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Communication

C_1-Symmetric Binap Derivative Featuring Single Diferrocenylphosphino-Donor Moiety

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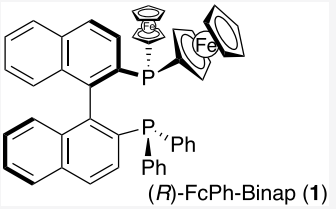
ABSTRACT: A C_1-symmetric chiral bisphosphine, FcPh-Binap (**1**), which possesses a single diferrocenylphosphino moiety together with a conventional Ph_2P-substituent, was prepared in enantiomerically pure forms. Ligand **1** is sterically less demanding than Fc-Segphos (**A**), which has two diferrocenylphosphino groups, and showed higher activity than **A** in the rhodium-catalyzed asymmetric conjugate addition of phenylboronic acid to 2-cyclohexenone. Ligand **1** was applied in the two palladium-catalyzed asymmetric reactions, namely the synthesis of axially chiral allenes and the intermolecular Heck reaction, and displayed higher enantioselectivity than parent Binap. The Pd/(*R*)-**1** species showed up to 47% ee enhancement over the Pd/(*R*)-Binap catalyst in the former reaction and up to 39% ee enhancement in the latter.



Chiral phosphines are arguably the most common chiral auxiliaries in asymmetric metal catalysis.[1] Accordingly, the design of novel chiral phosphines has been a central subject in the development of metal-catalyzed asymmetric transformations. In a metal catalyst coordinated with chiral phosphine(s), phosphorus-bound substituents are primal elements to create the chiral environment at the metal center in many cases. For example, upon the coordination of Binap to a metal atom, the orientation of the four phenyl groups are regulated by the chiral binaphthyl backbone to generate the effective chiral pocket around the metal (Figure 1).[2,3] Steric

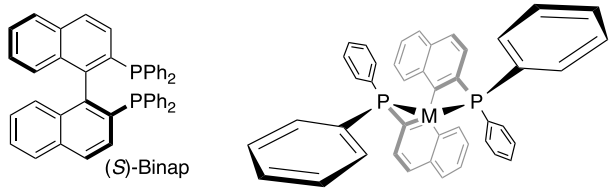


Figure 1. Structure of (*S*)-Binap and its 3D representation in a metal complex.

and electronic decorations of the phenyl groups are conventional strategies to improve the properties of chiral phosphines. Modified aryl groups, such as 3,5-dimethylphenyl (Xyl), 3,5-di-*tert*-butyl-4-methoxyphenyl (DTBM), 3,5-bis(trifluoromethyl)-phenyl, and so on, have been frequently used for these purposes.[4]

We have been interested in utilizing ferrocenyl (Fc) groups as components of ancillary phosphine ligands in metal catalysts. While ferrocene displays an aromatic character,[5] its steric properties are significantly different from those of benzenoid aromatics because of the cylindrical structure. Furthermore, the ferrocenyl group is highly electron-donating for an aryl substituent.[6] We recently quantified the steric and the electronic impacts of the ferrocenyl group in a series of organophosphines.[7] The electronic properties of the ferrocenyl group in organophosphines were estimated to be similar to those of primary alkyl groups. The steric influences of the ferrocenyl group are larger than those of typical bulky substituents, such as *tert*-butyl and *o*-tolyl groups, and comparable to those of the mesityl group.

In 2020, we reported a novel chiral bisphosphine ligand, Fc-Segphos **A**, in which the diphenylphosphino-substituents in parent Segphos **B** were replaced with the diferrocenylphosphino-groups (Figure 2).[8,9] Fc-Segphos was applied in the

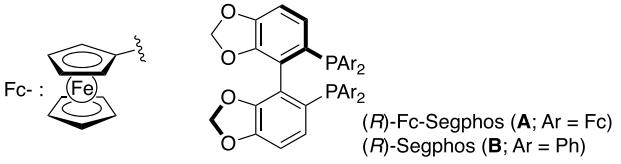


Figure 2. Structures of ferrocenyl group, (*R*)-Fc-Segphos **A**, and parent (*R*)-Segphos **B**.

palladium-catalyzed asymmetric synthesis of axially chiral allenes achieving higher enantioselectivity than **B**. In contrast, **A** was not effective in the rhodium-catalyzed asymmetric conjugate addition of phenylboronic acid to cyclohexenone. The catalytic inactivity of the Rh/**A** species could be

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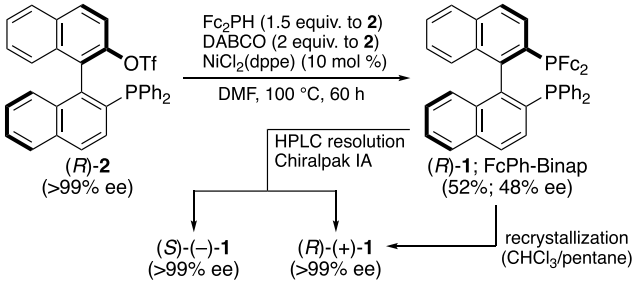
rationalized as the overcrowding at the rhodium center due to the presence of the four bulky ferrocenyl substituents in **A**.

Since the positive influences of the ferrocenyl substituents in **A** were proven in the palladium-catalyzed reaction, we intended to adjust its structure for wider applicability. In this Communication, the synthesis and applications of a C_1-symmetric Binap derivative having a single diferrocenylphosphino moiety (FcPh-Binap; **1**) are reported.

A major drawback of **A** is the overcrowding at the coordinating metal center. Our strategy to solve this problem is introducing one diferrocenylphosphino group in a chiral bisphosphine ligand instead of two in **A**, and C_1-symmetric FcPh-Binap (**1**) was designed. An axially chiral binaphthyl framework was employed in **1** instead of the bi(benzodioxolyl) skeleton in **A**, since the starting compound, (*S*)-/(*R*)-binaphthol, was commercially available. The synthesis of **1** is outlined in Scheme 1. Diphenylphosphino/triflate **2** (prepared

Scheme 1. Preparation of FcPh-Binap 1



from (*R*)-binaphthol[10] was reacted with diferrocenylphosphine[11] in the presence of DABCO and catalytic $NiCl_2$(dppe) in DMF. The reaction proceeded slowly, and **1** was obtained in 52% in 60 h. Similar conditions were used in the preparation of unsymmetric Binap derivatives,[12] and the coupling reactions proceeded with retention of the stereochemistry in **2**. However, the partial racemization was detected in the present reaction, and (*R*)-**1** was isolated in 48% ee. The enantiomeric purification of scalemic (*R*)-**1** was achieved by the preparative chiral HPLC on Daicel Chiralpak IA, and (*R*)- and (*S*)-**1** were obtained as pure enantiomers. Alternatively, enantiomerically pure (*R*)-**1** was isolated by recrystallization of scalemic (*R*)-**1** (48% ee) from chloroform/pentane. The X-ray crystallography of (*R*)-(+)-**1** confirmed its structure and the absolute configuration (see Supporting Information). Bisphosphine **1** is air-stable, and the ^{31}P NMR analysis of crystalline **1**, which had been stored under air for a few months, showed no oxidation.

A reaction of an equimolar mixture of (*S*)-**1** and $PdCl_2$(cod) in chloroform gave $PdCl_2$[(*S*)-FcPh-Binap] ((*S*)-**3**) quantitatively. The ^{31}P NMR signals of unligated (*S*)-**1**, detected at δ_P −35.0 and −14.0, shifted downfield to δ_P 14.4 and 26.1 upon the coordination to Pd(II). The single-crystals of (*S*)-**3** were grown as deep-red prisms by recrystallization from chloroform/hexane, and the crystal structure is shown in Figure 3 (see Supporting Information for details). The skewed seven-membered chelate and the alternating face-edge orientation of the phosphorus-bound Fc and Ph groups are similar to those in $PdCl_2$(Binap).[3] As observed in $PdCl_2$(Fc-Segphos),[8] both FeCp fragments are located away from Pd1 to avoid the steric congestion around Pd1. The nonbonding interactions are observed between **Fc2** and H6 as well as between the two

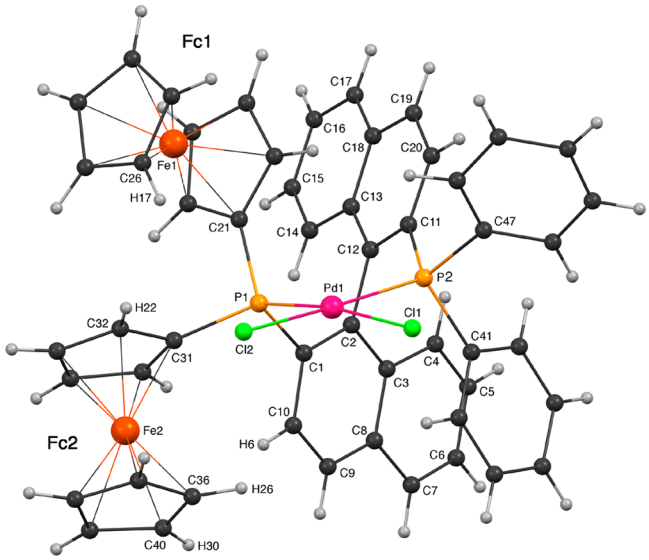


Figure 3. Ball-and-stick drawing of the X-ray structure of $PdCl_2$[(*S*)-FcPh-Binap] ((*S*)-**3**) with selected atom numbering. Cocrystallized solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd1−P1 = 2.252(1), Pd1−P2 = 2.287(2), Pd1−Cl1 = 2.347(2), Pd1−Cl2 = 2.333(2), C2−C12 = 1.508(8); P1−Pd1−P2 = 92.20(6), Cl1−Pd1−P2 = 86.61(7), Cl1−Pd1−Cl2 = 89.13(7), Cl2−Pd1−P1 = 92.54(6), dihedral angles between the two Cp planes in a Fc substituent = 6.41 (in **Fc1**) and 4.81 (in **Fc2**); nonbonding distances: H6−H26 = 2.382, H6−H30 = 2.438, H17−H22 = 2.325.

ferrocenyl substituents leading to the distortion of the ferrocenyl units. However, the distortion in **3** is smaller than that in $PdCl_2$(Fc-Segphos), which indicates that the overcrowding in **A** is somewhat reduced in **1**. The dihedral angle between the P1Pd1P2 plane and the Cl1Pd1Cl2 plane is 9.21°. The distortion at Pd1 is marginal, and the sum of the four angles at Pd1 involving Cl1, Cl2, P1, and P2 is 360.48. The bite angle, P1−Pd1−P2, in **3** is 92.20(6)°, which is comparable to that in $PdCl_2$(Binap) (92.69(8)°).[3] Likewise, the dihedral angle between the two naphthyl planes in **3** (71.64°) is only slightly larger than that in $PdCl_2$(Binap) (71.30°).

(*R*)-FcPh-Binap **1** was tested in several metal-catalyzed asymmetric reactions, and its performance was compared with that of parent Binap. The first reaction examined was the palladium-catalyzed asymmetric synthesis of axially chiral allenes (Table 1).[13] While the Pd/(*R*)-Binap catalyst provided allene (*R*)-**6ax** of 34% ee in 85% yield for the reaction of **4a** with malonate **5x** (entry 1), the enantioselectivity was improved to 81% ee by the use of Pd/(*R*)-**1** under the otherwise identical conditions (entry 2). Similarly, (*R*)-**1** showed higher enantioselectivity than (*R*)-Binap for the reaction of **4a** or **4b** with malonate **5y** to give (*R*)-**6ay** (82% ee vs 86% ee; entries 3 and 4) or (*R*)-**6by** (54% ee vs 88% ee; entries 5 and 6). The reaction with bissulfone **5z** also showed advantage of (*R*)-**1** over (*R*)-Binap. Allene (*R*)-**6cz** of 46% ee was obtained in 94% yield using Binap (entry 7). In comparison, the Pd/(*R*)-**1** catalyst afforded (*R*)-**6cz** of 86% ee in 94% yield (entry 8).

Whereas FcPh-Binap **1** was more effective than Binap in the reaction in Table 1, the validity of **1** was examined in the intermolecular asymmetric Heck reaction of aryl triflates **8** with 2,3-dihydrofuran **7** (Table 2).[3,15] The initial product in the reaction is **10**, which subsequently undergoes the isomerization to **9** under the palladium catalysis. The isomerization is also

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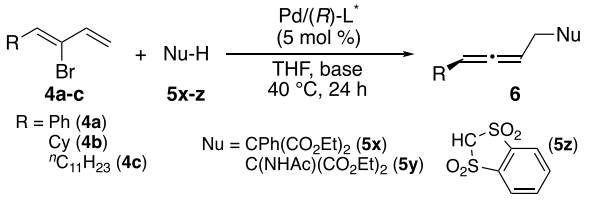
Table 1. Palladium-Catalyzed Asymmetric Synthesis of Axially Chiral Allenes[a]



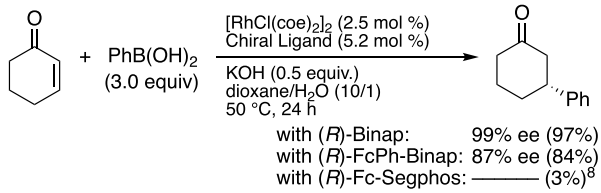
entry	4	5	base	L*	yield (%)[b]	% ee[c,d]
1	**4a**	**5x**	CsO^{t}Bu	Binap	85 (**6ax**)	34 (*R*)
2				FcPh-Binap	88 (**6ax**)	81 (*R*)
3	**4a**	**5y**	CsO^{t}Bu	Binap	90 (**6ay**)	82 (*R*)
4				FcPh-Binap	88 (**6ay**)	86 (*R*)
5	**4b**	**5y**	CsO^{t}Bu	Binap	81 (**6by**)	54 (*R*)
6				FcPh-Binap	85 (**6by**)	88 (*R*)
7	**4c**	**5z**	Me_3SiCH_2Li	Binap	94 (**6cz**)	46 (*R*)
8				FcPh-Binap	94 (**6cz**)	86 (*R*)

[a]All the reactions were carried out with **4** (0.20 mmol), **5** (0.23 mmol), and base (0.25 mmol) in THF (2.0 mL) for 24 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 HPLC on a chiral stationary phase. [d]The absolute configurations were deduced by the Lowe−Brewster rule [ref 14].

enantioselective, and major enantiomer (*R*)-**10** isomerizes faster than (*S*)-**10** with Pd/(*R*)-Binap. This kinetic resolution process enhances the enantiomeric purity of (*R*)-**9** by the selective concentration of the (*S*)-enantiomer in remaining **10**. Accordingly, the product ratios between **9** and **10** show strong influence on %ee of **9** and **10**. Under the conditions we employed, the yields of **10** were marginal, 7% at most. For the comparison of **1** with Binap at the carbon−carbon bond formation step, the mixtures of **9** and **10** were hydrogenated using the Wilkinson's catalyst, and the enantiomeric purities of 2-aryl-THFs **11** were determined by the chiral HPLC analysis. The reactions using the Pd/(*R*)-Binap catalyst provided **11** in modest enantioselectivity of ranging from 55 to 64% ee (entries 1, 3, and 5). On the other hand, the enantiomeric purities of **11** obtained by Pd/(*R*)-**1** were 91−95% ee (entries 2, 4, and 6). While minor products **10** obtained by Pd/(*R*)-Binap were (*S*)-enriched, the Pd/(*R*)-**1** catalyst provided (*R*)-enriched **10**. This is because the enantioselectivity of Pd/(*R*)-**1** was quite high at the initial carbon−carbon bond formation, and thus, remaining **10** were (*R*)-enriched even after the kinetic resolution/isomerization.

FcPh-Binap **1** showed decent performance in the rhodium-catalyzed asymmetric conjugate addition (Scheme 2).[16] For

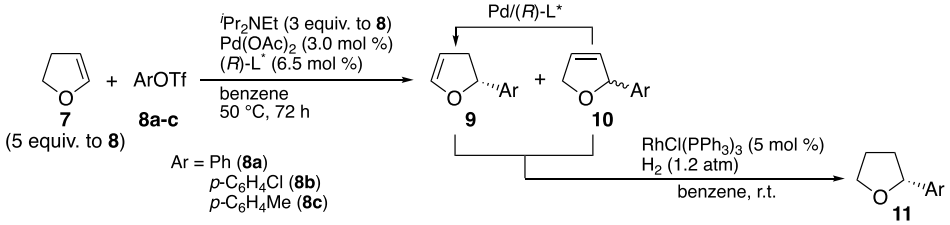
Scheme 2. Rhodium-Catalyzed Asymmetric 1,4-Addition of Phenylboronic Acid to 2-Cyclohexenone



the reaction between 2-cyclohexenone and phenylboronic acid, the Rh/(*R*)-**1** catalyst gave (*R*)-3-phenylcyclohexanone in 87% ee and 84% yield. Although the enantioselectivity was lower than that of the Rh/(*R*)-Binap catalyst (99% ee), the result is in striking contrast to the sluggishness of the Rh/(*R*)-**A** catalyst.[8] The catalytic inactivity of the Rh/(*R*)-**A** species could be attributed to the excessive congestion at the Rh center due to the presence of the four bulky Fc-substituents in **A**. Apparently, the rational design of (*R*)-**1**, reducing the number of ferrocenyl substituents to two, widens the available space around the Rh center and increases the catalytic activity of the Rh/(*R*)-**1** species.

In summary, a novel axially chiral C_1-symmetric bisphosphine ligand, FcPh-Binap **1**, was prepared. Ligand **1** possesses a single bulky and electron-donating Fc_2P-group instead of the two Fc_2P-groups in **A**. Because of the reduced steric congestion in **1**, the Rh complex of **1** showed better catalytic activity than that of **A** in the conjugate addition of phenylboronic acid to 2-cyclohexenone. Meanwhile, **1** displayed better enantioselectivity than Binap in the palladium-catalyzed asymmetric synthesis of axially chiral allenes as well as in the intermolecular asymmetric Heck reaction showing up to 47% ee and 39% ee enhancement, respectively,

Table 2. Palladium-Catalyzed Intermolecular Heck Reactions of 2,3-Dihydrofuran with Aryl Triflates[a]



entry	8	L*	yield of **9** + **10** (%)[b]	**9**/**10** ratio[c]	% ee of **9**[d]	% ee of **10**[d]	yield of **11** (%)[b]	% ee of **11**[d]
1	**8a**	Binap	>95 (**9a** + **10a**)	95/5	70 (*R*)	46 (*S*)	83 (**11a**)	64 (*R*)
2		FcPh-Binap (**1**)	>95 (**9a** + **10a**)	>99/<1	95 (*R*)	----	90 (**11a**)	95 (*R*)
3	**8b**	Binap	78 (**9b** + **10b**)	93/7	70 (*R*)	41 (*S*)	60 (**11b**)	58 (*R*)
4		FcPh-Binap (**1**)	67 (**9b**+ **10b**)	95/5	92 (*R*)	72 (*R*)	71 (**11b**)	91 (*R*)
5	**8c**	Binap	>95 (**9c** + **10c**)	96/4	55 (*R*)	25 (*S*)	84 (**11c**)	55 (*R*)
6		FcPh-Binap (**1**)	>95 (**9c** + **10c**)	98/2	94 (*R*)	57 (*R*)	83 (**11c**)	94 (*R*)

[a]All the reactions were carried out with **7** (2.5 mmol), **8** (0.50 mmol), and ^{i}Pr$_2$NEt (3.0 mmol) in benzene (2.0 mL) for 72 h in the presence of a Pd catalyst generated from $Pd(OAc)_2$ (3.0 mol %) and the chiral phosphine (6.5 mol %). [b]Isolated yield by silica gel chromatography. [c]Determined by the ^{1}H NMR analysis of the crude reaction mixture. [d]Determined by HPLC on a chiral stationary phase.

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over the palladium catalysts derived from parent Binap. Application of **1** in other transition-metal-catalyzed asymmetric reactions will be examined in due course.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.1c00132.

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

Accession Codes

CCDC 2060069 and 2060082 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.

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Notes

The authors declare no competing financial interest.

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