant features of the chiral ferrocenylphosphine ligands. (1) They all contain planar element of chirality due to 1,2-unsymmetrically substituted ferrocene structure, which must be highly asym-

metric enough to bring about high stereoselectivity in the catalytic asymmetric reactions. (2) Phosphines having either of the two configurations (*R* and *S*) of the carbon central chirality on the side chain of ferrocene and also those lacking this central chirality can be prepared: examples are (*S*)-(*R*)-**3a**, (*R*)-(*R*)-**3a**, and (*R*)-**25**. (3) Various kinds of functional groups such as an amino, alkoxyl, or hydroxyl can be introduced into the ferrocene side chain by nucleophilic substitution reactions, which proceed stereospecifically without any racemization or epimerization. (4) Both mono- and bisphosphines can be prepared from the same chiral source. They will coordinate with a transition metal as monodentate and bidentate ligands, respectively. The monophosphines with an amino group may possibly be a new type of chiral ligands that are capable of coordinating at both the phosphorus and nitrogen atoms.

The chiral ferrocenylphosphines have aforementioned advantages over other chiral phosphines, and they indeed gave rise to a high asymmetric induction in several transition metal complex catalyzed asymmetric reactions.[37-44] The high ability of the chiral ferrocenylphosphines is ascribed mainly to the attractive interactions between functional groups on a substrate and on the chiral ligand coordinated to a transition metal catalyst. The catalytic asymmetric reactions will be fully described elsewhere.

Experimental

All melting points are uncorrected. ^{1}H NMR spectra were recorded with a JEOL MH-100 or Varian EM-360 spectrometer, using tetramethylsilane as an internal standard in chloroform-*d*. The notations s, d, t, q, m, dd, and cm indicate singlet, doublet, triplet, quartet, multiplet, doublet of doublets, and complex multiplet, respectively. A letter b before these letters indicates broad. Infrared spectra were recorded with a Hitachi EPI-G3 grating spectrophotometer, UV spectra with a Hitachi EPS-3T spectrophotometer, and optical rotations were measured with a Yanagimoto OR-50 automatic polarimeter. ORD and CD spectra were obtained on a JASCO J-20 automatic recording spectropolarimeter. Wakogel (Silica gel) C-200 and Alumina Activated 200 (Nakarai) for column chromatography, and Alumina PF_{254} (Merck) and Silica gel 60 PF_{254} (Merck) for preparative TLC were used for the isolation and purification of the products.

dl-N,N-dimethyl-1-ferrocenylethylamine (**1**) was prepared by literature methods,[55,56] and optically resolved according to the reported procedure.[36]

Preparation of Chiral Ferrocenylphosphines. All manipulations for preparing phosphines were carried out in an oxygen-free dry nitrogen atmosphere. Melting points, optical rotations, and analytical data for the phosphines are summarized in Table 1.

*(S)-N,N-Dimethyl-1-[(R)-2-(diphenylphosphino)ferrocenyl]ethylamine [(S)-(R)-PPFA (**3a**)].* According to the procedure reported by Ugi *et al.*[36] for stereoselective lithiation of resolved *N,N*-dimethyl-1-ferrocenylethylamine (**1**), 12.4 ml of 1.4 M butyllithium in hexane was added to a solution of 3.60 g (14 mmol) of (*S*)-**1** ($[\alpha]_D^{24}$ −13.8° (*c* 1.5, ethanol)) in 20 ml of dry ether at 25—27 °C over a period of 20 min. The mixture was stirred at room temperature for 1.5 h and then 6.2 g (28 mmol) of chlorodiphenylphosphine in 10 ml of ether was added with heating under gentle reflux in the course of 45 min. After 4 h reflux aqueous sodium hydrogencarbonate was slowly added with cooling in an ice-bath. The resulting organic layer and benzene extracts from the aqueous layer were combined, washed with water, dried over anhydrous sodium sulfate, and concentrated *in vacuo* to afford a red oil. The oil was chromatographed on alumina (eluent: hexane/benzene, 3/1), and evaporated to give a crude product as orange crystals. The product was purified by recrystallization from ethanol to give 3.11 g (50% yield) of (*S*)-(*R*)-PPFA (**3a**), UV: λ_{max} ($CHCl_3$) 447 nm (ε 150), NMR: δ 1.19 (d, 3H, *J*=7 Hz, $CHC\underline{H}_3$), 1.77 (s, 6H, $NC\underline{H}_3$), 3.90 (s, 5H, $FeC_5\underline{H}_5$), 3.56—4.39 (m, 4H, $FeC_5\underline{H}_3C\underline{H}$), and 6.88—7.71 (cm 10H, $C_6\underline{H}_5$). The IR spectrum indicated the presence of the unsubstituted cyclopentadienyl ring (1105 and 1001 cm^{-1}) and phenyl groups (745 and 698 cm^{-1}). ORD (*c* 0.11 and 0.004, chloroform): $[\Phi]_{589}$ +1520°, $[\Phi]_{495}$ +3140° (pk), $[\Phi]_{434}$ +1590° (tr), and $[\Phi]_{294}$ +21900° (pk). The CD spectrum is shown in Fig. 1.

(*R*)-(*S*)-PPFA (**3a**) was prepared from (*R*)-**1** in a similar manner.

*(R)-N,N-Dimethyl-1-[(S)-2-(dimethylphosphino)ferrocenyl]ethylamine [(R)-(S)-MPFA (**3b**)].* At 27 °C, 3.14 g (12.2 mmol) of (*R*)-**1** ($[\alpha]_D^{24}$ +14.1° (*c* 1.6, ethanol)) was lithiated as described above. To the solution, 1.59 g (15.5 mmol) of chlorodimethylphosphine was added dropwise with stirring. A vigorous reaction occurred and the chlorodimethylphosphine was added at such a rate as to maintain boiling. The resulting mixture was heated under reflux for 3 h. Benzene/ether (1/1) (50 ml) and dilute sodium hydroxide solution (20 ml) were then added to the cooled reaction mixture. The organic layer was separated, dried over anhydrous sodium sulfate, and concentrated *in vacuo*. The residue was chromatographed on alumina (benzene) to give 1.10 g (31% yield) of (*R*)-(*S*)-MPFA (**3b**) as a red oil, UV: λ_{max} ($CHCl_3$) 446 nm (ε 131); NMR: δ 1.08 and 1.31 (a pair of d, 6H, *J*=2.6 Hz, $P(C\underline{H}_3)_2$), 1.34 (d, 3H, *J*=5.6 Hz, $CHC\underline{H}_3$), 2.14 (s, 6H, $NC\underline{H}_3$), 4.09 (s, 5H, $FeC_5\underline{H}_5$), 3.8—4.4 (cm, 3H, $FeC_5\underline{H}_3$). Methine proton resonances may lie under the cyclopentadienyl proton resonances. The IR spectrum indicated the presence of the unsubstituted cyclopentadienyl ring (1106 and 1000 cm^{-1}) and dimethylphosphino group (928 cm^{-1}). ORD (*c* 0.11 and 0.01, chloroform): $[\Phi]_{589}$ −425°, $[\Phi]_{473}$ −1120° (tr), $[\Phi]_{415}$ −615° (pk), $[\Phi]_{328}$ −1580° (tr), $[\Phi]_{304}$ −990° (pk), and $[\Phi]_{273}$ −8290° (tr). The CD spectrum is shown in Fig. 1.

*(S)-N,N-Dimethyl-1-[(R)-2-[bis(2-methylphenyl)phosphino]-ferrocenyl]ethylamine [(S)-(R)-**3c**].* (*S*)-(*R*)-**3c** was prepared in a similar manner to that for the preparation of (*S*)-(*R*)-**3a** starting with (*S*)-**1** and with chlorobis(2-methylphenyl)phosphine;[57a] recrystallized from methanol, 30% yield; NMR: δ 1.35 (d, 3H, *J*=7.5 Hz, $CHC\underline{H}_3$), 1.82 (s, 6H, $NC\underline{H}_3$) 2.15 and 2.96 (a pair of s, 6H, $C_6H_4C\underline{H}_3$), 3.88 (s, 5H, $FeC_5\underline{H}_5$), 3.75—4.48 (m, 4H, $C_5\underline{H}_3C\underline{H}$), 6.9—7.3 (cm, 8H, PC_6H_4).

*(R)-N,N-Dimethyl-1-[(S)-2-[bis(3-methylphenyl)phosphino]-ferrocenyl]ethylamine [(R)-(S)-**3d**].* Prepared from (*R*)-**1** and chlorobis(3-methylphenyl)phosphine,[57b] 35% yield; NMR: δ 1.28 (d, 3H, *J*=7.5 Hz, $CHC\underline{H}_3$), 1.80 (s, 6H, $NC\underline{H}_3$), 2.25 and 2.40 (a pair of s, 6H, $C_6H_4C\underline{H}_3$), 3.96 (s, 5H, $FeC_5\underline{H}_5$), 3.84—4.42 (m, 4H, $FeC_5\underline{H}_3C\underline{H}$), 6.90—7.63 (cm, 8H, $PC_6\underline{H}_4$).

*(S)-N,N-Dimethyl-1-[(R)-2-[bis(3,5-dimethylphenyl)phosphino]-ferrocenyl]ethylamine [(S)-(R)-**3e**].* Prepared from (*S*)-**1** and c lorobis(3,5-dimethylphenyl)phosphine (115—135 °C/0.015 mmHg, prepared by Yudina's method[57b]), 28% yield; NMR: δ 1.26 (d, 3H, *J*=7 Hz, $CHC\underline{H}_3$), 1.84 (s,

Table 1. Melting points, optical rotations, analytical data for chiral ferrocenylphosphines

Compound	Mp/°C	$[\alpha]_D^{25}$ (c, $CHCl_3$)	Found(Calcd) (%)		
			C	H	N
(*R*)-(*S*)-PPFA (**3a**)	139	−361° (0.6) [a]	70.74(70.76)	6.23(6.39)	2.95(3.17)
(*S*)-(*R*)-PPFA (**3a**)	139	+361° (0.6) [a]			
(*R*)-(*R*)-PPFA (**3a**)	oil	+364° (0.4)	70.46(70.76)	6.19(6.39)	3.05(3.17)
(*R*)-(*S*)-MPFA (**3b**)	oil	−134° (0.3)	60.61(60.59)	7.71(7.63)	4.51(4.42)
(*S*)-(*R*)-**3c**	123	+155° (0.4)	71.65(71.64)	6.81(6.87)	2.96(2.98)
(*R*)-(*S*)-**3d**	82.5—83	−349° (0.4)	71.58(71.64)	6.91(6.87)	3.03(2.98)
(*S*)-(*R*)-**3e**	oil	+280° (0.4)	72.67(72.44)	7.44(7.29)	2.91(2.82)
(*S*)-(*R*)-**3f**	111—112	+376° (0.4)	66.98(67.08)	6.39(6.43)	2.87(2.79)
(*S*)-(*R*)-BPPFA (**4a**)	139—140	+349° (0.5)	72.72(72.97)	6.00(5.96)	2.49(2.24)
(*R*)-(*S*)-BPPFA (**4a**)		−349° (0.5)			
(*R*)-(*R*)-BPPFA (**4a**)	oil	+335° (0.3)	72.68(72.97)	6.09(5.96)	2.32(2.24)
(*S*)-(*R*)-BMPFA (**4b**)	oil [b]	+14.8° (0.6)	57.47(57.31)	8.01(7.75)	3.62(3.71)
(*R*)-(*R*)-**6**	oil	+323° (0.5)			
(*S*)-(*R*)-**7**	oil	+5.95° (0.5)	48.75(48.62)	6.60(6.48)	3.32(3.34)
(*S*)-(*R*)-**8**	193.5—194	+477° (0.3)	65.83(65.83)	6.68(6.60)	4.54(4.52)
(*S*)-(*R*)-**9**	239—242 [c]	+161° (0.4)	68.54(68.28)	6.05(6.17)	2.92(3.06)
(*S*)-(*R*)-**10a**	175—178 [c]	+172° (0.4)	69.95(70.18)	6.93(7.07)	2.69(2.73)
(*S*)-(*R*)-**10b**	oil	+217° (0.4)	70.88(70.98)	7.46(7.45)	2.51(2.59)
(*S*)-(*R*)-**10c**	192—195 [c]	+140° (0.4)	69.28(69.58)	6.27(6.23)	2.60(2.90)
(*S*)-(*R*)-**10d**	200—210 [c]	+137° (0.4)	70.01(70.03)	6.61(6.48)	2.76(2.82)
(*S*)-(*R*)-**10e**	170	+192° (0.4)	68.05(67.98)	6.52(6.49)	5.36(5.47)
(*S*)-(*R*)-**10f**	217	+147° (0.4)	67.25(67.35)	5.90(6.06)	2.74(2.81)
(*S*)-(*R*)-**11a**	145.5—146	+359° (0.4)	72.16(72.43)	7.28(7.30)	2.78(2.82)
(*S*)-(*R*)-**11b**	oil	+389° (0.4)	72.79(73.14)	7.90(7.67)	2.50(2.67)
(*S*)-(*R*)-**11c**	102—103	+331° (0.3)	71.84(71.96)	6.67(6.47)	2.93(3.00)
(*S*)-(*R*)-**11d**	144—145	+331° (0.5)	72.32(72.36)	6.89(6.70)	2.97(2.91)
(*S*)-(*R*)-**11e**	101—102	+381° (0.4)	70.33(70.17)	6.72(6.70)	5·66(5.64)
(*S*)-(*R*)-**11f**	153	+343° (0.5)	69.86(69.58)	6.31(6.26)	3.07(2.90)
(*S*)-(*R*)-**11g**	124.5—125	+360° (0.4)	71.41(71.65)	6.80(6.87)	2.90(2.98)
(*S*)-(*R*)-**11h**	oil	+300° (0.4)	70.70(70.99)	7.25(7.11)	5.18(5.34)
(*R*)-(*S*)-**11i**	90—91	−275° (0.4)	70.98(70.99)	7.34(7.11)	5.23(5.34)
(*S*)-(*R*)-**11j**	128—129	+374° (0.5)	72.28(72.35)	6.91(6.70)	2.80(2.91)
(*S*)-(*R*)-**12**	117.5—118.5	+337° (0.9)	68.16(68.44)	5.68(5.96)	
(*R*)-(*S*)-**12**		−333° (0.4)			
(*R*)-(*S*)-**13**	153.5—155	−311° (0.5)	70.96(71.26)	5.05(5.35)	
(*R*)-(*S*)-**14a**	140—141	−302° (0.5)	72.35(72.37)	5.61(5.57)	2.30(2.34)
(*S*)-(*R*)-**14b**	190.5—191	+346° (0.4)	73.80(73.51)	6.38(6.32)	1.96(2.14)
(*S*)-(*R*)-**14c**	178	+344° (0.4)	73.54(73.74)	6.29(6.03)	2.06(2.15)
(*S*)-(*R*)-**14d**	150	+347° (0.4)	74.01(73.99)	6.19(6.21)	2.06(2.10)
(*S*)-(*R*)-**14e**	oil	+313° (0.2)	72.63(72.35)	6.33(6.22)	3.94(4.12)
(*R*)-(*S*)-**14f**	98—99	−327° (0.3)	73.73(73.74)	5.95(6.03)	2.06(2.15)
(*S*)-(*R*)-**14g**	oil	+313° (0.4)	71.83(72.14)	6.46(6.50)	3.77(4.10)
(*R*)-(*S*)-**14h**	137.5—138.5	−361° (0.4)	71.81(71.86)	6.25(6.33)	4.06(4.19)
(*R*)-(*S*)-**14i**	173—174.5	−368° (0.5)	71.47(71.46)	6.07(6.00)	1.98(2.14)
(*R*)-(*S*)-**14j**	163—164	−441° (0.5)	69.83(70.08)	6.12(6.03)	1.97(2.04)
(*R*)-(*S*)-**15**	120—121.5	−320° (0.2)	69.73(70.11)	5.84(5.88)	
(*R*)-(*S*)-**16**	164.5—165.5	−252° (0.7)	72.62(72.56)	5.55(5.60)	
(*R*)-(*S*)-PPFOH (**17**)	104.5—106	−271° (0.7)	69.32(69.58)	5.63(5.60)	
(*R*)-(*S*)-BPPFOH (**18**)	154—155	−285° (0.5)	72.31(72.25)	5.43(5.39)	
(*R*)-**20**	151.5—152	+118° (0.6)	69.75(69.58)	5.61(5.60)	
(*R*)-PPEF (**21**)	95.5	+273° (0.3)	72.36(72.38)	5.86(5.82)	
(*S*)-**22**	178.5—182	+83.3° (0.3)	74.37(74.50)	5.51(5.21)	
(*S*)-BPPEF (**23**)	166—167	−147° (0.3)	74.48(74.24)	5.58(5.54)	
(*R*)-(*S*)-**24**	oil	−330° (0.3)	74.53(74.24)	5.73(5.54)	
(*S*)-FcPN (**25**)	91.5	−325° (0.5)			
(*R*)-FcPN (**25**)	92	+324° (0.5)			
(*S*)-**26**	168—169.5	+50.2° (0.5) [d]	65.66(65.37)	5.94(5.70)	3.31(3.05)
(*R*)-**26**	169—171	−50.5° (0.5) [d]			
(*S*)-**27**	190—193 [c]		63.49(63.30)	4.87(4.89)	
(*S*)-**28**	192—194 [c]		63.51(13.90)	5.21(4.90)	
(*S*)-**29**	oil	−192° (0.4)			
(*S*)-**30**	135—136	−269° (0.3)	72.65(72.68)	5.74(5.77)	2.50(2.29)

a) Specific rotation in ethanol. b) Bp 157 °C/0.03 mmHg. c) Decomposition. d) $[\alpha]_{545}^{25}$ ($CHCl_3$).

6H, NC$\underline{H}_3$), 2.18 and 2.32 (a pair of s, 12H, $C_6H_3(C\underline{H}_3)_2$), 3.94 (s, 5H, $C_5\underline{H}_5$), 3.8—4.4 (m, 4H, $FeC_5\underline{H}_3C\underline{H}$), 6.7—7.3 (m, 6H, $PC_6\underline{H}_3$).

(S)-N,N-Dimethyl-1-[(R)-2-[bis(3-methoxyphenyl)phosphino]-ferrocenyl]ethylamine [*(S)-(R)-**3f***]. Prepared from (*S*)-**1** and chlorobis(3-methoxyphenyl)phosphine,[57b] 34% yield, recrystallized from hexane; NMR: δ 1.25 (d, 3H, J=7 Hz, CHC$\underline{H}_3$), 1.78 (s, 6H, NC$\underline{H}_3$), 3.66 and 3.76 (a pair of s, 6H, OC$\underline{H}_3$), 3.95 (s, 5H, $FeC_5\underline{H}_5$), 3.8—4.4 (m, 4H, $FeC_5\underline{H}_3C\underline{H}$), 6.6—7.3 (cm, 8H, $PC_6\underline{H}_4$).

(S)-N,N-Dimethyl-1-[(R)-1',2-bis(diphenylphosphino)ferrocenyl]-ethylamine [*(S)-(R)-BPPFA (**4a**)*]. To a solution of 3.6 g (14 mmol) of (*S*)-**1** in 22 ml of dry ether, 12.0 ml of 1.4 M butyllithium in hexane was added at 27 °C over a period of 20 min. The mixture was stirred at room temperature for 1 h and then a mixture of 1.9 g (16 mmol) of freshly distilled TMEDA and 13.0 ml of 1.4 M butyllithium in hexane was added in 15 min. After 5 h stirring at room temperature, 9.3 g (42 mmol) of chlorodiphenylphosphine was added to the cooled reaction mixture. After standing overnight it was hydrolyzed with aqueous sodium hydrogencarbonate. The resulting organic layer and extracts (benzene 50 ml) from the aqueous layer were combined, dried over anhydrous sodium sulfate, and concentrated *in vacuo*. The residue was chromatographed on alumina (hexane/benzene 2/1) to give the crude product, which was recrystallized from ethanol to give 5.08 g (58% yield) of pure (*S*)-(*R*)-**4a**; UV: λ_{max} ($CHCl_3$) 443 nm (ε 194); NMR: δ 1.12 (d, 3H, J=7 Hz, CHC$\underline{H}_3$), 1.75 (s, 6H, NC$\underline{H}_3$), 3.41—4.42 (m, 8H, $C_5\underline{H}_4FeC_5\underline{H}_3C\underline{H}$), 6.87—7.66 (cm, 20H, $PC_6\underline{H}_5$). The IR spectrum did not exhibit absorptions near 1100 and 1000 cm^{-1}, indicating the absence of the unsubstituted cyclopentadienyl ring. ORD (*c* 0.10 and 0.004, chloroform): $[\Phi]_{589}$ +2160°, $[\Phi]_{499}$ +3890° (pk), $[\Phi]_{446}$ +2680° (tr), and $[\Phi]_{299}$ +30,300° (pk). The CD spectrum is shown in Fig. 2.

(S)-N,N-Dimethyl-1-[(R)-1',2-bis(dimethylphosphino)ferrocenyl]-ethylamine [*(S)-(R)-BMPFA (**4b**)*]. (*S*)-**1** (14.0 g, 54.6 mmol) was lithiated first with 48 ml of 1.4 M butyllithium and then with 62 ml of 1.4 M butyllithium and 10.0 ml (66.8 mmol) of TMEDA as described in the preparation of (*S*)-(*R*)-BPPFA (**4a**). To the solution was added 16.0 ml (187 mmol) of chlorodimethylphosphine at 0 °C. After stirring at room temperature overnight, the reaction mixture was hydrolyzed with 100 ml of 2 M sodium hydroxide. The resulting solution was extracted with benzene (2× 100 ml). Evaporation of the solvent gave a red oil, which was distilled to give 19.5 g of a mixture of (*S*)-(*R*)-MPFA (**3b**) and (*S*)-(*R*)-BMPFA (**4b**) (1:2 mixture, 120—157 °C/0.03 mmHg) and 2.5 g (12% isolated yield) of pure (*S*)-(*R*)-BMPFA (**4b**) (157 °C/0.03 mmHg); NMR: δ 1.00—1.43 (cm, 12H, PC$\underline{H}_3$), 1.50 (d, 3H, J=7 Hz, CHC$\underline{H}_3$), 2.04 (s, 6H, NC$\underline{H}_3$), 3.58 (q, 1H, C$\underline{H}$CH$_3$), 3.8—4.4 (cm, 7H, $C_5\underline{H}_4FeC_5\underline{H}_3$).

(R)-N,N-dimethyl-1-[(R)-2-(diphenylphosphino)ferrocenyl]ethylamine [*(R)-(R)-PPFA (**3a**)*]. To a solution of 1.47 g (4.47 mmol) of (*R*)-α-[(*S*)-2-trimethylsilylferrocenyl]ethyldimethylamine[36] [(*R*)-(*S*)-**5**] in 15 ml of dry ether was added 5.3 ml of 1.27 M butyllithium in hexane at room temperature. After stirring at 30 °C for 2 h, 2.0 g (9.0 mmol) of chlorodiphenylphosphine was added. The reaction mixture was refluxed for 2 h, and then hydrolyzed with 30% sodium hydroxide at 0 °C. The resulting mixture was extracted with benzene (2×50 ml). The benzene solution was washed with brine, dried over anhydrous sodium sulfate, and the solvent was removed under reduced pressure. The NMR spectrum of the residue indicated that about 50% of **5** was phosphinated. Preparative TLC (alumina, hexane/benzene 2/1) gave 0.65 g of recovered (*R*)-(*S*)-**5** (R_f 0.4) and 1.03 g (45% yield) of (*R*)-*N*,*N*-dimethyl-1-[2-trimethylsilyl-5-(diphenylphosphino)ferrocenyl]ethylamine (**6**) (R_f 0.6). NMR of (*R*)-**6**: δ 0.27 (s, 9H, SiC$\underline{H}_3$), 1.68 (s, 6H, NC$\underline{H}_3$), 1.83 (d, 3H, J=7 Hz, CHC$\underline{H}_3$), 3.27 (q, 1H, C$\underline{H}$CH$_3$), 3.92 (s, 6H, $C_5\underline{H}_5FeC_5\underline{H}$), 4.18 (d, 1H, J=3.2 Hz, $FeC_5\underline{H}$), 7.08—7.72 (m, 10H, $PC_6\underline{H}_5$).

A solution of 0.296 g (0.58 mmol) of (*R*)-**6** and 0.067 g (0.63 mmol) of potassium *t*-butoxide in 10 ml of dry dimethyl sulfoxide was warmed at 43 °C for 20 min. Benzene (20 ml) was added and the benzene solution was washed with brine, dried over anhydrous sodium sulfate, and evaporated. Column chromatography (alumina, ether) gave 0.111 g (44%) of crude (*R*)-(*R*)-**3a** containing 10% of epimerized ferrocenylphosphine, (*S*)-(*R*)-**3a**. The latter was removed as follows: The crude (*R*)-(*R*)-**3a** was dissolved in pentane, and the pentane was evaporated slowly until small amounts of crystals appeared. The crystals which consisted of *ca.* 1:1 mixture of (*S*)-(*R*)-**3a** and (*R*)-(*R*)-**3a** were removed by filtration, and the filtrate was evaporated to give almost pure (*R*)-(*R*)-**3a** (0.093 g, 37% yield) as a red oil; NMR: δ 1.35 (d, 3H, J=7.5 Hz, CHC$\underline{H}_3$), 2.14 (s, 6H, NC$\underline{H}_3$), 3.60 (q, 1H, C$\underline{H}$CH$_3$), 3.98 (s, 5H, $FeC_5\underline{H}_5$), 3.71, 4.24, 4.35 (m, 3H, $FeC_5\underline{H}_3$), 7.15—7.65 (cm, 10H, $PC_6\underline{H}_5$).

(R)-N,N-Dimethyl-1-[(R)-1',2-bis(diphenylphosphino)ferrocenyl]-ethylamine [*(R)-(R)-BPPFA (**4a**)*]. To a solution of 0.738 g (1.45 mmol) of (*R*)-**6** in 25 ml of dry ether was added dropwise with stirring 2.1 ml (13.5 mmol) of TMEDA and 11.5 ml (13.5 mmol) of 1.25 M butyllithium in hexane succesively at 0 °C. After stirring at room temperature, a solution of 2.9 ml (15 mmol) of chlorodiphenylphosphine in 10 ml of ether was added at 0 °C. The mixture was refluxed for 1 h, and then hydrolyzed with 30% sodium hydroxide (50 ml). The mixture was extracted with benzene. The organic phase was washed with water, dried over anhydrous sodium sulfate, and evaporated. The residue was chromatographed on alumina (benzene/ether 1/1). An orange band was collected. The NMR spectrum showed that *ca.* 20% of (*R*)-**6** was converted to the bisphosphine derivative. This mixture was used for the desilylation without further purification.

To the mixture thus obtained was added 0.15 g (1.35 mmol) of potassium *t*-butoxide and 10 ml of dry dimethyl sulfoxide. The mixture was warmed with stirring at 40 °C for 20 min. After usual work up, preparative TLC (silica gel, benzene/ether 1/1) gave (*R*)-(*R*)-PPFA (**3a**) (R_f 0.3) and 0.080 g (9% yield) of (*R*)-(*R*)-BPPFA (**4a**) (R_f 0.6). For (*R*)-(*R*)-**4a**, NMR: δ 1.35 (d, 3H, J=7 Hz, CHC$\underline{H}_3$), 2.07 (s, 6H, NC$\underline{H}_3$), 3.32—4.48 (m, 8H, $C_5\underline{H}_4FeC_5\underline{H}_3C\underline{H}$), 7.00—7.55 (cm, 20H, $PC_6\underline{H}_5$).

(S)-N,N-Dimethyl-1-[(R)-2-(trimethylstannyl)ferrocenyl]ethylamine [*(S)-(R)-**7***]. (*S*)-**1** (5.0 g, 19.5 mmol) was lithiated as described above. To the solution was added a solution of 5.84 g (29.3 mmol) of trimethyltin chloride in 10 ml of dry ether over a period of 8 min. After refluxing for 2 h, the reaction mixture was hydrolyzed with aqueous sodium hydrogencarbonate at 0 °C. The organic layer was separated and extracted with dilute phosphoric acid. The aqueous solution was made alkaline with sodium carbonate and extracted with ether. The ether solution was washed with brine, dried over anhydrous magnesium sulfate, and evaporated under reduced pressure. The residue was chromatographed on alumina (benzene) to give 3.48 g (43% yield) of (*S*)-(*R*)-**7** as a red oil; NMR: δ 0.21 (s and d, 9H, J_{H-Sn}=37.7 Hz, SnC$\underline{H}_3$), 1.18 (d, 3H, J=6 Hz, CHC$\underline{H}_3$), 1.99 (s, 6H, NC$\underline{H}_3$), 3.82 (q, 1H, C$\underline{H}$CH$_3$), 4.00 (s, 5H,

$FeC_5\underline{H}_5$), 4.00 and 4.23 (m, 1H and 2H, $FeC_5\underline{H}_3$).

Bis[(R)-2-[(S)-1-(dimethylamino)ethyl]ferrocenyl]phenylphosphine [*(S)-(R)-**8***]. To a solution of 0.88 g (2.1 mmol) of *(S)-(R)-**7*** in 5 ml of dry ether was added 1.47 ml (2.2 mmol) of butyllithium in hexane (1.5 M) over a period of 10 min at 0 °C. After stirring at 0 °C for 30 min, 0.19 g (1.1 mmol) of dichlorophenylphosphine was slowly added (5 min). The reaction mixture was refluxed for 1 h and then hydrolyzed with aqueous sodium hydrogencarbonate at 0 °C. The resulting organic layer and ether extracts from the aqueous layer were combined and extracted with 10% phosphoric acid. The aqueous layer was made alkaline with sodium carbonate, and extracted with ether. The ether solution was washed with brine, dried over anhydrous sodium sulfate, evaporated under reduced pressure to give a red oil. The oil was chromatographed on alumina (benzene/ether 1/1) to give 0.157 g (21% yield) of *(S)-(R)-**8***. A pure sample was obtained by recrystallization from pentane; NMR: δ 1.24 and 1.48 (a pair of d, 6H, J=6.3 Hz, $CHC\underline{H}_3$), 1.64 and 2.30 (a pair of s, 12H, $NC\underline{H}_3$), 3.57 and 3.96 (a pair of s, 10H, $FeC_5\underline{H}_5$), 3.9—4.6 (m, 8H, $FeC_5\underline{H}_3C\underline{H}$), 7.13—7.76 (m, 5H, $PC_6\underline{H}_5$).

(S)-N,N-Dimethyl-1-[(R)-2-(diphenylphosphinyl)ferrocenyl]ethylamine [*(S)-(R)-**9***]. (a) A solution of 8.8 g (37 mmol) of diphenylphosphinic chloride in 30 ml of ether was added in 15 min to the refluxing solution of 5.08 g (19.8 mmol) of *(S)-**1*** which had been lithiated as described in the preparation of *(S)-(R)-**3a***. The mixture was refluxed for 9 h, and then hydrolyzed with aqueous sodium hydroxide. The resulting organic layer and benzene extracts from the aqueous layer were combined, dried over anhydrous sodium sulfate, and concentrated *in vacuo* to a minimum volume. The residue was chromatographed on alumina. Elution with benzene gave 2.5 g of starting amine *(S)-**1***. Elution with benzene/ethyl acetate (1/1) gave the crude product. The product was purified by recrystallization from dichloromethane/light petroleum ether (1/4) to give 2.74 g (30% yield) of *(S)-(R)-**9*** which gave brown crystals; UV: λ_{max} ($CHCl_3$) 446 nm (ε 145); NMR: δ 1.12 (d, 3H, J=6 Hz, $CHC\underline{H}_3$), 1.61 (s, 6H, $NC\underline{H}_3$), 4.13 (s, 5H, $FeC_5\underline{H}_5$), 3.76—4.51 (m, 4H, $FeC_5\underline{H}_3C\underline{H}$), 7.13—8.02 (m, 10H, $PC_6\underline{H}_5$); IR (KBr): 1192 (P→O) and 1107, 1010 cm^{-1} (FeC_5H_5).

(b) To a solution of 3.29 g (7.44 mmol) of *(S)-(R)-**3a*** in 60 ml of acetone was added dropwise 3 ml of 30% hydrogen peroxide. After 30 min at room temperature, aqueous sodium thiosulfate was added to decompose an excess of the hydrogen peroxide. The reaction mixture was extracted with dichloromethane. The extract was washed with water, dried over anhydrous sodium sulfate, and then evaporated. Purification of the residue by short-column chromatography (alumina, ethyl acetate) gave 3.31 g (97% yield) of *(S)-(R)-**9***.

(S)-1-[(R)-2-(Diphenylphosphinyl)ferrocenyl]ethylamines [*(S)-(R)-**10***]. The following procedure for the preparation of *(S)-(R)-**10a*** is typical. To a solution of 0.50 g (1.1 mmol) of *(S)-(R)-**9*** in 6 ml of acetonitrile was added 4 ml (64 mmol) of methyl iodide, and the mixture was stirred at room temperature for 1 h, then evaporated to *ca.* 2 ml. To the residue, 4 ml of acetonitrile and 4 ml (29 mmol) of diisopropylamine were added. The reaction mixture was kept stirring overnight, and the solvent was removed under reduced pressure. The product was extracted with dichloromethane, and the extract was washed with brine, dried over anhydrous magnesium sulfate, and evaporated. The residue was purified by column chromatography (alumina, ethyl acetate) to give 0.47 g (82% yield) of *(S)-(R)-**10a***, which was recrystallized from ethanol; NMR: δ 0.60 and 0.94 (a pair of d, 12H, J=7 Hz, $N(CH(C\underline{H}_3)_2)_2$), 1.50 (d, 3H, J=7.5 Hz, $C_5H_3CHC\underline{H}_3$), 3.05 (7, 2H, $NC\underline{H}$), 4.12 (s, 5H, $FeC_5\underline{H}_5$), 3.87—4.62 (m, 4H, $FeC_5\underline{H}_3C\underline{H}$), 7.20—7.92 (m, 10H, $PC_6\underline{H}_5$).

*(S)-(R)-**10b***. Prepared from *(S)-(R)-**9*** and diisobutylamine in 60% yield; NMR: δ 0.50 and 0.67 (a pair of d, 12H, J=7 Hz, $N(CH_2CH(C\underline{H}_3)_2)_2$), 1.49 (d, 3H, J=7.5 Hz, $C_5H_3CHC\underline{H}_3$), 1.20—1.60 (m, 2H, $N(CH_2C\underline{H}Me_2)_2$), 1.85—2.16 (m, 4H, $NC\underline{H}_2$), 4.02 (s, 5H, $FeC_5\underline{H}_5$), 4.00—4.59 (m, 4H, $FeC_5\underline{H}_3C\underline{H}$), 7.20—7.92 (cm, 10H, $PC_6\underline{H}_5$).

*(S)-(R)-**10c***. Prepared from *(S)-(R)-**9*** and pyrrolidine in 55% yield, and recrystallized from hexane; NMR: δ 0.96—1.15 and 1.96—2.41 (bm, 4H and 4H, 1-pyrrolidinyl), 1.32 (d, 3H, J=7.5 Hz, $C\underline{H}_3$), 4.18 (s, 5H, $FeC_5\underline{H}_5$), 3.88—4.56 (m, 4H, $FeC_5\underline{H}_3C\underline{H}$), 7.25—7.93 (m, 10H, $PC_6\underline{H}_5$).

*(S)-(R)-**10d***. Prepared from *(S)-(R)-**9*** and piperidine in 86% yield; NMR: δ 0.65—1.18 and 2.20 (b and deformed t, 6H and 4H, respectively, piperidino), 1.22 (d, 3H, J=7 Hz, $C\underline{H}_3$), 4.12 (s, 5H, $FeC_5\underline{H}_5$), 3.90—4.48 (m, 4H, $FeC_5\underline{H}_3C\underline{H}$), 7.12—7.93 (cm, 10H, $PC_6\underline{H}_5$).

*(S)-(R)-**10e***. Prepared from *(S)-(R)-**9*** and *N*-methylpiperazine in 81% yield; NMR: δ 1.24 (d, 3H, J=7 Hz, $CHC\underline{H}_3$), 1.45—1.80 (bm, 4H, $MeNC\underline{H}_2$), 1.89 (s, 3H, $NC\underline{H}_3$), 2.24—2.44 (m, 4H, $CHNC\underline{H}_2$), 4.12 (s, 5H, $FeC_5\underline{H}_5$), 3.93—4.58 (m, 4H, $FeC_5\underline{H}_3C\underline{H}$), 7.30—7.89 (m, 10H, $PC_6\underline{H}_5$).

*(S)-(R)-**10f***. Prepared from *(S)-(R)-**9*** and morpholine in 92% yield; NMR: δ 1.25 (d, 3H, J=7 Hz, $C\underline{H}_3$), 2.12—2.48 (m, 4H, $NC\underline{H}_2$), 2.68—3.04 (m, 4H, $OC\underline{H}_2$), 4.13 (s, 5H, $FeC_5\underline{H}_5$), 3.93—4.60 (m, 4H, $FeC_5\underline{H}_3C\underline{H}$), 7.25—7.92 (m, 10H, $PC_6\underline{H}_5$).

(S)-1-[(R)-2-(Diphenylphosphino)ferrocenyl]ethyl Acetate [*(S)-(R)-**12***]. In a degassed sealed glass tube, a mixture of 701 mg (1.59 mmol) of *(S)-(R)*-PPFA (***3a***) and 1.0 ml of acetic anhydride was heated at 100 °C for 2 h. It was then cooled in a refrigerator overnight and orange crystals formed were collected on a glass filter, washed with cold methanol, and dried *in vacuo* to give 646 mg (89% yield) of *(S)-(R)-**12***; NMR: δ 1.20 (s, 3H, $COC\underline{H}_3$), 1.64 (d, 3H, J=7 Hz, $CHC\underline{H}_3$), 4.04 (s, 5H, $FeC_5\underline{H}_5$), 3.80, 4.35, 4.56 (bm, 3H, $FeC_5\underline{H}_3$), 6.18 (dq, 1H, J_{H-P}=3 Hz, $C\underline{H}CH_3$), 7.05—7.65 (m, 10H, $PC_6\underline{H}_5$).

*(R)-(S)-**12*** was also prepared starting with *(R)-(S)-**3a*** in a similar manner.

(S)-1-[(R)-2-(Diphenylphosphino)ferrocenyl]ethylamines [*(S)-(R)-**11***].

*(S)-(R)-**11a***. To a solution of 0.175 g (4.6 mmol) of lithium aluminum hydride in 15 ml of dry dibutyl ether and 10 ml of dry benzene, was added with stirring 0.121 g (0.236 mmol) of *(S)-(R)-**10a***. The mixture was kept at 75 °C for 6 h, and then hydrolyzed by successive addition of water and 10% aqueous sodium hydroxide. The product was extracted with benzene, and the benzene solution was washed with brine and water, dried over anhydrous sodium sulfate, and evaporated to give a red oil. It was chromatographed (alumina, benzene) to give 83 mg (71% yield) of *(S)-(R)-**11a***, which was purified by recrystallization from ethanol; NMR: δ 0.74 and 1.01 (a pair of d, 12H, J=7 Hz, $CH(C\underline{H}_3)_2$), 1.59 (d, 3H, J=7.5 Hz, $C_5H_5CHC\underline{H}_3$), 3.10 (7, 2H, $C\underline{H}Me_2$), 3.87 (s, 5H, $FeC_5\underline{H}_5$), 4.00—4.55 (m, 4H, $FeC_5\underline{H}_3C\underline{H}$), 7.08—7.68 (m, 10H, $PC_6\underline{H}_5$).

*(S)-(R)-**11b***, ***11c***, ***11d***, and ***11f*** were prepared in a similar manner to that for the preparation of *(S)-(R)-**11a***, starting with *(S)-(R)-**10b***, ***10c***, ***10d***, and ***10f***, respectively.

*(S)-(R)-**11b***: 66% yield; NMR: δ 0.55 and 0.73 (a pair of d, 12H, J=7 Hz, $CH(C\underline{H}_3)_2$), 1.50 (d, 3H, J=7.5 Hz, $C_5H_3CHC\underline{H}_3$), 1.26—1.66 (m, 2H, $CH_2C\underline{H}(CH_3)_2$), 1.92 (d, 4H, $C\underline{H}_2CH(CH_3)_2$), 3.77 (s, 5H, $FeC_5\underline{H}_5$), 4.03—

4.40 (m, 4H, $FeC_5\underline{H}_3C\underline{H}$), 7.03—7.70 (m, 10H, $PC_6\underline{H}_5$).

(S)-(R)-11c: 87% yield; NMR: δ 1.04—1.25 and 2.03—2.43 (m and m, 4H and 4H, respectively, 1-pyrrolidinyl), 1.40 (d, 3H, J=7.5 Hz, $C\underline{H}_3$), 3.90 (s, 5H, $FeC_5\underline{H}_5$), 3.82—4.42 (m, 4H, $FeC_5\underline{H}_3C\underline{H}$), 7.11—7.66 (m, 10H, $PC_6\underline{H}_5$).

(S)-(R)-11d: 69% yield; NMR: δ 0.6—1.2 and 2.24 (bm and deformed t, 6H and 4H, respectively, piperidino), 1.27 (d, 3H, J=7 Hz, $C\underline{H}_3$), 3.89 (s, 5H, $FeC_5\underline{H}_5$), 3.85—4.41 (m, 4H, $FeC_5\underline{H}_3C\underline{H}$), 7.1—7.7 (m, 10H, $PC_6\underline{H}_5$).

(S)-(R)-11f: 29% yield; NMR: δ 1.30 (d, 3H, J= 7 Hz, $C\underline{H}_3$), 2.10—2.46 (m, 4H, $NC\underline{H}_2$), 2.67—3.13 (m, 4H, $OC\underline{H}_2$), 3.92 (s, 5H, $FeC_5\underline{H}_5$), 3.86—4.42 (m, 4H, $FeC_5\underline{H}_3C\underline{H}$), 7.14—7.66 (m, 10H, $PC_6\underline{H}_5$).

(*S*)-(*R*)-**11f** was also prepared from (*S*)-(*R*)-**12** (*vide infra*).

(S)-(R)-11e. To a solution of 0.57 g (1.11 mmol) of (*S*)-(*R*)-**10e** in 5 ml of benzene and 10 ml of dibutyl ether, a large excess of aluminum hydride, prepared from lithium aluminum hydride and aluminum chloride in ether, was added. The mixture was refluxed for 4 h, and then hydrolyzed with 20% aqueous sodium hydroxide at 0 °C. The organic layer was separated and the water layer was extracted with ether. The combined organic layer was washed with brine, dried over anhydrous sodium sulfate, and evaporated. The residue was purified by column chromatography (alumina, ether) to give 0.31 g (57% yield) of (*S*)-(*R*)-**11e**; NMR: δ 1.25 (d, 3H, J=7 Hz, $CHC\underline{H}_3$), 1.4—1.9 (bm, 4H, $CH_3NC\underline{H}_2$), 1.88 (s, 3H, $NC\underline{H}_3$), 2.18—2.50 (m, 4H, $CHNC\underline{H}_2$), 3.90 (s, 5H, $FeC_5\underline{H}_5$), 3.84—4.42 (m, 4H, $FeC_5\underline{H}_3C\underline{H}$), 7.12—7.71 (m, 10H, $PC_6\underline{H}_5$).

(S)-(R)-11f. A solution of 60 mg (0.13 mmol) of (*S*)-(*R*)-**12** and 0.6 ml of morpholine in 2.0 ml of methanol was refluxed for 5 h. Then the solvent was removed under reduced pressure, and 5 ml of benzene was added. The solution was washed with brine, dried over anhydrous sodium sulfate, and evaporated. The resulting red oil was column chromatographed (alumina, ether) to give 61.5 mg (98% yield) of (*S*)-(*R*)-**11f**.

(S)-(R)-11g. Prepared from (*S*)-(*R*)-**12** and diethylamine in 95% yield, recrystallized from dichloromethane/methanol; NMR: δ 0.65 (t, 6H, J=7 Hz, $NCH_2C\underline{H}_3$), 1.30 (d, 3H, J=7 Hz, $CHC\underline{H}_3$), 2.07—2.48 (cm, 4H, $NC\underline{H}_2$), 3.92 (s, 5H, $FeC_5\underline{H}_5$), 3.85—3.93, 4.19—4.52 (m, 4H, $FeC_5\underline{H}_3C\underline{H}$), 7.10—7.73 (m, 10H, $PC_6\underline{H}_5$).

(S)-(R)-11h. Prepared from (*S*)-(*R*)-**12** and (*S*)-2-(dimethylaminomethyl)pyrrolidine[58] in 70% yield; NMR: δ 1.26 (m, 4H, $CH_2C\underline{H}_2C\underline{H}_2CH$), 1.49 (d, 3H, J=7 Hz, $CHC\underline{H}_3$), 1.6—1.7 (m, 2H, $C\underline{H}_2NMe_2$), 2.06 (s, 6H, $NC\underline{H}_3$), 2.2—2.9 (m, 3H, $C\underline{H}_2NC\underline{H}$), 3.91 (s, 5H, $FeC_5\underline{H}_5$), 3.96—4.45 (m, 4H, $FeC_5\underline{H}_3C\underline{H}$), 7.10—7.75 (m, 10H, $PC_6\underline{H}_5$).

(R)-(S)-11i. Prepared from (*R*)-(*S*)-**12** and (*S*)-2-(dimethylaminomethyl)pyrrolidine[58] in 88% yield, recrystallized from ethanol; NMR: δ 1.30 (d, 3H, J=7 Hz, $CHC\underline{H}_3$), 2.18 (s, 6H, $NC\underline{H}_3$), 0.5—2.9 (m, 9H), 3.96 (s, 5H, $FeC_5\underline{H}_5$), 3.75, 4.22, 4.37 (m, 3H, $FeC_5\underline{H}_3$), 4.50 (m, 1H, $FeC_5H_3C\underline{H}$), 7.10—7.70 (m, 10H, $PC_6\underline{H}_5$).

(S)-(R)-11j. Prepared from (*S*)-(*R*)-**12** and (*R*)-2-methylpyrrolidine[59] (contaminated with 30% of piperidine), purified by preparative TLC (alumina, benzene R_f 0.5), 36% yield, recrystallized from ethanol; NMR: δ 0.17 (d, 3H, J=6 Hz, $CH_2CHC\underline{H}_3$), 1.1—1.4 (m, 4H, $CH_2C\underline{H}_2$-$C\underline{H}_2CH$), 1.55 (d, 3H, J=7 Hz, $C_5H_3CHC\underline{H}_3$), 2.1—2.7 (m, 2H, $NC\underline{H}_2$), 2.70—2.95 (m, 1H, $NC\underline{H}CH_2$), 3.88 (s, 5H, $FeC_5\underline{H}_5$), 4.00, 4.2—4.5 (m, 4H, $FeC_5\underline{H}_3C\underline{H}$), 7.1—7.7 (m, 10H, $PC_6\underline{H}_5$).

(R)-(S)-11k. Prepared from (*R*)-(*S*)-**12** and (*R*)-2-methylpyrrolidine[59] (contaminated with 30% of piperidine) in 50% yield. The (*R*)-(*S*)-**11k** contained 25% of (*R*)-(*S*)-**11d**, which could not be removed. NMR: δ 0.98 (d, 3H, J=6 Hz, $CH_2CHC\underline{H}_3$), 1.24 (d, 3H, J=7 Hz, C_5H_3-$CHC\underline{H}_3$), 0.4—1.6 (m, 4H, $CH_2C\underline{H}_2C\underline{H}_2CH$), 1.9—2.3 (m, 2H, $NC\underline{H}_2$), 2.49 (6, 1H, $NC\underline{H}CH_2$), 3.96 (s, 5H, $FeC_5\underline{H}_5$). 3.75, 4.20, 4.35 (m, 3H, $FeC_5\underline{H}_3$), 4.49 (double q, 1H, J_{H-P}= 3 Hz, $C_5H_3C\underline{H}$), 7.05—7.65 (m, 10H, $PC_6\underline{H}_5$).

(R)-1-[(S)-1',2-Bis(diphenylphosphino)ferrocenyl]ethyl acetate [(*R*)-(*S*)-**13**]. A mixture of 0.626 g (1.0 mmol) of (*R*)-(*S*)-BPPFA (**4a**) and 3 ml of acetic anhydride was heated at 100 °C for 1 h in a degassed sealed glass tube. After cooling the reaction mixture to room temperature, orange crystals formed were collected on a glass filter, and dried *in vacuo*. The crystals (0.576 g, 90% yield) were pure (*R*)-(*S*)-**13**; NMR: δ 1.16 (s, 3H, $COC\underline{H}_3$), 1.49 (d, 3H, J= 6.5 Hz, $CHC\underline{H}_3$), 3.60—4.56 (m, 7H, $C_5\underline{H}_4FeC_5\underline{H}_3$), 6.12 (double q, J=6.4 Hz and 2.4 Hz, 1H, $C\underline{H}CH_3$), 7.00—7.56 (m, 20H, $PC_6\underline{H}_5$). IR (KBr): 1734, 1372, and 1240 cm^{-1} (CH_3COO).

(R)-1-[(S)-1',2-Bis(diphenylphosphino)ferrocenyl]ethylamine [(*R*)-(*S*)-**14a**]. A mixture of 0.71 g (1.11 mmol) of (*R*)-(*S*)-**13** in 5 ml of saturated ammonia–methanol was heated at 100 °C for 7 h in a microautoclave. Benzene (20 ml) was added, and the solution was washed with dilute aqueous sodium hydroxide, dried over anhydrous sodium sulfate, and evaporated. The residue was chromatographed on alumina (ether/ethyl acetate 2/1) to give 0.57 g (86% yield) of (*R*)-(*S*)-**14a**, which was recrystallized from hexane/dichloromethane; NMR: δ 1.30 (d, J=7 Hz, $C\underline{H}_3$), 1.27—1.41 (bs, 2H, $N\underline{H}_2$), 3.63, 4.10, 4.39 (m, 8H, $C_5\underline{H}_4FeC_5\underline{H}_3C\underline{H}$), 7.14—7.63 (m, 20H, $PC_6\underline{H}_5$).

(*S*)-(*R*)-**14b**—**e** and (*R*)-(*S*)-**14f**—**j** were prepared by the reaction of **13** with the corresponding dialkylamine in methanol. The following procedure for the preparation of (*S*)-(*R*)-**14c** is typical.

(S)-(R)-14c. A solution of 0.450 g (0.70 mmol) of (*S*)-(*R*)-**13** and 4 ml of pyrrolidine in 15 ml of methanol was refluxed for 8 h. The solvent was removed under reduced pressure, and benzene was added. The solution was washed with brine, dried over anhydrous sodium sulfate, and evaporated. The residue was purified by column chromatography (alumina, ether) to give 0.368 g (81% yield) of (*S*)-(*R*)-**14c**, which was recrystallized from ethanol; NMR: δ 0.86—1.24 and 1.98—2.44 (bm, 4H and 4H, pyrrolidino), 1.26 (d, 3H, J=7 Hz, $C\underline{H}_3$), 3.46—4.46 (m, 8H, $C_5\underline{H}_4FeC_5$-$\underline{H}_3C\underline{H}$), 7.03—7.61 (m, 20H, $PC_6\underline{H}_5$).

(S)-(R)-14b. Prepared from (*S*)-(*R*)-**13** and diethylamine in 62% yield, recrystallized from benzene/hexane; NMR: δ 0.63 (t, 6H, J=7.5 Hz, $NCH_2C\underline{H}_3$), 1.20 (d, 3H, J=7.5 Hz, $CHC\underline{H}_3$), 2.22 (m, 4H, $NC\underline{H}_2$), 3.40—4.60 (m, 8H, $C_5\underline{H}_4FeC_5\underline{H}_3C\underline{H}$), 7.00—7.70 (m, 20H, $PC_6\underline{H}_5$).

(S)-(R)-14d. Prepared from (*S*)-(*R*)-**13** and piperidine in 88% yield, recrystallized from benzene/hexane; NMR: δ 0.66—1.20 and 2.03—2.40 (bm, 6H and 4H, respectively, piperidino), 1.19 (d, 3H, J=7.5 Hz, $C\underline{H}_3$), 3.40—4.40 (m, 8H, $C_5\underline{H}_4FeC_5\underline{H}_3C\underline{H}$), 6.98—7.60 (m, 20H, $PC_6\underline{H}_5$).

(S)-(R)-14e. Prepared from (*S*)-(*R*)-**13** and *N*-methylpiperazine in 62% yield; NMR: δ 1.12 (d, 3H, J=7.5 Hz, $CHC\underline{H}_3$), 1.23—1.90 (bs, 4H, $C\underline{H}_2NMeC\underline{H}_2$), 1.78 (s, 3H, $NC\underline{H}_3$), 2.02—2.46 (bs, 4H, $C\underline{H}_2N(CH)C\underline{H}_2$), 3.36—4.38 (m, 8H, $C_5\underline{H}_4FeC_5\underline{H}_3C\underline{H}$), 6.95—7.50 (m, 20H, $PC_6\underline{H}_5$).

(R)-(S)-14f. Prepared from (*R*)-(*S*)-**13** and *N*-methylallylamine, recrystallized from hexane, 81% yield; NMR: δ 1.15 (d, 3H, J=7.5 Hz, $CHC\underline{H}_3$), 1.66 (s, 3H, $NC\underline{H}_3$), 2.60—3.05 (m, 2H, $NC\underline{H}_2$), 3.52, 3.67, 3.97, 4.08, and 4.36 (m, 1H, 1H, 1H, 2H, and 2H, $C_5\underline{H}_4FeC_5\underline{H}_3$), 4.23 (m, 1H, $C\underline{H}CH_3$), 4.62—5.15 (m, 3H, $C\underline{H}$ $C\underline{H}_2$),

7.07—7.37 (m, 20H, $PC_6\underline{H}_5$).

*(R)-(S)-**14g***. Prepared from (*R*)-(*S*)-**13** and *N,N,N'*-trimethylethylenediamine in 74% yield; NMR: δ 1.07 (3H, J=7 Hz, $CHC\underline{H}_3$), 1.60 (s, 3H, $CHNC\underline{H}_3$), 1.45—1.70 and 2.07—2.41 (m, 4H, $NC\underline{H}_2C\underline{H}_2N$), 1.90 (s, 6H, $N(C\underline{H}_3)_2$), 3.37—4.30 (m, 8H, $C_5\underline{H}_4FeC_5\underline{H}_3C\underline{H}$), 6.80—7.50 (m, 20H, $PC_6\underline{H}_5$).

*(R)-(S)-**14h***. Prepared from (*R*)-(*S*)-**13** and *N,N'*-dimethylethylenediamine, recrystallized from hexane, 91% yield; NMR: δ 1.18 (d, 3H, J=7.5 Hz, $CHC\underline{H}_3$), 1.68 and 1.96 (s and s, 3H and 3H, $NC\underline{H}_3$), 2.12—2.86 (m, 5H, $NC\underline{H}_2C\underline{H}_2N\underline{H}$), 3.75, 3.86, 4.09, 4.34, and 4.42 (m, 1H, 1H, 1H, 2H, and 2H, respectively, $C_5\underline{H}_4FeC_5\underline{H}_3$), 4.22 (m, 1H, $C\underline{H}CH_3$), 7.10—7.40 (m, 20H, $PC_6\underline{H}_5$).

*(R)-(S)-**14i***. Prepared from (*R*)-(*S*)-**13** and 2-(methylamino)ethanol, recrystallized from ethanol, 88% yield; NMR: δ 1.18 (d, 3H, J=7.5 Hz, $CHC\underline{H}_3$), 1.62 (s, 3H, $NC\underline{H}_3$), 2.18—2.74 (m, 3H, $NC\underline{H}_2$ and $O\underline{H}$), 3.06—3.40 (m, 2H, $OC\underline{H}_2$), 3.47, 3.76, 3.90, 4.02—4.19, 4.34, and 4.43 (m, 1H, 1H, 1H, 2H, 1H, and 1H, respectively, $C_5\underline{H}_4FeC_5\underline{H}_3$), 4.26 (m, 1H, $C\underline{H}CH_3$), 7.10—7.38 (m, 20H, $PC_6\underline{H}_5$).

*(R)-(S)-**14j***. Prepared from (*R*)-(*S*)-**13** and di(2-hydroxyethyl)amine in 82% yield, recrystallized from hexane/methanol; NMR: δ 1.33 (d, 3H, J=7.5 Hz, $C\underline{H}_3$), 2.47 (t, 4H, J=5.5 Hz, $NC\underline{H}_2$), 3.16—3.38 (m, 4H, $OC\underline{H}_2$), 3.43, 3.71, 4.02, 4.05, and 4.18—5.03 (m, 1H, 1H, 1H, 1H, and 4H, $C_5\underline{H}_4FeC_5\underline{H}_3C\underline{H}$), 7.10—7.40 (m, 20H, $PC_6\underline{H}_5$).

(R)-1-[(S)-2-(Diphenylphosphino)ferrocenyl]ethyl methyl ether [*(R)-(S)-**15***]. A mixture of 92 mg (0.20 mmol) of (*R*)-(*S*)-**12** and 1.60 g of 3-aminopropylated silica gel[51] (0.236 meq/g nitrogen) in 10 ml of dry methanol was refluxed for 10 h. Methanol was evaporated, and 10 ml of ether was added. The silica gel was removed by short alumina column. Evaporation of the solvent gave crude (*R*)-(*S*)-**15**, which was recrystallized from methanol, 58% yield; NMR: δ 1.57 (d, 3H, J=7 Hz, $CHC\underline{H}_3$), 2.90 (s, 3H, $OC\underline{H}_3$), 3.98 (s, 5H, $FeC_5\underline{H}_5$), 3.83, 4.29, and 4.50 (bm, 3H, $FeC_5\underline{H}_3$), 4.45—4.75 (m, 1H, $C\underline{H}CH_3$), 7.1—7.7 (m, 10H, $PC_6\underline{H}_5$).

(R)-1-[(S)-1',2-Bis(diphenylphosphino)ferrocenyl]ethyl methyl ether [*(R)-(S)-**16***]. (a) A mixture of 72 mg (0.112 mmol) of (*R*)-(*S*)-**13** and 95 mg of 3-aminopropylated silica gel[51] (0.236 meq/g nitrogen), prepared from (3-aminopropyl)-triethoxysilane and activated silica gel, in 5 ml of methanol was refluxed for 29 h. The silica gel was filtered off. The filtrate was evaporated to give a quantitative yield of crude (*R*)-(*S*)-**16**, which was recrystallized from ethanol, 58 mg (85% yield).

(b) A solution of 81 mg (0.126 mmol) of (*R*)-(*S*)-**13** and 6.9 mg (0.128 mmol) of sodium methoxide in 10 ml of methanol was refluxed for 3 h, and then evaporated. The residue was passed through a short alumina column (ether/benzene) to give 67 mg (87% yield) of (*R*)-(*S*)-**16**; NMR: δ 1.45 (d, 3H, J=7.5 Hz, $CHC\underline{H}_3$), 2.88 (s, 3H, $OC\underline{H}_3$), 3.65, 3.95—4.20, 4.38, and 4.45 (m, 2H, 3H, 1H, and 1H, respectively, $C_5\underline{H}_3FeC_5\underline{H}_4$), 4.55 (m, 1H, $C\underline{H}CH_3$), 7.10—7.38 (m, 20H, $PC_6\underline{H}_5$).

(R)-1-[(S)-2-(Diphenylphosphino)ferrocenyl]ethanol [*(R)-(S)-**PPFOH (17)***]. To a solution of 60 mg (0.13 mmol) of (*R*)-(*S*)-**12** in 5 ml of dry ether was added 1.0 ml (1.25 mmol) of 1.25 M butyllithium in hexane. The mixture was kept stirring at room temperature for 1 h, and then hydrolyzed with water at 0 °C. Usual work up and column chromatography (alumina, ethyl acetate) gave 50 mg (92% yield) of (*R*)-(*S*)-**17**; NMR: δ 1.42 (d, 3H, J=7 Hz, $CHC\underline{H}_3$), 1.65 (bs, 1H, $O\underline{H}$), 3.95 (s, 5H, $FeC_5\underline{H}_5$), 3.71, 4.21, and 4.42 (m, 3H, $FeC_5\underline{H}_3$), 4.90 (dq, 1H, J_{H-P}=3 Hz, $C\underline{H}CH_3$), 7.05—7.55 (m, 10H, $PC_6\underline{H}_5$).

(R)-1-[(S)-1',2-Bis(diphenylphosphino)ferrocenyl]ethanol [*(R)-(S)-**BPPFOH (18)***]. To a suspension of 0.576 g (0.90 mmol) of (*R*)-(*S*)-**13** in 20 ml of dry ether, 1.7 ml of 1.27 M butyllithium in hexane was added at 0 °C. The resulting red solution was kept stirring at room temperature for 2 h, and hydrolyzed with water at 0 °C. The product was extracted with ether, and the ether solution was washed with water, dried over anhydrous sodium sulfate, and evaporated. The residue was chromatographed (alumina, ethyl acetate) to give 0.512 g (95% yield) of (*R*)-(*S*)-**18**. An analytically pure sample was obtained by recrystallization from ethanol; NMR: δ 1.38 (d, 3H, J=6.5 Hz, $CHC\underline{H}_3$), 1.78—1.98 (bs, 1H, $O\underline{H}$), 3.58—4.54 (m, 7H, $C_5\underline{H}_4FeC_5\underline{H}_3$), 4.88 (q, 1H, $C\underline{H}CH_3$), 6.94—7.70 (m, 20H, $PC_6\underline{H}_5$). IR (CCl_4): 3570 cm^{-1} (OH).

(R)-1-Diphenylphosphinyl-2-ethylferrocene [*(R)-**20***]. To a solution of 0.93 g (2.03 mmol) of (*S*)-(*R*)-**9** in 45 ml of acetone, 5.0 ml of methyl iodide was added at room temperature. The solution was refluxed for 15 min and concentrated *in vacuo* to *ca.* 15 ml. The residue was diluted with 30 ml of benzene, washed with 50 ml of 8.5% aqueous phosphoric acid and 50 ml of 10% aqueous sodium hydroxide, and dried over anhydrous sodium sulfate. After evaporation of the solvents, the residue was chromatographed on silica gel (benzene/ethyl acetate, 3/1) to give 0.61 g (73%) of crude (*R*)-1-diphenylphosphinyl-2-vinylferrocene (**19**) as a reddish-brown viscous oil; NMR: δ 4.12 (s, 3H, $FeC_5\underline{H}_3$), 4.22 (s, 5H, $FeC_5\underline{H}_5$), 4.7—5.5 (m, 2H, $CH{=}C\underline{H}_2$), 5.9—6.7 (m, 1H, $C\underline{H}{=}CH_2$), 7.1—7.9 (m, 10H, $PC_6\underline{H}_5$). IR: 1625 (vinyl), 1193 (P=O), and 1108 and 1002 cm^{-1} (FeC_5H_5).

The crude vinylferrocene (*R*)-**19** (0.57 g) in 5 ml of benzene solution was hydrogenated in a 50-ml steel autoclave at 130 kg/cm^2 of hydrogen in the presence of 10 mg of chlorotris(triphenylphosphine)rhodium to give, after chromatography on alumina (benzene/ethyl acetate 2/1), 0.29 g of (*R*)-**20**; NMR: δ 0.95 (t, 3H, J=7 Hz, $C\underline{H}_3$), 2.26—2.77 (cm, 2H, $C\underline{H}_2$), 4.25 (s, 5H, $FeC_5\underline{H}_5$), 3.72, 4.17, and 4.32 (m, 3H, $FeC_5\underline{H}_3$), 7.22—7.96 (m, 10H, $PC_6\underline{H}_5$).

(R)-1-Diphenylphosphino-2-ethylferrocene [*(R)-**PPEF (21)***]. A solution of 0.23 g (0.55 mmol) of (*R*)-**20** in 5 ml of benzene was added at room temperature to a solution of 0.1 g of lithium aluminum hydride in 4 ml of dry dibutyl ether over a period of 10 min. The reaction mixture was heated at 80—85 °C for 4.5 h. After work up in the usual way, chromatography on alumina using benzene as an eluent gave 0.17 g (78% yield) of (*R*)-**21**; UV: λ_{max} ($CHCl_3$) 446 nm (ε 155); NMR: δ 1.01 (t, 3H, J=7 Hz, $C\underline{H}_3$), 2.19—2.71 (m, 2H, $C\underline{H}_2$), 3.94 (s, 5H, $FeC_5\underline{H}_5$), 3.56, 4.10, and 4.27 (m, 3H, $FeC_5\underline{H}_3$), 6.76—7.62 (m, 10H, $PC_6\underline{H}_5$). ORD (*c* 0.12 and 0.005, chloroform): $[\Phi]_{589}$ +1080°, $[\Phi]_{474}$ +2450° (pk), $[\Phi]_{428}$ +1880° (tr), and $[\Phi]_{294}$ +14400° (pk). The CD spectrum is shown in Fig. 2.

(S)-1,1'-Bis(diphenylphosphino)-2-vinylferrocene [*(S)-**22***]. A solution of 1.17 g (1.83 mmol) of (*R*)-(*S*)-**13** in 10 ml of 10% potassium hydroxide in methanol was refluxed for 1 h. After usual work up, column chromatography (alumina) gave 0.360 g (34% yield) of (*S*)-**22** (benzene elution) and 0.431 g (39% yield) of (*R*)-(*S*)-**18** (ethyl acetate elution). (*S*)-**22**; NMR: δ 3.57, 3.68, 4.12, 4.23, 4.33, and 4.68 (m, 1H, 1H, 1H, 2H, 1H, 1H, respectively, $C_5\underline{H}_4FeC_5\underline{H}_3$), 4.95—5.40 (m, 2H, $CH{=}C\underline{H}_2$), 6.48—6.94 (m, 1H, $C\underline{H}{=}CH_2$), 7.0—7.6 (m, 20H, $PC_6\underline{H}_5$).

(S)-1,1'-Bis(diphenylphosphino)-2-ethylferrocene [*(S)-**BPPEF (23)***]. A solution of 85 mg (0.15 mmol) of (*S*)-**22** and 7 mg (0.015 mmol) of chlorotris(triphenylphosphine)-rhodium in 5 ml of benzene was placed in a microautoclave, and magnetically stirred with hydrogen at 50 atm for 18 h.

Column chromatography (alumina, benzene) gave 50 mg (57% yield) of (*S*)-**23**; NMR: δ 0.93 (t, 3H, J=7.5 Hz, $CH_2C\underline{H}_3$), 2.37 (q, 2H, $C\underline{H}_2CH_3$), 3.30—3.55, 3.55—3.75, 3.85—4.17, and 4.20—4.40 (bm, 1H, 1H, 3H, and 2H, respectively, $C_5\underline{H}_4FeC_5\underline{H}_3$), 6.8—7.6 (m, 20H, $PC_6\underline{H}_5$).

[(R)-1-[(S)-2-(Diphenylphosphino)ferrocenyl]ethyl]diphenylphosphine [(R)-(S)-**24**]. A solution of 69.2 mg (0.15 mmol) of (*R*)-(*S*)-**12** and 280 mg (1.5 mmol) of diphenylphosphine in 4.5 ml of methanol was refluxed under argon for 7 h. The solvent was removed under reduced pressure, and the residue was chromatographed on alumina (benzene) to give 74 mg (85% yield) of (*R*)-(*S*)-**24** as a red oil; NMR: δ 1.51 (dd, 3H, J_{H-H}=7.2 Hz, J_{H-P}=5.8 Hz, $PCHC\underline{H}_3$), 3.97 (s, 5H, $FeC_5\underline{H}_5$), 3.75—4.44 (m, 4H, $FeC_5\underline{H}_3C\underline{H}$), 7.31—7.95 (m, 20H, $PC_6\underline{H}_5$).

dl-*1-Diphenylphosphino-2-(dimethylaminomethyl)ferrocene* [dl-*FcPN* (**25**)]. *dl*-**25** was prepared according to the reported procedure,[52] mp 101.5—102 °C; NMR: δ 2.01 (s, 6H, $NC\underline{H}_3$), 3.48 (deformed AB, 2H, J=14 Hz, $\Delta\nu$=17 Hz, $C\underline{H}_2$), 3.94 (s, 5H, $FeC_5\underline{H}_5$), 3.87, 4.29, and 4.52 (m, 3H, $FeC_5\underline{H}_3$), 7.15—7.71 (m, 10H, $PC_6\underline{H}_5$).

dl-*1-Diphenylthiophosphinyl-2-(dimethylaminomethyl)ferrocene* [dl-**26**]. A solution of 26.9 g (62.9 mmol) of *dl*-**25** and 2.22 g (69.2 mmol) of sulfur in 60 ml of benzene was refluxed for 1 h. The solvent was removed under reduced pressure and the residue was purified by short-column chromatography (alumina) to give 25.8 g (89% yield) of *dl*-**26**, mp 166 °C; NMR: δ 1.92 (s, 6H, $NC\underline{H}_3$), 3.52 (AB, 2H, J=13 Hz, $\Delta\nu$=67 Hz, $C\underline{H}_2$), 4.27 (s, 6H, $FeC_5\underline{H}_5$ and one of $FeC_5\underline{H}_3$), 3.82 and 4.60 (m, 2H, $FeC_5\underline{H}_3$), 7.25—7.96 (m, 10H, $PC_6\underline{H}_5$).

(S)- and (R)-26. *dl*-**26** (5.72 g, 12.4 mmol) dissolved in 20 ml of hot benzene was added to a hot benzene (20 ml) solution of 4.68 g (12.4 mmol) of dibenzoyl-*d*-tartaric acid.[60] The benzene was removed by evaporation under reduced pressure to give ammonium salts as an orange powder. The ammonium salts were dissolved in 100 ml of warm (40 °C) ethanol. Very soon orange crystals started to separate out. After 8 h the crystals were collected and set free with aqueous sodium carbonate. The partially optically active **26** (2.05 g) obtained and 1.58 g of dibenzoyl-*d*-tartaric acid were mixed in 7 ml of dichloromethane. Ethanol (50 ml) was added, and the solution was kept at 50 °C. As dichloromethane was evaporated, orange needle crystals were formed. After 8 h 2.90 g of the crystals ($[\alpha]_D^{25}$ +12° (*c* 0.4, chloroform)) were obtained; this was converted with aqueous sodium carbonate to **26**, which was purified by a short alumina column (ether) to give 1.63 g (57% yield) of optically pure (*S*)-**26**; $[\alpha]_{545}^{25}$ +50.2° (*c* 0.5, chloroform). From the mother liquor of the first crystallization, was recovered 3.15 g of *R*-rich **26**, which was fractionally recrystallized using dibenzoyl-*l*-tartaric acid to give 1.50 g (52% yield) of (*R*)-**26**; $[\alpha]_{545}^{25}$ −50.5° (*c* 0.5, chloroform).

(S)-FcPN (**25**). To a solution of 1.38 g (3.0 mmol) of (*S*)-**26** in 20 ml of dry dioxane was added 0.6 g of lithium aluminum hydride, and the mixture was refluxed for 22 h. It was hydrolyzed with 10% aqueous sodium hydroxide, and then extracted with benzene. Column chromatography (alumina, ether) gave 1.06 g (83% yield) of crude (*S*)-**25**. Recrystallization from pentane (4 ml) gave 0.77 g of pure (*S*)-**25** as red cubic crystals. The CD spectrum is shown in Fig. 3.

In the same manner, (*R*)-**25** was obtained from (*R*)-**26** in 80% yield.

(S)-1-Diphenylthiophosphinyl-2-(acetoxymethyl)ferrocene [(S)-**27**]. In a degassed sealed glass tube, a mixture of 0.23 g (0.50 mmol) of (*S*)-**26** and 2.0 ml of acetic anhydride was heated at 100 °C for 20 h. Benzene (5 ml) was added and the benzene solution was washed with aqueous sodium hydroxide and water, dried over anhydrous sodium sulfate, and evaporated. Column chromatography (alumina, ethyl acetate) gave 0.20 g (84% yield) of (*S*)-**27**, $[\alpha]_{545}^{25}$ +59° (*c* 0.5, chloroform), mp 190—193° (decomp); NMR: δ 1.56 (s, 3H, $COC\underline{H}_3$), 4.35 (s, 6H, $FeC_5\underline{H}_5$ and one of $FeC_5\underline{H}_3$), 3.81 and 4.59 (m, 2H, $FeC_5\underline{H}_3$), 5.24 (AB, 2H, J=12 Hz, $\Delta\nu$=45 Hz, $C\underline{H}_2$), 7.22—7.90 (m, 10H, $PC_6\underline{H}_5$).

(S)-1-Diphenylthiophosphinyl-2-(hydroxymethyl)ferrocene [(S)-**28**]. A solution of 0.20 g (0.42 mmol) of (*S*)-**27** in 8 ml of 3 M aqueous potassium hydroxide and 18 ml of methanol was refluxed for 1 h. The solvent was removed, and 10 ml of benzene was added. The benzene solution was washed with water, dried over anhydrous sodium sulfate, and evaporated. The product was purified by column chromatography (alumina, chloroform/methanol 15/1) to give 0.16 g (88% yield) of (*S*)-**28**, mp 192—194 °C (decomp); NMR: δ 3.34 (dd, 1H, J=6 and 8 Hz, O$\underline{H}$), 4.31 (s, 5H, $FeC_5\underline{H}_5$), 3.70—4.78 (m, 5H, $FeC_5\underline{H}_3C\underline{H}_2$), 7.21—7.95 (m, 10H, $PC_6\underline{H}_5$).

dl-**28** was also prepared from *dl*-**26**; NMR of *dl*-**28** in the presence of 30 mol% of Eu(facam)$_3$: δ 5.30 and 5.88 (a pair of s, $FeC_5\underline{H}_5$).

(S)-1,1'-Bis(diphenylphosphino)-2-(dimethylaminomethyl)ferrocene [(S)-**30**]. To a solution of 1.02 g (2.4 mmol) of (*S*)-**25** in 25 ml of dry ether was added a solution of butyllithium in hexane (4.0 ml of a 1.25 M solution). After stirring at room temperature for 1.5 h, 1.5 ml (12 mmol) of chlorotrimethylsilane was added with heating under gentle reflux. The reaction mixture was refluxed for 2 h, hydrolyzed with 10 ml of water and 10 ml of 30% aqueous sodium hydroxide, and then extracted with benzene (2×40 ml). The combined benzene extracts were washed with brine and dried over anhydrous sodium sulfate. Evaporation of the solvent followed by column chromatography (alumina, benzene/ether 1/1) gave 1.02 g (85% yield) of 1-diphenylphosphino-2-dimethylaminomethyl-3-(trimethylsilyl)ferrocene [(*S*)-**29**]. Elution with ethyl acetate gave 0.15 g of recovered (*S*)-**25**. NMR of (*S*)-**29**: δ 0.28 (s, 9H, $SiC\underline{H}_3$), 1.78 (s, 6H, $NC\underline{H}_3$), 3.47 (ABX, 2H, $J_{H_A-H_B}$=13 Hz, J_{H_A-P}=3 Hz, J_{H_B-P}=0 Hz, $\Delta\nu$=16 Hz, $C\underline{H}_2$), 3.90 (s, 5H, $FeC_5\underline{H}_5$), 3.97 (d, 1H, J=3 Hz, one of $FeC_5\underline{H}_2$), 4.20 (d, 1H, one of $FeC_5\underline{H}_2$), 7.12—7.72 (m, 10H, $PC_6\underline{H}_5$).

(*S*)-**29** (1.02 g, 2.04 mmol) was lithiated with butyllithium (4.9 ml of 1.25 M hexane solution) and TMEDA (0.92 ml, 6.13 mmol). To the solution was added with stirring 1.5 ml (7.96 mmol) of chlorodiphenylphosphine at 0 °C. The reaction mixture was refluxed for 1.5 h, hydrolyzed with 30% aqueous sodium hydroxide at 0 °C, and extracted with benzene (2×30 ml). The benzene extracts were washed with brine, dried over anhydrous sodium sulfate, and evaporated. Column chromatography (alumina, hexane/benzene 1/1) gave 0.747 g of recovered (*S*)-**29** and 0.393 g of a mixture of recovered (*S*)-**29** and the desired phosphinated product (3:7).

The above-obtained mixture (0.318 g) was desilylated by treatment with 0.052 g (0.46 mmol) of potassium *t*-butoxide in 10 ml of dimethyl sulfoxide. Usual work up and preparative TLC (silica gel, benzene/acetone 1/1) gave 0.160 g of (*S*)-**30** (R_f 0.65); NMR: δ 1.94 (s, 6H, $NC\underline{H}_3$), 3.11, 3.14, 3.47, 3.57, 3.71, 3.99, 4.09, 4.16, 4.27, and 4.52 (m, 9H, $C_5\underline{H}_4FeC_5\underline{H}_3C\underline{H}_2$), 7.0—7.7 (m, 20H, $PC_6\underline{H}_5$).

The reaction of (R)-1 with Acetic Anhydride. A solution of 0.186 g (0.726 mmol) of (*R*)-(+)-**1** ($[\alpha]_D^{25}$ +14.1° (*c* 1.7, ethanol)) in 0.3 ml of acetic anhydride was heated at 100 °C for 2 h. Saturated aqueous sodium hydrogencarbonate was added at room temperature, and the product

was extracted with ether. The ether solution was washed with brine, dried over anhydrous sodium sulfate, and evaporated *in vacuo* to give 0.192 g (97% yield) of 1-ferrocenylethyl acetate, $[\alpha]_D^{25}$ −26.6° (*c* 1.0, ethanol), (lit,[49] (*R*)-1-ferrocenylethyl acetate, $[\alpha]_D^{25}$ −28.5° (*c* 1.4, ethanol)).

We thank the Ministry of Education for Grant-in-Aid (No. 235053, 303523, 311709, 355370) and the Asahi Glass Foundation for the Contribution to Industrial Technology for financial support of this work. We are indebted to Professor Y. Imanishi, Department of Polymer Chemistry, Kyoto University, for CD measurements.

References

1) a) J. D. Morrison and H. S. Mosher, "Asymmetric Organic Reactions," Prentice-Hall Englewood Cliffs, New Jersey (1971); b) H. B. Kagan and J. C. Fiaud, "Topics in Stereochemistry," ed by E. L. Eliel and N. L. Allinger, Wiley-Interscience, New York (1978), Vol. 10, p. 175.

2) a) J. W. Scott and D. Valentine, Jr., *Science*, **184**, 943 (1974); b) D. Valentine, Jr. and J. W. Scott, *Synthesis*, **1978**, 329.

3) For a review: J. D. Morrison, W. F. Masler, and M. K. Neuberg, *Adv. Catal.*, **25**, 81 (1976).

4) L. Horner, H. Winkler, A. Rapp, A. Mentrup, H. Hoffman, and P. Beck, *Tetrahedron Lett.*, **1961**, 161.

5) L. Horner, H. Siegel, and H. Büthe, *Angew. Chem.*, **80**, 1034 (1968).

6) W. S. Knowles and M. J. Sabacky, *Chem. Commun.*, **1968**, 1445.

7) a) O. Korpiun and K. Mislow, *J. Am. Chem. Soc.*, **89**, 4784 (1967); b) K. Naumann, G. Zon, and K. Mislow, *ibid.*, **91**, 7012 (1969).

8) a) W. S. Knowles, M. J. Sabacky, and B. D. Vineyard, *J. Chem. Soc., Chem. Commun.*, **1972**; 10, b) W. S. Knowles, M. J. Sabacky, and B. D. Vineyard, *Chem. Tech.*, **1972**, 591; c) W. S. Knowles, M. J. Sabacky, and B. D. Vineyard, *Ann. N. Y. Acad. Sci.*, **214**, 119 (1973).

9) a) W. S. Knowles, M. J. Sabacky, B. D. Vineyard, and D. J. Weinkauff, *J. Am. Chem. Soc.*, **97**, 2567 (1975); b) B. D. Vineyard, W. S. Knowles, M. J. Sabacky, G. L. Bachman, and D. J. Weinkauff, *ibid.*, **99**, 5946 (1977).

10) a) T. P. Dang and H. B. Kagan, *Chem. Commun.*, **1971**, 481; b) H. B. Kagan and T. P. Dang, *J. Am. Chem. Soc.*, **94**, 6429 (1972).

11) a) H. B. Kagan, N. Langlois, and T. P. Dang, *J. Organomet. Chem.*, **90**, 353 (1975); b) G. Gelbard, H. B. Kagan, and S. Stern, *Tetrahedron*, **32**, 233 (1976) and references cited therein.

12) R. Glaser and B. Vainas, *J. Organomet. Chem.*, **121**, 249 (1976) and their previous papers cited therein.

13) M. Tanaka, Y. Watanabe, T. Mitsudo, Y. Yasunori, and Y. Takegami, *Chem. Lett.*, **1974**, 137.

14) A. P. Stoll and R. Süess, *Helv. Chim. Acta*, **57**, 2487 (1974).

15) B. R. James, D. K. W. Wang, and R. F. Voigt, *J. Chem. Soc., Chem. Commun.*, **1975**, 574.

16) A. Levi, G. Modena, and G. Scorrano, *J. Chem. Soc., Chem. Commun.*, **1975**, 6.

17) a) B. Heil, S. Törös, S. Vastag, and L. Marko, *J. Organomet. Chem.*, **94**, C47 (1975); b) S. Törös B. Heil, and L. Marko, *ibid.*, **159**, 401 (1978).

18) a) I. Ojima, T. Kogure, M. Kumagai, S. Horiuchi, and T. Sato, *J. Organomet. Chem.*, **122**, 83 (1976); b) I. Ojima, T. Kogure, and M. Kumagai, *J. Org. Chem.*, **42**, 1671 (1977) and their previous papers cited therein.

19) T. Hayashi, Dissertation, Kyoto University, 1975.

20) W. Dumont, J. C. Poulin, T. P. Dang, and H. B. Kagan, *J. Am. Chem. Soc.*, **95**, 8295 (1973).

21) R. J. P. Corriu and J. J. E. Moreau, *J. Organomet. Chem.*, **85**, 19 (1975).

22) a) G. Consiglio, C. Botteghi, C. Salomon, and P. Pino, *Angew. Chem.*, **85**, 663 (1973); b) G. Consiglio, C. Botteghi, C. Solomon, and P. Pino, *Chimia*, **27**, 215 (1973); c) G. Consiglio and P. Pino, *Helv. Chim. Acta*, **59**, 642 (1976).

23) R. Stern, A. Hirshauer, and L. Sajus, *Tetrahedron Lett.*, **1973**, 3247.

24) a) M. Tanaka, Y. Ikeda, and I. Ogata, *Chem. Lett.*, **1975**, 1115; b) Y. Kawabata, T. M. Suzuki, and I. Ogata, *ibid.*, **1978**, 361.

25) G. Consiglio and C. Botteghi, *Helv. Chim. Acta*, **56**, 460 (1973).

26) Y. Kiso, K. Tamao, N. Miyake, K. Yamamoto, and M. Kumada, *Tetrahedron Lett.*, **1974**, 3.

27) a) B. M. Trost and P. E. Strege, *J. Am. Chem. Soc.*, **99**, 1649 (1977); b) J. C. Fiaud, A. Hibon de Gournay, M. Larcheveque, and H. B. Kagan, *J. Organomet. Chem.*, **154**, 175 (1978).

28) J. D. Morrison, R. E. Burnett, A. M. Aguiar, C. J. Morrow, and C. Phillips, *J. Am. Chem. Soc.*, **93**, 1301 (1971).

29) a) J. D. Morrison and W. F. Masler, *J. Org. Chem.*, **39**, 270 (1974); b) A. M. Aguiar, C. J. Morrow, J. D. Morrison, R. E. Burnett, W. F. Masler, and N. S. Bhacca, *J. Org. Chem.*, **41**, 1545 (1976). See also: M. Tanaka and I. Ogata, *Bull. Chem. Soc. Jpn.*, **48**, 1094 (1975). Y. Kiso, K. Yamamoto, K. Tamao, and M. Kumada, *J. Am. Chem. Soc.*, **94**, 4373 (1972).

30) B. Bogdanović, B. Henc, A. Lösler, B. Meister, H. Pauling, and G. Wilke, *Angew. Chem.*, **85**, 1013 (1973).

31) I. Ogata, F. Mizukami, Y. Ikeda, and M. Tanaka, Japan. Kokai, 76-43754; *Chem. Abstr.*, **85**, 124144z (1976); Japan Kokai, 76-39662; *Chem. Abstr.*, **85**, 124143y (1976).

32) a) K. Achiwa, *J. Am. Chem. Soc.*, **98**, 8265 (1976); b) K. Achiwa, Y. Ohga, Y. Iitaka, and H. Saito, *Tetrahedron Lett.*, **1978**, 4683, and their previous papers cited therein.

33) a) G. Descotes, D. Lafont, and D. Sinou, *J. Organomet. Chem.*, **150**, C14 (1978); b) D. Lafont, D. Sinou, and G. Descotes, *ibid.*, **169**, 87 (1979).

34) a) M. D. Fryzuk and B. Bosnich, *J. Am. Chem. Soc.*, **99**, 6262 (1977); b) M. D. Fryzuk and B. Bosnich, *ibid.*, **100**, 5491 (1978).

35) K. Tamao, H. Yamamoto, H. Matsumoto, N. Miyake, T. Hayashi, and M. Kumada, *Tetrahedron Lett.*, **1977**, 1389.

36) D. Marquarding, H. Klusacek, G. Gokel, P. Hoffmann, and I. Ugi, *J. Am. Chem. Soc.*, **92**, 5389 (1970).

37) T. Hayashi, T. Mise, S. Mitachi, K. Yamamoto, and M. Kumada, *Tetrahedron Lett.*, **1976**, 1133.

38) W. R. Cullen and E-S. Yeh, *J. Organomet. Chem.*, **139**, C13 (1977).

39) a) T. Hayashi, T. Mise, and M. Kumada, *Tetrahedron Lett.*, **1976**, 4351; b) T. Hayashi, A. Katsumura, M. Konishi, and M. Kumada, *ibid.*, **1979**, 425.

40) T. Hayashi, M. Nakatsuka, A. Katsumura, and M. Kumada, unpublished results.

41) T. Hayashi, K. Yamamoto, and M. Kumada, *Tetrahedron Lett.*, **1974**, 4405.

42) T. Hayashi, K. Tamao, Y. Katsuro, I. Nakae, and M. Kumada, *Tetrahedron Lett.*, in press.

43) a) T. Hayashi, M. Tajika, K. Tamao, and M. Kumada,

J. Am. Chem. Soc., **98**, 3718 (1976); b) K. Tamao, T. Hayashi, H. Matsumoto, H. Yamamoto, and M. Kumada, *Tetrahedron Lett.*, **1979**, 2155.
44) T. Hayashi, M. Konishi, S. Kawakami, and M. Kumada, unpublished results.
45) H. Kumobayashi, S. Akutagawa, and S. Otsuka, *J. Am. Chem. Soc.*, **100**, 3949 (1978).
46) M. D. Rausch and D. J. Ciappenelli, *J. Organomet. Chem.*, **10**, 127 (1967).
47) C. C. Price and J. R. Sowa, *J. Org. Chem.*, **32**, 4126 (1967).
48) B. J. Wakefield, "The Chemistry of Organolithium Compounds," Pergamon Press, New York (1974), p. 66.
49) G. W. Gokel, D. Marquarding, and I. Ugi, *J. Org. Chem.*, **37**, 3052 (1972).
50) A. N. Nesmeyanov, E. G. Perevalova, L. S. Shilovtseva, and V. D. Tyurin, *Izv. Akad. Nauk. SSSR, Otd. Khim. Nauk*, **1962**, 1997; *Chem. Abstr.*, **58**, 9132 (1963).
51) J. S. Fritz and J. N. King, *Anal. Chem.*, **48**, 570 (1976).
52) G. Marr and T. Hunt, *J. Chem. Soc., C*, **1969**, 1070.
53) G. R. Sullivan, "Topics in Stereochemistry," ed by E. L. Eliel and N. L. Allinger, Wiley-Interscience, New York, (1978), Vol. 10, p. 287.
54) M. Rosenblum, "Chemistry of the Iron Group Metallocenes," Wiley-Interscience, New York (1965), p. 40.
55) M. Rosenblum, A. K. Banerjee, N. Danieli, R. W. Fish, and V. Schlatter, *J. Am. Chem. Soc.*, **85**, 316 (1963).
56) C. R. Hauser and J. K. Lindsay, *J. Org. Chem.*, **22**, 906 (1957).
57) a) T. P. Dang, J.-C. Poulin, and H. B. Kagan, *J. Organomet. Chem.*, **91**, 105 (1975); b) K. S. Yudina, T. Ya. Medved, and M. I. Kabachnik, *Izv. Akad. Nauk. SSSR, Ser. Khim.*, **1966**, 1954; *Chem. Abstr.*, **66**, 76096u (1967).
58) T. Sone, K. Hiroi, and S. Yamada, *Chem. Pharm. Bull.*, **21**, 2331 (1973).
59) L. A. Paquette, J. P. Freeman, and S. Maiorana, *Tetrahedron*, **27**, 2599 (1971).
60) C. L. Butler and L. H. Cretcher, *J. Am. Chem. Soc.*, **55**, 2605 (1933).