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SYNTHESIS OF OPTICALLY ACTIVE P-CHIROGENIC FERROCENE-FUSED BENZOPHOSPHOLE BY DIASTEREOSELECTIVE INTRAMOLECULAR CYCLIZATION OF PHOSPHANYLFERROCENE DERIVATIVES

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Abstract – A novel optically active P-chirogenic ferrocene-fused benzophosphole, (S_{Fc},R_P)-4-phenylbenzo[*b*]ferroceno[*d*]phosphole, was synthesized by diastereoselective intramolecular cyclization of (S_{Fc})-1-(diphenylphosphanyl)-2-(2-lithiophenyl)ferrocene intermediates in two routes. The geometry of the new P-chirogenic ferrocenophosphole including absolute configuration of the phosphorous was disclosed by single crystal X-ray analysis of the palladium complex derived from the reaction of the phosphole with di-μ-dichloro-bis{2-[(dimethylamino)methyl]phenyl-C^1,N}dipalladium (II).

INTRODUCTION

The chemistry of asymmetric catalysts is an interesting research field in asymmetric reactions and has recently been the focus of attention.[1] The most popular and actively investigated examples are optically active phosphorous compounds which are proved to be an important synthetic tool for ligand chemistry in asymmetric synthesis. Accompanied by the wide applicability of optically active phosphorous compounds for asymmetric reactions, studies on P-chirogenic optically active phosphorous compounds and their application in asymmetric synthesis have also been the subject of much interest.[2] As for the typical methods for the preparation of P-chirogenic phosphorous compounds, stereoselective nucleophilic

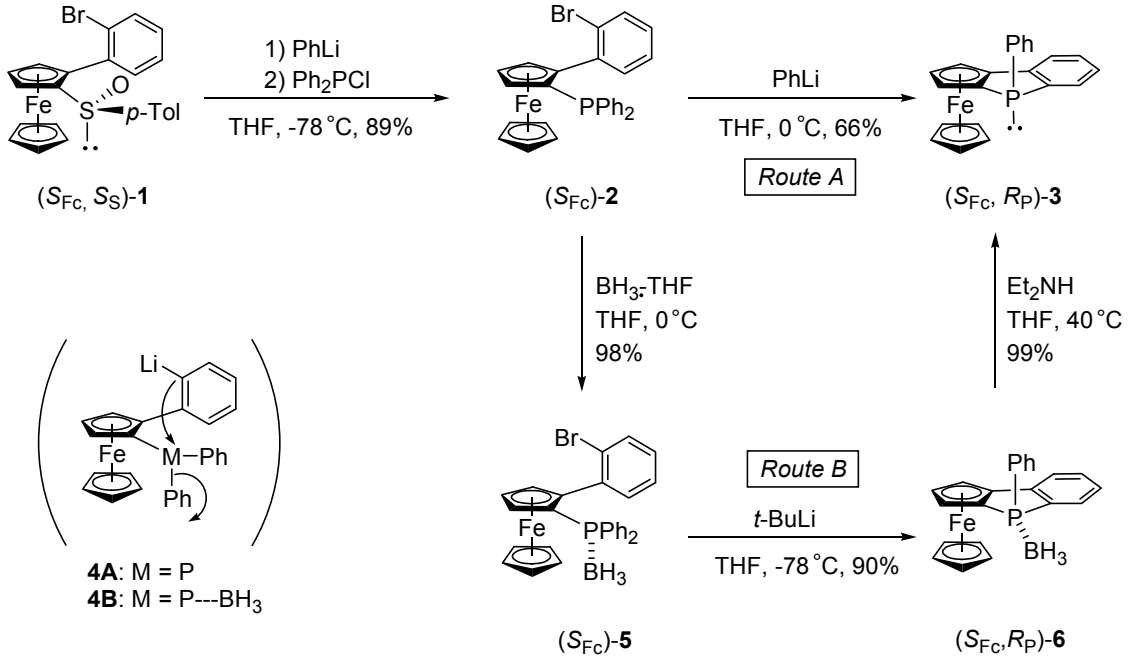
displacement of the substituents on phosphorous with organometallic reagents has been extensively investigated. For instance, reactions of chiral phosphinates and phosphorous-borane complexes with organolithiums and Grignard reagents result in nucleophilic substitution to afford appropriate new P-chirogenic phosphorous compounds.[3] Additionally, the synthesis of optically active cyclic phosphorous compounds has also been widely studied along with its application into a variety of asymmetric syntheses as a chiral auxiliary.[4] However, optically active P-chirogenic ferrocene-fused phospholes have not been reported so far, although the ferrocene back bone was known to provide effective enantiocontrol environment for a wide variety of asymmetric reactions.[5]

We recently reported that the 1,4-dilithio compound, generated from 1-bromo-2-[(*Z*)-2-bromoethenyl]-benzene on treatment with BuLi, reacted with group 15 dihalides (MX_2: M = PPh, AsPh, SbPh, and BiPh) to afford the corresponding benzoheteroles in good yields.[6] In the course of our continuing studies on the synthesis of new heterocyclic compounds, we are interested in the synthesis of novel ferrocene-fused benzoheteroles. Here we report the synthesis of optically active P-chirogenic ferrocene-fused benzophosphole, (S_{Fc},R_P)-4-phenylbenzo[*b*]ferroceno[*d*]phosphole [(–)-**3**], from (S_{Fc},S_S)-1-(2-bromophenyl)-2-(*p*-tolylsulfinyl)ferrocene (**1**) by intramolecular diastereoselective cyclization as a key step in two routes via (S_{Fc})-1-(diphenylphosphanyl)-2-(2-lithiophenyl)ferrocene intermediates (**4**). The absolute configuration of [(–)-**3**] was determined by single crystal X-ray analysis of the palladium complex (**8**) obtained by the reaction of [(–)-**3**] with di-μ-dichlorobis{2-[(dimethylamino)methyl]phenyl-C^1,N}-dipalladium(II) (**7**).

RESULTS AND DISCUSSION

The synthetic routes to P-chirogenic ferrocene-fused benzophosphole (**3**) are shown in Scheme 1. (S_{Fc}, S_S)-1-(2-Bromophenyl)-2-(*p*-tolylsulfinyl)ferrocene (**1**),[7] prepared from (S_S)-ferrocenyl *p*-tolyl sulfoxide by diastereoselective *ortho*-lithiation and Suzuki-Miyaura cross-coupling, was treated with PhLi (3 eq) in dry THF at –78 °C in an argon atmosphere to form 2-lithioferrocene intermediate.[8] Successive addition of chlorodiphenylphosphane (Ph_2PCl) furnished (S_{Fc})-1-(2-bromophenyl)-2-diphenylphosphanylferrocene (**2**) in 89% yield. This reaction afforded **2** exclusively and the bromine moiety on the phenyl group remained intact. In contrast, when *t*-BuLi was employed instead of PhLi for the present reaction, no chemoselective lithium exchange reaction of the *p*-tolylsulfinyl group over the bromine moiety on the phenyl group was observed and the reaction gave a complex mixture. It has been reported that the reaction of 2-bromo-2'-diphenylphosphanyl-1,1'-biphenyl[9] and 2-diphenylphosphanyl-2'-diphenylphosphinyl-1,1'-binaphthyl[10] with BuLi resulted in intramolecular cyclization to form phosphole derivatives via the corresponding lithio intermediates. Thus, we first examined the straightforward transformation of **2** into ferrocenophosphole (**3**) using lithium reagents (Route A). Treatment of **2** with PhLi in THF cooling in an ice bath brought about the expected intramolecular cyclization to give

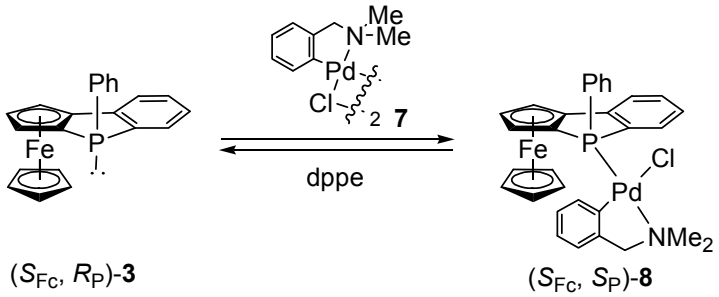
optically active ferrocenophosphole [(–)-**3**] via 2-lithiophenyl intermediate (**4A**) as a red oil in moderate yield (66%). However, the phosphole [(–)-**3**] was formed in low yield (28%) by use of *t*-BuLi instead of PhLi under the same reaction conditions.



As noted above, phosphorous-borane complexes are known to be useful for the synthesis of P-chirogenic phosphorous compounds due to the enhanced stability of quarternary phosphorous by coordination.[3] We next examined an alternative route for the preparation of **3** from **2** via phosphorous-borane complex (Route B). The borane complex (**5**) was prepared from **2** on treatment with borane in THF with ease (98% yield). The reaction of **5** thus obtained with 4 eq of *t*-BuLi in THF at –78 ºC for 10 min, followed by quenching the reaction mixture with methanol gave ferrocene-fused benzophosphole borane complex (**6**) via intermediate **4B** in 90% yield. This result is inconsistent with that of the Hayashi's report, in that the reaction of 2-diphenylphosphanyl-2'-diphenylphosphinyl-1,1'-binaphthyl borane complex with BuLi resulted in chemoselective replacement of the diphenylphosphinyl moiety with lithium to form 2-deuterio-2'-diphenylphosphanyl-1,1'-binaphthyl after quenching with methanol-*d*.[10] In the above reaction of binaphthyl derivative, the phosphorous-borane complex moiety remained unchanged. Finally, the borane complex (**6**) underwent ligand exchange reaction on treatment with diethylamine to give (–)-**3** quantitatively.[11] These results show that the latter Route B (87%) via borane complexes **5** and **6** is superior to the former direct Route A (66%) with respect to the yield of **3**.

The ferrocenophosphole (**3**) isolated here is optically active with the value being $[\alpha]_D^{24}$ –1200 (c 0.81, chloroform). Additionally, the ^{1}H and ^{13}C NMR spectra of (–)-**3** showed a single set of signals, and ^{31}P NMR spectrum also showed only one singlet peak at –21.1 ppm. A similar spectral future was observed in the ^{1}H, ^{13}C and ^{31}P NMR spectra of the borane complex **6** [δ_p: +19.2 ppm (s)]. These results imply that

the intramolecular cyclization of the borane complex (**5**) gave only one of the two diastereomers [(S_{Fc},R_P)-**6** or (S_{Fc},S_P)-**6**].



Scheme 2

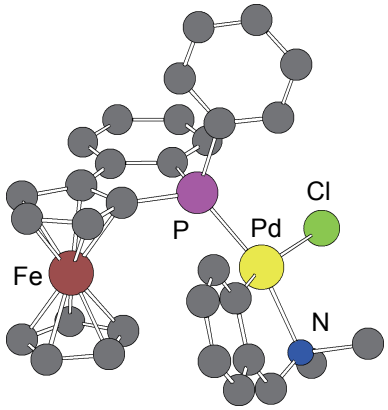


Fig. 1 X-Ray structure of **8**

In order to gain deeper insight into the stereochemistry of the oily ferrocenophosphole (–)-**3**, we examined a derivatization of (–)-**3** into a solid palladium complex (Scheme 2). It has been reported that di-μ-dichloro-bis{2-[(dimethylamino)methyl]phenyl-C^1,N}dipalladium(II) (**7**) reacts with phosphorous (III) compounds to form solid palladium complexes, and is useful not only for the optical resolution but also for the determination of the absolute configuration of P-chirogenic compounds.[12] Treatment of (–)-**3** with **7** in dichloromethane (CH_2Cl_2) at room temperature resulted in coordination of the phosphorus(III) to palladium to give palladium complex (**8**) in 99% yield. The complex (**8**) thus formed is optically active {$[\alpha]_D^{25}$ –1450 (c 0.56, $CHCl_3$)} and ^{31}P NMR spectrum of **8** exhibits a sole singlet peak at +28.6 ppm. These results were suggestive to the predominant formation of one of the two diastereomers [(S_{Fc},S_p)-**8** or (S_{Fc},R_p)-**8**]. The X-ray crystal structure for **8** is illustrated in Fig. 1. The geometry of the cyclopentadienyl and fused benzophosphole moieties are almost planar (mean deviation 0.0404 Å), and the phenyl group on the phosphorous is oriented in the opposite direction to the iron, out of plane to the C_4-P unit of the phosphole ring. Thus, the palladium occupies the endo position and the absolute configuration of the phosphorus center is determined to be *S*. The ligand exchange reaction of **8** with 1,2-bis-(diphenylphosphanyl)ethane in CH_2Cl_2 regenerated **3** {$[\alpha]_D^{24}$ –1198, δ_p: –21.1 ppm} quantitatively.[13] Similar $[\alpha]_D$ values were observed for the phospholes (**3**) obtained by Routes A and B noted above. These results show that the intramolecular cyclizations with Routes A and B afforded only one of the two diastereomers exclusively. It has been reported that the inversion barriers of the P-chirogenic phosphorous atoms of phosphole, phosphindole, and dibenzophosphole derivatives were evaluated to be 67 kJ mol^{-1}, 98 kJ mol^{-1}, and 110 kJ mol^{-1}, respectively.[14] Thus, isolation of optically pure P-chirogenic phosphole derivatives is known to be hard under ambient conditions, although tertiary phosphines are isolable in optically pure form.[3,4,14] However, the diastereomerically pure P-chirogenic phosphole

(S_{Fc},R_P)-(**3**) isolated here is optically stable and no racemization on the chiral phosphorus center was observed at room temperature in chloroform over 24 h. The results imply that the inversion of the phenyl group on the phosphorous in **3** to form endo derivative was strongly interrupted by the steric repulsion between the phenyl group and cyclopentadienyl moiety.

In order to evaluate the ability of P-chirogenic phosphole (**3**) for a chiral auxiliary in asymmetric reaction, we finally examined the Pd-catalyzed hydrosilylation of styrene by the use of (S_{Fc},R_P)-(**3**), because enantiomerically pure monodentate phosphine ligands based on ferrocenyl scaffolds have proved to be so successful in the asymmetric hydrosilylation of olefines.[15,16] The reaction of styrene with trichlorosilane in the presence of $[PdCl(C_3H_5)]_2$ (0.1 mol%) and (S_{Fc},R_P)-(**3**) (0.4 mol%) at 0 °C to rt resulted in the enantioselective hydrosilylation to afford (*R*)-1-phenylethanol (49 %ee) in 39% yield. This preliminary benchmark test showed that the optically active (S_{Fc},R_P)-(**3**) displays moderate catalytic activity and enantioselectivity in the transition metal-catalyzed asymmetric hydrosilylation of styrene.

In conclusion, we succeeded in the synthesis of a novel optically pure P-chirogenic ferrocene-fused benzophosphole (–)-**3** by intramolecular diastereoselective cyclization of 1-diphenylphosphanyl-2-(2-lithiophenyl)ferrocene intermediates. To the best of our knowledge, the ferrocenophosphole (–)-**3** would be the first isolated example of an optically pure phosphole, which is stable under ambient conditions. The X-ray analysis of (–)-**3** revealed that the phenyl group is placed at the opposite direction of iron moiety. Further studies in this area, including application of the phosphole for asymmetric synthesis as a chiral auxiliary and preparation of optically active benzo[*b*]ferroceno[*d*]heteroles consisting of a variety of hetero atoms, are in progress.

EXPERIMENTAL

All reactions were carried out in pre-dried glassware under an argon atmosphere. Dehydrated diethyl ether and THF ware purchased from Kanto Chemical Co., Inc. and used directly without further dehydration. Melting points were taken on a Yanagimoto micro melting point hot-stage apparatus and are not corrected. ^{1}H NMR (TMS: δ 0.00 as an internal standard), ^{13}C NMR ($CDCl_3$: δ 77.00 as an internal standard) and ^{31}P NMR (85% H_3PO_4: δ 0.00 as an external standard) spectra were recorded on JEOL JNM-ECA (400 MHz for ^{1}H and 100 MHz for ^{13}C) and JEOL JNM-ECX (162 MHz for ^{31}P) spectrometers in $CDCl_3$ unless otherwise stated. Mass spectra (MS) and high-resolution mass spectra (HRMS) were obtained on a JEOL JMP-DX300 instrument (70 eV, 300 μA). Optical rotations were measured on a JUSCO DIP-370 digital polarimeter. All chromatographic separations were accomplished with Silica Gel 60N (Kanto Chemical Co., Inc.). Thin-layer chromatography (TLC) was performed with Macherey-Nagel pre-coated TLC plates Sil G25 UV_{254}. (S_{Fc},S_S)-1-(2-Bromophenyl)-2-(*p*-tolylsulfinyl)-ferrocene (**1**)[6] was prepared according to the reported procedures.

(S_{Fc})-1-(2-Bromophenyl)-2-(diphenylphosphanyl)ferrocene (2)

To a stirred solution of PhLi (1.14 M solution in cyclohexane–ether, 13.2 mL, 15 mmol) was added a solution of **1** (2.40 g, 5 mmol) in anhydrous THF (35 mL) dropwise over 15 min at –78 ºC and the solution was stirred for 10 min at the same temperature. Chlorodiphenylphosphine (2.75 mL, 15 mmol) was added at –78 ºC. The reaction mixture was stirred for 1 h at the same temperature. The mixture was allowed to warm slowly to room temperature and stirred for 1 h. The reaction mixture was quenched with water (70 mL) and diluted with CH_2Cl_2 (70 mL). The resulting organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (20 mL x 2). The combined organic layer was washed with brine, dried over $MgSO_4$, and evaporated in vacuo. The residue was subjected to silica gel column chromatography with hexane–CH_2Cl_2 (4:1) to give **2**; orange powder (2.33 g, 89% yield), mp 141–144 ºC (from hexane–CH_2Cl_2). $[\alpha]_D^{25}$ –191 (c 0.63, $CHCl_3$); ^{1}H NMR (400 MHz) δ: 3.79 (1H, br-s, Fc-H), 4.10 (5H, s, Fc-H), 4.45 (1H, br-s, Fc-H), 4.81 (1H, br-s, Fc-H), 7.03-7.57 (13H, m, Ar-H), 8.29 (1H, d, J = 7.8 Hz, Ar-H); ^{13}C NMR (100 MHz) δ: 69.1 (CH), 70.5 (CH), 70.9 (CH), 74.2 (CH), 94.2 (Cq, $J_{c,p}$ = 22.9 Hz), 125.4 (Cq), 126.4 (CH), 127.8 (CH), 128.2 (CH, $J_{c,p}$ = 7.6 Hz), 128.4 (CH), 129.3 (Cq), 131.5 (Cq), 132.1 (CH, $J_{c,p}$ = 18.1 Hz), 132.4 (CH), 134.9 (CH, $J_{c,p}$ = 7.6 Hz), 135.1 (CH, $J_{c,p}$ = 21.0 Hz), 136.9 (Cq); ^{31}P NMR (162 MHz) δ: –21.5 (s); MS (EI) 524 (M^+); Anal. Calcd for $C_{28}H_{22}BrFeP$: C, 64.03; H, 4.22. Found: C, 64.52; H, 4.22.

(S_{Fc},R_P)-4-Phenylbenzo[*b*]ferroceno[*d*]phosphole (3): (S_{Fc},R_P)-4-Phenyl-(η^5-2,4-cyclopentadien-1-yl)-{benzo[*b*](1,2,3,3$_a$,8$_b$-η)-1-hydro-2-cyclopenteno[*d*]phosphol-1-yl} iron from 2

To a solution of **2** (100 mg, 0.19 mmol) in anhydrous THF (7 mL) was added a solution of PhLi (1.14 M solution in cyclohexane–ether, 0.43 mL, 0.5 mmol) over 5 min at 0 ºC and the mixture was stirred for 1 h. The reaction mixture was quenched with water (20 mL) and diluted with CH_2Cl_2 (40 mL). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (20 mL x 2). The combined organic layer was washed with brine, dried over $MgSO_4$, and evaporated in vacuo. The residue was subjected to silica gel column chromatography with hexane–CH_2Cl_2 (3:1) to give (S_{Fc},R_P)-**3** as a red oil, (46 mg, 66% yield); $[\alpha]_D^{24}$ –1200 (c 0.81, chloroform); ^{1}H NMR (400 MHz) δ: 3.98 (5H, s, Fc-H), 4.43 (1H, t, J = 2.3 Hz, Fc-H), 4.71 (1H, d, J = 2.3 Hz, Fc-H), 4.79 (1H, d, J = 2.3 Hz, Fc-H), 7.12–7.29 (7H, m, Ar-H), 7.47 (1H, d, J = 7.3 Hz, Ar-H), 7.52 (1H, t, J = 6.8 Hz); ^{13}C NMR (100 MHz) δ: 62.0 (CH), 69.0 (CH, $J_{c,p}$ = 12.4 Hz), 71.0 (CH), 72.6(CH, $J_{c,p}$ = 2.9 Hz), 84.3 (Cq), 93.4 (Cq), 120.8 (CH), 125.4 (CH, $J_{c,p}$ = 7.6 Hz), 128.3 (CH, $J_{c,p}$ = 6.7 Hz), 128.5 (CH), 128.7 (CH), 130.8 (CH, $J_{c,p}$ = 22.8 Hz), 131.7 (CH, $J_{c,p}$ = 20.0 Hz), 138.9 (Cq, $J_{c,p}$ = 11.9 Hz), 143.2 (Cq), 146.5 (Cq, $J_{c,p}$ = 8.5 Hz); ^{31}P NMR (162 MHz) δ: –21.1 (s); MS (EI) 368 (M^+); HRMS Calcd for $C_{22}H_{17}FeP$ 368.0417. Found 368.0417.

(S_{Fc})-2-(Boranatodiphenylphosphanyl)-1-(2-bromophenyl)ferrocene (5)

To a solution of **2** (1.57 g, 3 mmol) in anhydrous THF (30 mL) was added borane–THF complex (1.03 M solution in THF, 14.6 mL, 15 mmol) dropwise over 10 min at 0 ºC. After stirring for an additional 1 h at the same temperature, the mixture was allowed to warm slowly to room temperature and stirred for 1 h. The reaction mixture was quenched with water (50 mL) and diluted with CH_2Cl_2 (100 mL). The resulting organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (20 mL x 2). The combined organic layer was washed with brine, dried over $MgSO_4$, and evaporated in vacuo. The residue was subjected to silica gel column chromatography with hexane–CH_2Cl_2 (3:1) to give **5**; orange prisms (1.57 g, 98% yield), mp 203–205 ºC (from hexane–CH_2Cl_2). $[\alpha]_D^{25}$ –48 (c 0.14, $CHCl_3$); ^{1}H NMR (400 MHz) δ: 1.17–1.44 (3H, br, BH_3), 4.41 (6H, s, Fc-H), 4.63 (1H, s, Fc-H), 4.68 (1H, s, Fc-H), 6.88–7.62 (14H, m, Ar-H); ^{13}C NMR (100 MHz) δ: 70.1 (CH, $J_{c,p}$ = 7.7 Hz), 70.6 (Cq), 71.1 (CH), 74.1 (CH, $J_{c,p}$ = 11.4 Hz), 75.9 (CH, $J_{c,p}$ = 5.7 Hz), 93.8 (Cq, $J_{c,p}$ = 6.7 Hz), 125.9 (Cq), 126.1 (CH), 128.1 (CH, $J_{c,p}$ = 10.5 Hz), 128.2 (CH, $J_{c,p}$ = 7.5 Hz), 128.5 (CH), 129.0 (Cq, $J_{c,p}$ = 58.1 Hz), 130.6 (CH, $J_{c,p}$ = 2.8 Hz), 130.7 (CH, $J_{c,p}$ = 2.8 Hz), 131.6 (Cq, $J_{c,p}$ = 59.1 Hz), 131.6 (CH), 132.8 (CH, $J_{c,p}$ = 9.6 Hz), 133.4 (CH, $J_{c,p}$ = 9.6 Hz), 135.4 (Cq), 136.0 (CH); ^{31}P NMR (162 MHz) δ: +17.5 (d, J = 56.4 Hz); MS (EI) 538 (M^+); Anal. Calcd for $C_{28}H_{25}BBrFeP$: C, 62.39; H, 4.67. Found: C, 61.31; H, 4.74.

(S_{Fc},R_P)-4-Phenylbenzo[*b*]ferroceno[*d*]phosphole borane complex (6)

To a solution of **5** (1.00 g, 1.86 mmol) in anhydrous THF (17 mL) was added *t*-BuLi (1.58 M in pentane, 4.7 mL, 7.42 mmol) dropwise over 10 min at –78 ºC and the solution was stirred for 10 min at the same temperature. The reaction mixture was quenched with methanol (3 mL) and diluted with water (30 mL) and CH_2Cl_2 (50 mL). The resulting organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (20 mL x 2). The combined organic layer was washed with brine, dried over $MgSO_4$, and evaporated in vacuo. The residue was subjected to silica gel column chromatography with hexane–CH_2Cl_2 (2:1) to give **6**; orange amorphous (639 mg, 90% yield). $[\alpha]_D^{24}$ –1,210 (c 0.94, chloroform); ^{1}H NMR (400 MHz) δ: 1.25–1.55 (3H, br, BH_3), 4.21 (5H, s, Fc-H), 4.63 (1H, dt, J = 2.2, 2.3 Hz, Fc-H), 4.66 (1H, d, J = 2.2 Hz, Fc-H), 4.92 (1H, d, J = 2.3 Hz, Fc-H), 7.21–7.59 (9H, m, Ar-H); ^{13}C NMR (100 MHz) δ: 63.8 (CH, $J_{c,p}$ = 4.8 Hz), 68.3 (CH, $J_{c,p}$ = 10.5 Hz), 71.6 (CH), 74.1 (CH, $J_{c,p}$ = 6.6 Hz), 75.2 (Cq, $J_{c,p}$ = 70.5 Hz), 92.8 (Cq, $J_{c,p}$ = 11.5 Hz), 121.3 (CH, $J_{c,p}$ = 5.8 Hz), 126.7 (CH, $J_{c,p}$ = 10.5 Hz), 128.5 (CH, $J_{c,p}$ = 9.5 Hz), 130.7 (CH, $J_{c,p}$ = 13.3 Hz), 130.9 (Cq, $J_{c,p}$ = 48.7 Hz), 130.9 (CH, $J_{c,p}$ = 2.8 Hz), 131.3 (CH), 131.4 (CH, $J_{c,p}$ = 6.8 Hz), 137.4 (Cq, $J_{c,p}$ = 60.1 Hz), 143.3 (Cq, $J_{c,p}$ = 4.8 Hz); ^{31}P NMR (162 MHz) δ: +19.2 (d, J = 56.4 Hz); MS (EI) 382 (M^+); HRMS Calcd for $C_{22}H_{20}BFeP$ 382.0745. Found 382.0755.

(S_{Fc},R_P)-4-Phenylbenzo[*b*]ferroceno[*d*]phosphole (3) from borane complex (6)

To a solution of **6** (600 mg, 1.57 mmol) in anhydrous THF (18 mL) was added diethylamine (2.60 mL, 25 mmol) at room temperature, and the mixture was stirred at 40 ºC for 1 h. The reaction mixture was concentrated in vacuo and the resulting residue was subjected to column chromatography on silica gel with hexane–CH_2Cl_2 (1:1) to give (S_{Fc},R_P)-**3** (572 mg, 99% yield). The ^{1}H NMR of the product **3** obtained here was superimposable to that of (S_{Fc}, R_P)-**3** shown above.

(S_{Fc},S_P)-4-Phenylbenzo[*b*]ferroceno[*d*]phosphole palladium complex (8)

To a stirred solution of (–)-**3** (200 mg, 0.54 mmol) in CH_2Cl_2 (10 mL), solids of di-μ-dichloro-bis-{2-[(dimethylamino)methyl]phenyl-C^1, N}dipalladium(II) (**7**) (152 mg, 0.272 mmol) was added in small portions at room temperature and the mixture was stirred for 1 h. The reaction mixture was concentrated in vacuo, and the resulting residue was subjected to silica gel column chromatography with CH_2Cl_2 to give **8**; orange prisms (346 mg, 99% yield), mp 207–209 ˚C (from benzene). $[\alpha]_D^{25}$ –1450 (c 0.56, $CHCl_3$); ^{1}H NMR (400 MHz) δ: 2.71 (3H, s, NMe), 3.00 (3H, br-s, NMe), 3.60 (1H, d, J = 13.7 Hz, CH), 4.19 (5H, s, Fc-H), 4.51 (2H, br-s, Fc-H), 4.59 (1H, d, J = 13.7 Hz, CH), 4.84 (1H, s, Fc-H), 6.81 (1H, t, J = 7.3 Hz, Ar-H), 6.94 (1H, t, J = 7.3 Hz, Ar-H), 7.04 (1H, t, J = 7.3 Hz, Ar-H), 7.13 (1H, d, J = 7.3 Hz, Ar-H), 7.26–7.82 (8H, m, Ar-H), 8.15 (1H, br, Ar-H); ^{13}C NMR (100 MHz) δ: 48.9 (CH_3), 51.6 (CH_3), 63.4 (CH, $J_{c,p}$ = 4.7 Hz), 72.0 (CH), 73.2 (CH_2), 73.7 (CH, $J_{c,p}$ = 7.7 Hz), 75.5(Cq), 93.4 (Cq), 120.6 (CH, $J_{c,p}$ = 5.7 Hz), 123.1 (CH), 124.6 (CH), 125.2 (CH, $J_{c,p}$ = 6.7 Hz), 125.9 (CH, $J_{c,p}$ = 10.4 Hz d), 128.3 (CH), 128.5 (CH, $J_{c,p}$ = 10.4 Hz), 130.3 (CH), 130.6 (CH), 132.9 (CH, $J_{c,p}$ = 13.3 Hz), 133.0 (Cq), 135.1 (CH), 136.9 (CH, $J_{c,p}$ = 14.3 Hz), 141.7 (Cq), 148.2 (Cq), 149.6 (Cq); ^{31}P NMR (162 MHz) δ: +28.6 (s); MS (EI) 643 (M^+); Anal. Calcd for $C_{31}H_{29}ClFeNPPd$: C, 57.79; H, 4.54; N, 2.17. Found: C, 58.57; H, 4.70; N, 2.18.

Ligand exchange reaction of 8

To a stirred solution of **8** (193 mg, 0.3 mmol) in CH_2Cl_2 (10 mL) was added 1,2-bis(diphenyl-phosphanyl)ethane (131 mg, 0.33 mmol) at room temperature and the mixture was stirred for 30 min. The reaction mixture was concentrated in vacuo and the resulting residue was subjected to column chromatography on silica gel with hexane–CH_2Cl_2 (2:1) to afford **3**; red oil (108 mg, 98% yield), $[\alpha]_D^{23}$ –1198 (c 0.55, $CHCl_3$). The ^{1}H NMR spectrum of the product was superimposable to that of (S_{Fc}, R_P)-**3** shown above.

Enantioselective hydrosilylation of styrene by the use of (S_{Fc}, R_P)-3

To a mixture of $[PdCl(C_3H_5)]_2$ (3.6 mg, 0.01 mmol), (S_{Fc}, R_P)-**3** (14.9 mg, 0.04 mmol), and styrene (1.1 mL, 10 mmol) was added trichlorosilane (1.2 mL, 12 mmol) at 0 °C, and the mixture was stirred for 24 h

at rt. The reaction mixture was poured into a suspension of KF (10 g) in methanol (80 mL) and stirred for 30 min. After concentration of the reaction mixture in vacuo, the resulting residue was suspended in DMF (100 mL) and 30% H_2O_2 aq (10 mL) and then the mixture was heated at 65 °C for 1 h. The reaction mixture was dissolved with CH_2Cl_2 (100 mL) and water (50 mL). The organic layer was separated, and the water layer was re-extracted with CH_2Cl_2 (50 mL × 2). The combined organic layer was washed with water (100 mL × 5), dried over anhydrous Na_2SO_4, and concentrated in vacuo. The resulting residue was subjected to column chromatography on silica gel with CH_2Cl_2–AcOEt (10:1) to give (*R*)-1-phenylethano (455 mg, 39% yield). The absolute configuration (*R*) and enantiomeric excess (49%ee) of the product were determined by chiral HPLC column [Dicel, Chiral OD-H, eluent: hexane–*i*-PrOH (95:5)].[16]

Crystal data for [(S_{Fc},S_P)-3] palladium complex (8)

Crystal dimensions 0.45 x 0.40 x 0.23 mm^3; $C_{37}H_{35}ClFeNPPd$, M = 722.33; triclinic space group $P1$, a = 9.8984(12) Å, b = 10.0882(12) Å, c = 17.851(2) Å, α = 85.935(2)º, β = 79.986(2)º, γ = 64.404(2)º, V = 1583.1(3) $Å^3$, Z = 2, D_{calc} = 1.515 $g \cdot cm^{-3}$, T = 90 K, 8309 unique and 7812 observed [$I > 2\sigma(I)$] reflections, 761 parameters, final [$I > 2\sigma(I)$] R_1 = 0.0333, wR_2 = 0.0839, S = 1.069, Flack parameter = -0.007(18), Data collections were performed using a Bruker SMART 1000 CCD area detector diffractometer with Mo Kα radiation(λ = 0.71073 Å). The structure was solved by direct methods and refined by full-matrix least squares refinements based on F^2. All hydrogen atoms were anisotropically refined. Hydrogen atoms were added geometrically and refined with a riding model. Structure solutions were performed with the SHELXS-97 and SHELXL-97.[17] Full details of the crystallographic results have been deposited with the Cambridge Crystallographic Data Center [no. CCDC 747789].

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REFERENCES

1. I. Ojima, Ed., 'Catalytic Asymmetric Synthesis, Second Edition,' Wiley-VCH, New York, 2000.
2. For selected recent reviews, see; P.-H. Leung, *Acc. Chem. Res*., 2004, **37**, 169; K.-V. L. Crépy and T. Imamoto, *Adv. Synth. Catal*., 2003, **345**, 79; K.-V. L. Crépy and T. Imamoto, 'Topics in current Chemistry: New Aspects in Phosphorous Chemistry III, New P-Chirogenic Phosphine ligands and Their Use in Catalytic Asymmetric Synthesis,' Vol. 229, Springer, Berlin, 2003, pp. 1-40.

3. A. Grabulosa, J. Granell, and G. Muller, *Coord. Chem. Rev*., 2007, **251**, 25.
4. J. Holz, M.-N. Gensow, O. Zayas, and A. Börner, *Curr. Org. Chem*., 2007, **11**, 61.
5. P. Štěpnička, Ed., 'Ferrocenes: Ligands, Materials and Biomolecules,' John Wiley & Sons, Ltd., England, 2008; R. G. Arrayás, J. Adrio, and J. C. Carretero, *Angew. Chem. Int. Ed*., 2006, **45**, 7674.
6. J. Kurita, M. Ishii, S. Yasuike, and T. Tsuchiya, *J. Chem. Soc., Chem. Commun.*, 1993, 1309; J. Kurita, M. Ishii, S. Yasuike, and T. Tsuchiya, *Chem. Pharm. Bull*., 1994, **42**, 1437; A. Muranaka, S. Yasuike, C.-Y. Li, J. Kurita, N. Kakusawa, T. Tsuchiya, M. Okuda, N. Kobayashi, Y. Matsumoto, K. Yoshida, D. Hashizume, and M. Uchiyama, *J. Phys. Chem. A*, 2009, **113**, 464.
7. J. F. Jensen, I. Stofte, H. O. Srensen, and M. Johannsen, *J. Org. Chem*., 2003, **68**, 1258.
8. R. J. Kloetzing and P. Knochel, *Tetrahedron: Asymmetry*, 2006, **17**, 116.
9. H. Bruner and M. Janura, *Synthesis*, 1998, 45.
10. T. Shimada, H. Kurushima, Y.-H. Cho, and T. Hayashi, *J. Org. Chem*., 2001, **66**, 8854.
11. T. Imamoto, T. Kusumoto, N. Suzuki, and K. Sato, *J. Am. Chem. Soc*., 1985, **107**, 5301; E. A. Colby and T. F. Jamison, *J. Org. Chem*., 2003, **68**, 156.
12. J. Leitch, G. Salem, and D. C. R. Hockless, *J. Chem. Soc., Dalton Trans*., 1995, 649.
13. S.-K. Loh, G.-K. Tan, L. L. Koh, S. Selvaratnam, and P.-H. Leung, *J. Organomet. Chem*., 2005, **690**, 4933.
14. W. Egan, R. Tang, G. Zon, and K. Mislow, *J. Am. Chem. Soc*., 1971, **93**, 6205.
15. S. E. Gibson and M. Rudd, *Adv. Synth. Catal*., 2007, **349**, 781; T. Hayashi, *Acc. Chem. Res*., 2000, **33**, 354.
16. S. Yasuike, S. Kawara, S. Okajima, H. Seki, K. Yamaguchi, and J. Kurita, *Tetrahedron Lett*., 2004, **45**, 9135.
17. G. M. Sheldrick, *Acta Cryst*., 2008, **A64**, 112**.**