reported quite frequently in crystal structure determinations; e.g., there are two examples of such disorder in 1979 alone.[12,38]

It would have been desirable to treat the adjacent atoms similarly but the corresponding positions would be below the limit of the resolution. Except for those attached to C^{γ} (proline) of the first molecule, evidence was found for all hydrogen atoms in a difference map. Hydrogen atom positions were calculated for those of the two C^{γ} sites. Final refinement utilized anisotropic thermal parameters for all heavier atoms and isotropic parameters for hydrogen atoms. All parameters, except for the thermal parameters of the hydrogen atom involved in the disorder, were refined. It was assumed that the population parameters for all disordered sites were 0.5 and no refinement was attempted. The final R factor was 3.7%; final parameters for the heavier atoms and for the hydrogen atoms are given as supplementary material. The refinement was carried out by full-matrix least-squares techniques although the structure was partitioned into many groups of atoms because of computer size limitations. No evidence of unexplained density was apparent in a final difference map. A table of observed and calculated structure factors has been also deposited. (See paragraph at end of paper concerning supplementary material.)

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Registry No. I, 76805-10-2; II, 76805-09-9; III, 47450-18-0; III methyl ester, 51782-77-5; III dicyclohexylammonium salt, 27483-24-5; IV, 79663-88-0; V, 79663-89-1; VI, 79663-90-4; carbobenzoxy-D-valine, 1685-33-2; L-proline methyl ester, 2577-48-2; D-valyl-L-prolylsarcosine, 79663-91-5; *N-tert*-butoxycarbonyl-*O*-benzyl-L-threonine, 15260-10-3; *N-tert*-butoxycarbonyl-*N*-methyl-L-alanine, 16948-16-6; *O*-benzyl-L-threonyl-D-valyl-L-prolylsarcosine methyl ester, 79663-92-6; *N-tert*-butoxycarbonyl-*N*-methyl-L-alanyl-*O*-benzyl-L-threonyl-D-valyl-L-prolylsarcosine, 79663-93-7.

Supplementary Material Available: A table of observed and calculated structure factors, table of benzyl dimensions, table of positional and thermal parameters for the heavier atoms, table of parameters for hydrogen atoms and a stereopacking diagram (33 pages). See current masthead page for ordering information.

Asymmetric Synthesis Catalyzed by Chiral Ferrocenylphosphine–Transition Metal Complexes. 2.[1] Nickel- and Palladium-Catalyzed Asymmetric Grignard Cross-Coupling[2]

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Abstract: Various kinds of chiral ferrocenylphosphines, which have both planar and central elements of chirality and also a functional group on the side chain, have been used as ligands for nickel or palladium complex catalyzed asymmetric cross-coupling of secondary alkyl (1-phenylethyl, 2-octyl, and 2-butyl) Grignard reagents with organic halides such as vinyl bromide, (*E*)-β-bromostyrene, 2-bromopropene, and bromobenzene. (*S*)-*N*,*N*-Dimethyl-1-[(*R*)-2-(diphenylphosphino)ferrocenyl]ethylamine [(*S*)-(*R*)-PPFA] was one of the most effective ligands giving the coupling product, 3-phenyl-1-butene, of up to 68% ee in the reaction of 1-phenylethylmagnesium chloride with vinyl bromide, and it was found that the ferrocene planar chirality is more important than the carbon central chirality and the dimethylamino group is the first requisite for the high stereoselectivity. The stereoselectivity was not affected by introduction of substituents onto the diphenylphosphino group of the ligand, but was strongly affected by changing the steric bulkiness of the secondary amino group on the ferrocenylphosphine side chain. A mechanism, where the coordination of the amino group on the ligand with the magnesium atom in the Grignard reagent plays a key role in a diastereomeric transition state, is proposed to account for the ferrocenylphosphine ligands causing a high asymmetric induction.

Asymmetric synthesis catalyzed by chiral transition metal complexes has been intensively studied in the last several years and is now recognized to be a promising method for the synthesis of optically active compounds. One of the most crucial points in obtaining high stereoselectivity in the catalytic asymmetric synthesis is the choice of the ligand which will fit in with a given reaction as efficiently in stereoselectivity as possible. In the asymmetric hydrogenation of α-acylaminoacrylic acids catalyzed by chiral rhodium complexes, over 90% optical yields have been achieved[4] and the dependence of the stereoselectivity on structural

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Table I. Asymmetric Cross-Coupling of 1-Phenylethylmagnesium Chloride (1a) with Vinyl Bromide (2a) Catalyzed by Chiral Ferrocenylphosphine-Nickel or -Palladium Complexes[a]

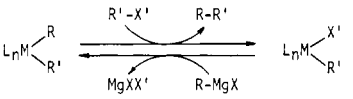
entry	chiral catalyst[b]	1a/2a	reaction temp (°C)	yield[c] of 3a (%)	$[\alpha]^{22}_D$[d] (neat), deg	% ee (confign)
1	(*S*)-(*R*)-PPFA/$NiCl_2$	4	0	>95	−3.75	63 (*R*)
2	(*S*)-(*R*)-PPFA/$NiCl_2$	2	0	>95	−3.59	61 (*R*)
3	(*S*)-(*R*)-PPFA/$NiCl_2$	1	0	83	−3.32	56 (*R*)
4	(*S*)-(*R*)-PPFA/$NiCl_2$	2[e]	0	>95	−3.62	61 (*R*)
5	(*S*)-(*R*)-PPFA/$NiCl_2$	4	−20	>95	−3.92	66 (*R*)
6	(*R*)-(*S*)-PPFA/$NiCl_2$[f]	4	−20	>95	+4.04	68 (*S*)
7	(*S*)-(*R*)-PPFA/$NiCl_2$	4	45	>95	−3.30	56 (*R*)
8	(*S*)-(*R*)-PPFA/$NiCl_2$[f]	4	0	>95	−3.75	63 (*R*)
9	(*S*)-(*R*)-PPFA/$NiCl_2$[g]	3	0	80[h]	−3.75	63 (*R*)
10	$PdCl_2$[(*S*)-(*R*)-PPFA]	3	25[i]	82	−3.58	61 (*R*)
11	(*R*)-(*R*)-PPFA/$NiCl_2$	2	0	>95	−3.19	54 (*R*)
12	(*S*)-FcPN/$NiCl_2$[f]	4	0	>95	+3.82	65 (*S*)
13	(*R*)-PPEF/$NiCl_2$[f]	4	0	86	+0.27	5 (*S*)
14	(*S*)-(*R*)-4a/$NiCl_2$	3	0	79	−1.93	33 (*R*)
15	(*S*)-(*R*)-4b/$NiCl_2$	3	0	>95	−3.85	65 (*R*)
16	(*S*)-(*R*)-4c/$NiCl_2$	3	0	90	−3.87	65 (*R*)
17	(*S*)-(*R*)-4d/$NiCl_2$	3	0	>95	−3.39	57 (*R*)
18	(*S*)-(*R*)-5a/$NiCl_2$	3	0	65	−2.07	35 (*R*)
19	(*S*)-(*R*)-5b/$NiCl_2$	3	0	49	+0.42	7 (*S*)
20	(*S*)-(*R*)-5c/$NiCl_2$	3	0[j]	50	+0.91	15 (*S*)
21	(*S*)-(*R*)-5d/$NiCl_2$	3	0	>95	−3.67	62 (*R*)
22	(*S*)-(*R*)-5e/$NiCl_2$	3	0	43	+2.50	42 (*S*)
23	(*S*)-(*R*)-5f/$NiCl_2$	3	0	68	−1.02	17 (*R*)
24	(*S*)-(*R*)-5g/$NiCl_2$	3	0	>95	−3.84	65 (*R*)
25	(*S*)-(*R*)-6/$NiCl_2$	2	0	95	−3.39	57 (*R*)
26	(*S*)-(*R*)-BPPFA/$NiCl_2$	4	0	73	−3.82	65 (*R*)
27	$PdCl_2$[(*S*)-(*R*)-BPPFA]	3	25[k]	93	−3.61	61 (*R*)

[a] Catalyst/2a = 5×10^{-3}. Concentration of 1a in ether was 1.2–1.5 M unless otherwise noted. Reaction time is 24 h unless otherwise noted. [b] Nickel catalyst was prepared in situ by mixing nickel chloride with 1 equiv of a ligand unless otherwise noted. [c] Yields based on 2a used were determined by GLC. Isolated yields were usually over 70%. [d] Optically pure (*R*)-(−)-3-phenyl-1-butene has $[\alpha]^{22}_D$ −5.91 ± 0.04° (neat); see text. [e] 1a of 0.5 M was used. [f] Chiral ligand:$NiCl_2$ = 2:1. [g] (*S*)-(*R*)-PPFA:$NiCl_2$ = 1:10. [h] 2-Phenylbutane (10%), 5-phenyl-1-hexene (5%), and styrene (20%) were formed as by-products. [i] Reacted for 70 h. [j] For 120 h. [k] For 60 h.

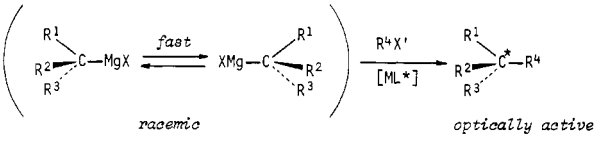
features of the chiral ligands and substrates has been elucidated.[4i,5] However, the choice of the ligand is still quite empirical in other fields of catalytic asymmetric synthesis, especially in asymmetric carbon–carbon bond forming reactions;[6] little has been known about structural features of a ligand giving rise to the highest stereoselectivity.

We have prepared various kinds of optically active ferrocenylphosphines starting with Ugi's chiral *N,N*-dimethyl-1-ferrocenylethylamine[1] and used them successfully as ligands for several transition metal catalyzed asymmetric reactions, viz., hydrogenation of olefins,[4a] ketones,[7] and imines[8] catalyzed by rhodium complexes, hydrosilylation of ketones by rhodium complexes[9] and of olefins by a palladium complex,[10] and Grignard cross-coupling by nickel complexes.[2,11] The ferrocenylphosphines have been also reported by other research groups to be effective ligands for some asymmetric reactions.[12-14] The chiral ferrocenylphosphines are quite unique in that they contain both planar and central elements of chirality, and also a functional group such as an amino on the side chain. Moreover, the ferrocenylphosphines have advantages over other chiral phosphines in that they permit one to estimate separately the role which each element of chirality and the functionality play in a catalytic asymmetric reaction by appropriate structural modifications. In this paper, we describe the asymmetric cross-coupling of secondary alkyl Grignard reagents with organic halides catalyzed by chiral ferrocenylphosphine–nickel and –palladium complexes, focusing attention upon the factors influencing the high stereoselectivity obtained.

Scheme I



Scheme II



Phosphine–nickel and –palladium complexes have been used as catalysts for the reaction of Grignard reagents (RMgX) with vinyl or aryl halides (R′X′) producing cross-coupling products (R–R′) selectively, and the catalytic cycle of the reaction is proposed to consist of a sequence of steps involving a diorganometal

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Table II. Asymmetric Cross-Coupling of 1 with 2 Catalyzed by Nickel or Palladium Complexes with PPFA or BPPFA Ligand[a]

entry	Grignard reagent	halide	chiral catalyst[b]	product (yield %)	$[\alpha]_D$, deg	% ee[c] (confign)
28	1a	2b	(S)-(R)-PPFA/$NiCl_2$	3b (62)[d,e]	+27.4[f]	52 (R)
29	1a	2b	$PdCl_2$[(S)-(R)-BPPFA]	3b (78)[d,e]	+24.3[f]	46 (R)
30	1a	2c	$PdCl_2$[(S)-(R)-BPPFA]	3c (48)[g,h]	+3.38[i]	5 (S)
31	1b	2a	(S)-(R)-PPFA/$NiCl_2$	3d (>95)[g]	+5.35[j]	37 (S)
32	1b	2a	(S)-(R)-BPPFA/$NiCl_2$	3d (>95)[g]	+3.48[j]	24 (S)
33	1c	2a	(R)-(S)-PPFA/$NiCl_2$	3e (>95)[g]	−9.73[k]	30 (R)
34	1c	2c	$PdCl_2$[(R)-(S)-BPPFA]	3f (65)[d]	−1.60[l]	12 (R)
35	1c	2d	$PdCl_2$[(S)-(R)-BPPFA]	3g (60)[g,m]	−0.54[n]	22 (R)

[a] Catalyst/2 = 5 × 10^{-3}. 1/2 = 2. The coupling reaction was carried out at 0 °C for 24 h unless otherwise noted. [b] See footnote in Table I. [c] Calculated on the basis of values for the optically pure compounds: (R)-3b, $[\alpha]^{20}_D$ + 52.9° (c 3, benzene), see text; (R)-3c, $[\alpha]^{25}_D$ +76° (c 1.55, benzene) [Clark, D. R.; Mosher, H. S. *J. Org. Chem.* **1970**, *35*, 1114]; (S)-3d, $[\alpha]^{20}_D$ +14.6° (neat), see text; (S)-3e, $[\alpha]^{17}_D$ +32.86° (neat), ref 41; (S)-3f, $[\alpha]^{25}_D$ +13.29° (neat), ref 42; (R)-3g, α^{23}_D −24.3° (1 dm, neat), ref 31. [d] Isolated yield. [e] Styrene (5–10%) was formed as a by-product. [f] $[\alpha]^{20}_D$ (benzene). [g] GLC yield. [h] Styrene (40%) was formed as a by-product. [i] $[\alpha]^{25}_D$ (benzene). [j] $[\alpha]^{20}_D$ (neat). [k] $[\alpha]^{17}_D$ (neat). [l] $[\alpha]^{25}_D$ (neat). [m] Reaction at room temperature. [n] α^{23}_D (0.1 dm, neat).

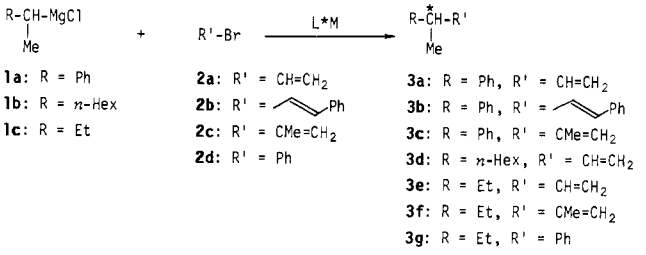
complex ($L_nM(R)R'$) as a key intermediate (Scheme I).[15,16]

Use of an optically active phosphine ligand L* for the reaction of a racemic Grignard reagent must bring about kinetic resolution of it to make the reaction rate of the enantiomers different.[17] Those Grignard reagents in which the magnesium atom attaches to a chiral carbon center undergo racemization because of the stereochemical instability of the magnesium–carbon bond,[18] and if the inversion at this chiral carbon is much faster than the cross-coupling reaction, the optical purity of the coupling product should be kept constant throughout the reaction since the Grignard reagent always exists in a racemic form (Scheme II).

Results and Discussion

Chiral ferrocenylphosphines[1] used are shown in Figure 1[19a] and the results are summarized in Tables I and II.

In the first set of experiments, the reaction of 1-phenylethylmagnesium chloride (**1a**) with vinyl bromide (**2a**) was examined using (S)-*N*,*N*-dimethyl-1-[(R)-2-(diphenylphosphino)-ferrocenyl]ethylamine [(S)-(R)-PPFA] as a ligand under various reaction conditions (entries 1–10). Reaction of 4 equiv of **1a** (1.5



M in ether) with **2a** in the presence of 0.5 mol% nickel catalyst prepared in situ from nickel chloride and the ligand (1:1) gave,

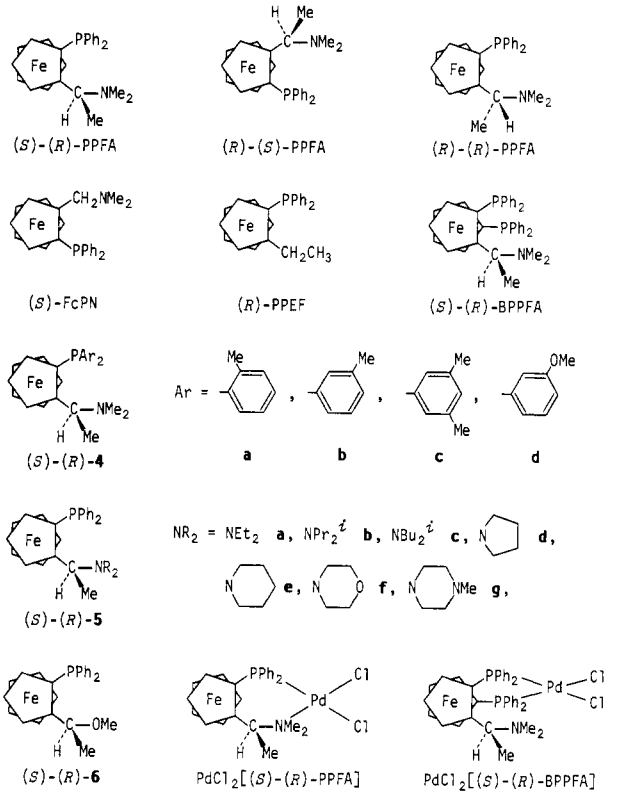


Figure 1. Ferrocenylphosphines and their palladium complexes.

after 24 h at 0 °C, 3-phenyl-1-butene (**3a**) in quantitative yield, which was found to possess $[\alpha]^{22}_D$ of −3.75° (entry 1). This value corresponds to 63% enantiomeric purity enriched in the *R* configuration (determination of the maximum optical rotation of **3a** will be described later). The stereoselectivity obtained here with the PPFA ligand is much higher[19b] than that obtained with 2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane (DIOP) (7–16% ee),[17] 1,2-bis(diphenylphosphino)propane (prophos) (0% ee),[20] and 2,2′-bis(diphenylphosphinomethyl)-1,1′-binaphthyl (NAPHOS (1,1)) (11% ee).[21]

The coupling product **3a** of almost the same optical purity (61 and 56% ee) was obtained in the reaction of **1a** with **2a** in a 2:1 and 1:1 ratio (entries 2 and 3). Use of the Grignard reagent **1a** in a low concentration (0.5 M) also gave **3a** of 61% ee (*R*) (entry 4). Thus, the optical purity of **3a** was not largely affected by the initial **1a**/**2a** ratio, indicating that the inversion of the Grignard reagent **1a** is relatively fast as compared with the coupling reaction.

(15) For a pertinent review, see: Tamao, K.; Kumada, M. In "Organometallic Reactions and Syntheses"; Becker, E. I.; Tsutsui, M., Eds.; Plenum: New York, in press.

(16) (a) Tamao, K.; Sumitani, K.; Kiso, Y.; Zembayashi, M.; Fujioka, A.; Kodama, S.; Nakajima, I.; Minato, A.; Kumada, M. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 1958, and references cited therein. (b) Morrell, D. G.; Kochi, J. K. *J. Am. Chem. Soc.* **1975**, *97*, 7262. (c) Corriu, R. J. P.; Massé, J. P. *J. Chem. Soc., Chem. Commun.* **1972**, 144. (d) Hayashi, T.; Konishi, M.; Kumada, M. *Tetrahedron Lett.* **1979**, 1871, and references cited therein.

(17) The first two reports concerning the asymmetric Grignard cross-coupling appeared in 1973–1974: (a) Consiglio, G.; Botteghi, C. *Helv. Chim. Acta* **1973**, *56*, 460. (b) Kiso, Y.; Tamao, K.; Miyake, N.; Yamamoto, K.; Kumada, M. *Tetrahedron Lett.* **1974**, 3.

(18) For inversion of Grignard reagents, see, for example: (a) Whitesides, G. M.; Roberts, J. D. *J. Am. Chem. Soc.* **1965**, *87*, 4878. (b) Maercker, A.; Geuss, R. *Angew. Chem.* **1971**, *83*, 288. (c) Krieghoff, N. G.; Cowan, D. O. *J. Am. Chem. Soc.* **1966**, *88*, 1322. (d) Jensen, F. R.; Nakamaye, K. L. *Ibid.* **1966**, *88*, 3437.

(19) (a) For the ferrocenylphosphines containing both central and planar elements of chirality, the symbols *R* and *S* are used in the order: first, central, and second, planar chirality. (b) Recently we have found that chiral β-dimethylaminoalkyldiphenylphosphines derived from amino acids are more effective than the ferrocenylphosphines for the cross-coupling of **1a** with **2a** (ref 20). See also, Hayashi, T.; Nagashima, N.; Kumada, M. *Tetrahedron Lett.* **1980**, *21*, 4623. Hayashi, T.; Kanehira, K.; Hioki, T.; Kumada, M. *Ibid.* **1981**, *22*, 137.

(20) Hayashi, T.; Fukushima, M.; Konishi, M.; Kumada, M. *Tetrahedron Lett.* **1980**, *21*, 79.

(21) Tamao, K.; Yamamoto, H.; Matsumoto, H.; Miyake, N.; Hayashi, T.; Kumada, M. *Tetrahedron Lett.* **1977**, 1389.

It should be emphasized that the present asymmetric reaction can produce an optically active coupling product even if all the Grignard reagent is consumed, though the reaction may be classified as kinetic resolution of a racemic reagent.

The temperature dependency of the stereoselectivity was tested (entries 5, 6, and 7). As expected, the optical purity of **3a** went up to 66–68% in the reaction at −20 °C and down to 56% at 45 °C. At a temperature lower than −40 °C, the coupling reaction was very slow, the yield being below 10% even after 2 weeks.

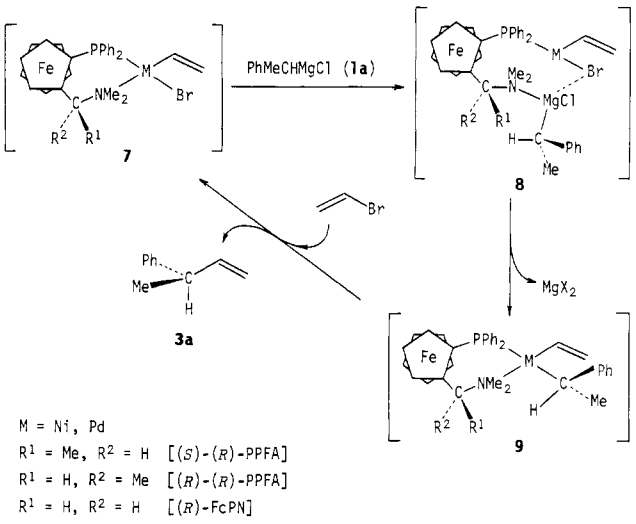
Several attempts to isolate the PPFA–nickel complex by reacting the ligand with nickel(II) salts have failed,[22] but the palladium complex could be easily obtained. Dichlorobis(acetonitrile)palladium(II) and PPFA react easily to afford $PdCl_2$(PPFA) where both the phosphorus and nitrogen atoms are bonded to the palladium to form a chelate ring. Chelation through the phosphorus and nitrogen atoms is demonstrated by the NMR spectrum which shows the presence of inequivalent methyl groups on the nitrogen. The PPFA–palladium complex $PdCl_2$[(*S*)-(*R*)-PPFA] was also found to catalyze the asymmetric cross-coupling of **1a** with **2a** at 25 °C to give (*R*)-**3a** of 61% ee (entry 10), the stereoselectivity being almost the same as that in the reaction catalyzed by the (*S*)-(*R*)-PPFA–nickel catalyst. In can therefore be assumed that the in situ nickel catalyst is structurally analogous to the palladium catalyst consisting of the ligand and the metal in a one-to-one ratio, not in a two-to-one ratio forming "$Ni(PPFA)_2$". The optical purity of **3a** obtained with the in situ catalyst prepared from nickel chloride and the PPFA ligand in a ratio of 1:2 and 10:1 was 63% ee each, exactly the same as that obtained with the 1:1 catalyst (entries 8 and 9). In the reaction with the 1:2 nickel catalyst, an excess of PPFA is imagined to be free from nickel and to have no effect on the catalytic reaction. Since nickel chloride itself does not catalyze the present cross-coupling reaction, the presence of an excess of it does not reduce the optical purity of the coupling product. Nevertheless, use of a large excess of nickel chloride should be avoided. It brought about side reactions forming 2-phenylbutane and 5-phenyl-1-hexene, probably originating from 3-phenylbutylmagnesium chloride formed by the nickel chloride catalyzed Grignard exchange reaction[23] of **1a** with the coupling product **3a**.

The mechanism to account for the PPFA ligand causing a high asymmetric induction in the present cross-coupling reaction was investigated by use of several other types of chiral ferrocenylphosphine ligands. As mentioned above, some chiral ferrocenylphosphines contain both planar and central elements of chirality, and also a functional group on the ferrocene side chain, while others lack one or two of these features. (*S*)-(*R*)-PPFA has an *S* configuration of carbon central chirality and an *R* configuration of ferrocene planar chirality, and the dimethylamino group in addition. (*R*)-(*R*)-PPFA is a diastereomeric isomer of (*S*)-(*R*)-PPFA, with the carbon central chirality *R*. (*S*)-FcPN lacks the central chirality, but still bears the dimethylamino group. (*R*)-PPEF possesses the planar chirality only, containing neither the central chirality nor this functional group.

(*R*)-(*R*)-PPFA and (*S*)-FcPN gave the coupling product of 54% ee (*R*) and 65% ee (*S*), respectively (entries 11 and 12). These optical purities and configurations are comparable to those obtained with the (*S*)-(*R*)- or (*R*)-(*S*)-PPFA ligand. On the other hand, a dramatic decrease in the asymmetric induction was observed with (*R*)-PPEF as a ligand (entry 13). These results demonstrate that the ferrocene planar chirality plays a dominant role and that the dimethylamino group is the first requisite for the high stereoselectivity. In the same cross-coupling reaction with chiral β-aminoalkylphosphine ligands,[20] we have also observed that the presence of the dimethylamino group on the ligands is responsible for high optical yields.

The important role of the amino group may be visualized by its strong ability to coordinate with the magnesium atom in the Grignard reagent, and the mechanism shown in Scheme III can be proposed based on the catalytic cycle assumed for the nickel- or palladium-catalyzed cross-coupling. This scheme illustrates the reaction with ferrocenylphosphines containing *R* planar chirality. When the Grignard reagent **1a** approaches the intermediate **7**, the dimethylamino group in the ferrocenylphosphine ligand dissociates from the metal M and coordinates with the magnesium atom in the Grignard reagent to form the diastereomeric transition state (or intermediate) **8**. This coordination should occur selectively with one of the enantiomers of the racemic Grignard reagent and allow it to readily undergo subsequent transmetalation to form the diorganonickel or -palladium intermediate **9**.[24a] The optical purity of the coupling product is mainly determined at this stage (vide infra). The stereoselection by the coordination must be much more effective than that by simple steric repulsion, since the coordination brings about the enhanced steric interactions.[24b] Reductive elimination to give optically active coupling product **3a** is followed by oxidative addition of vinyl bromide to reproduce **7**. Supposing that both transmetalation and reductive elimination occur with retention of configuration at carbon[25] on the 1-phenylethyl group, it may be said that the *S* isomer of the Grignard reagent **1a** is more subject to coordination with the amino group than the *R* isomer.

Scheme III



The data obtained with several other ferrocenylphosphines, which contain bis(substituted phenyl)phosphino groups or dialkylamino groups, could provide further insight into the present asymmetric Grignard cross-coupling reaction. The phosphine ligands ((*S*)-(*R*)-**4a**, **-4b**, **-4c**, and **-4d** with a 2-methylphenyl, 3-methylphenyl, 3,5-dimethylphenyl, and 3-methoxyphenyl group on the phosphorus atom gave the coupling product (*R*)-**3a** of 33, 65, 65, and 57% ee, respectively (entries 14, 15, 16, and 17). These figures are close to the value obtained with the (*S*)-(*R*)-PPFA ligand, except that (*S*)-(*R*)-**4a** results in a little lower selectivity. It has been reported[26] that a dramatic change in stereoselectivity is caused by substitution at the diarylphosphino groups in the

(22) It has been reported that $Ni(CO)_3$(PPFA) can be prepared by the reaction of nickel carbonyl with PPFA (ref 12).

(23) Farády, L.; Markó, L. *J. Organomet. Chem.* **1971**, *28*, 159, and their previous papers cited therein.

(24) (a) One referee suggested an alternative explanation that there might be no kinetic resolution of **1a** but fast epimerization of the benzylic center within the complex **8** and preferential fast transformation of one epimer into **9**. (b) The efficiency of the coordination for stereoselection observed here is in good agreement with Meyers' methodology in his studies on stoichiometric asymmetric carbon–carbon bond forming reactions that a high degree of asymmetric induction can be attained by steric effects generated via chelation: Meyers, A. I. *Acc. Chem. Res.* **1978**, *11*, 375.

(25) To our knowledge there has been no report establishing the stereochemistry of transmetalation and reductive elimination on nickel or palladium complexes. Transmetalation of the *endo*-2-norbornyl Grignard reagent to copper has been reported to proceed with retention: Whitesides, G. M.; Filippo, J. S., Jr.; Stredronsky, E. R.; Casey, C. P. *J. Am. Chem. Soc.* **1969**, *91*, 6542.

(26) (a) Dang, T. P.; Poulin, J.-C.; Kagan, H. B. *J. Organomet. Chem.* **1975**, *91*, 105. (b) Brown, J. M.; Murrer, B. A. *Tetrahedron Lett.* **1980**, *21*, 581.

asymmetric hydrogenation with chiral phosphine–rhodium complexes, where the stereocontrol by orientation of the aryl rings has been proposed. The present results that introduction of the substituents on to the phenyl ring did not exert a great influence upon the stereoselectivity appear consistent with the mechanism shown in Scheme III, in which the surroundings around the nitrogen rather than phosphorus atom should control the stereoselectivity.

In fact, the steric bulkiness of the amino substituent had a powerful effect on the stereoselection. Thus, the ferrocenylphosphines ((*S*)-(*R*)-) with the dimethylamino (PPFA), diethylamino (**5a**), and pyrrolidino group (**5d**) afforded the coupling product (*R*)-**3a** of 63, 35, and 62% ee, respectively (entries 1, 18, and 21), while the use of phosphines with the diisopropylamino (**5b**), diisobutylamino (**5c**), and piperidino (**5e**) group resulted in the formation of (*S*)-**3a** of 7, 15, and 42% ee, respectively (entries 19, 20, and 22). It follows that a larger substituent on the amino group tends to form the coupling product with *S* configuration. Morpholino and *N*-methylpiperazino groups are considered to have almost the same size of steric bulkiness as the piperidino group, but the phosphines **5e**, **5f**, and **5g** gave very different stereochemical results (entries 22, 23, and 24). Chelate formation is expected in the reaction with **5g** or **5f**, with two nitrogen atoms or both nitrogen and oxygen atoms, respectively, coordinating to the magnesium atom in the Grignard reagent. The piperidino group, by contrast, cannot make a chelate.

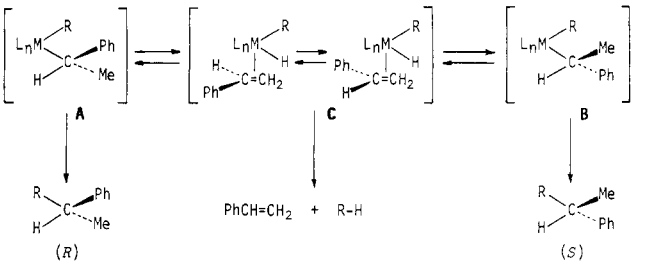
Reversal of the configuration of product **3a** observed in the reaction with **5b**, **5c**, and **5e** as a ligand may be attributed either to the reversal of stereoselection at the magnesium–nitrogen coordination step (**8** in Scheme III) caused by a change of stereochemical requirements around the nitrogen atom with a sterically hindered substituent or to the change of the manner of stereoselection for an alternative one where the steric hindrance around the nitrogen atom no longer allows the coordination of nitrogen with magnesium; consequently, simple steric repulsion controls the stereochemistry. The latter seems more likely in view of the fact that the reaction forming (*S*)-**3a** is slower than that forming (*R*)-**3a** (as judged from the yields in Table I). The slower reaction rate can be accounted for by the absence of the acceleration of the transmetalation step by magnesium–nitrogen coordination (**8** → **9** in Scheme III).

(*S*)-1-[(*R*)-2-(Diphenylphosphino)ferrocenyl]ethyl methyl ether (**6**), which has the methoxyl group on the ferrocene side chain instead of an amino group, gave (*R*)-**3a** of 57% ee (entry 25); the similar stereoselectivity to that obtained with (*S*)-(*R*)-PPFA indicates that the methoxyl group coordinates to the magnesium atom of the Grignard reagent **1a** in the same manner as the dimethylamino group.

The optically active bisphosphine ligand, (*S*)-*N*,*N*-dimethyl-1-[(*R*)-1′,2-bis(diphenylphosphino)ferrocenyl]ethylamine [(*S*)-(*R*)-BPPFA], also exhibited about the same stereoselectivity as (*S*)-(*R*)-PPFA in both nickel and palladium catalysts (entries 26 and 27). According to X-ray crystallographic studies,[27] $PdCl_2$(BPPFA) has the structure in which both the diphenylphosphino groups coordinate to the palladium atom, leaving the dimethylamino group free. The similarity in the stereoselectivity between PPFA and BPPFA indicates again that the steric factors around the amino group, and not the other moieties of the ligand, are responsible for asymmetric induction in the present coupling reaction. The results make a strong contrast to rhodium complex-catalyzed asymmetric hydrogenation where PPFA and BPPFA ligands produce acylamino acids with different configurations.[4a,12]

The reaction of 1-phenylethylmagnesium chloride (**1a**) with the other alkenyl halides **2b** and **2c** was also examined (entries 28, 29, 30 in Table II). From (*E*)-β-bromostyrene (**2b**), (*R*)-(*E*)-1,3-diphenyl-1-butene (**3b**) of 52 and 46% ee was obtained in the presence of the (*S*)-(*R*)-PPFA/$NiCl_2$ and $PdCl_2$[(*S*)-(*R*)-BPPFA] catalyst, respectively, the optical purity being slightly lower than that of **3a** obtained with the same catalysts. In the reaction with 2-bromopropene (**2c**), $PdCl_2$[(*S*)-(*R*)-BPPFA] gave coupling product **3c** of *S* configuration with very low stereoselectivity (5%). It should be noted that the reaction of **2b** and **2c** was accompanied by the formation of styrene in about 10 and 40%, respectively. The interrelation between a decrease in stereoselectivity and an increase in the formation of styrene as a by-product leads us to propose the mechanism shown in Scheme IV. The diorganometal intermediate A, having a chiral 1-phenylethyl group, isomerizes to its diastereomeric isomer B via the hydridostyrene metal intermediate C formed by β-hydride elimination.[28] When the reductive elimination forming a coupling product is fast compared with the β-hydride elimination, the isomerization does not take place and the coupling product with high optical purity can be obtained. When it is slow, the optical purity of the coupling product is lowered by the isomerization and the hydridostyrene metal intermediate is liable to afford styrene. It seems likely that a bulkier alkenyl group such as isopropenyl retards the reductive elimination, allowing the β-hydride elimination to proceed.

Scheme IV



The results obtained in the reaction of 2-octylmagnesium chloride (**1b**) and 2-butylmagnesium chloride (**1c**) are also given in Table II. These Grignard reagents reacted also quantitatively with vinyl bromide in the presence of the PPFA/$NiCl_2$ or BPPFA/$NiCl_2$ catalyst to afford the corresponding coupling products with moderate optical purity. Here, the configuration of the Grignard reagents (**1b** and **1c**) consumed predominantly is the same as that of the 1-phenylethyl Grignard reagent (**1a**). The nickel catalysts, PPFA/$NiCl_2$ and BPPFA/$NiCl_2$, failed to catalyze the coupling of **1c** with 2-bromopropene (**2c**) or bromobenzene (**2d**).[29] The palladium complex $PdCl_2$(BPPFA) was found to catalyze the reaction with modest stereoselectivity. The relatively low stereoselectivity observed in the reaction of **1b** and **1c** is thought to be due to the difficulty in the chiral recognition of these racemic Grignard reagents; that is, a distinction between methyl and ethyl or between methyl and *n*-hexyl is more difficult than that between methyl and phenyl as usually recognized in studies on asymmetric synthesis.[30]

Optical Rotation of Coupling Products. The maximum values for the optical rotation of 3-phenyl-1-butene (**3a**), (*E*)-1,3-diphenyl-1-butene (**3b**), and 3-methyl-1-nonene (**3d**) were determined by converting the optically active olefins **3a**,**b**,**d** into several related compounds of which the maximum rotation values were established.

Scheme V summarizes the conversion of (*R*)-**3a**, $[\alpha]^{22}_D$ −3.55° (neat), into (*R*)-3-phenyl-1-butanol (**10**) and (*R*)-2-phenylbutane (**11**), the maximum rotation values of which have been reported to be α^{25}_D −39.0° (1 dm, neat)[31] and α^{23}_D −24.3° (1 dm, neat),[31] respectively. Since the optical purity of **10** and **11** obtained here is 60.1 ± 0.4%, the optical rotation for the optically pure **3a** is calculated back to be $[\alpha]^{22}_D$ 5.91 ± 0.04° (neat). The reported

(27) Higuchi, T.; Hirotsu, K.; Hayashi, T.; Konishi, M.; Kumada, M., unpublished results.

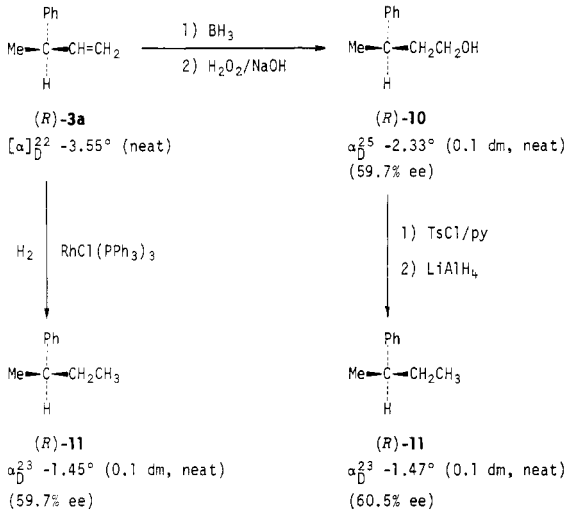
(28) (a) Tamao, K.; Kiso, Y.; Sumitani, K.; Kumada, M. *J. Am. Chem. Soc.* **1972**, *94*, 9268. (b) Kiso, Y.; Tamao, K.; Kumada, M. *J. Organomet. Chem.* **1973**, *50*, C12.

(29) Recently Consiglio and co-workers have reported that a prophosnickel complex can catalyze the coupling reaction of the 2-butyl Grignard reagents with halobenzenes in up to 44% optical yield: Consiglio, G.; Piccolo, O. *J. Organomet. Chem.* **1979**, *177*, C13.

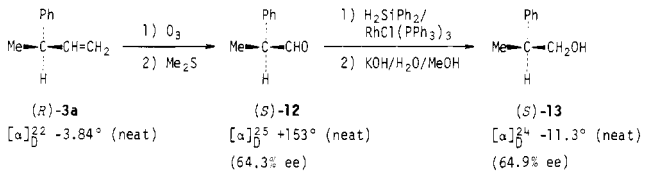
(30) Morrison, J. D.; Mosher, H. S. "Asymmetric Organic Reactions"; Prentice-Hall: Englewood Cliffs, N.J., 1971.

(31) Cram, D. J. *J. Am. Chem. Soc.* **1952**, *74*, 2137.

Scheme V



Scheme VI



value, $[\alpha]^{22}_D$ 6.39° (neat),[31] is a little too high. (*R*)-**3a** was also converted to (*S*)-2-phenylpropanal (**12**) and (*S*)-2-phenyl-1-propanol (**13**) (Scheme VI). From reported values of the maximum rotation of **12**, $[\alpha]^{25}_D$ 238° (neat),[32] and **13**, $[\alpha]^{24}_D$ 17.4° (neat),[33] the optical purities are calculated to be 64.3 and 64.9%, respectively. The optical purity (65.0%) of the starting (*R*)-**3a**, $[\alpha]^{22}_D$ −3.84° (neat), calculated on the basis of the above-obtained $[\alpha]^{22}_D$ max 5.91°, is in very good agreement with these figures.[34]

In the same manner as in Scheme VI, (+)-**3b**, $[\alpha]^{20}_D$ +27.4° (benzene), was converted into (*S*)-**13** of 52% ee via aldehyde **12**, and the maximum optical rotation of (*R*)-**3b** was determined to be $[\alpha]^{20}_D$ +52.9° (benzene).

The maximum rotation of (*S*)-**3d** was calculated to be $[\alpha]^{20}_D$ +14.6° (neat) from the rotation data of 3-methylnonane[36] obtained by catalytic hydrogenation of **3d**.

Conclusions

We have emphasized the importance of the design of chiral phosphine ligands for asymmetric synthesis catalyzed by chiral transition metal complexes[1] and demonstrated here that the high stereoselectivity can be achieved by use of appropriately functionalized chiral ferrocenylphosphines in asymmetric Grignard cross-coupling reaction, which is regarded as a most potentially useful method for the synthesis of optically active olefins. The chiral ferrocenylphosphines are far superior to others in that structural modification can be readily made by introduction of an appropriate functional group on to the side chain. The high stereoselectivity in the present study is ascribed mainly to the efficient stereocontrol by coordination of an amino group on the ligand to the magnesium atom on the racemic Grignard reagent.[24b] This type of stereocontrol, i.e., the one which, in general, is based on attractive interactions between functional groups on a substrate and on a chiral ligand, should be applicable to other catalytic asymmetric syntheses. Our current research is directed toward the synthesis of new optically active ligands designed for several catalytic asymmetric carbon–carbon bond forming reactions.

Experimental Section

Optical rotations were measured with a Yanagimoto OR-50 or Perkin-Elmer 241 polarimeter. ^{1}H NMR spectra were measured with a JEOL MH-100 spectrometer. Gas chromatographic data were obtained with a Shimadzu GC-4B or GC-4C chromatograph (30% Silicone DC550 on Celite) using an appropriate internal standard. A Varian Aerograph Model 920, equipped with a 20-ft column packed with Silicone DC 550 (30% on Celite) or PEG 20M (30% on Celite), was used for isolation and purification of the products. The preparation of chiral ferrocenylphosphines has been described in the previous paper.[1] 2-Bromopropene,[37] (*E*)-β-bromostyrene[38] and 1-phenylethyl chloride[39] were prepared as reported previously. 2-Octyl chloride was prepared by the reaction of 2-octanol with thionyl chloride in pyridine.[40] Vinyl bromide, bromobenzene, and 2-butyl chloride were commercially available and used without further purification. Grignard reagents were prepared in a standard manner by adding slowly a solution of an organic halide in ether to magnesium ribbons which had been dried in a rapid stream of dry nitrogen by flaming.

Preparation of $PdCl_2$[(*S*)-(*R*)-PPFA]. To a suspension of 259 mg (1.0 mmol) of dichlorobis(acetonitrile)palladium(II) in 10 mL of benzene was added with stirring a solution of 441 mg (1.0 mmol) of (*S*)-*N*,*N*-dimethyl-1-[(*R*)-2-(diphenylphosphino)ferrocenyl]ethylamine [(*S*)-(*R*)-PPFA] in 10 mL of benzene. After 12 h at room temperature, the reddish brown precipitate formed was collected by filtration, washed with benzene, and dried in vacuo. The precipitate was recrystallized from dichloromethane/hexane to give $PdCl_2$[(*S*)-(*R*)-PPFA] (550 mg, 90% yield) as red needles: mp 170 °C dec, $[\alpha]^{25}_D$ −335° (*c* 0.41, chloroform); NMR ($CDCl_3$) δ 1.42 (d, *J* = 7 Hz, 3 H, $CHCH_3$), 2.78, 3.58 (a pair of s, 6 H, $N(CH_3)_2$), 3.4–3.7 (m, 1 H, $CHCH_3$), 3.80 (s, 5 H, FeC_5H_5), 4.28, 4.50 (m, 1 H and 2 H, respectively, FeC_5H_3), 7.2–7.7, 8.1–8.4 (m, 10 H, $P(C_6H_5)_2$). Anal. Calcd for $C_{26}H_{28}NCl_2PFePd$: C, 50.48; H, 4.56; N, 2.26; Cl, 11.46. Found: C, 50.09; H, 4.62; N, 2.17; Cl, 11.49.

Preparation of $PdCl_2$[(*R*)-(*S*)-BPPFA]. To a suspension of 259 mg (1.0 mmol) of dichlorobis(acetonitrile)palladium(II) in 9 mL of benzene was added with stirring a solution of 626 mg (1.0 mmol) of (*R*)-*N*,*N*-dimethyl-1-[(*S*)-1′,2-bis(diphenylphosphino)ferrocenyl]ethylamine [(*R*)-(*S*)-BPPFA] in 9 mL of benzene. After the solution was stirred overnight, 779 mg (97%) of the palladium complex was obtained by filtration. An analytically pure sample was obtained by recrystallization from chloroform: mp 215–220 °C dec, $[\alpha]^{25}_D$ + 321° (*c* 0.3, chloroform); NMR ($CDCl_3$) δ 1.31 (d, *J* = 7 Hz, 3 H, $CHCH_3$), 2.33 (s, 6 H, $N(CH_3)_2$), 3.43–3.65, 4.13–4.68 (m, 7 H, $C_5H_4FeC_5H_3$), 5.49–5.76 (m, 1 H, $CHCH_3$), 6.91–8.55 (m, 20 H, $P(C_6H_5)_2$). Anal. Calcd for $C_{38}H_{37}NCl_2P_2FePd$: C, 56.85; H, 4.65; N, 1.74. Found: C, 56.68; H, 4.70; N, 1.75.

$PdCl_2$[(*S*)-(*R*)-BPPFA] was also prepared from (*S*)-(*R*)-BPPFA in a similar manner.

Asymmetric Grignard Cross-Coupling Reactions. The reaction conditions and data obtained are listed in Tables I and II. Densities of the coupling products used for the calculation of specific rotations are as follows: 3-phenyl-1-butene (**3a**), d_4^{22} 0.8809;[31] 3-methyl-1-nonene (**3d**), d_4^{20} 0.7365; 3-methyl-1-pentene (**3e**), d^{17}_4 0.6703;[41] 2,3-dimethyl-1-pentene (**3f**), d^{25}_4 0.7009.[42] Detailed procedures for coupling of 1-phenylethylmagnesium chloride (**1a**) with vinyl bromide (**2a**) in the presence of (*S*)-(*R*)-PPFA/$NiCl_2$ (entry 2) and with (*E*)-β-bromostyrene (**2b**) in the presence of $PdCl_2$[(*S*)-(*R*)-BPPFA] (entry 29) are described below. All other reactions were carried out in essentially the same manner.

(a) Reaction of 1-Phenylethylmagnesium Chloride (1a) with Vinyl Bromide (2a). A 100-mL pressure glass tube containing 13 mg (0.10 mmol) of anhydrous nickel chloride and 44 mg (0.10 mmol) of (*S*)-(*R*)-PPFA was filled with argon after evacuation and cooling at −78 °C. To it were added 2.14 g (20 mmol) of vinyl bromide by a precooled syringe and 27 mL (40 mmol) of 1.5 M 1-phenylethylmagnesium chlo-

(32) Botteghi, C.; Consiglio, G.; Pino, P. *Justus Liebigs Ann. Chem.* **1974**, 864.
(33) Bakshi, S. P.; Turner, E. E. *J. Chem. Soc.* **1961**, 171.
(34) It should be noted that no racemization was observed in the reduction of **12** to **13** by the use of rhodium-catalyzed hydrosilylation.[35] The reduction of **12** with lithium aluminum hydride or catalytic hydrogenation has been reported to be accompanied by partial racemization (ref 32).
(35) (a) Ojima, I.; Nihonyanagi, M.; Kogure, T.; Kumagai, M.; Horiuchi, S.; Nakatsugawa, K.; Nagai, Y. *J. Organomet. Chem.* **1975**, *94*, 449, and references cited therein. (b) Hayashi, T.; Yamamoto, K.; Kasuga, K.; Omizu, H.; Kumada, M. *Ibid.* **1976**, *113*, 127, and references cited therein.
(36) Lardicci, L.; Botteghi, C.; Benedetti, E. *J. Org. Chem.* **1966**, *31*, 1534.
(37) Braude, E. A.; Evans, E. A. *J. Chem. Soc.* **1956**, 3333.
(38) Dolby, L. J.; Wilkins, C.; Frey, T. G. *J. Org. Chem.* **1966**, *31*, 1110.
(39) Goerner, G. L.; Hines, W. G. *J. Am. Chem. Soc.* **1948**, *70*, 3511.
(40) Cason, J.; Correira, J. S. *J. Org. Chem.* **1961**, *26*, 3645.
(41) Pino, P.; Lardicci, L.; Centoni, L. *J. Org. Chem.* **1959**, *24*, 1399.
(42) Lardicci, L.; Rossi, R.; Pucci, S.; Aglietto, M.; Botteghi, C.; Pino, P. *Chim. Ind. (Milan)* **1968**, *50*, 227; *Chem. Abstr.* **1968**, *68*, 113956p.

ride in ether. The glass tube was stoppered and allowed to warm up to 0 °C. The mixture was kept standing at 0 °C for 24 h, and hydrolyzed with 20 mL of 10% hydrochloric acid. GLC analysis of the organic layer indicated the formation of 19.8 mmol (99%) of 3-phenyl-1-butene. The organic layer and ether extracts from the aqueous layer were combined, washed with saturated sodium hydrogen carbonate solution and then water, and dried over anhydrous sodium sulfate. After evaporation of solvent, distillation through a short Vigreux column under reduced pressure gave 2.43 g (92%) of 3-phenyl-1-butene (~96% pure by GLC), 65 °C (20 mmHg), which was purified by preparative GLC (Silicone DC 550), $[\alpha]^{22}_D$ −3.59° (neat).

(b) Reaction of 1-Phenylethylmagnesium Chloride (1a) with (*E*)-β-Bromostyrene (2b). $PdCl_2$[(*S*)-(*R*)-BPPFA] (40 mg, 0.05 mmol) was placed in a 50-mL two-necked flask equipped with a stirring bar, a serum cap, and a three-way stopcock. The reaction vessel was then filled with argon after evacuation and at −78 °C charged with 1.83 g (10 mmol) of (*E*)-β-bromostyrene and 1-phenylethylmagnesium chloride in ether (20 mmol, 17 mL of 1.2 M solution) through the serum cap with a syringe. The reaction mixture was stirred at 0 °C for 24 h and hydrolyzed with 10% hydrochloric acid. Workup as above and distillation under reduced pressure gave a crude product (121–25 °C (3 mmHg)). Purification by preparative GLC gave 1.62 g (78%) of (*E*)-1,3-diphenyl-1-butene: $[\alpha]^{20}_D$ +24.3° (*c* 3, benzene); NMR ($CDCl_3$) δ 1.45 (d, *J* = 7 Hz, 3 H, CH_3), 3.45–3.78 (m, 1 H, C*H*CH_3), 6.30–6.45 (m, 2 H, CH=CH), 7.04–7.45 (m, 10 H, C_6H_5).

Optical Rotation of 3-Phenyl-1-butene (3a). (*R*)-3-Phenyl-1-butanol (10). According to the procedure of Brown[43] for preparing 2-phenyl-1-propanol from α-methylstyrene by hydroboration, 3.62 g of (*R*)-**3a** with $[\alpha]^{22}_D$ −3.55° (neat) was converted to (*R*)-**10**. The crude sample obtained by distillation (95–98 °C (2 mmHg)) was purified by preparative GLC (PEG 20M): 2.50 g (61% yield), α^{25}_D −2.33° (0.1 dm, neat) (59.7% ee); α^{25}_D max 39.0° (1 dm, neat)).[31]

(*R*)-2-Phenylbutane (11). (a) To a solution of 1.44 g (9.6 mmol) of (*R*)-**10** (α^{25}_D −2.33° (0.1 dm, neat)) in 4.5 mL of pyridine was added 1.83 g (9.6 mmol) of tosyl chloride. The mixture was stirred at room temperature for 8 h. After hydrolysis with dilute HCl, the product was extracted with ether, and the extract was washed with dilute HCl, water, aqueous $NaHCO_3$, and saturated NaCl, and dried over anhydrous sodium sulfate. Evaporation of the solvent in vacuo gave 2.17 g (74% yield) of crude 3-phenylbutyl tosylate. An ether (10 mL) solution of the crude tosylate thus obtained was added to a suspension of 0.3 g (7.9 mmol) of lithium aluminum hydride in 5 mL of ether at 0 °C. The reaction mixture was stirred at room temperature for 10 min, and then refluxed for 5 h. After hydrolysis by successive addition of 0.3 mL of water, 0.3 mL of 15% NaOH, and 0.9 mL of water, the precipitate formed was filtered off. The filtrate was washed with aqueous $NaHCO_3$ and saturated NaCl, and dried over magnesium sulfate. The solvent was removed in vacuo, and (*R*)-**11** was isolated by preparative GLC (Silicone DC 550): 0.85 g (66% overall yield), α^{23}_D −1.47° (0.1 dm, neat) (60.5% ee); α^{23}_D max 24.3° (1 dm, neat).[31]

(b) A solution of 2.0 g (15.1 mmol) of (*R*)-**3a** ($[\alpha]^{22}_D$ −3.55° (neat)) and 70 mg (0.15 mmol) of chlorotris(triphenylphosphine)rhodium(I) in 4 mL of benzene was placed in a stainless micro autoclave, and magnetically stirred with hydrogen at 50 atm for 20 h. The reaction mixture was distilled to give 1.7 g (84% yield) of (*R*)-**11**, α^{23}_D −1.45° (0.1 dm, neat) (59.7% ee); (α^{23}_D max 24.3° (1 dm, neat)).[31]

(*S*)-2-Phenylpropanal (12). The reported procedure[44] for ozonolysis of 1-octene was modified as follows: Through a solution of 2.0 g (15.1 mmol) of (*R*)-**3a**, $[\alpha]^{22}_D$ −3.84° (neat), in 17 mL of dry methanol was passed ozonized oxygen at −78 °C until no starting olefin was detected by GLC. An excess of ozone in the reaction mixture was purged at −78 °C by nitrogen bubbling and then 1.6 mL (21.8 mmol) of dimethyl sulfide was added. The mixture was stirred at −10 °C for 1 h and at room temperature for 1 h. The solvent was evaporated and the residue was extracted with ether. The ether extract was washed with water and saturated NaCl, dried over anhydrous sodium sulfate, and evaporated. Distillation (65–70 °C (3 mmHg)) gave 1.2 g (59% yield) of (*S*)-**12** (97–98% pure by GLC analysis), $[\alpha]^{25}_D$ +153° (neat) (64.3% ee); $[\alpha]^{25}_D$ max 238° (neat).[32] An attempted purification of **12** by preparative GLC resulted in complete racemization.

(*S*)-2-Phenyl-1-propanol (13). Diphenylsilane (1.8 mL, 9.7 mmol) was added to a solution of 1.0 g (7.5 mmol) of (*S*)-**12**, $[\alpha]^{25}_D$ +153° (neat), and 32 mg (0.07 mmol) of chlorotris(triphenylphosphine)rhodium(I) in 3 mL of dry benzene at 0 °C under an argon atmosphere. The reaction mixture was stirred at room temperature for 1 day, and the solvent was removed under reduced pressure to give crude 2-phenylpropyl diphenylsilyl ether. To the silyl ether was added at 0 °C with stirring 4 mL of 30% KOH in 90% methanol. The hydrolysis was completed within 10 min. After workup in the usual manner, distillation (78–80 °C (7 mmHg)) gave 0.85 g (84% yield) of (*S*)-**13**, which was purified by preparative GLC (PEG 20M), $[\alpha]^{24}_D$ −11.3° (neat) (64.9% ee); $[\alpha]^{24}_D$ max 17.4° (neat).[33]

Optical Rotation of (*E*)-1,3-Diphenyl-1-butene (3b). In a similar manner to that described for the conversion of 3-phenyl-1-butene (**3a**) into 2-phenyl-1-propanol (**13**), 3.29 g (15.8 mmol) of 1,3-diphenyl-1-butene, $[\alpha]^{20}_D$ +27.4° (*c* 0.35, benzene), was ozonized in methanol and then treated with dimethyl sulfide. After workup, distillation (30–90 °C (3 mmHg)) gave 2.60 g of a 1:1 mixture of benzaldehyde and 2-phenylpropanal. The mixture of the aldehydes was hydrosilylated with diphenylsilane (32 mmol) in the presence of a catalytic amount of chlorotris(triphenylphosphine)rhodium(I). Hydrolysis of the reaction mixture with 30% KOH in 90% methanol followed by workup in the usual manner gave a mixture of benzyl alcohol and 2-phenyl-1-propanol (**13**). The latter was isolated by preparative GLC (PEG 20M), 1.08 g (51%), $[\alpha]^{24}_D$ −9.02° (neat) (52% ee); $[\alpha]^{24}_D$ max 17.4° (neat).[33]

Optical Rotation of 3-Methyl-1-nonene (3d). 3-Methyl-1-nonene (1.24 g, 8.8 mmol, $[\alpha]^{20}_D$ +3.48° (neat), NMR ($CDCl_3$) δ 0.90 (t, *J* = 6 Hz, 3 H, CH_2CH_3), 0.98 (d, *J* = 7 Hz, 3 H, $CHCH_3$), 1.12–1.41 (broad s, 10 H, $(CH_2)_5$), 1.86–2.28 (m, 1 H, CH), 4.82–5.08 (m, 2 H, CH=CH_2), 5.55–5.92 (m, 1 H, C*H*=CH_2)) was hydrogenated in the presence of a catalytic amount of chlorotris(triphenylphosphine)rhodium(I) in a stainless micro autoclave. Distillation (60–80 °C (17 mmHg), bath temperature) gave 1.06 g (85%) of 3-methylnonane, $[\alpha]^{25}_D$ −2.30° (neat) (24% ee); ($[M]^{25}_D$ max 13.7°, $[\alpha]^{25}_D$ max 9.65° (neat),[36] d^{25}_4 0.730[45]).

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Registry No. (*S*)-**3g**, 5787-28-0; $NiCl_2$[(*S*)-(*R*)-**4a**], 79746-09-1; $NiCl_2$[(*S*)-(*R*)-**4b**], 79746-08-0; $NiCl_2$[(*S*)-(*R*)-**4c**], 79746-07-9; $NiCl_2$[(*S*)-(*R*)-**4d**], 79746-06-8; $NiCl_2$[(*S*)-(*R*)-**5a**], 79723-29-8; $NiCl_2$[(*S*)-(*R*)-**5b**], 79735-33-4; $NiCl_2$[(*S*)-(*R*)-**5c**], 79723-30-1; $NiCl_2$[(*S*)-(*R*)-**5d**], 79723-31-2; $NiCl_2$[(*S*)-(*R*)-**5e**], 79723-32-3; $NiCl_2$[(*S*)-(*R*)-**5f**], 79746-05-7; $NiCl_2$[(*S*)-(*R*)-**5g**], 79746-04-6; $NiCl_2$-[(*S*)-(*R*)-**6**], 79746-03-5; $PdCl_2$[(*S*)-(*R*)-PPFA], 79767-72-9; $PdCl_2$-[(*R*)-(*S*)-BPPFA], 79723-33-4; $PdCl_2$[(*S*)-(*R*)-BPPFA], 79767-73-0; $NiCl_2$[(*S*)-(*R*)-PPFA], 72776-01-3; $NiCl_2$[(*R*)-(*S*)-PPFA], 79768-51-7; $NiCl_2$[(*R*)-(*R*)-PPFA], 79767-74-1; $NiCl_2$[(*S*)-FcPN], 79723-34-5; (±)-**1a**, 79722-36-4; (±)-**1b**, 79722-37-5; (±)-**1c**, 79722-38-6; **2a**, 593-60-2; **2b**, 588-72-7; **2c**, 557-93-7; **2d**, 108-86-1; (*R*)-**3a**, 36617-88-6; (*S*)-**3a**, 58717-85-4; (*R*)-**3b**, 79767-68-3; (*S*)-**3b**, 79767-69-4; (*R*)-**3c**, 23406-53-3; (*S*)-**3c**, 25145-46-4; (*R*)-**3d**, 54541-44-5; (*S*)-**3d**, 54541-45-6; (*R*)-**3e**, 39914-58-4; (*S*)-**3e**, 5026-95-9; (*R*)-**3f**, 79722-39-7; (*S*)-**3f**, 20205-10-1; (*R*)-**3g**, 5787-29-1; (*R*)-PPEF, 55650-55-0; $NiCl_2$[(*S*)-(*R*)-BPPFA], 65137-74-8; (*S*)-(*R*)-PPFA, 55650-58-3; (*R*)-(*S*)-BPPFA, 74311-59-4; (*S*)-(*R*)-BPPFA, 55650-59-4; dichlorobis(acetonitrile)palladium(II), 14592-56-4.

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