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Communication

Synthesis, Characterization, and Application of Segphos Derivative Having Diferrocenylphosphino-Donor Moieties

Hao Hu, Hiroki Ichiryu, Naoki Seki, Kiyohiko Nakajima, Yasuhiro Ohki, and Masamichi Ogasawara*

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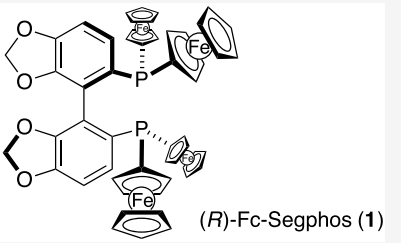
ABSTRACT: An axially chiral bisphosphine, Fc-Segphos (**1**), which possesses diferrocenylphosphino-donor moieties, was prepared as a racemate, and its optical resolution was achieved by the use of chiral HPLC. Ligand **1** coordinated to a palladium(II) cation in a bidentate fashion to construct a unique chiral environment at the palladium center due to the sterically demanding ferrocenyl groups. Ligand (*R*)-**1** was applied in the palladium-catalyzed asymmetric synthesis of axially chiral allenes showing good enantioselectivity of up to 92% ee. In general, (*R*)-**1** displayed better enantioselectivity than the parent Segphos in the palladium-catalyzed reaction, and the Pd/(*R*)-**1** species showed up to 18% ee enhancement over the (*R*)-Segphos-derived palladium catalyst.



Many conventional chiral bisphosphine ligands, such as Diop,[1] Binap,[2] and Segphos,[3] possess diphenylphosphino groups as their donor moieties.[4] Upon their chelate coordination to a transition-metal atom/cation, the conformations of the four phosphorus-bound phenyl groups are regulated by a chiral backbone to create an effective chiral environment around the metal center (Figure 1). In other words, the phosphorus-bound phenyl groups are primal components constructing the chiral pockets in the chiral metal complexes. Consequently, steric and electronic modifications of the phenyl groups have been common strategies to modify the properties of the chiral phosphine ligands. Some representative aryl groups frequently used for these purposes include 4-methylphenyl (*p*-tolyl; Tol), 3,5-dimethylphenyl (3,5-xylyl; Xyl), 3,5-di-*tert*-butyl-4-methoxyphenyl (DTBM), 3,5-bis(trifluoromethyl)phenyl, etc.

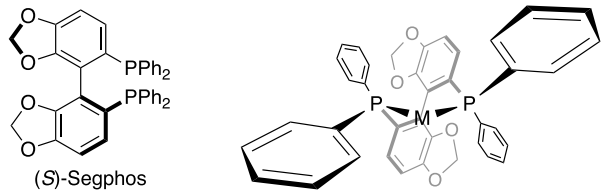


Figure 1. Structure of (*S*)-Segphos and its 3D representation in a metal complex.

Ferrocene is an 18-electron organometallic compound with an aromatic character.[5] While classical benzenoid aromatics are flat-shaped molecules, ferrocene is a cylinder-shaped three-dimensional compound. Ferrocene is also known to be a very electron rich molecule showing the high activity in electrophilic aromatic substitution reactions. Ferrocene derivatives have played important roles in organophosphine chemistry as frameworks in chelating bisphosphine ligands. For example, 1,1′-bis(diphenylphosphino)ferrocene (dppf)[6] has been utilized as a useful ancillary ligand in the palladium-catalyzed cross-coupling reaction[7] as well as in the palladium-catalyzed amination.[8] Unsymmetrically substituted (1,2-ferrocenylene)-phosphine derivatives, such as PPFA[9] and Josiphos,[10] are planar-chiral, and they are one of the most successful classes of chiral phosphine ligands to date.[11] On the other hand, applications of a monovalent ferrocenyl group in organophosphine chemistry have received little attention.[12] Since the ferrocenyl (Fc) group possesses peculiar electronic/steric properties,[13] which are significantly different from those of benzenoid aryl groups, we are interested in introducing diferrocenylphosphino groups in a chiral bisphosphine ligand in place of the diphenylphosphino groups.

In this communication, the synthesis and applications of a Segphos derivative having diferrocenylphosphino moieties (Fc-Segphos **1**) are reported in detail.

The designed Fc-Segphos **1** was prepared as outlined in Scheme 1. Commercially available 5-bromo-1,3-benzodioxole was converted to the corresponding Grignard reagent, and a subsequent reaction with chlorodiferrocenylphosphine followed by oxidative workup with hydrogen peroxide gave phosphine oxide **2** in 63% yield. Deprotonation of **2** with lithium 2,2,6,6-tetramethylpiperidide (LTMP) took place highly regioselectively at the 4-position of the benzodioxole moiety, and a subsequent oxidative homocoupling using iron(III) chloride afforded axially chiral *rac*-**3** in 50% yield. The enantiomeric resolution of *rac*-**3** was achieved by HPLC on a chiral stationary phase column (Daicel Chiralpak IA), and

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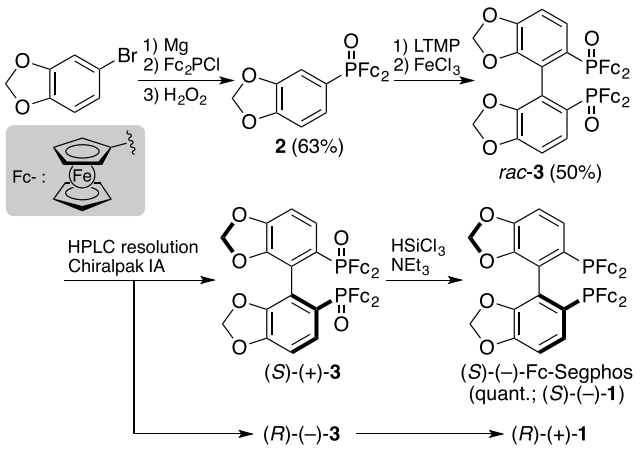
Scheme 1. Preparation of (*S*)- and (*R*)-Fc-Segphos



(+)- and (−)-**3** were obtained in enantiomerically pure forms. Reduction of the respective enantiomers of **3** using trichlorosilane/triethylamine furnished (*S*)- and (*R*)-Fc-Segphos **1** quantitatively. Bisphosphine **1** is reasonably air stable in the solid state, and the crystalline sample of **1** stored under air for a few months showed oxidation of less than the detection limit by the ^{31}P NMR analysis.

The dextrorotatory enantiomer of **3** was recrystallized by slow diffusion of diethyl ether into its concentrated dichloromethane solution, yielding red-orange prisms. Single-crystal X-ray crystallography revealed that the compound was a single enantiomer. The unit cell contains two independent molecules, having slightly different conformations. The Flack parameter was determined to be −0.009(18), and the absolute configuration of (+)-**3** was unambiguously assigned to be *S* (see the Supporting Information for details). Interestingly, all the ferrocenyl substituents take eclipsed conformations with slightly distorted dihedral angles between the two Cp planes ranging from 2.20 to 4.29°.

Dissolving an equimolar mixture of Fc-Segphos **1** and $PdCl_2$(cod) in chloroform showed quantitative conversion to $PdCl_2$(Fc-Segphos) (**4**) in the time of mixing. The ^{31}P NMR signal of free **1**, detected at δ_P −38.5, shifted downfield to δ_P 11.6 upon the coordination to the Pd(II) center. The racemic complex showed better crystallinity, and single crystals of *rac*-**4** were grown as deep red prisms by recrystallization from chloroform/dichloromethane/pentane. X-ray crystallography disclosed that the unit cell contained the pair (*R*)-**4** and (*S*)-**4**, which were nearly isostructural with each other, and the structure of (*S*)-**4** is shown in Figure 2 with selected bond lengths and angles (see the Supporting Information for space-filling drawings of the X-ray structure of *rac*-**4**). The seven-membered chelate is highly skewed. The four ferrocenyl substituents are located in an alternating "face and edge" manner. In complex **4**, all the FeCp fragments are located away from Pd1, minimizing the steric congestion around the palladium atom. The two ferrocenyl substituents, **Fc1** and **Fc3**, show nonbonding interactions with H6 and H13, respectively, leading to the distortion of the ferrocenyl units. The dihedral angles between the two cyclopentadienyl planes are 7.32° in **Fc1** and 8.85° in **Fc3**. Due to the steric hindrance between Cl1 and **Fc1** as well as between Cl2 and **Fc3**, the Cl1 and Cl2 atoms are situated above and below the P1−Pd1−P2 plane, respectively. The dihedral angle between the P1Pd1P2 plane and the Cl1Pd1Cl2 plane is 17.95°. The geometry

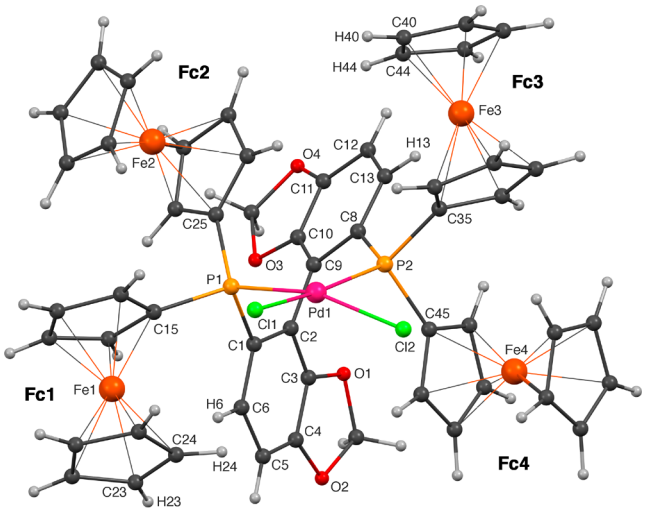


Figure 2. Ball-and-stick drawing of the X-ray structure of *rac*-$PdCl_2$(Fc-Segphos) with selected atom numbering. Cocrystallized solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd1−P1 = 2.246(1), Pd1−P2 = 2.296(1), Pd1−Cl1 = 2.330(1), Pd1−Cl2 = 2.358(1), C2−C9 = 1.484(9); P1−Pd1−P2 = 94.07(5), Cl1−Pd1−P1 = 92.33(6), Cl1−Pd1−Cl2 = 87.96(6), Cl2−Pd1−P2 = 87.77(6), dihedral angles between the two Cp planes in a Fc substituent 7.32 (in **Fc1**), 3.88 (in **Fc2**), 8.85 (in **Fc3**), and 2.26 (in **Fc4**); nonbonding distances H6−H23 = 2.394, H6−H24 = 2.361, H13−H40 = 2.493, and H13−H44 = 2.369.

around Pd1 is distorted square planar, the sum of four angles at Pd1 involving Cl1, Cl2, P1, and P2 being 362.13°. The bite angle, P1−Pd1−P2, in **4** is 94.07°, which is considerably larger than those in $PdCl_2$(Segphos) (90.95°)[14] and $PdCl_2$(Binap) (92.63°).[15] This can be attributed to the bulkiness of the ferrocenyl substituents. In accordance with this, the biarylic dihedral angle between the two 1,3-benzodioxole planes in **4** (66.00°) is much larger than that in $PdCl_2$(Segphos) (59.30°).

While the two faces of the each phenyl substituent in Segphos are homotopic, the two faces of each phosphorus-bound C_5H_4 moiety in Fc-Segphos are heterotopic due to the η^5 coordination of the FeCp fragment onto one side of the planar C_5H_4. The ferrocenyl groups are fairly bulky, and the four Fc groups in **4** protrude in different directions to avoid steric congestion, which breaks the symmetry of the complex. Hence, the overall geometry of **4** in the solid state is C_1 symmetric and significantly different from that in $PdCl_2$(Segphos), which is roughly C_2 symmetric (Figure 3a).[14] The side view of the X-ray structure of **4** clearly

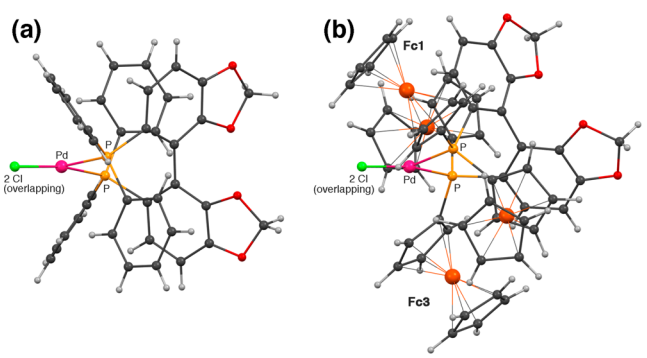


Figure 3. Side views of the X-ray structures of (a) $PdCl_2$(Segphos) and (b) $PdCl_2$(Fc-Segphos) (**4**).

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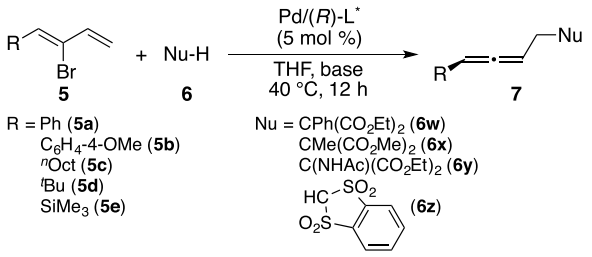
Organometallics XXXX, XXX, XXX−XXX

displays the bulkiness of the ferrocenyl substituents; the two ferrocenyl groups, **Fc1** and **Fc3**, stick out over the Pd−Cl bonds and are shielding certain spaces of the potential reaction sites in the d^8 complex (Figure 3b).

The potential of Fc-Segphos **1** was examined in the Pd-catalyzed asymmetric synthesis of axially chiral allenes.[16] For a direct comparison between Segphos and **1**, two reactions, one with (*R*)-Segphos and the other with (*R*)-**1**, were set up simultaneously and carried out side by side under identical conditions. The results are summarized in Table 1. While the

Table 1. Palladium-Catalyzed Asymmetric Synthesis of Axially Chiral Allenes[a]



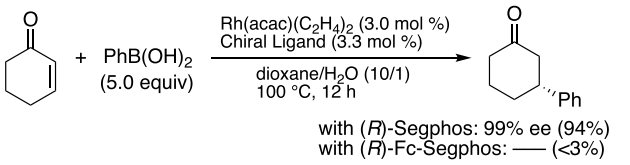
entry	5	6	base	Ar in L*	yield (%)[b]	% ee[c,d]
1	**5a**	**6w**	CsO^{t}Bu	Ph	95 (**7aw**)	73 (*R*)
2				DTBM	84 (**7aw**)	74 (*R*)
3				Fc	86 (**7aw**)	86 (*R*)
4	**5b**	**6x**	NaH	Ph	98 (**7bx**)	66 (*R*)
5				Fc	95 (**7bx**)	84 (*R*)
6	**5c**	**6x**	NaH	Ph	95 (**7cx**)	68 (*R*)
7				Fc	92 (**7cx**)	74 (*R*)
8	**5d**	**6y**	CsO^{t}Bu	Ph	91 (**7dy**)	90 (*R*)
9				Fc	90 (**7dy**)	92 (*R*)
10	**5e**	**6z**	NaH	Ph	96 (**7ez**)	76 (*R*)
11				Fc	82 (**7ez**)	87 (*R*)

[a]All reactions were carried out with **5** (0.20 mmol), **6** (0.23 mmol), and base (0.25 mmol) in THF (2.0 mL) for 12 h in the presence of a Pd catalyst (5 mol %) generated from $Pd(dba)_2$ and the chiral phosphine. [b]Isolated yield by chromatography on alumina. [c]Determined by chiral HPLC (Chiralpak AS-H (**7aw**), Chiralpak AD-H (**7bx**), Chiralpak IB (**7cx** and **7ez**)), or Chiralpak IA (**7dy**). [d]The absolute configurations were deduced by the Lowe−Brewster rule.[17]

Pd/(*R*)-Segphos and the Pd/(*R*)-DTBM-Segphos catalysts gave the axially chiral allene (*R*)-**7aw** in 73% ee and 74% ee, respectively, for the reaction of **5a** with **6w** (entries 1 and 2), the Pd/(*R*)-**1** catalyst afforded (*R*)-**7aw** in 86% ee under otherwise identical conditions except for the ligand (entry 3). In the same way, (*R*)-**1** exhibited better enantioselectivity than the parent (*R*)-Segphos for the reaction of **5b** and **6x** to give (*R*)-**7bx** (66% ee vs 84% ee; entries 4 and 5), **5c** and **6x** to give (*R*)-**7cx** (68% ee vs 74% ee; entries 6 and 7), and **5d** and **6y** to give (*R*)-**7dy** (90% ee vs 92% ee; entries 8 and 9). The reaction with a nucleophile derived from bis-sulfone **6z** and NaH also showed the advantage of (*R*)-**1** over (*R*)-Segphos. The axially chiral allene **7ez** in 76% ee was obtained in 96% yield using Segphos (entry 10). In comparison, the Pd/Fc-Segphos system afforded **7ez** with 87% ee in 82% yield under the same conditions (entry 11).

In contrast, Fc-Segphos **1** was not effective in rhodium-catalyzed asymmetric conjugate addition.[18] For the reaction of cyclohexenone with phenylboronic acid, the Rh/(*R*)-Segphos catalyst gave (*R*)-3-phenylcyclohexanone in 99% ee and 94% yield. On the other hand, Rh/(*R*)-**1** was catalytically nearly inert, and the addition product was obtained in less than 3% yield. The stereodetermining intermediates in the two reactions, shown in Table 1 and Scheme 2, are quite different

Scheme 2. Rhodium-Catalyzed Asymmetric 1,4-Addition of Phenylboronic Acid to 2-Cyclohexenone



from each other. While the palladium-catalyzed reaction proceeds via a (1,2,3-η^3-butadien-3-yl)palladium intermediate,[16a,19] the key intermediate of the rhodium-catalyzed reaction was suggested to be Rh(Ph)(η^2-cyclohexenone)(bisphosphine).[18] Apparently, the Rh/Fc-Segphos species could not accommodate the phenyl group and η^2-cyclohexenone simultaneously due to the sterically demanding ferrocenyl substituents in the bisphosphine ligand. Accordingly, the Rh/Fc-Segphos species was inactive for the 1,4-addition reaction.

In summary, a novel axially chiral bisphosphine ligand, Fc-Segphos **1**, was prepared. Upon its chelate coordination to a transition metal, **1** creates a unique chiral environment in the complex due to the diferrocenylphosphino-donor moieties. Ligand **1** was used in the palladium-catalyzed asymmetric synthesis of axially chiral allenes, showing up to 18% ee enhancement over a palladium catalyst derived from parent Segphos. Although the superiority of **1** is not universal, we believe that **1** should prove useful for other transition-metal-catalyzed asymmetric reactions.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.9b00865.

Full experimental procedures, NMR spectra (^{1}H, ^{13}C, and ^{31}P) for all of the new compounds, and chiral HPLC chromatograms (PDF)

Accession Codes

CCDC 1972843 and 1972914 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

■ AUTHOR INFORMATION

Corresponding Author

Masamichi Ogasawara − *Department of Natural Science, Graduate School of Science and Technology and Research Cluster on "Innovative Chemical Sensing", Tokushima University, Tokushima 770-8506, Japan;* orcid.org/0000-0002-1893-3306; Email: ogasawar@tokushima-u.ac.jp

Authors

Hao Hu − *Department of Natural Science, Graduate School of Science and Technology, Tokushima University, Tokushima*

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Organometallics XXXX, XXX, XXX−XXX

770-8506, Japan
Hiroki Ichiryu − *Department of Natural Science, Graduate School of Science and Technology, Tokushima University, Tokushima 770-8506, Japan*
Naoki Seki − *Faculty of Integrated Arts and Sciences, Tokushima University, Tokushima 770-8502, Japan*
Kiyohiko Nakajima − *Department of Chemistry, Aichi University of Education, Kariya 448-8542, Japan*
Yasuhiro Ohki − *Department of Chemistry, Graduate School of Science, Nagoya University, Nagoya 464-8602, Japan;* orcid.org/0000-0001-5573-2821

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.organomet.9b00865

Notes

The authors declare no competing financial interest.

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Organometallics XXXX, XXX, XXX−XXX