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A novel P-chirogenic phosphine ligand, (*S*,*S*)-1,2-bis-[(ferrocenyl)methylphosphino]ethane: synthesis and use in rhodium-catalyzed asymmetric hydrogenation and palladium-catalyzed asymmetric allylic alkylation

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Abstract—A new P-chirogenic diphosphine ligand, (*S*,*S*)-1,2-bis[(ferrocenyl)methylphosphino]ethane, was prepared via phosphine–borane intermediates. The ligand was used in the rhodium-catalyzed asymmetric hydrogenation of dehydroamino acid derivatives (up to 77% enantioselectivity) and in the palladium-catalyzed asymmetric allylic alkylation of 1,3-diphenyl-2-propenyl acetate (up to 95% enantioselectivity).

Hundreds of optically active phosphine ligands containing a ferrocenyl moiety have been designed, synthesized, and used in a variety of enantioselective transition metal-catalyzed reactions.[1] Most of the ligands are planar chiral and/or possess chirality due to a stereogenic carbon center, and have been proven to be highly effective in many asymmetric catalyses. In contrast, relatively less attention has been paid to P-chirogenic phosphines bearing ferrocenyl groups despite their potential utility as ligands in asymmetric reactions.[2] Previously, we prepared P-chirogenic bis(trialkyl-phosphine), (*S*,*S*)-1,2-bis(alkylmethylphosphino)-ethanes (BisP*), in which a bulky alkyl group and the smallest alkyl group (methyl group) were bonded to each phosphorus atom, and demonstrated that they exhibited excellent asymmetric induction in rhodium catalyzed hydrogenation.[3] On the other hand, non-racemic 1,2-bis(arylmethylphosphino)ethanes have been prepared by other groups and their catalytic performance in a few representative catalytic asymmetric reactions evaluated.[2c,4,5] To the best of our knowledge, however, a similar ligand bearing a ferrocenyl group as the aryl group has not yet been reported. We envisioned that the steric and electronic effects of the ferrocenyl group may result in the high catalytic efficiency of the ligand compared with that of previously reported 1,2-bis(arylmethylphosphino)ethanes. Herein we report the preparation of enantiomerically pure 1,2-bis[(ferrocenyl)methylphosphino]ethane and its use in rhodium-catalyzed asymmetric hydrogenation and palladium-catalyzed asymmetric allylic alkylation.

Previously, we reported that ethylene bridged P-chirogenic diphosphines are prepared via phosphine–borane intermediates.[3,6] This methodology and Evans et al.'s (−)-sparteine assisted enantioselective deprotonation procedure[5] permitted the short-step preparation of enantiomerically pure 1,2-bis-[(ferrocenyl)methylphosphino]ethane **1** from ferrocene (Scheme 1). The mono-lithioferrocene, that was generated directly from ferrocene using Guilanex and Kagan's procedure,[7] was treated sequentially with phosphorus trichloride, methyl magnesium bromide, and a borane–THF complex to give ferrocenyl(dimethyl)phosphine–borane **2** in a 30–40% yield. One of the enantiotopic methyl groups of **2** was selectively deprotonated with a (−)-sparteine/*sec*-BuLi complex[5] and the resulting carbanion subjected to oxidative dimerization by treatment with copper(II) chloride to give the diphosphine–borane crude product **3**. Recrystallization of the product from hot toluene afforded an enantiomerically pure compound in 25–35% yield based on **2**. Compound **3** was subjected to

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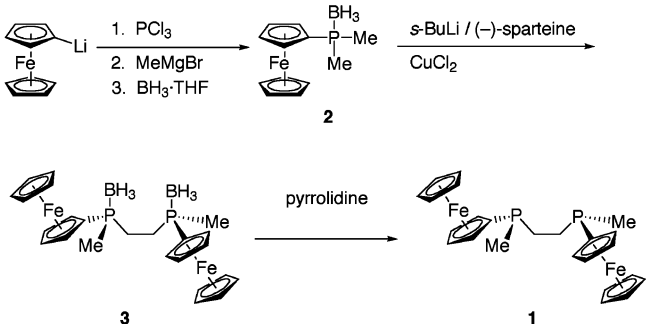


Scheme 1.

single-crystal X-ray analysis to confirm its molecular structure and to determine the absolute configurations at the phosphorus atoms using the Flack parameter method. The ORTEP drawing of **3** in Figure 1 indicated an (*S*,*S*)-configuration at the chiral phosphorus atoms. The configuration is consistent with the stereochemistry that was predicted based on previously reported results.[5,3] Compound **3** was heated with a large excess of pyrrolidine at 65°C for 90 min to furnish the desired ligand **1** without any loss of enantiomeric purity.[8]

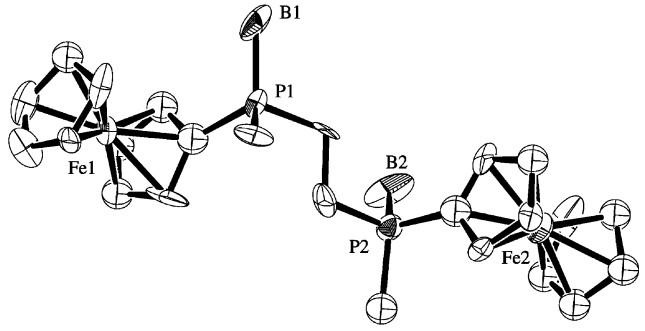


Figure 1. An ORTEP drawing of **3**.

The pure ligand was obtained as orange plates by recrystallization from methanol. Surprisingly, this ligand was quite stable in air: it remained unchanged on exposure to air at least for one month. The molecular structure of **1** was determined not only from spectroscopic data but also by single-crystal X-ray analysis. The ORTEP drawing of **1** in Figure 2 indicated an (*S*,*S*)-configuration at the phosphorus atoms in agreement with retention of the configuration occurring at the phosphorus atom in the deboranation step.[9] The catalytic efficiency of ligand **1** was tested first in the rhodium catalyzed asymmetric hydrogenation of some dihydroamino acid derivatives. The catalyst precursor was generated in situ by mixing ligand **1** with $[RhCl(cod)]_2$ in methanol, and the hydrogenation was carried out in the same solvent. The results are summarized in Table 1.[10] The reaction proceeded slowly at room temperature and required a higher temperature (50°C) for completion within a short time. The observed enantioselectivity was moderate to good, and was higher than that observed by the use of 1,2-bis-(methylphenylphosphino)ethane (e.g. 22% enantioselectivity for α-(*N*-benzoylamino)cinnamic acid).[4] It is noteworthy that the reactions of β,β-disubstituted derivatives gave rise to higher enantioselectivity than those of β-monosubstituted derivatives. In all the cases, (*R*)-configuration products were obtained. These stereochemical outcomes are consistent with the prediction based on our reformulated quadrant rule[11] since the ferrocenyl group is bulkier than the methyl group.

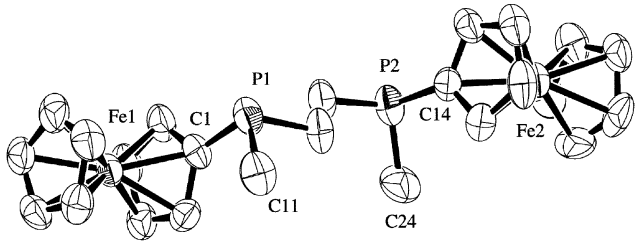
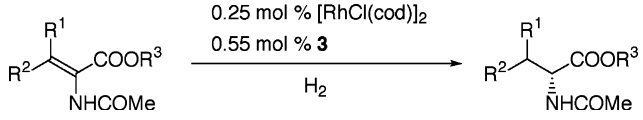


Figure 2. An ORTEP drawing of **1**.

Table 1. Asymmetric hydrogenation of dehydroamino acid derivatives by rhodium complexes coordinated with **3**



Entry	R^1	R^2	R^3	Temp. (°C)	Atm.	Time (h)	Yield (%)[a]	Ee (%)[b] (config.)[c]
1	H	Ph	Me	rt	2	1	56	35 (*R*)
2	H	Ph	Me	50	2	1	>99	52 (*R*)
3	H	Ph	Me	50	6	1	>99	46 (*R*)
4	H	Ph	H	50	2	1	>99	28 (*R*)
5	H	H	Me	50	2	1	>99	45 (*R*)
6	Me	Me	Me	50	6	3	>99	66 (*R*)
7	$-(CH_2)_4-$		Me	50	6	3	>99	77 (*R*)

[a] Determined by GC or HPLC.
[b] The ee% values were determined by HPLC using Daicel Chiralcel OJ or chiral capillary GC using Chrompack's Chiral-L-Val Column (25 m). The acids were converted to the corresponding methyl esters by the reactions with diazomethane.
[c] Absolute configurations were confirmed by comparison of chiral HPLC or GC elution orders with those reported in the literature.

Next, we focused our attention on the enantioselectivity of ligand **1** in palladium-catalyzed asymmetric allylic alkylation.[12] Experiments using 1,3-diphenyl-2-propenyl acetate and dimethyl malonate with various solvents and conventional base/additive conditions (Table 2, entries 1–5) revealed that the reaction proceeded smoothly in THF at room temperature to give the substitution product in an almost quantitative yield with 95% ee (entry 5). Other nucleophiles also reacted under similar conditions to give the corresponding products with high enantioselectivity (entries 6–9). The number of reaction runs is limited; however, we believe that this ligand may exhibit high catalytic efficiency in other asymmetric allylic alkylation reactions.

We have prepared a new P-chirogenic diphosphine ligand, (*S*,*S*)-1,2-bis[(ferrocenyl)methylphosphino]-ethane. The ligand is a solid crystal that is stable in air and can be easily handled without special precautions. The ligand gave moderate to good enantioselectivity of up to 77% in the rhodium-catalyzed asymmetric hydrogenation and high enantioselectivity of up to 95% in the palladium-catalyzed asymmetric allylic alkylation of 1,3-diphenyl-2-propenyl acetate.

1. Experimental

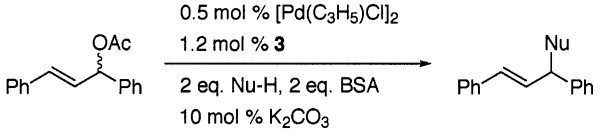
1.1. General

All reactions were carried out under argon atmosphere. All pieces of glassware were dried in an oven before use. Solvents were treated prior to use according to the standard method. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a JMN-LA300 spectrometer (JEOL). Chemical shifts were referenced to solvent peaks or internal TMS (^{1}H, ^{13}C), or external 85% H_3PO_4 (^{31}P). High-resolution mass spectra were obtained on a JMS-DX303 mass spectrometer (JEOL). FT-IR spectra were obtained on an FT/IR-430 spectrometer (JASCO). Melting points were determined with MP-V500 (Yanako) or FP-62 (Mettler). Specific rotation was measured on SEPA-300 polarimeter (HORIBA). TLC was performed on glass plates pre-coated with silica gel 60 F-254 (0.2 mm) from Merck.

1.2. Preparation of ferrocenyldimethylphosphine–borane 2

t-BuLi (56 mL, 1.43 M, 80 mmol) was added dropwise to a solution of ferrocene (14.88 g, 80 mmol) in THF (40 mL) and hexane (40 mL) at 0°C. After stirring for 1 h, the mixture was added to a solution of phosphorus trichloride (10.99 g, 80 mmol) in THF (160 mL) at −78°C through a cannula over a period of 30 min under argon. The mixture was stirred at the same temperature for 1 h, and then gradually raised to 0°C. Methyl magnesium bromide (200 mL, 0.93 M THF solution, 192 mmol) was added to the solution, and the mixture warmed to 50°C. After stirring for 1 h, the mixture was cooled to 0°C, and a borane–THF complex (87 mL, 1.03 M THF solution, 90 mmol) added. The reaction mixture was carefully poured into a mixture of ice-water containing HCl. The organic layer was separated, and the aqueous layer extracted with ethyl acetate. The combined organic extracts were sequentially washed with 1 M HCl, water and brine, dried over Na_2SO_4, and concentrated in vacuo. Unreacted ferrocene and volatiles were removed in vacuo at 100°C under vacuum (0.1 torr), and the residue recrystallized from ethyl acetate/hexane to afford practically pure product (7.9 g, 38%). Orange needles: mp 105–106°C; ^{1}H NMR ($CDCl_3$) δ 0.75 (br q, $J_{HB}=95.6$ Hz, 3H), 1.49 (d, $^{2}J_{HP}=10.4$ Hz, 6H), 4.29 (s, 5H), 4.41 (s, 2H), 4.44 (s, 2H); ^{13}C NMR δ 14.03 (d, $J_{CP}=20.0$ Hz), 69.49 (s),

Table 2. Asymmetric allylic alkylation catalyzed by palladium complexes coordinated with **3**



Entry[a]	Nu	Solvent	Temp. (°C)	Time (h)	Yield (%)[b]	Ee (%)[c], (config.)[d]
1	$CH(COOMe)_2$	CH_3CN	rt	24	44	29 (*S*)
2	$CH(COOMe)_2$	DMF	rt	24	55	95 (*S*)
3	$CH(COOMe)_2$	CH_2Cl_2	rt	5	99	94 (*S*)
4	$CH(COOMe)_2$	Toluene	rt	3	99	95 (*S*)
5	$CH(COOMe)_2$	THF	rt	1	99	95 (*S*)
6	$CH(COO^tBu)_2$	THF	rt	4	99	93 (*S*)
7[e]	$CH(COMe)_2$	THF	40	10	99	94 (*S*)
8[e,f]	$AcNC(COOMe)_2$	THF	40	4	99	92 (*R*)
9[e,f]	$AcNC(COOEt)_2$	THF	40	3	98	94 (*R*)

[a] 1 mmol% catalyst and 1 mL/mmol of solvents were used, unless otherwise stated.
[b] Isolated yields.
[c] The ee% values were determined by HPLC using Daicel Chiralcel AD-H.
[d] Determined by HPLC elution order.
[e] 2 mol% catalyst and high reaction temperature was required for rapid completion of the reaction.
[f] 3 mL/mol solvent was needed for the solubility of Nu-H.

70.75 (d, $^2J_{CP}=10.6$ Hz), 71.28 (d, $^3J_{CP}=7.47$ Hz); ^{31}P NMR (^{1}H decoupled, $CDCl_3$) δ 0.25 (br q, $J_{PB}=59.5$ Hz); IR (KBr) 3078, 2920, 2377, 1421, 1287, 1072, 819 cm^{-1}; HRMS calcd for $C_{12}H_{18}BPFe$ (M^+) 260.0589, found 260.0591.

1.3. Preparation of (*S*,*S*)-1,2-bis[boranato(ferrocenyl)-methylphosphino]ethane 3

s-BuLi (34 mL, 0.99 M, 33 mmol) was added to a solution of (−)-sparteine (7.73 g, 33 mmol) in Et_2O (65 mL) at −78°C. After stirring for 30 min, ferrocenyl(dimethyl)phosphine–borane (3.9 g, 15 mmol) in toluene (20 mL) was slowly added to the solution and the mixture kept at the same temperature for 5 h. Copper(II) chloride (3.09 g, 23 mmol) was added in one portion with vigorous stirring. The cooling bath was removed and the mixture warmed to rt over 2 h. The stirring was then continued for another 15 h before quenching the reaction with aqueous NH_3 (25%, 45 mL). Most of the organic solvent was removed on an evaporator, and the residue was vigorously stirred with aqueous NH_3 (25%, 45 mL) and chloroform (100 mL). The organic layer was separated and the aqueous layer extracted with chloroform. The combined organic layers were washed with 5% aqueous NH_3, 2 M HCl, and brine, and dried over Na_2SO_4. Purification by flash column chromatography on silica gel using chloroform as the eluent, followed by recrystallization from chloroform/hexane, afforded the desired (*S*,*S*) coupling product (1.7 g) that contained a small amount (ca. 2%) of *meso*-isomer (HPLC analysis: Daicel Chiralpak AD-H, 2-PrOH:hexane:AcOH = 5:95:0.05, 1 mL/min, (*R*,*R*) $t_1=17.0$ min, (*S*,*S*) $t_2=18.5$ min, *meso* $t_3=20.4$ min).. Further recrystallization from hot toluene (ca. 60 mL) furnished enatiomerically pure **3** (1.3 g, 33%). Orange needles: mp 238°C (dec.); ^{1}H NMR ($CDCl_3$) δ 0.65 (br q, $J_{HB}=114.8$ Hz, 6H), 1.50–1.54 (m, 6H), 1.65–1.93 (m, 4H), 4.23 (br s, 12H), 4.43 (br s, 6H); ^{13}C NMR δ 11.03 (d, $J_{CP}=39.7$ Hz), 22.50 (d, $J_{CP}=34.7$ Hz), 69.57 (s), 69.92 (m), 71.5–71.8 (m), 72.2–72.4 (m); ^{31}P NMR (^{1}H decoupled, $CDCl_3$) δ 8.5–11.5 (m); IR (KBr) 3096, 2920, 2371, 1417, 1298, 1066, 823 cm^{-1}; HRMS calcd for $C_{24}H_{34}B_2P_2Fe_2$ (M^+) 518.1031, found 518.1052; $[\alpha]_D^{25}$ −53.0 (*c* 0.52, $CHCl_3$).

1.4. *meso*-1,2-Bis[(Ferrocenyl)methylphosphino]ethane

Orange needles: mp 228°C (dec.); ^{1}H NMR ($CDCl_3$) δ 0.05–1.25 (br q, 6H), 1.45–1.55 (m, 6H), 1.65–1.82 (m, 4H), 4.22–4.28 (m, 2H), 4.28–4.32 (br s, 10H), 4.42–4.48 (br s, 6H); ^{13}C NMR δ 10.65 (d, $J_{CP}=40.3$ Hz), 22.77 (d, $J_{CP}=33.5$ Hz), 69.61 (s), 71.5–71.8 (m), 72.5–72.7 (m); ^{31}P NMR (^{1}H decoupled, $CDCl_3$) δ 13.8–16.2 (m); IR (KBr) 3097, 2915, 2380, 1417, 1293, 1067, 821 cm^{-1}; HRMS calcd for $C_{24}H_{34}B_2P_2Fe_2$ (M^+) 518.1031, found 518.1018.

1.5. Crystal data of (*S*,*S*)-1,2-bis[boranato(ferrocenyl)-methylphosphino]ethane 3[13]

An orange plate crystal of $C_{24}H_{34}B_2P_2Fe_2$ having approximate dimensions of 0.40×0.20×0.10 nm was mounted on a glass needle. All measurements were conducted on a Rigaku RAXIS-II Imaging Plate diffractometer with graphite monochromated Mo Kα radiation ($\lambda=0.71070$ Å) at −100°C. Cell constants and an orientation matrix for data collection corresponded to a primitive orthorhombic cell. The data were collected at a temperature of −100±1°C to a maximum 2θ value of 49.9°. A total of 126.00° oscillation images were collected, each being exposed for 8.0 min. Crystal data: $C_{24}H_{34}B_2P_2Fe_2$, $M_w=517.79$, orthorhombic, space group $P2_12_12_1$ (#19), $a=14.24(1)$ Å, $b=15.27(2)$ Å, $c=11.41(3)$ Å, $V=2481(7)$ Å^3, $Z=4$, $D_{calcd}=1.386$ g/cm^3, $F(000)=1080.00$, μ (Mo Kα) = 13.06 cm^{-1}. The structure was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full matrix least-squares refinement was based on 867 observed reflections ($I>2.00\sigma(I)$, $2\theta<49.92$) and 271 variable parameters and converged (largest parameter shift was 0.05 times its esd) with unweighted and weighted agreement factors of: $R=0.071$, $R_w=0.067$. The absolute configuration was determined by the Flack parameter method, value = 0.054865 (0.182087).

1.6. Preparation of (*S*,*S*)-1,2-bis[(ferrocenyl)methylphosphino]ethane 1

A solution of **3** (104 mg, 0.2 mmol) in pyrrolidine (3 mL) was stirred at 65°C under argon. After 90 min, pyrrolidine was removed in vacuo, and the residue passed through a column of basic alumina using degassed toluene. The eluent was evaporated in vacuo to leave 77 mg of practically pure ligand **3** (78% yield). Further purification by recrystallization from methanol afforded orange plates: mp 133–134°C. ^{1}H NMR ($CDCl_3$) δ 1.19–1.20 (m, 6H), 1.40–1.50 (m, 4H), 4.06–4.09 (m, 2H), 4.07 (s, 10H), 4.05–4.08 (m, 2H), 4.19–4.23 (m, 4H); ^{13}C NMR δ 11.38–11.54 (m), 22.77 (br), 68.70 (s), 68.8–69.0 (m), 69.83 (s), 70.10–70.18 (m), 72.68–72.99 (m); ^{31}P NMR (^{1}H decoupled, $CDCl_3$) δ −35.87 (s); IR (KBr) 3080, 2920, 1420, 1285, 1023, 817 cm^{-1}; HRMS calcd for $C_{24}H_{28}P_2Fe_2$ (M^+) 490.0365, found 490.0397.

1.7. Crystal data of (*S*,*S*)-1,2-bis[(ferrocenyl)methylphosphino]ethane 1

An orange plate crystal of $C_{24}H_{28}P_2Fe_2$ having approximate dimensions of 0.60×0.40×0.10 nm was mounted on a glass needle. All measurements were conducted on a Rigaku RAXIS-II Imaging Plate diffractometer with graphite monochromated Mo Kα radiation ($\lambda=0.71070$ Å) at 15°C. Cell constants and an orientation matrix for data collection corresponded to a primitive orthorhombic cell. The data were collected at a temperature of 15±1°C to a maximum 2θ value of 50.1°. A total of 196.00° oscillation images were collected, each being exposed for 4.0 min. Crystal data:[13] $C_{24}H_{28}P_2Fe_2$, $M_w=490.13$, orthorhombic, space group $P2_12_12_1$ (#19), $a=13.888(8)$ Å, $b=10.698(2)$ Å, $c=15.12(1)$ Å, $V=2245(2)$ Å^3, $Z=4$, $D_{calcd}=1.449$ g/cm^3, $F(000)=1080.00$, μ (Mo Kα) = 14.40 cm^{-1}. The structure was

solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full matrix least-squares refinement was based on 2915 observed reflections ($I > 2.00\sigma(I)$, $2\theta < 50.14$) and 253 variable parameters and converged (the largest parameter shift was 0.08 times its esd) with unweighted and weighted agreement factors of: $R = 0.057$, $R_w = 0.070$.

1.8. General procedure for rhodium-catalyzed asymmetric hydrogenation of dehydroamino acid derivatives

Ligand **1** (5.8 mg, 0.012 mmol) was added to a solution of $[RhCl(cod)]_2$ (1.2 mg, 0.005 mmol) in MeOH (5 mL). After stirring for 10 min, the catalyst solution was transferred by syringe to a 50 mL pressure tight glass vessel containing dihydroamino acid derivative (1 mmol). The vessel was immersed in a dry ice–ethanol bath, evacuated and filled with hydrogen gas to a predefined pressure. After four vacuum/H_2 cycles, the vessel was closed and the cooling bath removed. The solution was magnetically stirred at ambient temperature until no further hydrogen uptake was observed.

1.9. General procedure for palladium-catalyzed asymmetric allylic alkylation of *rac*-1,3-diphenyl-2-propenyl acetate

To a 10 mL flask containing a magnetic stirrer bar was added *rac*-1,3-diphenyl-2-propenyl acetate (252 mg, 1 mmol), solvent (1 mL), malonate derivative (2 mmol), *N*,*O*-bis(trimethylsilyl)acetamide (470 μL, 2 mmol) and K_2CO_3 (14 mg, 0.1 mmol) in this order under argon. To this solution was added $[Pd(\pi\text{-}C_3H_5)Cl]_2$ (1.8 mg, 0.005 mmol), and ligand **1** (5.8 mg, 0.012 mmol) in one portion. The mixture was stirred at ambient temperature with occasional monitoring by TLC. The reaction mixture was diluted with the minimum amount of ethyl acetate and purified by flash chromatography on silica gel (ethyl acetate/hexane = 1/7) to give the pure product.

Acknowledgements

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References

1. For representative reviews and accounts, see: (a) Hayashi, T.; Kumada, M., *Acc. Chem. Res.* **1982**, *15*, 395; (b) Hayashi, T. *Pure Appl. Chem.* **1988**, *60*, 7; (c) Sawamura, M.; Ito, Y. *Chem. Rev.* **1992**, *92*, 857; (d) Hayashi, T. *Ferrocenes*; Togni, A.; Hayashi, T., Eds.; Wiley-VCH: Weinheim, 1995; pp. 105–142; (e) Togni, A. *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1475; (f) Kagan, H. B.; Riant, O. *Advance in Asymmetric Synthesis*; Hassner, A., Ed.; JAI Press Inc.: Greenwich, CT, 1997; 2, pp. 189–235; (g) Richards, C. J.; Locke, A. J. *Tetrahedron: Asymmetry* **1998**, *9*, 2377.
2. (a) Nettekoven, U.; Widhalm, M.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *Tetrahedron: Asymmetry* **1997**, *8*, 3185; (b) Brown, J. M.; Laing, J. C. P. *J. Organometal. Chem.* **1997**, *529*, 435; (c) Maienza, F.; Wörle, M.; Steffanut, P.; Mezzetti, A. *Organometallics* **1999**, *18*, 1041; (d) Tsuruta, H.; Imamoto, T. *Tetrahedron: Asymmetry* **1999**, *10*, 877; (e) Maienza, F.; Spindler, F.; Thommen, M.; Pugin, B.; Malan, C.; Mezzetti, A. *J. Org. Chem.* **2002**, *67*, 5239.
3. (a) Imamoto, T.; Watanabe, J.; Wada, Y.; Masuda, H.; Yamada, H.; Tsuruta, H.; Matsukawa, S.; Yamaguchi, K. *J. Am. Chem. Soc.* **1998**, *120*, 1635; (b) Imamoto, T. *Pure Appl. Chem.* **2001**, *73*, 373; (c) Gridnev, I. D.; Yamanoi, Y.; Higashi, N.; Tsuruta, H.; Yasutake, M.; Imamoto, T. *Adv. Synth. Catal.* **2001**, *343*, 118.
4. Horner, L.; Simons, G. *Z. Naturforsch.* **1984**, *396*, 512.
5. Evans and his co-workers reported many enantiomerically pure borane adducts of 1,2-bis(arylmethylphosphino)ethanes. See: Muci, A. R.; Campos, K. R.; Evans, D. A. *J. Am. Chem. Soc.* **1995**, *117*, 9075.
6. (a) Imamoto, T.; Kusumoto, T.; Suzuki, N.; Sato, K. *J. Am. Chem. Soc.* **1985**, *107*, 5301; (b) Imamoto, T.; Oshiki, T.; Onozawa, T.; Kusumoto, T.; Sato, K. *J. Am. Chem. Soc.* **1990**, *112*, 5244; (c) Imamoto, T. *Pure Appl. Chem.* **1993**, *65*, 655.
7. Guilaneux, D.; Kagan, H. B. *J. Org. Chem.* **1995**, *60*, 2502.
8. No epimerization under these conditions was confirmed by HPLC analysis of the phosphine–borane adduct which was obtained by the reaction of crude product **1** with borane–THF.
9. (a) Imamoto, T; Kusumoto, T.; Suzuki, N.; Sato, K. *J. Am. Chem. Soc.* **1985**, *107*, 5301; (b) Imamoto, T.; Oshiki, T.; Onozawa, T.; Kusumoto, T.; Sato, K. *J. Am. Chem. Soc.* **1990**, *112*, 5244.
10. Use of cationic rhodium complex $[Rh(nbd)_2]^+BF_4^-$ or $[Rh(cod)_2]^+BF_4^-$ instead of $[RhCl(cod)]_2$ resulted in sluggish reaction providing very low enantioselectivity.
11. (a) Gridnev, I. D.; Higashi, N.; Asakura, K.; Imamoto, T. *J. Am. Chem. Soc.* **2000**, *122*, 7183; (b) Crépy, K. V. L.; Imamoto, T. *Adv. Synth. Catal.* **2003**, *345*, 79.
12. For representative reviews, see: (a) Trost, C. G.; Howarth, J.; Williams, J. M. J. *Tetrahedron: Asymmetry* **1992**, *3*, 1089; (b) Hayashi, T. In *Catalytic Asymmetric Synthesis*; Ojima, I., Ed.; Wiley-VCH: New York, 1993; pp. 325–365; (c) Trost, B. M.; van Vranken, D. L. *Chem. Rev.* **1996**, *96*, 395; (d) Trost, B. M.; Lee, C. in *Catalytic Asymmetric Synthesis*, 2nd ed.; Ojima, I., Ed.; Wiley-VCH: New York, 2000; pp. 593–649; (e) Pflatz, A.; Lautens, M. In *Comprehensive Asymmetric Catalysis II*; Jacobsen, E. N.; Pflatz, A.; Yamamoto, H., Eds; Springer: Berlin, pp. 833–884.
13. CCDC 212697 for compound **3** and CCDC 212698 for compound **1** contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk).