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Divalent Samarium Triflate Mediated Stereoselective Pinacol Coupling of Planar Chiral Phosphanyl and Phosphoryl Ferrocenecarbaldehyde

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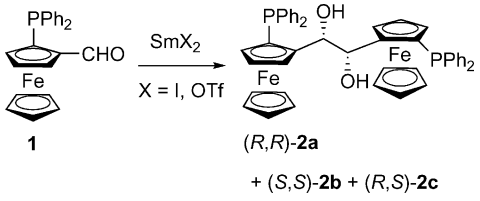
The pinacol coupling reaction of (*Rp*)-2-diphenylphosphanyl ferrocenecarbaldehyde (**1**) was smoothly mediated by divalent samarium triflate to give (*R*,*R*)-diol **2a** predominantly, whereas the use of samarium(II) iodide resulted in low selectivity as described in the previous literature. In contrast, the coupling reaction of (*Rp*)-2-diphenylphosphoryl ferrocenecarbaldehyde (**3**) with $Sm(OTf)_2$ gave the (*S*,*S*)-diol as the major isomer, which was the opposite stereochemistry of that obtained in the reaction with **1**. The rhodium complexes of diphosphanes **2a** were good catalysts for the asymmetric hydrogenation of α-acetamidocinnamic acid, and the product was obtained quantitatively with up to 92 % *ee*.

Introduction

Thousands of ferrocenyl phosphane ligands, which are useful tools for metal-catalyzed asymmetric reactions, have been designed.[1] C_2-symmetrical bisferrocenyl diphosphanes are expected to be efficient ligands for metal-complex-catalyzed asymmetric synthesis. The bifep [2,2′′-bis(diphenylphosphanyl)1,1′-bisferrocene][2] ligand was first prepared by Sawamura and Ito as an analogue of well-established binap and related biaryl diphosphanes[3] by optical resolution of its racemate. Weissensteiner et al. and Widhalm et al. reported an alternative synthetic method of bifep without optical resolution, and applied it to metal-complex-catalyzed asymmetric reactions.[4–5] Bisferrocenyl methane diphosphane homologues, which are more readily accessible than bifep,[6–7] have been applied to the rhodium-complex-catalyzed asymmetric hydrogenation of alkenes and ketones. In these asymmetric reactions, bifep and its homologues have provided moderate-to-good enantioselectivities.

Kagan et al. prepared C_2-symmetrical bisferrocenyl diol diphosphanes by pinacol coupling reactions of planar chiral *ortho*-phosphanyl ferrocenecarbaldehyde by samarium(II) iodide and showed that they are efficient ligands for the rhodium-catalyzed asymmetric hydrogenation of α-acetamidocinnamic acid.[8] Although readily prepared by a simple procedure, the diol diphosphane was obtained as a mixture of three diastereomers with fairly low selectivity. We previously reported highly diastereoselective pinacol coupling reactions of chiral *ortho*-oxazoline-substituted ferrocenecarbaldehyde by divalent samarium triflate [$Sm(OTf)_2$].[9] We attempted to prepare a single isomer of diol diphosphane by $Sm(OTf)_2$ selectively.[10] In this paper we report our results of the pinacol coupling reaction of (*Rp*)-**1** (Scheme 1) together with the results for *ortho*-phosphoryl derivative **3** and the benchmark rhodium-catalyzed asymmetric hydrogenation.[11]



Scheme 1. Pinacol coupling reaction of **1** with divalent samarium reagents.

Results and Discussion

(*Rp*)-2-Diphenylphosphanyl ferrocenecarbaldehyde (**1**) was prepared starting from the optically active ferrocenyl sulfoxide according to the literature,[7] and it was used to verify the SmI_2-induced pinacol coupling reaction of Kagan[8] and Uemura.[11] Table 1 summarizes the pinacol coupling reaction together with reference results. The product was a mixture of three diol diphosphane diastereomers, (*R*,*R*)-**2a**, (*S*,*S*)-**2b**, and (*R*,*S*)-**2c**. The isomeric ratio was determined by ^1H NMR spectroscopic integration of alcoholic methine protons and/or Cp ring protons of the crude product, (*R*,*R*)-**2a**/(*S*,*S*)-**2b**/(*R*,*S*)-**2c**, 32:16:52

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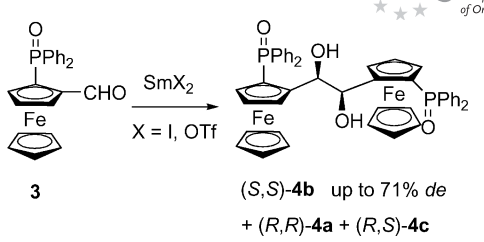
(Table 1, Entry 5). The isomers could be separated by flash column chromatography. In the previous two studies, the *Sp* isomer of **1** was used, so the present three diastereomers **2a**–**c** are enantiomers of the previous diol diphosphanes. In experiments performed by Kagan and Uemura, the isomeric ratios were *ent*-**2a**/*ent*-**2b**/*ent*-**2c**, 30:40:30 (r.t.) and 52:24:24 (0 °C), respectively (Table 1, Entries 1 and 3).[8,12] Our results are different, but the stereochemical outcome is similar in that the selectivity was fairly low. We next carried out the pinacol coupling of **1** by using divalent samarium triflate, which was prepared by the reduction of $Sm(OTf)_3$ with *s*BuLi at 0 °C in THF. The reaction was complete in 5 min as seen by the decolorization of the initial deep purple color. ^{1}H NMR spectroscopic analysis revealed that the selectivity for (*R*,*R*)-**2a** was remarkably enhanced with a ratio of (*R*,*R*)-**2a**/(*S*,*S*)-**2b**/(*R*,*S*)-**2c**, 79:8:13, **2a** = 58%*de* (Table 1, Entry 7). The structure of major product (*R*,*R*)-**2a** was confirmed by X-ray crystallographic analysis. This higher diastereoselectivity was reproducible and was almost the same at room temperature (Table 1, Entry 6) and at 0 °C. Kagan et al. improve their diastereoselectivity by lowering the reaction temperature from room temperature to –25 °C in the SmI_2-mediated reaction (Table 1, Entry 2),[8] but Uemura et al. reported that no reaction occurs at –78 °C.[12] Therefore, the control of stereochemistry by temperature has limitations with SmI_2, whereas $Sm(OTf)_2$-mediated reactions can achieve high diastereoselectivity at either room temperature or at 0 °C.

Table 1. Pinacol coupling of (*Rp*)-**1** with divalent samarium reagents.[a]

Entry	SmX_2	*T* [°C]	Yield [%]	**2a/2b/2c**[b]
1[c]	SmI_2	25	80	30:40:30[d]
2[c]	SmI_2	–25	–	25:65:10[d]
3[e]	SmI_2	0	41	52:24:24[d]
4	SmI_2	25	90	17:19:64
5	SmI_2	0	90	32:16:52
6	$Sm(OTf)_2$	25	>99	79:10:11
7	$Sm(OTf)_2$	0	>99	79:8:13

[a] **1** (0.5 mmol), SmX_2 (1.2 mmol), THF (5 mL). [b] Determined by ^{1}H NMR spectroscopy. [c] Ref.[8] [d] When (*Sp*)-**1** was used, the isomeric ratio was *ent*-**2a**/*ent*-**2b**/*ent*-**2c**. [e] Ref.[12]

We next examined the pinacol coupling reaction of (*Rp*)-2-diphenylphosphoryl ferrocenecarbaldehyde **3** with SmI_2 and $Sm(OTf)_2$ in THF at 0 °C for 0.5–1 h (Scheme 2). It is interesting that the analysis of the crude product by ^{1}H NMR spectroscopy showed the presence of (*S*,*S*)-pinacol **4b** predominantly (70–71%*de*) with both SmI_2 and $Sm(OTf)_2$; for SmI_2 **4a/4b/4c**, 4:86:10 and for $Sm(OTf)_2$ **4a/4b/4c**, 5:85:10. Combined pinacols **4a**–**c** were obtained quantitatively and are separable by flash silica gel column chromatography. The structure of main product (*S*,*S*)-**4b** was confirmed by X-ray crystallographic analysis, and its X-ray structure is shown in Figure 1. Reduction of the phosphoryl group[5] in **4b** afforded diphosphane **2b**, which was a minor product in the reaction of **1** with $Sm(OTf)_2$. Thus, either diastereomer **2a** or **2b** can be obtained selectively by the pinacol coupling reaction of **1** or **3** with $Sm(OTf)_2$.



Scheme 2. Pinacol coupling reaction of **3** with divalent samarium reagents.

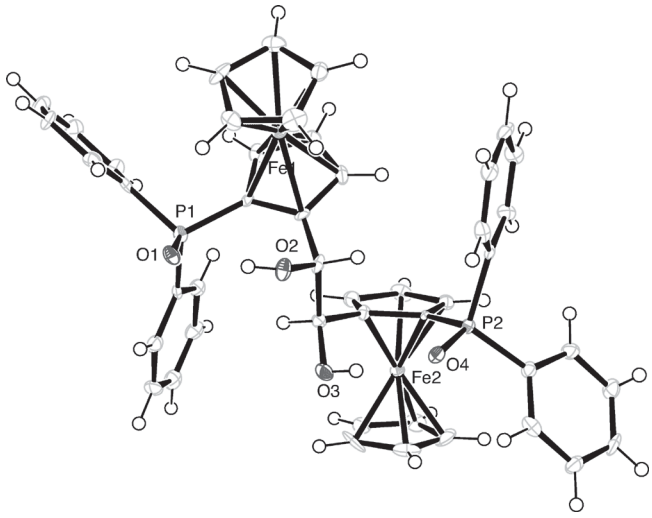
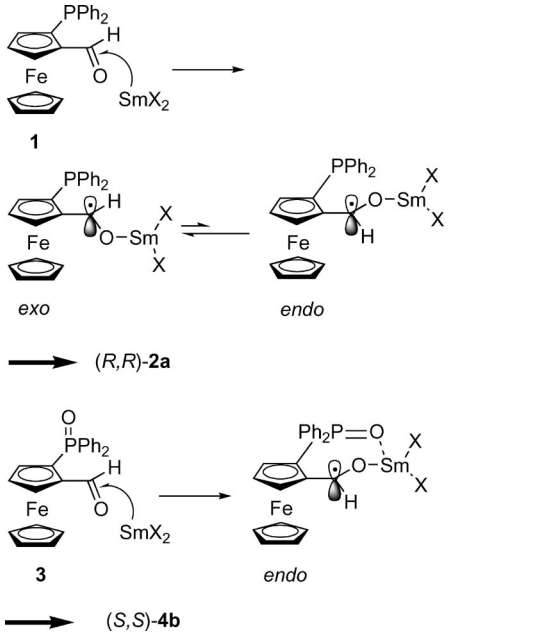


Figure 1. Molecular structure of **4b** (ORTEP plot). Selected bond lengths [Å]: P1–O1 1.49, P2–O4 1.48, C18–C19 1.55, O2–C18 1.40, O3–C19 1.40. Selected bond angles [°]: O1–P1–C13 113.0, O4–P2–C24 114.7, O2–C18–C17 115.3, O2–C18–C19 112.3, O3–C19–C20 115.6, O3–C19–C18 112.4.

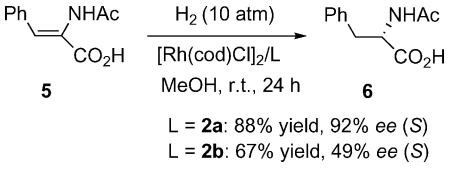
Although the detailed mechanism is not yet clear, the transition-state model discussed in the previous reaction of *ortho*-substituted ferrocenecarbaldehyde may also explain the stereochemistry of the reaction of **1** (Scheme 3).[9,12] The carbonyl oxygen atom is oriented away from the *ortho* phosphane group by steric effects and Sm^{II} attacks the carbonyl group from the *exo* side to form the corresponding *exo* ketyl radical intermediate. The sterically demanding triflate group prevents diastereomerization, and the predominant *exo* ketyl radicals could couple with each other at the less-hindered *re* face to give (*R*,*R*)-diol **2a**. In contrast, in the reaction of **3**, the phosphoryl oxygen atom can coordinate to the samarium atom and the *endo* ketyl radical is favored, which then self-couples to form (*S*,*S*)-diol **4b**.[13]

The catalytic activities of diol diphosphanes **2a** and **2b** were checked by the benchmark rhodium-catalyzed asymmetric hydrogenation of α-acetamidocinnamic acid (**5**) (Scheme 4).[14] The reaction was carried out by using 0.01 mol and 0.02 mol equivalents of $[Rh(cod)Cl]_2$ and the ligand to **5**, respectively, in MeOH at room temperature under 10 atm of hydrogen. The enantiomeric excess and absolute configuration of product **6** were determined by HPLC analysis after methyl esterification. The results are shown in Table 2. The complex of **2a** catalyzed the hydrogenation smoothly to give (*S*)-**6** quantitatively with high enantio-



Scheme 3. Proposed nonchelation and chelation mechanism for the pinacol coupling reaction.

selectivity (92%*ee*; Table 2, Entry 1), whereas the complex of **2b** gave low enantioselectivity (49%*ee*; Table 2, Entry 2). We also examined the selectivity and reactivity of the reaction by using *ent*-**2a**,**b** and the results were consistent with those obtained with **2a**,**b** (Table 2, Entries 3 and 5). These results were different from those of Kagan's rhodium-catalyzed asymmetric hydrogenation of **5** by using *ent*-**2a**,**b**; *ent*-**2a** and *ent*-**2b** give the product in 40% yield with 85%*ee* and 100% yield with 89%*ee*, respectively (Table 2, Entries 4 and 6).[15] Ligand **2a**, which is obtained as the major product of the pinacol coupling of **1** by $Sm(OTf)_2$, was a more efficient ligand in our studies.



Scheme 4. Asymmetric hydrogenation of **5** by using rhodium/**2a**,**b** complexes.

Table 2. Asymmetric hydrogenation of **5** by using rhodium/diol diphos complexes.[a]

Entry	L	Conv. [%]	*ee* [%][b]	Config.
1	**2a**	>99	93	*S*
2	**2b**	92	49	*S*
3	*ent*-**2a**	>99	80	*R*
4[c]	*ent*-**2a**	40	85	*R*
5	*ent*-**2b**	90	40	*R*
6[c]	*ent*-**2b**	100	89	*R*

[a] **5** (1 mmol), Rh (0.010 mol), L (0.011 mol), MeOH (2 mL), room temp., 24 h, H_2 (10 atm). [b] The %*ee* were determined by HPLC (Chiralcel AD-H) after esterification with MeOH/$SOCl_2$. [c] Data from Ref.[8]

Conclusions

$Sm(OTf)_2$-mediated pinacol coupling reactions of *ortho*-phosphanyl and phosphoryl-substituted ferrocenecarbaldehyde with high diastereoselection was achieved and C_2-symmetric (*R*,*R*)- or (*S*,*S*)-diol diphosphanes were obtained selectively from each aldehyde. It was revealed that the (*R*,*R*)-diol diphosphane worked more efficiently in the rhodium-catalyzed asymmetric hydrogenation of α-acetamidocinnamic acid.

Experimental Section

General: The ^1H and ^{13}C NMR spectra were recorded with a Varian Mercury 300 NMR (300 MHz) spectrometer as solutions in $CDCl_3$. The chemical shifts are reported in δ units downfield from the internal reference, Me_4Si. The optical rotations were determined with a JASCO DIP-370 instrument. The HPLC analyses were carried out with a Hitachi L-7100 apparatus equipped with a UV detector by using chiral columns (Chiralcel OD-H, AS-H, OB). Column chromatography was performed by using a Yamazen YFLC-254 and a Michael Miller column equipped with a UV detector by using Merck Silica Gel 60. Preparative TLC was conducted with the use of a 20 × 20 cm glass sheet coated with a 2 mm thick layer of Merck Kieselgel 60 PF_{254}.

Crystallography: The diffraction data were collected at room temperature with a Rigaku AFC7R four-circle automated diffractometer with graphite monochromated Mo-K_α radiation and the ω-2θ scan technique to a maximum 2θ value of 50 or 55°. The structure solution and refinements were carried out by using the teXsan and Crystal Structure crystallographic software packages. The positions of the non-hydrogen atoms were determined by Patterson methods (DIRDIF PATTY) or direct methods (SIR92) and expanded by using Fourier techniques (DIRDIF94 or 99). The carbon atoms of the solvating CH_2Cl_2 molecules were refined isotropically.

CCDC-697469 [for (*R*,*Rp*;*R*,*Rp*)-**2a**] and -697470 [for (*S*,*Rp*;*S*,*Rp*)-**4b**] contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

General Procedure for the $Sm(OTf)_2$-Mediated Pinacol Coupling Reaction of 1: Under a nitrogen atmosphere, $Sm(OTf)_3$ (0.72 g, 1.2 mmol) was placed in a 50-mL Schlenk tube and equipped with a septum inlet. The tube was heated at 180 °C in vacuo for 2 h. After the tube was cooled to room temperature, a magnetic stirring bar was placed in the flask, which was flushed with nitrogen. THF (5 mL) was added by syringe through the rubber septum, and the mixture was stirred at room temperature for 1 h. Then, a solution of *s*BuLi (1.0 M in cyclohexane, 1.2 mL, 1.2 mmol) was injected slowly into the suspension at 0 °C. The solution was warmed to room temperature over a period of 0.5 h during which time a purple solution of the divalent samarium triflate was obtained. To the resulting THF solution of $Sm(OTf)_2$ was added **1** (199 mg, 0.5 mmol) at 0 °C. The deep purple color of the solution faded in 5 min, and the solution was stirred for an additional 30 min. The solution was quenched with saturated NH_4Cl, and the aqueous phase was extracted with ethyl acetate. The combined organic extract was washed with brine and dried ($MgSO_4$). Evaporation of the solvent left a pale-yellow residue, and ^1H NMR measurements of the crude product revealed the presence of three diol diphosphane dia-

stereomers. (*R*,*R*)-Isomer **2a** was produced as the major product. The diastereomers were isolated by flash column chromatography on silica gel (hexane/ethyl acetate, 4:1 to 2:1).

(*R*,*Rp*;*R*,*Rp*)-2a: Yield: 155 mg, 78%. Brown solid, m.p. 94–95 °C. $[\alpha]_D^{25}$ = +310 (*c* = 0.41, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.73 (br. s, 2 H), 3.66 (s, 2 H), 3.76 (s, 10 H, Cp), 4.24 (t, *J* = 2.3 Hz, 2 H), 4.36 (s, 2 H), 4.53 (s, 2 H, CHO), 7.3–7.5 (m, 20 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 69.1, 69.2, 69.6 (Cp), 71.7, 72.0, 74.7(C-O), 93.9 (C-P), 128.0, 128.8, 133.1 (d, *J* = 10 Hz), 133.3 (d, *J* = 10 Hz), 134.9 (d, *J* = 10.5 Hz), 135.1 (d, *J* = 10.5 Hz), 140.1 ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = –26.4 (s) ppm. HRMS (ESI): calcd. for $C_{46}H_{40}Fe_2O_2P_2$ 798.1171; found 798.1178. Crystals suitable for X-ray analysis were obtained by recrystallization from hexane/CH_2Cl_2.

(*S*,*Rp*;*S*,*Rp*)-2b: Yield: 20 mg, 10%. Brown solid, m.p. 210–211 °C. $[\alpha]_D^{25}$ = +320 (*c* = 0.5, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.63 (br. s, 2 H), 3.80 (s, 2 H), 4.10 (s, 10 H), 4.24 (t, *J* = 2.3 Hz, 2 H), 4.40 (s, 2 H), 4.84 (d, *J* = 6.2 Hz, 2 H, CHO), 7.3–7.4 (m, 16 H), 7.5–7.6 (m, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 69.4, 69.8 (Cp), 71.1 (d, *J* = 3.8 Hz), 71.3 (d, *J* = 3.2 Hz), 73.0 (d, *J* = 6.3 Hz), 75.3 (d, *J* = 8.9 Hz, C-O), 94.4 (d, *J* = 22.5 Hz, C-P), 128.1, 128.2, 128.3, 129.1, 132.7 (d, *J* = 18.9 Hz), 134.9 (d, *J* = 20.9 Hz), 137.1 (d, *J* = 8.2 Hz), 139.9 (d, *J* = 9.5 Hz), 140.1 ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = –23.8 (s) ppm. HRMS (ESI): calcd. for $C_{46}H_{40}Fe_2O_2P_2$ 798.1171; found 798.1200.

(*R*,*Rp*;*S*,*Rp*)-2c: Yield: 22 mg, 11%. Brown solid, m.p. 189–190 °C $[\alpha]_D^{25}$ = +287 (*c* = 0.17, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.78 (t, *J* = 5.0 Hz, 1 H), 3.80 (s, 5 H), 3.86 (s, 1 H), 3.88 (s, 1 H), 3.90 (s, 5 H), 4.00 (s, 1 H), 4.18 (t, *J* = 2.5 Hz, 1 H), 4.20 (t, *J* = 2.5 Hz, 1 H, CHO), 4.76 (m, 1 H, CHO), 7.3–7.4 (m, 16 H), 7.5–7.6 (m, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 68.3–69.8 (several Cp signals), 71.1 72.0, 73.0 (d, *J* = 10.1 Hz), 73.5, 76.0 (C-O), 92.4 (d, *J* = 21.5 Hz), 95.5 (d, *J* = 23.7 Hz, C-P), 127.7–128.3 (several Ph signals), 128.9, 129.1, 132.5 (d, *J* = 17.5 Hz), 133.4 (d, *J* = 19.5 Hz), 134.6 (d, *J* = 21.3 Hz), 135.2 (d, *J* = 21.3 Hz), 137.0 (d, *J* = 9.3 Hz), 137.3 (d, *J* = 5.1 Hz), 139.6 (d, *J* = 10.2 Hz), 139.8 (d, *J* = 4.3 Hz) ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = –22.8 (s), –26.4 (s) ppm. HRMS (ESI): calcd. for $C_{46}H_{40}Fe_2O_2P_2$ 798.1171; found 798.1180.

(*Rp*)-3: To a methanol solution (5 mL) of **1** (1.12 g, 2.8 mmol) was added H_2O_2 (30%, 0.5 mL) at room temperature. The completion of the oxidation reaction was monitored by TLC, and after 5 h aqueous $Na_2S_2O_3$ was added to the solution. Methanol was evaporated in vacuo, and the residue was diluted with CH_2Cl_2. The solution was dried by $MgSO_4$ and filtered. The solvent was evaporated in vacuo, and the crude product was purified by flash column chromatography on silica gel (ethyl acetate). Yield: 0.75 g, 1.8 mmol, 64%. Brown solid, m.p. 176–177 °C. $[\alpha]_D^{25}$ = –512 (*c* = 0.31, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.17 (s, 1 H), 4.34 (s, 5 H), 4.71 (s, 1 H), 4.36 (s, 2 H), 5.17 (s, 1 H, CHO), 7.3–7.5 (m, 10 H, Cp), 10.3 (s, 1 H, CH = O) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 69.5, 71.2, 74.3 (d, *J* = 10.7 Hz), 75.8, 78.6 (d, *J* = 14.0 Hz), 82.4 (d, *J* = 10.1 Hz), 128.2 (d, *J* = 10.5 Hz), 128.3 (d, *J* = 10.5 Hz), 133.1 (d, *J* = 7.6 Hz), 133.3 (d, *J* = 7.6 Hz), 131.7, 131.8, 133.2 (d, *J* = 17.7 Hz), 134.8, 194.2 ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 27.6 (s) ppm. $C_{23}H_{19}FeO_2P$ (414.21): calcd. C 66.69, H 4.62; found C 66.63, H 4.64.

Pinacol Coupling Reaction with 3: The reaction of **3** with $Sm(OTf)_2$ and SmI_2 was carried out with a similar procedure to that of **1**.

(*R*,*Rp*;*R*,*Rp*)-4a: Yield: 10 mg, 5%. Brown solid, m.p. 184–185 °C. $[\alpha]_D^{25}$ = +66.4 (*c* = 0.41, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.82 (s, 2 H), 4.23 (s, 10 H, Cp), 4.33 (dd, *J* = 2.5, 4.9 Hz, 2 H), 4.65 (s, 2 H), 4.75 (d, *J* = 4.0 Hz, 2 H), 5.21 (d, *J* = 4.0 Hz, 2 H), 7.2–7.8 (m, 20 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 68.5 (d, *J* = 115.2 Hz), 69.6, 70.0 (d, *J* = 12.0 Hz), 71.4 (Cp), 72.3 (d, *J* = 15.6 Hz), 73.0 (d, *J* = 9.6 Hz), 97.2 (d, *J* = 9.6 Hz), 128.0 (d, *J* = 12.0 Hz), 128.2 (d, *J* = 12.0 Hz), 131.3 (d, *J* = 10.8 Hz), 131.6 (d, *J* = 9.6 Hz), 132.7, 133.6, 134.0, 134.9 ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 32.7 (s) ppm. $C_{46}H_{40}Fe_2O_4P_2$ (830.44): calcd. C 66.53, H 4.85; found C 66.61, H 4.52.

(*S*,*Rp*;*S*,*Rp*)-4b: Yield: 176 mg, 85%. Brown solid, m.p. >300 °C (decomp.). $[\alpha]_D^{25}$ = +247 (*c* = 0.17, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.46 (s, 2 H), 3.79 (d, *J* = 9.1 Hz, 2 H), 3.89 (s, 2 H), 4.06 (s, 10 H, Cp), 5.92 (d, *J* = 9.4 Hz, 2 H, CHO), 7.5–7.6 (m, 16 H), 7.8–7.9 (m, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 69.4 (d, *J* = 67.1 Hz), 69.9 (d, *J* = 34.8 Hz), 70.4, 73.0 (d, *J* = 15.6 Hz), 74.0 (d, *J* = 10.8 Hz), 74.8, 95.1 (d, *J* = 10.9 Hz), 128.2 (d, *J* = 12.0 Hz), 128.3 (d, *J* = 12.0 Hz), 131.6 (d, *J* = 9.7 Hz), 131.7 (d, *J* = 9.6 Hz), 132.2, 133.1, 133.8, 134.7 ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 30.2 (s) ppm. HRMS (ESI): calcd. for $C_{46}H_{40}Fe_2O_4P_2Na^+$ 853.0967; found 853.0963. Crystals suitable for X-ray analysis were obtained by recrystallization from hexane/CH_2Cl_2.

(*R*,*Rp*;*S*,*Rp*)-4c: Yield: 21 mg, 9.6%. Brown solid, m.p. >300 °C (decomp.). $[\alpha]_D^{25}$ = +111 (*c* = 0.17, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.70 (s, 1 H), 3.89 (s, 1 H), 4.00 (d, *J* = 8.9 Hz, 1 H), 4.23 (s, 5 H), 4.24 (s, 5 H), 4.00 (s, 1 H), 4.29 (dd, *J* = 2.9, 5.2 Hz, 1 H), 4.35 (d, *J* = 9.0 Hz, 1 H), 4.43 (dd, *J* = 2.3, 4.5 Hz, 1 H), 4.63 (s, 1 H), 5.03 (s, 1 H), 6.04 (s, 1 H), 6.64 (d, *J* = 11.3 Hz, 1 H), 7.3–7.8 (m, 20 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 68.3–69.8 (several Cp signals), 70.0 70.3, 72.7, 72.9, 73.0, 73.2 (d, *J* = 15.5 Hz), 73.9 (d, *J* = 10.8 Hz), 75.5 (d, *J* = 10.8 Hz), 97.1 (d, *J* = 9.6 Hz), 97.7 (d, *J* = 10.2 Hz), 127.7–131.9 (several Ph signals), 132.8, 133.1, 133.2, 134.2 ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 33.9 (s), 35.1 (s) ppm. HRMS (ESI): calcd. for $C_{46}H_{40}Fe_2O_4P_2Na^+$ 853.0967; found 853.0947.

[Rh(cod)Cl]$_2$/2a-Complex Catalyzed Asymmetric Hydrogenation of α-Acetamidocinnamic Acid (5): In a 20-mL Schlenk tube containing a stirring bar was dissolved $[Rh(cod)Cl]_2$ (4.9 mg, 2 mol-%) and **2a** (8.0 mg, 2 mol-%) in MeOH (4 mL), and the mixture was stirred under a nitrogen atmosphere at room temperature. After 30 min, the in situ formed catalyst solution was transferred to stainless autoclave containing α-acetamidocinnamic acid (**5**; 102 mg, 0.5 mmol) by using a cannula. The autoclave was purged three times with hydrogen, and placed under hydrogen pressure (10 atm). The mixture was stirred at room temperature for 24 h under an atmosphere of hydrogen (10 atm). The solvent was removed under reduced pressure, and the residue was treated with MeOH/$SOCl_2$. The inorganic part was removed by short column chromatography on silica gel to give almost pure product. The enantiomeric excess (92%*ee*, *S*) of the crude product was determined by HPLC [Chiralpack AD-H; 25 cm; hexane/*i*PrOH, 90:10; 0.8 mL min^{-1}; t_R (*R*) = 14.7 min, t_R (*S*) = 18.7 min]. The pure methyl ester of **6** was obtained by flash column chromatography on silica gel. Yield: 91 mg, 4.4 mmol, 88%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.97 (s, 3 H), 3.07 (dd, *J* = 5.9, 13.8 Hz, 1 H), 3.14 (dd, *J* = 5.8, 13.8 Hz, 1 H), 3.71 (s, 3 H), 4.87 (ddd, *J* = 5.8, 5.9, 7.8 Hz, 1 H), 6.11 (d, *J* = 7.8 Hz, 1 H), 7.1–7.3 (m, 5 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 22.9, 37.7, 52.2, 53.0, 127.0, 128.5, 129.1, 135.8, 169.6, 172.1 ppm.

Supporting Information (see footnote on the first page of this article): ^{1}H and ^{13}C NMR spectra of **1**, **2a**–**c**, **3**, and **4a**–**c**.

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