Optically Active Ruthenocenylbis(phosphines): New Efficient Chiral Phosphine Ligands for Catalytic Asymmetric Reactions

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Contribution from the Catalysis Research Center and Graduate School of Pharmaceutical Sciences, Hokkaido University, Kita-ku, Sapporo 060, Japan, and Tsukuba Research Laboratory, Sumitomo Chemical Company, Ltd., 6 Kitahara, Tsukuba, Ibaraki 300-32, Japan

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Abstract: New optically active ruthenocenylbis(phosphines) (*R*)-*N*,*N*-dimethyl-1-[(*S*)-1′,2-bis(diphenylphosphino)-ruthenocenyl]propylamine [(*R*)-(*S*)-Et-BPPRA] (**5a**) and its ethylamine analog [(*R*)-(*S*)-BPPRA] (**5b**) were prepared by way of stereoselective lithiation of (*R*)-*N*,*N*-dimethyl-1-ruthenocenylalkylamines (**4**), which were obtained by the asymmetric ethylation or methylation (>96% ee) of ruthenocenecarboxaldehyde with the corresponding dialkylzincs in the presence of a catalytic amount of an optically active aminoalcohol **2** followed by stereoretentive amination of the resulting (*R*)-1-ruthenocenylalkanols (**3**). An X-ray diffraction study of the crystal structure of $PdCl_2$[(*R*)-(*S*)-Et-BPPRA] (**6a**) revealed that the P–Pd–P bite angle of the ruthenocenylbis(phosphine) complex (100.47°) is larger than that of the ferrocene analog and the phenyl rings on the phosphorus atoms are located closer to the chlorine ligand and palladium atom, suggesting that the ruthenocenylphosphines are more enantioselective chiral ligands for asymmetric reactions catalyzed by transition metal complexes. Actually, the ruthenocenylphosphines gave high enantioselectivity (higher than the ferrocene analog) in the palladium-catalyzed asymmetric silylation of allylic chlorides with 1,1-dichloro-1-phenyl-2,2,2-trimethyldisilane ($PhCl_2SiSiMe_3$) (up to 92% ee) and in the palladium-catalyzed cyclization of 2-butenylene dicarbonate with methyl acetylacetate forming a vinyldihydrofuran (up to 86% ee).

Introduction

We have developed optically active ferrocenylphosphines[1] which are effective as chiral ligands for several types of asymmetric reactions catalyzed by transition metal complexes.[2] The ferrocenylphosphines have been demonstrated to be superior to others in that structural modification can be readily made by introduction of a desired functional group on the side chain according to the demand of the reaction type. The functional group on the pendant side chain is controlled, by the ferrocenyl and methyl groups on the chiral carbon center at the ferrocenylmethyl position, to face to the reaction site on the catalyst coordinated with phosphorus atoms on the ferrocenylphosphine ligand, and it interacts attractively with a functional group on a substrate in a catalytic asymmetric reaction (Figure 1). By this secondary interaction between functional groups on the phosphine ligand and the reacting substrate,[3] the ferrocenylphosphines can bring about higher enantioselectivity in a variety of catalytic asymmetric reactions, including rhodium(I)-catalyzed hydrogenation,[4] palladium(0)-catalyzed allylic substitution reactions,[5,6] and gold(I)- or silver(I)-catalyzed aldol-type reactions of isocyanocarboxylates.[7-9]

On the other hand, the basic chiral surroundings created by the four phenyl rings on the 1,1′-bis(diphenylphosphino)ferrocene skeleton are not always efficient enough to bring about high enantioselectivity simply by steric interactions. It has been sometimes observed that (*R*)-*N*,*N*-dimethyl-1-[(*S*)-1′,2-bis-(diphenylphosphino)ferrocenyl]ethylamine [(*R*)-(*S*)-BPPFA (**1**)],

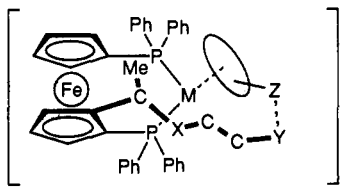
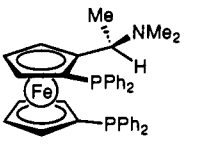


Figure 1. Stereocontrol by the attractive interaction.



(*R*)-(*S*)-BPPFA (1)

which is the chiral ferrocenylbis(phosphine) lacking the pendant side chain, is less effective than some of other types of chiral bis(phosphine) ligands represented by BINAP[10] for the catalytic asymmetric reactions of the substrates that do not contain any particular functional groups.[11]

The basic ability of chiral phosphines containing two diphenylphosphino groups to induce enantioselectivity is determined mainly by a chiral array of the four phenyl groups on the

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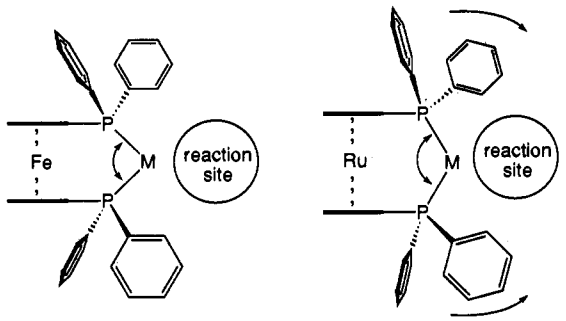


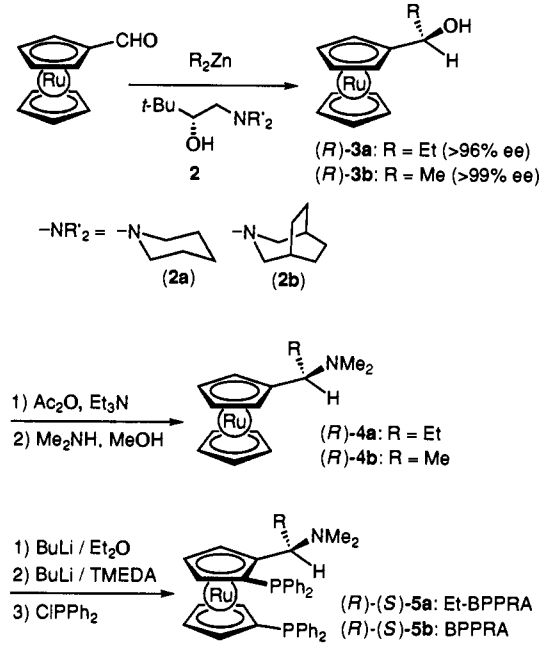
Figure 2. Proposed chiral surroundings on ferrocenylbis(phosphines) and ruthenocenylbis(phosphines).

phosphorus atoms on their chelate coordination to a metal,[12] and it is related to the bite angle (∠P–M–P) of the bis(phosphine) ligand to the metal. The wider bite angle is able to create more effective chiral surroundings on the catalyst because the phenyl rings on a chiral bis(phosphine) ligand will come close to the reaction site on the metal center.[13] The distances between two cyclopentadienyl rings in ferrocene and ruthenocene are known to be 3.32 and 3.68 Å, respectively.[14] The longer distance by about 10% in ruthenocene suggests that ruthenocenylbis(phosphines) will form the wider bite angle on coordination to a metal than their ferrocene analogs and hence will give rise to higher enantioselectivity (Figure 2). Here we report the preparation of new optically active ruthenocenylbis(phosphines) and their use for some palladium-catalyzed asymmetric reactions which demonstrate their higher enantioselectivity than their ferrocene analogs.

Results and Discussion

Preparation of Chiral Ruthenocenylbis(phosphines). The optically active ferrocenylphosphines have previously been prepared via Ugi's[15] stereoselective lithiation of optically active *N,N*-dimethyl-1-ferrocenylethylamine,[1,2] which is obtained by optical resolution of its racemate with tartaric acid.[15] The ruthenocenylphosphines are expected to be prepared in a similar manner by the stereoselective lithiation of the ruthenocene analog of the optically active amine as a key step. We have succeeded in the preparation of optically active *N,N*-dimethyl-1-ruthenocenylalkylamines by way of the asymmetric alkylation of ruthenocenecarboxaldehyde with dialkylzincs in the presence of a catalytic amount of an optically active aminoalcohol **2**,[16] which gives 1-ruthenocenylalkanols of over 96% ee (Scheme 1). Thus, alkylation of ruthenocenecarboxaldehyde with diethylzinc in toluene in the presence of 5 mol % of (*R*)-1-*tert*-butyl-2-piperidinoethanol (**2a**)[16] at −10 °C gave a quantitative yield of (*R*)-1-ruthenocenylpropanol (**3a**) ($[\alpha]_D^{20}$ −49.0 (*c* 1.0, benzene)) with over 96% enantioselectivity.[17] The minor enantiomer was not detected by NMR studies using Eu(hfc)$_3$. The aminoalcohol **2a** was not as stereoselective (at highest 90% ee) for the methylation of ruthenocenecarboxaldehyde with dimethylzinc,[17] but the use of 3-azabicyclo[3.2.2]nonane derivative **2b**[16] in ether–benzene solvent gave (*R*)-1-ruthenocenylethanol (**3b**) ($[\alpha]_D^{20}$ −26.5 (*c* 1.7, benzene)) in over 99% enantiomerically purity, which was confirmed by HPLC analysis with a chiral stationary phase column. The alcohols (*R*)-**3** were readily converted into dimethylamines (*R*)-**4** without racemization by acetylation of the alcohols followed by amination of the resulting acetates with dimethylamine.[18] Thus, (*R*)-*N,N*-dimethyl-1-ruthenocenylpropylamine (**4a**) ($[\alpha]_D^{20}$ +13.2 (*c* 1.0, benzene), 94% yield from **3a**) and ethylamine (*R*)-**4b** ($[\alpha]_D^{20}$ +24.8 (*c* 1.4, benzene), 94% yield from **3b**) were obtained as key intermediates for the chiral ruthenocenylphosphines.

Scheme 1



Treatment of (*R*)-**4b** with 2.6 equiv of butyllithium in ether in the presence of 1,2-bis(dimethylamino)ethane (TMEDA)

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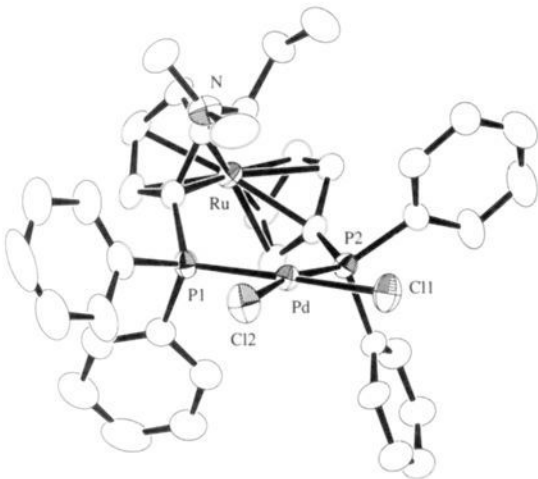


Figure 3. Molecular structure of $PdCl_2[(R)$-(S)-Et-BPPRA]·CH_3COCH_3 (**6a**). The acetone molecule is omitted for simplicity. Selected bond distances (Å) and angles (deg): Pd–P(1) = 2.317(2), Pd–P(2) = 2.316(2), Pd–Cl(1) = 2.342(2), Pd–Cl(2) = 2.332(2), P(1)–Pd–P(2) = 100.49(5), Cl(1)–Pd–Cl(2) = 87.05(7), P(1)–Pd–Cl(1) = 175.86(6), P(1)–Pd–Cl(2) = 88.81(6), P(2)–Pd–Cl(1) = 83.64(6), P(2)–Pd–Cl(2) = 169.04(6).

followed by diphenylphosphination of the resulting dilithiated ruthenocene with chlorodiphenylphosphine gave 51% yield of ruthenocenylbis(phosphine) (*R*)-*N*,*N*-dimethyl-1-[(*S*)-1′,2-bis(diphenylphosphino)ruthenocenyl]ethylamine ((*R*)-(*S*)-**5b** (BPPRA)) ($[\alpha]_D^{20}$ −275 (*c* 1.2, benzene)) together with a minor amount (17%) of ruthenocenylmono(phosphine) (*R*)-*N*,*N*-dimethyl-1-[(*S*)-2-(diphenylphosphino)ruthenocenyl]ethylamine. Their diastereomeric isomers that contain *R* planar chirality have not been detected, indicating that the diastereoselectivity of the ortho-lithiation is very high.[19] In a similar manner, ethyl analog (*R*)-(*S*)-**5a** (Et-BPPRA) ($[\alpha]_D^{20}$ −302 (*c* 0.6, chloroform)) was obtained in 29% yield by starting with (*R*)-**4a**.

X-ray Structure of the Ruthenocenylbis(phosphine)–Palladium Complex. The manner of coordination of the ruthenocenylbis(phosphine) to a transition metal was studied by X-ray crystal structure analysis of the palladium complex $PdCl_2[(R)$-(S)-Et-BPPRA (**5a**)]·CH_3COCH_3 (**6a**) (Figure 3), which was obtained by the reaction of the ruthenocenylbis(phosphine) with $PdCl_2(MeCN)_2$ in benzene and recrystallized from acetone and hexane. It is important to compare its structure with that of ferrocenylbis(phosphine) analog $PdCl_2[(R)$-(S)-BPPFA(**1**)].[20] As we expected, the P–Pd–P bond angle (bite angle) of the ruthenocenylphosphine complex (100.47°) is larger than that of ferrocenylbis(phosphine) complex (98.79°), and the phenyl rings, especially rings A and B, on the phosphorus atoms are located closer to the chlorine ligand and palladium atom, which is caused by the larger bite angle. Some of the distances characteristic to those complexes are shown in Figure 4. The closer location of the phenyl rings to the metal, where the catalytic reaction takes place, promises us that the ruthenocenylphosphine is more enantioselective than the ferrocenylphosphine. The absolute configuration of the phosphine ligand **5a**, which was assigned by an empirical rule at the enantioselective alkylation of aldehydes,[17] was confirmed to be *R* on the 1-(dimethylamino)propyl side chain and *S* on the ruthenocene planar chirality on the basis of an *R*-value significance test[21] during the X-ray analysis.

Catalytic Asymmetric Reactions. The enantiocontrolling abilities of the chiral ruthenocenylbis(phosphines) (*R*)-(*S*)-**5** obtained above were examined for two types of palladium-

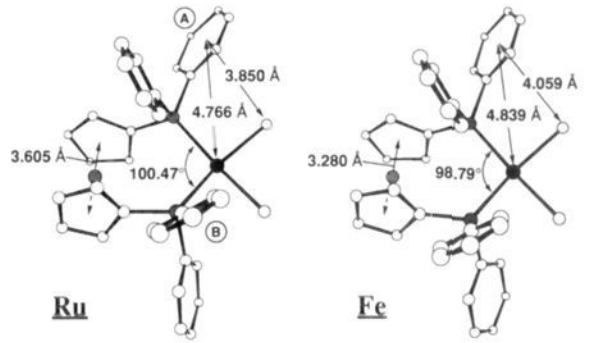
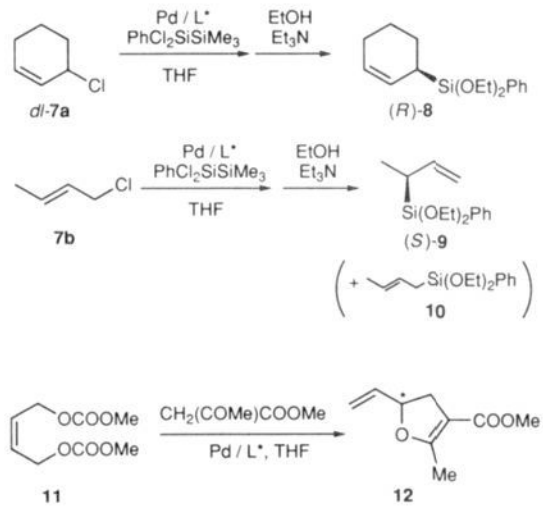


Figure 4. Comparison of the molecular structure of $PdCl_2[(R)$-(S)-Et-BPPRA (**5a**)] (**6a**) (Ru) with that of $PdCl_2[(R)$-(S)-BPPFA (**1**)] (Fe). The side chains are omitted for simplicity.

Scheme 2



catalyzed asymmetric allylic substitution reactions, *i.e.*, the silylation of allylic chlorides[22] and cyclization of 2-butenylene dicarbonate forming a vinyldihydrofuran[23] (Scheme 2). Both reactions are of current interest to us because the unfunctionalized ferrocenylphosphine, BPPFA (**1**), has so far given higher enantioselectivity than other types of chiral bis(phosphine) ligands but the selectivity is still not high enough. The results obtained are summarized in Tables 1 and 2, which also include those obtained with BPPFA (**1**) and BINAP for comparison.

In the silylation of allylic chlorides with 1,1-dichloro-1-phenyl-2,2,2-trimethyldisilane ($PhCl_2SiSiMe_3$), the palladium catalysts coordinated with ruthenocenylbis(phosphines) **5a**,**b** gave much higher enantioselectivity than those of the ferrocenylphosphine analog **1** and BINAP for both 3-chlorocyclohexene (**7a**) and 1-chloro-2-butene (**7b**) (Table 1). Thus, 3-silylcyclohexene **8** of over 40% ee was obtained with ruthenocenylphosphines **5a**,**b** (entries 1 and 2), while BPPFA (**1**) and BINAP gave **8** of not higher than 10% ee[22] under the same reaction conditions (entries 3 and 4). For the silylation of **7b**, the enantiomeric purity of the silylation product, 3-silyl-1-butene **9**, was raised to 92% ee by use of the ruthenocenylphosphine **5a** (entry 5).

A great improvement of the enantioselectivity was also observed in the cyclization forming vinyldihydrofuran **12** (Table 2). The reaction of dimethyl (*Z*)-2-butenylene dicarbonate (**11**) with methyl acetylacetate in the presence of a palladium catalyst generated from $Pd_2(dba)_3$·$CHCl_3$ and ruthenocenylphosphine **5a** in THF at −20 °C for 48 h gave 83% yield of the cyclization product **12** in 83% ee (entry 1). The dihydrofuran **12** was found

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Table 1. Asymmetric Silylation of Allylic Chlorides **7** with 1,1-Dichloro-1-phenyl-2,2,2-trimethyldisilane Catalyzed by Chiral Palladium–Phosphine Complexes[a]

entry	7	ligand	temp (°C)	time (h)	product	yield (%)[b]	% ee (config.)
1	**7a**	(*R*)-(*S*)-Et-BPPRA (**5a**)	40	10	**8**	>99	47 (*R*)
2	**7a**	(*R*)-(*S*)-BPPRA (**5b**)	40	2	**8**	93	42 (*R*)
3[c]	**7a**	(*R*)-(*S*)-BPPFA (**1**)	40	0.5	**8**	93	10 (*R*)
4[c]	**7a**	(*R*)-BINAP	60	44	**8**	80	7 (*R*)
5	**7b**	(*R*)-(*S*)-Et-BPPRA (**5a**)	20	15	**9, 10**	83 (42/58)[d,e]	92 (*S*)
6	**7b**	(*R*)-(*S*)-BPPRA (**5b**)	20	16	**9, 10**	94 (43/57)[d,e]	73 (*S*)
7[c]	**7b**	(*R*)-(*S*)-BPPFA (**1**)	20	4	**9, 10**	99 (21/79)[d,e]	61 (*S*)

[a] All reactions were carried out in THF under nitrogen. The catalyst was generated in situ by mixing $[PdCl(\pi\text{-allyl})]_2$ with a ligand (P:Pd = 2.2:1). 7:disilane:catalyst = 1:1.4–1.6:0.01. For the determination of enantiomeric purity and absolute configuration, see ref 22. [b] Isolated yield by bulb-to-bulb distillation. [c] Reported in ref 22. [d] The ratio of **9** to **10**. [e] Determined by GLC analysis.

Table 2. Asymmetric Cyclization of 2-Butenylene Dicarbonate **11** with Methyl Acetylacetate Catalyzed by Chiral Palladium–Phosphine Complexes[a]

entry	ligand	time (h)	yield (%)[b] of **12**	% ee[c]
1	(*R*)-(*S*)-Et-BPPRA (**5a**)	48	83	83
2	(*R*)-(*S*)-Et-BPPRA (**5a**)	23	52	86[d]
3	(*R*)-(*S*)-BPPRA (**5b**)	48	76	58
4[e]	(*R*)-(*S*)-BPPFA (**1**)	26	80	34
5	(*R*)-BINAP	66	28	31

[a] A mixture of $Pd_2(dba)_3{\cdot}CHCl_3$ (0.006 mmol), phosphine ligand (0.013 mmol), **11** (0.9 mmol), and methyl acetylacetate (0.6 mmol) in 9.0 mL of THF was stirred at −20 °C under nitrogen. [b] Isolated yield based on acetylacetate by silica gel column chromatography. [c] Determined by GLC analysis with a chiral stationary phase column, CP Cyclodex β236M. [d] $[\alpha]_D^{20}$ −103 (*c* 0.6, CCl_4). [e] The highest enantioselectivity reported in the previous paper with **1** (ref 23) is corrected to be 45% ee on the basis of its optical rotation value ($[\alpha]_D^{20}$ −54.1 (CCl_4)).

to undergo a slow racemization under the reaction conditions, and hence **12** with a little higher enantiomeric purity (86% ee) was obtained at lower conversion (entry 2). The enantioselectivity was much lower in the reaction with BPPFA (**1**) under similar reaction conditions (entry 4). In the presence of BINAP–palladium catalyst, the reaction is very slow (entry 5).

Interestingly, the ruthenocenylphosphine **5a**, which has an ethyl group on the stereogenic center at the ruthenocenylmethyl position, is always more enantioselective than the methyl analog **5b**. This suggests that a proper modification of the alkyl substituent on the ruthenocenylmethyl position will bring us more stereoselective ruthenocenylphosphine ligands.

Conclusion. The ruthenocenylphosphines prepared here were demonstrated to have the wider bite angle than the corresponding ferrocene analogs as expected and hence to be more enantioselective ligands for palladium-catalyzed asymmetric reactions. It is expected that they can be modified according to the demand of the reacting substrates, in a manner similar to that of ferrocenylphosphines, by introduction of functionalized pendant groups on the side chain and will be more enantioselective chiral ligands for a wide variety of reactions where the functionalized ferrocenylphosphines have been used.[1-9]

Experimental Section

General Procedure. Melting points were measured with a hot stage microscope (YANACO MP-S3) and are uncorrected. ^1H NMR spectra were measured on a JEOL JNM-EX270 spectrometer (270 MHz) or JEOL JNM-EX400 spectrometer (400 MHz) in $CDCl_3$. Chemical shifts of protons are reported in δ ppm referred to tetramethylsilane as an internal standard. IR spectra were recorded on a Perkin Elmer 1720X FT-IR spectrometer. Silica gel column chromatography was carried out using Merck silica gel 60 (70–325 mesh ASTM). Air- and moisture-sensitive reactions were performed under usual inert atmosphere techniques. All dry solvents were distilled under N_2. THF and Et_2O were distilled from sodium/benzophenone ketyl. Dichloromethane was distilled from CaH_2. Ruthenocenecarboxaldehyde was prepared according to the reported procedures.[24]

(*R*)-1-Ruthenocenylpropanol (3a). Under an oxygen-free argon atmosphere, a mixture of 16.8 mL (16.8 mmol) of 1.0 M diethylzinc in hexane and 0.135 mL (0.662 mmol) of (*R*)-1-*tert*-butyl-2-(1-piperidino)-ethanol (**2a**) was stirred at 20 °C for 30 min. To the mixture was added a solution of 3.28 g (12.7 mmol) of ruthenocenecarboxaldehyde in 15 mL of toluene at −10 °C, and the mixture was kept stirring at −10 °C for 5 days. It was hydrolyzed by addition of methanol and water and extracted with ether. The ether extracts were dried over anhydrous magnesium sulfate and evaporated under a reduced pressure. The residue was chromatographed on silica gel (ether/hexane = 1/1) to give 3.66 g (99%) of (*R*)-**3a** as a white solid: ^1H NMR ($CDCl_3$) δ 0.94 (t, *J* = 7.3 Hz, 3 H), 1.58–1.75 (m, 2 H), 1.93 (d, *J* = 3.3 Hz, 1 H), 4.15–4.26 (m, 5 H), 4.20 (s, 5 H); $[\alpha]_D^{20}$ −49.0 (*c* 1.1, benzene); IR (KBr) 3468, 1101, 998 cm^{-1}. Anal. Calcd for $C_{13}H_{16}ORu$: C, 53.97; H, 5.57. Found: C, 54.00; H, 5.59. The enantiomeric purity of (*R*)-**3a** was determined to be over 96% ee by ^1H NMR studies in the presence of chiral europium shift reagent $Eu(hfc)_3$.

(*R*)-1-Ruthenocenylethanol (3b). Under an oxygen-free argon atmosphere, a mixture of 46.0 mL (46.0 mmol) of 1.0 M dimethylzinc in ether and 438 mg (1.94 mmol) of (*R*)-1-*tert*-butyl-2-(3-azabicyclo[3.2.2]-nonyl)ethanol (**2b**) was stirred at 20 °C for 30 min. To the mixture was added a solution of 10.0 g (38.7 mmol) of ruthenocenecarboxaldehyde in 50 mL of benzene, and the mixture was kept stirring at 20 °C for 14 days. Hydrolysis and ether extraction followed by chromatography on silica gel (ethyl acetate/hexane = 1/3) gave 10.3 g (96%) of (*R*)-**3b** as a yellow solid: ^1H NMR ($CDCl_3$) δ 1.34 (d, *J* = 6.3 Hz, 3 H), 1.44 (d, *J* = 5.0 Hz, 1 H), 4.28 (dq, *J* = 5.0, 6.3 Hz, 1 H), 4.53–4.68 (m, 4 H), 4.61 (s, 5 H); $[\alpha]_D^{20}$ −26.5 (*c* 1.7, benzene); IR (KBr) 3244, 1101, 996 cm^{-1}. Anal. Calcd for $C_{12}H_{14}ORu$: C, 52.35; H, 5.13. Found: C, 52.41; H, 5.13. The enantiomeric purity of alcohol (*R*)-**3b** was determined to be over 99% ee by HPLC analysis of its 3,5-dinitrophenyl carbamate ester with Sumichiral OA-1000 (hexane/1,2-dichloroethane/ethanol = 250/20/1), the carbamate ester being obtained by treatment of 4 mg (0.015 mmol) of (*R*)-**3b** with 3.2 mg (0.015 mmol) of 3,5-dinitrophenyl isocyanate and 10 μL of pyridine in 1.0 mL of toluene.

(*R*)-*N,N*-Dimethyl-1-ruthenocenylpropylamine (4a). To a solution of 10.6 g (36.5 mmol) of (*R*)-1-ruthenocenylpropanol (**3a**) in 60 mL of dichloromethane were added 6.6 mL (47.4 mmol) of triethylamine and a catalytic amount of 4-(dimethylamino)pyridine. At 0 °C 4.1 mL (43.5 mmol) of acetic anhydride was added dropwise, and the mixture was stirred at room temperature for 25 h. Water was added, and the mixture was extracted with dichloromethane. The extracts were dried over anhydrous magnesium sulfate and evaporated. To the residue were added 25 mL (0.28 mol) of 50% aqueous dimethylamine and 100 mL of ethanol, and the mixture was stirred at room temperature for 62 h. The solvent was evaporated under a reduced pressure, and the residue was diluted with ether. The amine was extracted with 10% phosphoric acid, and after the aqueous layer was made alkaline (pH 9) with saturated sodium bicarbonate, it was extracted with ether. The ether extracts were dried over anhydrous potassium carbonate and concentrated under a reduced pressure to give 10.9 g (94%) of (*R*)-**4a** as a yellow solid: ^1H NMR ($CDCl_3$) δ 0.98 (t, *J* = 7.3 Hz, 3 H), 1.52–1.85 (m, 2 H), 2.10 (s, 6 H), 3.02 (dd, *J* = 4.1, 10.1 Hz, 1 H), 4.45–4.83 (m, 4 H), 4.51 (s, 5 H); $[\alpha]_D^{20}$ +13.2 (*c* 1.0, benzene); IR (KBr) 2815, 2773, 1101, 991 cm^{-1}. Anal. Calcd for $C_{15}H_{21}NRu$: C, 56.94; H, 6.69; N, 4.43. Found: C, 56.99; H, 6.81; N, 4.35.

(*R*)-*N,N*-Dimethyl-1-ruthenocenylethylamine (4b). In a manner similar to the preparation of **4a**, 10.3 g (37.2 mmol) of (*R*)-1-ruthenocenylethanol (**3b**) was treated with 6.8 mL (48.8 mmol) of

(24) Kamiyama, S.; Suzuki, T. M.; Kimura, T.; Kasahara, A. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 909.

triethylamine, a catalytic amount of 4-(dimethylamino)pyridine, and 4.2 mL (44.5 mmol) of acetic anhydride in 70 mL of dichloromethane, and the resulting acetate was treated with 34 mL (0.38 mol) of 50% aqueous dimethylamine and 100 mL of ethanol. The extractions of the amine followed by distillation (bulb-to-bulb, 150 °C, 0.1 mmHg) gave 10.6 g (94%) of (*R*)-**4b**: ^{1}H NMR ($CDCl_3$) δ 1.27 (d, J = 6.9 Hz, 3 H), 2.17 (s, 6 H), 3.32 (q, J = 6.9 Hz, 1 H), 4.47–4.55 (m, 4 H), 4.52 (s, 5 H); $[\alpha]_D^{20}$ +24.8 (*c* 1.4, benzene); IR (KBr) 2819, 2777, 1101, 999 cm^{-1}. Anal. Calcd for $C_{14}H_{19}NRu$: C, 55.61; H, 6.33; N, 4.63. Found: C, 55.58; H, 6.22; N, 4.65.

(*R*)-*N,N*-Dimethyl-1-[(*S*)-1′,2-bis(diphenylphosphino)ruthenocenyl]-propylamine (5a). To a solution of 10.85 g (34.3 mmol) of (*R*)-*N,N*-dimethyl-1-ruthenocenylpropylamine (**4a**) in 100 mL of dry diethyl ether was added dropwise 30.5 mL (41.2 mmol) of 1.35 M butyllithium in hexane at room temperature. The mixture was stirred at room temperature for 1.5 h, and then 6.2 mL (41.1 mmol) of TMEDA and 30.5 mL (41.2 mmol) of 1.35 M butyllithium in hexane were added successively. After 20 h of stirring at room temperature, 15.4 mL (85.8 mmol) of chlorodiphenylphosphine was added at −78 °C. The mixture was refluxed for 1 h, diluted with 50 mL of ether, and hydrolyzed with aqueous sodium bicarbonate. The resulting organic layer and extracts from the aqueous layer were combined, dried over anhydrous sodium sulfate, and concentrated under a reduced pressure. The residue was chromatographed on silica gel (ethyl acetate/hexane = 1/1) to give 6.70 g (29%) of (*R*)-(*S*)-**5a** as yellow crystals: mp 147–148 °C; ^{1}H NMR ($CDCl_3$) δ 0.95 (t, J = 6.3 Hz, 3 H), 1.51–1.59 (m, 2 H), 1.86 (s, 6 H), 3.55–3.62 (m, 1 H), 3.89–3.91 (m, 1 H), 4.09–4.11 (m, 1 H), 4.14–4.16 (m, 1 H), 4.36–4.39 (m, 1 H), 4.45–4.47 (m, 1 H), 4.61–4.63 (m, 1 H), 4.65–4.67 (m, 1 H), 7.2–7.4 (m, 20 H); ^{31}P{^{1}H} NMR ($CDCl_3$) δ −23.8 (s), −16.2 (s); $[\alpha]_D^{20}$ −302 (*c* 0.6, chloroform); IR (KBr) 1478, 1433, 1156, 742, 697 cm^{-1}. Anal. Calcd for $C_{39}H_{39}NP_2Ru$: C, 68.41; H, 5.74; N, 2.05. Found: C, 68.63; H, 5.91; N, 2.15. Ruthenocenylmono(phosphine) (*R*)-*N,N*-dimethyl-1-[(*S*)-2-(diphenylphosphino)ruthenocenyl]-propylamine (3.35 g, 20%) was also isolated by the chromatography: ^{1}H NMR ($CDCl_3$) δ 1.03 (t, J = 7 Hz, 3 H), 1.63–1.76 (m, 2 H), 1.89 (s, 6 H), 3.61–3.70 (m, 1 H), 4.29 (m, 1 H), 4.33 (s, 5 H), 4.61–4.69 (m, 1 H), 4.70–4.72 (m, 1 H), 7.2–7.4 (m, 10 H); ^{31}P{^{1}H} NMR ($CDCl_3$) δ −23.3 (s).

(*R*)-*N,N*-Dimethyl-1-[(*S*)-1′,2-bis(diphenylphosphino)ruthenocenyl]-ethylamine (5b). To a solution of 7.86 g (26.0 mmol) of (*R*)-*N,N*-dimethyl-1-ruthenocenylethylamine (**4b**) in 60 mL of dry diethyl ether was added dropwise 22.0 mL (34.3 mmol) of 1.56 M butyllithium in hexane at room temperature. The mixture was stirred at room temperature for 1.5 h, and then 5.1 mL (33.8 mmol) of TMEDA and 22.0 mL (34.3 mmol) of 1.56 M butyllithium in hexane were added successively. After 12 h at room temperature, 13.0 mL (72.4 mmol) of chlorodiphenylphosphine was added at −78 °C. The mixture was refluxed for 1 h, diluted with 50 mL of ether, and hydrolyzed with aqueous sodium bicarbonate. The resulting organic layer and extracts from the aqueous layer were combined, dried over anhydrous sodium sulfate, and concentrated under a reduced pressure. The residue was chromatographed on silica gel with ethyl acetate and hexane (1:1) as the eluent to give the crude product, which was recrystallized from ethanol to give 8.91 g (51%) of (*R*)-(*S*)-**5b**: mp 115–117 °C; ^{1}H NMR ($CDCl_3$) δ 1.04 (d, J = 6.9 Hz, 3 H), 1.85 (s, 6 H), 3.81–3.88 (m, 1 H), 3.97–3.99 (m, 1 H), 4.04–4.06 (m, 1 H), 4.26–4.28 (m, 1 H), 4.34–4.36 (m, 1 H), 4.47–4.49 (m, 1 H), 4.65–4.67 (m, 2 H), 7.21–7.41 (m, 20 H); ^{31}P{^{1}H} NMR ($CDCl_3$) δ −22.9 (s), −16.3 (s); $[\alpha]_D^{20}$ −275 (*c* 1.2, benzene); IR (KBr) 1478, 1433, 1156, 742, 696 cm^{-1}. Anal. Calcd for $C_{38}H_{37}NP_2Ru$: C, 68.05; H, 5.56; N, 2.09. Found: C, 67.99; H, 5.60; N, 2.13. Ruthenocenylmono(phosphine) (*R*)-*N,N*-dimethyl-1-[(*S*)-2-(diphenylphosphino)ruthenocenyl]ethylamine (2.16 g, 17%) was also isolated by the chromatography: ^{1}H NMR ($CDCl_3$) δ 1.17 (d, J = 7 Hz, 3 H), 1.89 (s, 6 H), 3.83–3.96 (m, 1 H), 4.20–4.24 (m, 1 H), 4.33 (s, 5 H), 4.57–4.60 (m, 1 H), 4.74–4.80 (m, 1 H), 7.14–7.51 (m, 10 H); ^{31}P{^{1}H} NMR ($CDCl_3$) δ −22.6 (s).

Dichloro[(*R*)-*N,N*-dimethyl-1-[(*S*)-1′,2-bis(diphenylphosphino)ruthenocenyl]propylamine]palladium(II) (6a). To a suspension of 10.0 mg (0.039 mmol) of dichlorobis(acetonitrile)palladium(II) in 0.6 mL of benzene was added with stirring a solution of 30.0 mg (0.044 mmol) of (*R*)-(*S*)-**5a** in 0.4 mL of benzene. After the mixture was stirred for 1 h at room temperature, the orange precipitate formed was collected by filtration, washed with benzene, and dried in vacuo. It was recrystallized from acetone/hexane to give 25.9 mg (77%) of **6a** (as orange crystals), which contains one molecule of acetone: mp 260 °C (decomp); ^{1}H NMR ($CDCl_3$) δ 1.33 (t, J = 7.6 Hz, 3 H), 1.90–2.09 (m, 1 H), 2.11–2.20 (m, 1 H), 2.56 (s, 6 H), 3.90–3.92 (m, 2 H), 4.47–4.56 (m, 2 H), 4.60–4.62 (m, 1 H), 4.71–4.73 (m, 1 H), 5.03–5.06 (m, 1 H), 5.19–5.24 (m, 1 H), 6.98–7.01 (m, 2 H), 7.19–7.63 (m, 12 H), 7.83–7.96 (m, 4 H), 8.49–8.53 (m, 2 H); ^{31}P{^{1}H} NMR ($CDCl_3$) δ 29.5 (d, J = 33 Hz), 36.0 (d, J = 33 Hz); $[\alpha]_D^{25}$ +72.9 (*c* 1.0, chloroform); IR (KBr) 1434, 1157, 743, 696 cm^{-1}. Anal. Calcd for $C_{39}H_{39}NCl_2P_2RuPd{\cdot}C_3H_6O$: C, 54.82; H, 4.93; N, 1.52; Cl, 7.71. Found: C, 54.64; H, 4.82; N, 1.43; Cl, 7.86.

Table 3. Crystal Data and Details of the Structure Determination for $PdCl_2$[(*R*)-(*S*)-Et-BPPRA]·MeCOMe (**6a**)

formula	$C_{39}H_{39}Cl_2PdRuNP_2{\cdot}C_3H_6O$
formula weight	920.16
crystal size, mm	0.40 × 0.20 × 0.20
crystal system	orthorhombic
space group	$P2_12_12_1$
a, Å	17.859(1)
b, Å	18.544(1)
c, Å	11.740(1)
V, Å^3	3888.0
Z	4
d_{calcd}, g cm^{-3}	1.57
μ(Mo Kα), cm^{-1}	10.9
F(000)	1864
radiation	Mo Kα (λ = 0.710 73 Å)
monochromator	graphite crystal, incident beam
data collected	$+h,+k,+l$
maximum 2θ, deg	50.0
scan type	ω–2θ
scan width, deg	0.8 + 0.35 tan θ
scan rate, deg min^{-1}	2–10 (in ω)
temperature, K	298
no. of reflns measd	3816
no. of reflns included	3466 with $I > 3\sigma(I)$
no. of params refined	452
R	0.030
R_w	0.046
S	1.62
max and min peak, e/Å^3	0.70, −0.16

X-ray Diffraction Study of $PdCl_2$[(*R*)-(*S*)-Et-BPPRA]·CH_3COCH_3 (6a). A single crystal (0.4 × 0.2 × 0.2 mm) of the palladium complex **6a** obtained above was sealed in a glass capillary tube. Intensity data were collected on an Enraf-Nonius CAD4 diffractometer. Unit cell dimensions were obtained from a least-squares treatment of the setting angles of 25 reflections in the range $10 < \theta < 12°$. The cell dimensions suggested an orthorhombic cell, and systematic absences in the diffractometer data indicated the space group $P2_12_12_1$. Diffraction data were collected in the range $3 < \theta < 25°$ using the $\omega/2\theta$ scan technique. The scan rate varied from 2 to 10 deg/min in ω. Three standard reflections, monitored by every 80 h of X-ray exposure, showed no significant variation in the intensities during the data collection. The data were corrected for Lorenz and polarization effects. Of the 3816 reflections measured, 3466 were classed as observed ($I > 3\sigma(I)$), and these were used for the solution and refinement of the structure.

Calculations were performed on a VAX Station 4000/60 computer using the MolEN software. The scattering factors were taken from ref 25. The palladium and ruthenium atoms were located on a Patterson map, and other non-hydrogen atoms were found from subsequent difference Fourier syntheses. Hydrogen atoms were not located. The structure was refined by full-matrix least squares with anisotropic thermal parameters for all non-hydrogen atoms. The function minimized in least squares was $\Sigma w(|F_o| - |F_c|)^2$ ($w = 4I/[\sigma^2(I) + (0.05I)^2]$). The final R index was 0.030 (R_w = 0.046, S = 1.62). $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$, and $S = [\Sigma w(|F_o| - |F_c|)^2/(N_o - N_p)]^{1/2}$, where N_o is the number of observed data and N_p is the number of parameters varied. The absolute configuration of the complex **6a** was determined to be (*R*)-(*S*), as shown in Figure 3. The refinement of the enantiomeric structure gave R and R_w values of 0.033 and 0.050, respectively. This configuration was rejected on the basis of the R-value significance test.[21] Crystal data and details of data collection and refinement are summarized in Table 3. Positional parameters, the atomic numbering scheme, anisotropic thermal parameters, and bond distances and angles are reported in the supplementary material.

Palladium-Catalyzed Asymmetric Silylation of Allylic Chlorides. The reaction was carried out in essentially the same manner as reported in ref 22. The reaction conditions and results are summarized in Table 1.

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The absolute configurations were determined by oxidation of the allylic silanes into known allylic alcohols, (*R*)-1-cyclohexen-3-ol[26] and (*S*)-1-buten-3-ol,[27] by oxidation with hydrogen peroxide in the presence of potassium fluoride and potassium hydrogen carbonate.[28] Enantiomeric purities of the alcohols were determined by HPLC analysis of their 3,5-dinitrophenyl carbamate derivatives with a chiral stationary phase column, Sumichiral OA-4100 (hexane/1,2-dichloroethane/ethanol = 50/15/1).

Palladium-Catalyzed Asymmetric Cyclization of 2-Butenylene Dicarbonate with Methyl Acetylacetate. The reaction conditions reported in ref 23 were slightly modified by three times dilution of the reaction mixture in order to obtain a higher chemical yield of the monomeric cyclization product. The conditions and results are summarized in Table 2. The enantiomeric purity of **12** was determined by GLC analysis with a chiral stationary phase column, CP Cyclodex β236M.

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Supplementary Material Available: Figure showing the atomic numbering scheme for $PdCl_2[(R)\text{-}(S)\text{-Et-BPPRA}]\cdot CH_3COCH_3$ (**6a**) and tables of positional parameters, anisotropic thermal parameters, and bond distances and angles for **6a** (9 pages); listings of observed and calculated structure factors for **6a** (17 pages). The material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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