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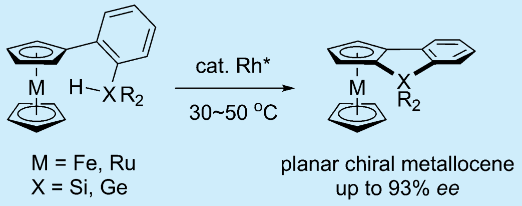
Rhodium-Catalyzed Synthesis of Benzosilolometallocenes via the Dehydrogenative Silylation of C(sp^2)−H Bonds

Masahito Murai,*,[†] Koji Matsumoto,[†] Yutaro Takeuchi,[†] and Kazuhiko Takai*,[†,‡]

[†]Division of Applied Chemistry, Graduate School of Natural Science and Technology and [‡]Research Center of New Functional Materials for Energy Production, Storage and Transport, Okayama University, 3-1-1 Tsushimanaka, Kita-ku, Okayama 700-8530, Japan

Supporting Information

ABSTRACT: Use of a rhodium catalyst with electron-rich and bulky chiral diphosphine ligands having C_2-symmetry allowed efficient dehydrogenative silylation of the C(sp^2)−H bond of ferrocenes leading to chiral benzosiloloferrocenes. The substrate scope was expanded to hydrogermane and hydrosilanes having a ruthenocene backbone, which resulted in a new approach to benzosilole- and benzogermole-fused metallocenes.



Metallocenes are useful in material sciences as well as in bioorganometallic chemistry due to their unique stimuli-responsiveness based on redox activity.[1] They are also important and privileged units in catalysts and ligands for synthetic organic chemistry.[2] Therefore, development of practical and efficient functionalization methods is important for determining their inherent electronic characteristics. Introduction of electron-donating or -withdrawing substituents into the metallocene backbone is the most frequently used strategy for functionalization. An alternative approach is through extension of the π-system by annulation with aromatic rings. Introduction of fused heteroaromatics is an especially promising method because it can perturb the electronic structure of the parent metallocene frameworks and provide them with new properties such as charge-carrier mobility and luminescence.[3] On the basis of these past results, the synthesis of several metallocenes, such as pyrrole-,[3a] thiophene-,[3b] and phosphole-fused ferrocenes,[3c,d] have been reported. These compounds were obtained mainly via complexation between the lithium salt of the heterocycle and iron chloride,[3a−c] with the sole exception of cyclization of 1-phosphanyl-2-(2-lithiophenyl)ferrocene, which led to a phosphole-fused ferrocene.[3d] Although these methods are useful, the use of highly reactive lithium salt limits their application in the construction of complexed metallocene frameworks.

A recent report described the catalytic synthesis of polycyclic aromatic compounds fused by silicon-, germanium-, boron-, and phosphorus-containing heterocycles based on the dehydrogenative functionalization of C(sp^2)−H bonds.[4,5] The success of these syntheses prompted an examination of transition-metal-catalyzed dehydrogenative functionalization of C−H bonds of metallocenes as a facile and efficient method to tailor functionality. Preliminary data on the effect of π-conjugation were estimated by DFT calculations (Figure 1). The results suggested that the choice of the bridging atom had a significant effect on the energy levels of the frontier orbital and that those of the LUMO were most effectively stabilized by the silicon bridge due to the interaction between the low-lying σ^* orbital of the silicon and the π^* orbital of the conjugated π-system of the backbone.[6] This unique electronic structure prompted development of a facile and efficient route to benzosilolometallocenes. The present report describes the rhodium-catalyzed dehydrogenative silylation and germylation of C(sp^2)−H bonds of ferrocenes and ruthenocenes as a new approach to benzosilolo- and benzogermolometallocenes.[7,8]

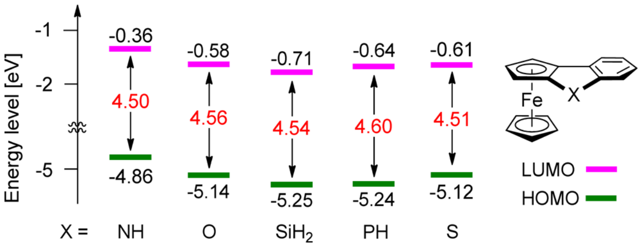


Figure 1. Comparison of the HOMO and LUMO energies of heterocycle-fused ferrocenes estimated by DFT calculations (LanL2DZ for Fe and B3LYP/6-31G(d) for other elements were used). The values between each level are the energy gaps of the frontier orbitals.

Treatment of hydrosilane **1a**, which can be readily prepared from commercially available ferrocene in two steps, with a catalytic amount of $[RhCl(cod)]_2$ and *rac*-BINAP in dioxane at 70 °C afforded benzosiloloferrocene **2a** in 44% yield (Table 1). The yield increased to 72% when 3,3-dimethyl-1-butene was added as a hydrogen acceptor. In this case, competitive formation of the hydrosilylation product **3** with 3,3-dimethyl-1-butene was obtained in 14% yield as a side product. In contrast to a previous report on the synthesis of 9-silafluorenes,[4a]

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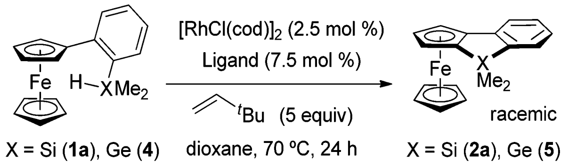
Table 1. Rh-Catalyzed Dehydrogenative Silylation and Germylation of C(sp^2)−H Bonds of 1a and 4



entry	X	ligand	product	yield (%)
1	Si	*rac*-BINAP	**2a**	72 (44[a])
2	Ge	PPh_3[b]	**5**	68 (45[a])

[a]Without 3,3-dimethyl-1-butene. [b]15 mol %.

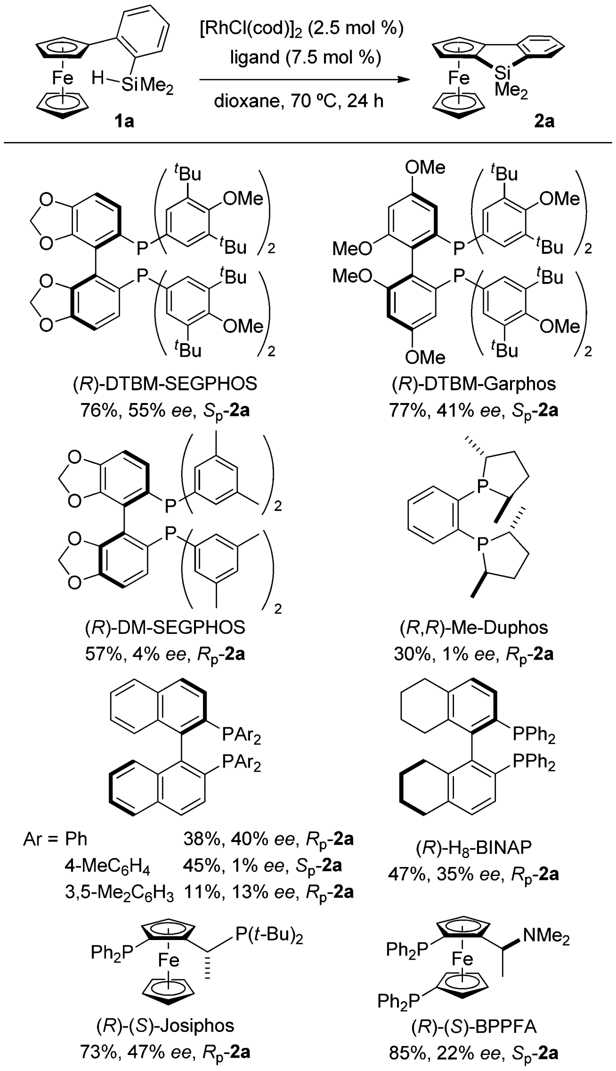


Figure 2. Effect of phosphine ligands on enantioselective dehydrogenative silylation of the C(sp^2)−H bond of **1a**. (Isolated yields, ee, and absolute configuration for the major isomer are shown. Ee was determined on a CHIRALPAK IB column with hexane/^{i}PrOH = 99/1 as the eluent.)

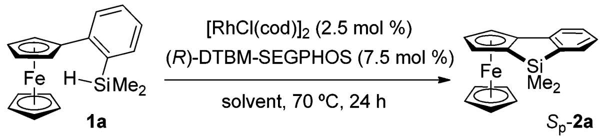
silylative cyclization leading to **2a** did not occur efficiently with Wilkinson catalyst, $RhCl(PPh_3)_3$.[9] On the other hand, benzogermoloferrocene **5** was obtained in 68% yield by using PPh_3 as a ligand in the presence of 3,3-dimethyl-1-butene via the dehydrogenative germylation of C(sp^2)−H bond of **4**.[4e]

Despite advances in dehydrogenative C−H bond silylation, few studies on the enantioselectivity of this transformation have been reported.[4c,7,10b,11] Controlling both reactivity and stereoselectivity is challenging, and we have developed the rhodium-catalyzed construction of axially chiral spirosilabifluorenes via 2-fold dehydrogenative silylation of bis(biaryl)dihydrosilanes.[4c] Enantioselective desymmetrization via dehydrogenative silylation of C(sp^3)−H bonds using chiral diphosphine ligands with C_2-symmetry also has been reported from our group.[10b] On the basis of these results, the asymmetric synthesis of benzosilolometallocenes to induce planar chirality was investigated (Figure 2).[12−14] Fortunately, (*R*)-DTBM-SEGPHOS, which was an effective ligand for the enantioselective silylation of the C(sp^3)−H bond,[10b] gave **2a** in 76% yield with 55% ee. In contrast to the results shown in eq 1, reaction with (*R*)-DTBM-SEGPHOS did not require a hydrogen acceptor.[15] The absolute configuration of **2a** was assigned as S_p by a comparison of the HPLC retention times for the major enantiomer obtained from **1a** with that for the literature-reported compound.[7] Among the ligands examined, (*R*)-DTBM-Garphos, (*R*)-BINAP, and (*R*)-(*S*)-Josiphos were effective for enantioselective silylation to provide **2a** in 40% ee, 41% ee, and 47% ee, respectively. The (*R*)-(*S*)-BPPFA with a ferrocene backbone afforded **2a** in high yield (85%) but with low enantioselectivity (22% ee). Although the combination of $[Rh(OMe)(cod)]_2$ with (*R*)-DTBM-SEGPHOS possessed similar catalytic activity (79% yield, 52% ee), the use of other rhodium and iridium precatalysts, such as $[Rh(cod)(OTf)]_2$, $[IrCl(cod)]_2$, or $[Ir(OMe)(cod)]_2$, decreased both the yield and enantioselectivity.[16] Other transition-metal complexes, including $Ru_3(CO)_{12}$, $Ir_4(CO)_{12}$, $Re_2(CO)_{10}$, $Pd(OAc)_2$, $Pd_2(dba)_3$, and $In(OTf)_3$, were completely ineffective, with the reaction resulting in recovery of precursor **1a**.

The effect of solvent and temperature on enantioselectivity was also examined (Table 2). Acetonitrile and toluene were ineffective at achieving enantioselectivity, while 1,2-dichloroethane and cyclohexane provided **2a** in moderate yield with good enantioselectivity (entries 1−6). Further screening revealed that using 1,2-dichloroethane as a solvent at a reaction temperature of 50 °C increased the yield of **2a** without loss of enantioselectivity (entry 7). The reaction proceeded, even at 30 °C, with ee up to 83%, although prolonged reaction time (48 h) was required for the complete conversion of **1a** (entry 8). In the course of these investigations, Shibata et al. reported enantioselective C(sp^2)−H bond silylation of ferrocene using a combination of the rhodium complex and chiral diene ligand.[7a] Although the maximum enantioselectivity was 86% ee, their catalytic system requires 10 mol % of expensive rhodium complex together with 10 equiv of a hydrogen acceptor to prevent competitive hydrosilylation of the chiral diene ligand at high temperature (135 °C). In contrast to the report of Shibata et al., no side reactions, including cleavage of the C−Si bond, occurred using the current rhodium−chiral diphosphine system.

Under the reaction conditions shown in Table 2, hydrosilane with an electron-withdrawing trifluoromethyl group afforded the corresponding benzosiloloferrocene **2b** in 93% yield with 80% ee (Figure 3).[17] A chloride group, which allows further derivatization through a transition-metal-catalyzed cross-coupling reaction, was also tolerated to afford **2c** in 80% yield and 77% ee. In contrast to our previous report, reductive dechlorination leading to **2a** did not occur when (*R*)-DTBM-SEGPHOS was used as a ligand, which indicates the potential utility of the current reaction in various functional material

Table 2. Effect of Solvent and Temperature on Enantioselective Dehydrogenative Silylation of the C(sp^2)−H Bond of 1a



entry	solvent	yield (%)	ee[a] (%)
1	dioxane	76	55
2	THF	87	61
3	MeCN	24	3
4	CH_2ClCH_2Cl	67	77
5	cyclohexane	86	74
6	toluene	83	37
7[b]	CH_2ClCH_2Cl	93	79
8[c]	CH_2ClCH_2Cl	88	83

[a] Isolated yields, ee, and absolute configuration for the major isomer are shown. ee was determined on a CHIRALPAK IB column with hexane/^{i}PrOH = 99/1 as the eluent. The absolute configuration of the major enantiomer was S_p. [b] 50 °C. [c] 30 °C, 48 h.

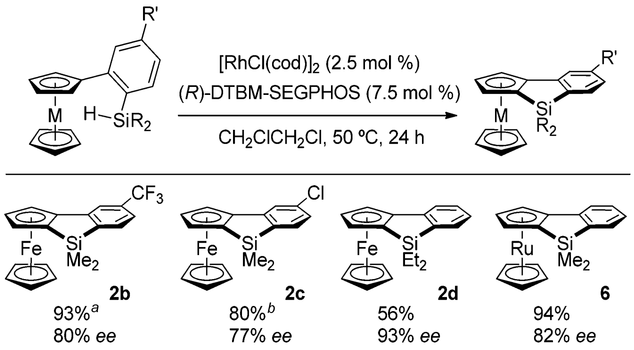
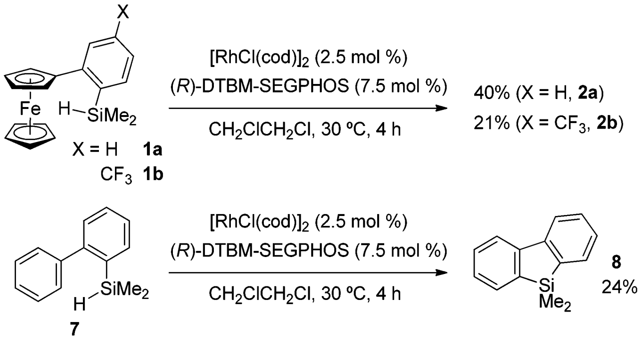


Figure 3. Rh-catalyzed enantioselective synthesis of benzosilole-fused metallocenes. (Ee was determined on a CHIRALPAK OD column with hexane/^{i}PrOH = 99/1 as the eluent. [a] At 30 °C for 48 h. [b] With 3,3-dimethyl-1-butene (2 equiv).)

syntheses.[4a] Cyclization of diethylsilane leading to **2d** proceeded with excellent enantiocontrol (93% ee). The substrate scope could be expanded to hydrosilanes with a ruthenocene backbone to furnish **6** in 94% yield with 82% ee.[18]

To obtain insight into the reaction mechanism, the parallel competitive cyclization of hydrosilanes **1a** without any substituents and **1b** having an electron-withdrawing trifluoromethyl group was carried out in a separate flask. The result demonstrated that formation of **2a** proceeded faster than that of **2b** (Scheme 1, upper), reflecting the nucleophilic nature of the silylrhodium species, which can be generated via oxidative addition of the rhodium center to H−Si bond of **1**. On the other hand, 2-(dimethylsilyl)biphenyl **7** gave 9-silafluorene **8** in 24% yield under the same reaction conditions (Scheme 1, lower).[4a] Although the dehydrogenative silylation of C(sp^2)−H bonds has previously been reported to proceed via the C−H bond activation rather than the electrophilic metalation,[19] the conversion of electron-rich **1a** was faster than that of **7** under the current reaction conditions using (*R*)-DTBM-SEGPHOS.[20]

Scheme 1. Parallel Competitive Silylation of 1a, 1b, and 7 in the Separated Flask To Elucidate the Electronic Effects on the Reactivity



The UV−vis absorption study indicates that the benzosiloloferrocene **2a** showed a maximum peak at 306 nm along with a broad shoulder peak in the region of 400−550 nm (Figure S2, Supporting Information). The bathochromic shifts of the absorption of **2a** with respect to phenylferrocene reflect (1) effective electronic interaction between the ferrocene and the benzosilole moieties and (2) a decreased HOMO−LUMO energy gap as a consequence of the expanded π-conjugation. These values are summarized in Table 3 along with the redox potentials determined by cyclic voltammetry. CV charts of **2a** in Figure S3 contained reversible waves for the Fe(III)/Fe(II) oxidation processes of the ferrocene moieties giving the monocation radical. The oxidation potential of **2a** shifted cathodically by 33 mV when compared to that of phenylferrocene, again indicating the effective expansion of the π-conjugated system.

Table 3. Photophysical and Electrochemical Properties

compd	λ_{abs} (nm) ($\varepsilon \times 10^{-3}$, M^{-1} cm^{-1})[a]	$E_{1/2}$ (mV vs Fc/Fc^+)[b]
phenylferrocene	288 (10.6), 440 (0.9)	−9
2a	306 (14.3), 348 (9.6), 456 (2.9)	−42

[a] In CH_2Cl_2 (1×10^{-5} M). [b] In CH_2Cl_2 (1×10^{-3} M) with ^{n}Bu_4NPF_6 (0.1 M) as a supporting electrolyte.

In conclusion, several benzosilole- and benzogermole-fused ferrocenes and ruthenocene were prepared by rhodium-catalyzed enantioselective intramolecular C−H silylation and germylation. The process did not require the severe reaction conditions or oxidants and may offer a practical and environmentally friendly route to functionalized planar chiral metallocenes. These results are of potential significance for materials science as well as enantioselective synthesis. Further investigation into enantioselective C(sp^3)−H and C(sp^2)−H bond functionalization as well as applications of the resulting chiral metallocenes are currently underway.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures, spectroscopic data for all new compounds, and copies of ^{1}H and ^{13}C NMR spectra. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b01373.

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: masahito.murai@okayama-u.ac.jp.
*E-mail: ktakai@cc.okayama-u.ac.jp.

Notes

The authors declare no competing financial interest.

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(7) During our detailed investigation, we have learned that Prof. Takanori Shibata (Waseda University, Japan) also examined the rhodium-catalyzed asymmetric synthesis of ferrocene-fused benzosiloles. We thank Prof. Shibata for providing this information prior to their publication. For their recent report, see: (a) Shibata, T.; Shizuno, T.; Sasaki, T. *Chem. Commun.* **2015**, *51*, 7802. Part of our current work has already been reported: *95th Annual Meeting of the Chemical Society of Japan*; Chemical Society of Japan: Tokyo, March 2015; 2E5−33. During the review of the current manuscript, He et al. reported enantioselective silylation of ferrocene using the rhodium−chiral phosphine catalyst system. See: (b) Zhang, Q.-W.; An, K.; Liu, L.-C.; Yue, Y.; He, W. *Angew. Chem., Int. Ed.* **2015**, *54*, 6918.

(8) The frontier energy levels for dibenzogermoloferrocene (X = $\mathrm{GeH_2}$ in Figure 1) are −5.26 eV (HOMO) and −0.68 eV (LUMO), respectively.

(9) Effect of other achiral ligands on the dehydrogenative silylation of hydrosilane **1a** with $\mathrm{[RhCl(cod)]_2}$ in dioxane at 70 °C: $\mathrm{PPh_3}$, 48%; $\mathrm{P(4\text{-}MeOC_6H_4)_3}$, 54%; $\mathrm{PCy_3}$, 24%; $\mathrm{P(4\text{-}CF_3C_6H_4)_3}$, 30%; $\mathrm{P(2\text{-}furyl)_3}$, 2%; $\mathrm{P(OPh)_3}$, 23%; Xantphos, 32%.

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(15) When (*R*)-DTBM-SEGPHOS and 3,3-dimethyl-1-butene were used as ligand and hydrogen acceptor, respectively, **2a** was obtained in 73% yield with 50% ee.

(16) Effect of metal complexes with (*R*)-DTBM-SEGPHOS at 70 °C: $\mathrm{[Rh(OMe)(cod)]_2}$, 79%, 52% ee ($S_\mathrm{p}$ major); $\mathrm{[Rh(OTf)(cod)]_2}$, 46%, 21% ee ($S_\mathrm{p}$ major); $\mathrm{[IrCl(cod)]_2}$, 44%, 3% ee (R_p major); $\mathrm{[Ir(OMe)(cod)]_2}$, 35%, 5% ee ($R_\mathrm{p}$ major).

(17) The reaction of 2-(hydrodimethylgermyl)phenylferrocene **4** in the presence of $\mathrm{[RhCl(cod)]_2}$ and the chiral phosphines listed in Figure 2 afforded the inseparable mixture of products.

(18) The absolute configuration of **2b**, **2c**, **2d**, and **6** was deduced from the configuration of **2a**, which was assigned in ref 7a.

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(20) The reaction with $\mathrm{PPh_3}$ (15 mol%) in place of (*R*)-DTBM-SEGPHOS at 50 °C for 4 h gave 7% yield of **2a** (from **1a**) and 16% yield of **8** (from **7**). The conversion of **7** was slower than that of **1a** only when (*R*)-DTBM-SEGPHOS was used as a ligand (Scheme 1), probably because the bulky rhodium center having a (*R*)-DTBM-SEGPHOS ligand distorted the rhodacycle intermediate generated from **7** and decreases its stability. Thus, we believe the present reaction mechanism contains C(sp^2)−H bond activation, a mechanism similar to that reported in ref 19.