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COMMUNICATION

Enantioselective Synthesis of Planar-Chiral Benzosiloloferochenes by Rh-Catalyzed Intramolecular C-H Silylation

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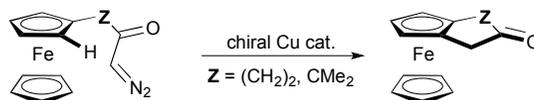
The intramolecular reaction of 2-(dimethylhydrosilyl)arylferrocenes achieved the first synthesis of planar-chiral benzosiloloferochenes. The enantioselective cross dehydrogenative coupling of an sp^2 C-H bond of ferrocene with a Si-H bond proceeded efficiently with the use of a Rh-chiral diene catalyst.

Dibenzosilole (9-silafluorene) is an important skeleton of many functional molecules that are useful as conjugated organosilicon materials in organic electronics and photonics.¹ Therefore, a facile method for the synthesis of multi-substituted dibenzosilole is strongly desired. Among various catalytic protocols, Pd-catalyzed intramolecular C-H arylation of diarylsilane² and consecutive coupling of 2,2'-diiodo-1,1'-biphenyl with dihydrosilane³ are typical examples. However, these reactions require halogenated substrates and suffer from the formation of by-products derived from halogens, based on atom-economical concerns. The Ir-catalyzed [2+2+2] cycloaddition of silanylbenzene-tethered 1,6-diyne with alkyne affords a perfectly atom-economical transformation for the synthesis of multi-substituted dibenzosiloles.⁴ As another approach, the Rh-catalyzed intramolecular dehydrogenative coupling of sp^2 C-H and Si-H bonds has been reported⁵ and asymmetric variants followed, in which a chiral spirocyclic silicon center was created by a Rh-chiral diphosphine catalyst.⁶

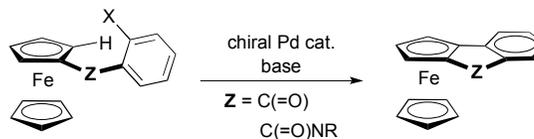
In contrast, the catalytic creation of planar chirality in disubstituted ferrocenes initiated by enantioselective C-H bond cleavage has attracted much attention over the past few years.⁷ Aminomethyl group-directed asymmetric C-H arylation, Heck-type reaction, and annulation have been realized through the use of Pd-chiral amino acid catalysts.⁸ We also reported isoquinolyl directed-C-H alkylation with alkenes by using an Ir-chiral diene catalyst.⁹ As for the intramolecular reaction, carbene C-H insertion of diazoketone-tethered ferrocenes by a chiral Cu catalyst is a pioneering work, and planar-chiral cyclic ketone-fused ferrocenes

have been prepared (Scheme 1-a).¹⁰ In 2014, three groups independently reported C-H arylation with haloarenes by using chiral Pd catalysts in the presence of more than a stoichiometric amount of base. Planar-chiral indenone- and quinolinone-fused ferrocenes were obtained in excellent ee (Scheme 1-b).¹¹ In this communication, we report the cross dehydrogenative coupling (CDC) of ferrocene and hydrosilane or hydrogermane by using a Rh-chiral diene catalyst. This is the first example of the enantioselective synthesis of planar-chiral heterole-fused ferrocenes (Scheme 1-c).¹²

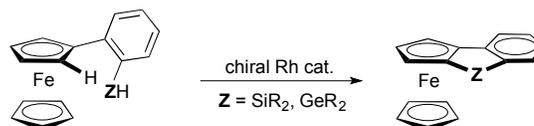
a) C-H insertion of carbene (ref. 10)



b) C-H arylation by haloarene (ref. 11)

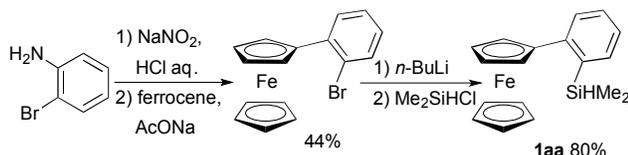


c) This work: Si-H/C-H coupling



Scheme 1 Enantioselective and intramolecular reaction for the synthesis of planar-chiral ring-fused ferrocenes

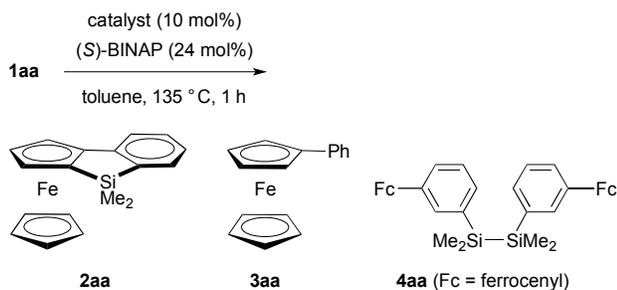
We chose 2-(dimethylhydrosilyl)phenylferrocene (**1aa**) as a model substrate, which was readily prepared in two steps (Scheme 2). Diazotization of 2-bromoaniline followed the reaction with ferrocene,¹³ and aryllithium prepared from the obtained bromide underwent silylation by dimethylhydrosilane.



Scheme 2 Preparation of 2-(dimethylhydrosilyl)phenylferrocene **1aa**

According to the literature,⁶ we intended to perform the intramolecular reaction of ferrocene **1aa** in the presence of a chiral Rh catalyst prepared from [RhCl(cod)]₂ and (*S*)-BINAP (Table 1, Entry 1). Desired CDC product **2aa** was obtained in good yield and enantioinduction was ascertained, albeit in low selectivity. The major by-product was disilane **4aa**, which resulted from the self-coupling of hydrosilanes. The iridium counterpart was less effective with respect to both yield and ee, and a significant amount of desilylated product **3aa** was formed (Entry 2).¹⁴ Cationic Rh catalyst gave a higher yield along with the formation of **3aa** (Entry 3). We also investigated several chiral diphosphine ligands, but without success.¹⁵

Table 1 Rh- or Ir-BINAP-catalyzed C-H silylation of **1aa**

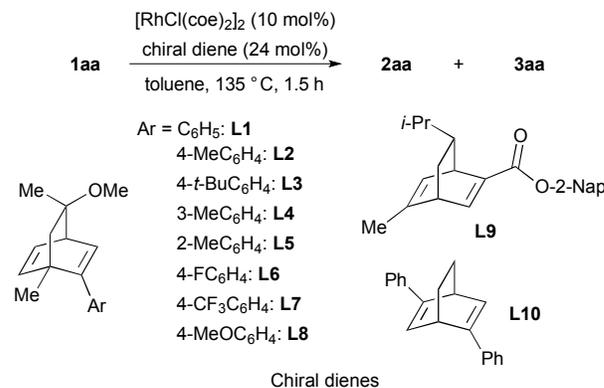


Entry	Catalyst	Yield (%) ^a	2aa:3aa ^b	Ee (%) ^c	Yield (%) ^d
1	[RhCl(cod)] ₂	78	1:0	-27	31
2	[IrCl(cod)] ₂	65	1:0.42	7	6
3	[Rh(cod)] ₂ BF ₄ ^e	97	1:0.20	-21	ND

^a Total yield of **2aa** and **3aa**. ^b The ratio was determined by NMR analysis. ^c Ee of **2aa**. ^d NMR yield of **4aa**. ^e (*S*)-BINAP (12 mol%) was used.

We next examined chiral dienes as ligands (Table 2). We were pleased to find that Carreira's dienes¹⁶ drastically improved the enantioselectivity: chiral Rh catalysts prepared from [RhCl(cod)]₂ and dienes generally realized moderate enantioselectivity (ca. 60%), but the ratio of **2aa** and **3aa** differed depending on the aryl group (Entries 1-8). In each entry, disilane **4aa** was formed as a by-product to some extent. We determined that **L1** was the best ligand, and most strongly suppressed the formation of **3aa**. Hayashi's dienes **L9**¹⁷ and **L10**¹⁸ were ineffective in the present reaction.

Table 2 Screening of chiral diene ligands



Entry	Chiral diene	Yield (%) ^a	2aa:3aa ^b	Ee (%) ^c
1	L1	78	1:0.17	58
2	L2	80	1:0.29	63
3	L3	82	1:0.23	65
4	L4	89	1:0.24	59
5	L5	73	1:0.46	35
6	L6	61	1:1.31	62
7	L7	75	1:0.39	52
8	L8	61	1:0.24	60
9	L9	64	1:0.29	-33
10	L10	82	1:0.12	<2

^a Total yield of **2aa** and **3aa**. ^b The ratio was determined by NMR analysis. ^c Ee of **2aa**.

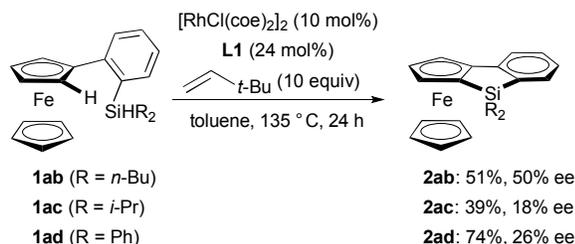
To improve the yield and ee, we screened several alkenes as hydrogen acceptors (Table 3).¹⁹ Norbornene surely increased the yield of **2aa** and decreased the yield of **3aa** with comparable ee (Entry 2). Unstrained cyclic alkene gave negative results (Entry 3). In the presence of 4-vinylcyclohexene, the reaction proceeded quantitatively with the almost perfect suppression of disilane formation, but the ee was significantly decreased (Entry 4). In contrast, 3,3-dimethylbut-1-ene realized a drastic increase in enantiomeric excess and greater amounts of the alkene slightly suppressed the formation of **3aa** (Entries 5 and 6).²⁰ The hydrogen acceptor probably prevented the hydrogenation of the chiral diene ligand and the enantioselectivity was improved.

Table 3 Effect of alkenes as a hydrogen acceptor

Entry	Alkene	Yield (%) ^a	2aa:3aa ^b	Ee (%) ^c
1	none	78	1:0.17	58
2	norbornene	89	1:0.03	57
3	cyclooctene	50	1:0.34	59
4	4-vinylcyclohexene	>99	1:0.01	40
5	3,3-dimethylbut-1-ene	72	1:0.11	82
6 ^d	3,3-dimethylbut-1-ene	67	1:0.07	85

^a Total yield of **2aa** and **3aa**. ^b The ratio was determined by NMR analysis. ^c Ee of **2aa**. ^d Alkene (10 equiv) was added.

The present reaction was sensitive to the bulkiness around the silicon atom (Scheme 3). Both the yield and ee decreased as the substituents (R) increase in size. 2-(Diphenylhydrosilyl)phenylferrocene (**1ad**) was transformed into the corresponding benzosiloloferrrocene **2ad** in good yield, but the ee was low.



Scheme 3 Effect of substituents on the silicon atom

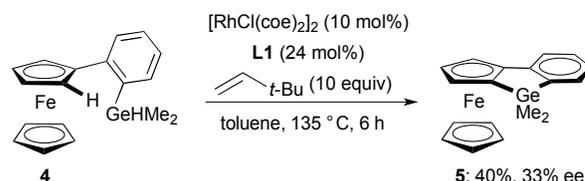
We checked the substrate scope by introducing several substituents on the benzene ring of 2-(dimethylhydrosilyl)phenylferrocene (Table 4). Both of electron-donating and -withdrawing groups could be installed into the para- and meta-positions with respect to the silyl group: moderate yield and good ee were achieved (Entries 1-5). A methyl group at the 3-position slightly affected the enantioselectivity (Entry 6). Introduction adjacent to the silyl group gave a poor ee (Entry 7)

Table 4 Substrate scope of 2-(dimethylhydrosilyl)arylferrocenes

Entry	R	Time (h)	Yield (%) ^a	2:3 ^b	Ee (%) ^c
1	4-Me (1ba)	24	56	1:0.11	74
2	4-CF ₃ (1ca)	4	55	1:0.14	78
3	5-Me (1da)	4	44	1:0.06	86
4	5-CF ₃ (1ea)	9	53	1:0.17	80
5	5-OCF ₃ (1fa)	2	55	1:0.16	76
6	3,5-Me ₂ (1ga)	5	75	1:0.13	55
7	6-Me (1ha)	24	67	1:0.09	5

^a Total yield of **2** and **3**. ^b The ratio was determined by NMR analysis. ^c Ee of **2**.

The reaction of (dimethylhydrogermyl)phenylferrocene (**4**) also proceeded to afford benzogermoloferrrocene **5** (Scheme 4).²¹ The low yield and ee were probably due to the bulkiness of a germanium atom compared with a silicon atom.



Scheme 4 Reaction of 2-(dimethylhydrogermyl)phenylferrocene (**4**)

In conclusion, we first prepared ferrocene-fused benzosiloles and benzogermole by enantioselective and intramolecular cross dehydrogenative coupling of an sp^2 C-H bond of ferrocene with a Si-H or Ge-H bond. We will evaluate the potential of a new class of planar-chiral molecules as electronic organic materials.

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Notes and references

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[†] Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/c000000x/
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- 14 Compounds **2aa** and **3aa** have similar polarity and could not be separated by preparative TLC, but could be separated by GPC (gel permeation chromatography), and **2aa** was fully characterized.
- 15 (a) The representative ee of **2aa** by using chiral diphosphines: tolBINAP (9% ee); xylylBINAP (15% ee); Me-DUPHOS (<2% ee). (b) We have recently learned that Prof. Kazuhiko Takai (Okayama University) also examined a rhodium-cihral diphosphine-catalyzed asymmetric synthesis of ferrocene-fused benzosiloles. We thank Prof. Takai for exchanging information prior to the publication.
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- 20 Recrystallization of **2aa** gave a single crystal with improved ee (99% ee), and its absolute structure was determined by X-ray analysis; The crystal data of compound **2aa**: C₁₈H₁₈FeSi, *M* = 318.27, orthorhombic, space group *P*2₁2₁2₁ (no. 19), *a* = 9.6741(4) Å, *b* = 10.9465(6) Å, *c* = 29.0292(11) Å, *V* = 3074.1(2) Å³, *Z* = 8, $\mu(\text{Mo-K}\alpha)$ = 10.447 cm⁻¹; number of reflections measured: total 29429 and unique 6966, *R*₁ = 0.0371, *wR*₂ = 0.1036, Flack parameter (Friedel pairs = 2036) 0.003(8). CCDC 1045375.
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