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Synthesis and Properties of Sila[*n*]helicenes via Dehydrogenative Silylation of C−H Bonds under Rhodium Catalysis

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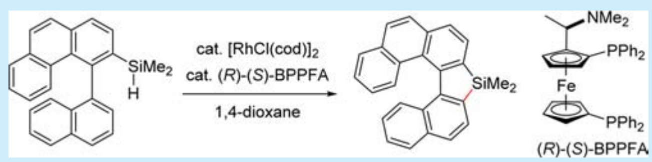
Supporting Information

ABSTRACT: Use of a rhodium catalyst with (*R*)-(*S*)-BPPFA ligand allows efficient synthesis of sila[*n*]helicenes via dehydrogenative silylation of C−H bonds. By selecting the proper ligands, the current method provides the ability to prepare unsymmetrical sila[*n*]helicene derivatives without any oxidants. The resulting sila[6]helicene is a rare example of a five-membered ring-fused [6]helicene, which was isolated as a single pure enantiomer without substituents on the terminal benzene rings.



Silicon-containing *π*-conjugated molecules show promise as materials useful in the areas of electro- and photo-luminescence.[1] The incorporated silicon atom has a significant impact on the energy levels of the frontier orbital, and that of the LUMO is effectively stabilized by the interaction between the low lying *σ** orbital of two exocyclic *σ*-bonds of the silicon atom and the *π** orbital of the conjugated *π*-system of the backbone. Catalytic dehydrogenative silylation of C−H bonds is a straightforward, atom-efficient, and sustainable route toward these silicon-containing *π*-conjugated molecules.[2−5] Since our first report in 2010 on the synthesis of silafluorenes,[3a] rhodium-catalyzed dehydrogenative silylation has been developed for the synthesis of various silicon-containing *π*-conjugated molecules, such as silicon-bridged *p*-terphenyl,[3a] spirosilabifluorenes,[3b,j] benzosilolometallocenes,[3e−g] dihydrobenzosilole,[3i] and phenazasilines[3d] (Figure 1). To further demonstrate the utility of this silylative cyclization, development of a robust catalyst system with improved reaction efficiency is highly desirable for the synthesis of more challenging silicon-containing *π*-systems. The present paper describes the synthesis of sila[*n*]helicenes (*n* = 4, 5, and 6) with uniquely merged *π*-conjugated systems of helicene and silole. This study also demonstrates that the amino group-substituted (*R*)-(*S*)-BPPFA ((*R*)-*N*,*N*-dimethyl-1-[(*S*)-1′,2-bis(diphenylphosphino)ferrocenyl]ethylamine) ligand is highly effective for the rhodium-catalyzed dehydrogenative silylation of C−H bonds.

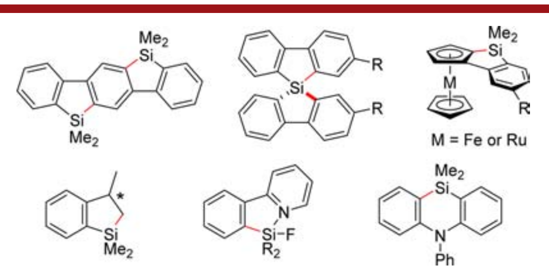


Figure 1. Silicon-containing *π*-conjugated molecules synthesized by dehydrogenative silylation of C−H bonds.

Helicene possesses a unique screw-shaped *π*-system consisting of all *ortho*-annelated aromatic rings.[6] In addition to a unique function as an optoelectronic material, these compounds can be utilized as ligands and organocatalysts.[6c] Despite their promising potential for functional materials, few examples of helicenes with fused-silacycles have been reported.[7] Sila[*n*]helicenes (*n* = 5 or 7) have been synthesized by reaction of dilithiobiaryls with dichlorosilane,[7a−d] rhodium- or iridium-catalyzed [2 + 2 + 2] cycloaddition of silicon-tethered polyynes,[7e,g] and platinum-catalyzed arylative cyclization of 2-alkynylbiaryls with a dibenzosilole backbone.[7f] While these methods provide a route to sila[*n*]helicenes, their utility can be limited by requiring complicated precursors containing the proper reactive functional groups. Thus far, no syntheses of sila[*n*]helicenes with an unsymmetrical structure have been reported. Development of flexible and convenient synthetic methods for sila[*n*]helicenes could allow customization of their properties, and dehydrogenative silylation with the activation of ubiquitous C−H bonds is thought to allow a more straightforward approach.

We previously reported that Wilkinson's catalyst, RhCl(PPh_3)$_3$, is effective for the silylative cyclization of 2-(2-hydrosilylphenyl)naphthalene **1a** to benzosilafluorene **2a** in the presence of 3,3-dimethyl-1-butene as a hydrogen acceptor (Scheme 1a).[3a] However, the corresponding cyclization of its isomer **1b** under the same reaction conditions resulted in formation of the expected sila[4]helicene **2b** in low yield (Scheme 1b).[8] This reactivity difference was rationalized by the steric repulsion between the two hydrogen atoms in the terminal benzene ring of helicene structures (see Figure S4 in Supporting

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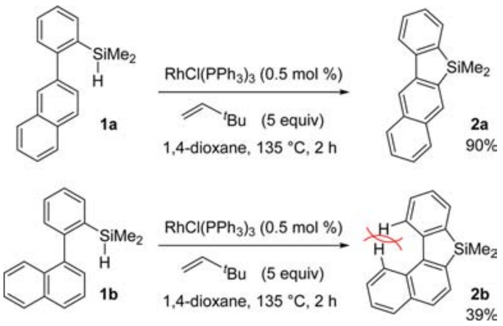
Scheme 1. Comparison of Reactivity



Information (SI)). Considering our previous study on the promotion of dehydrogenative silylation with the proper choice of ligand,[3e,i,j] the effect of ligands was investigated in the reaction of **1b** with $[RhCl(cod)]_2$ as the precatalyst.

The study revealed that the use of electron-rich monodentate phosphine ligands, such as PCy_3 and $P(4\text{-}MeOC_6H_4)_3$, furnished the expected **2b** in low yield, whereas the electron-deficient phosphine and phosphite ligands failed to promote the reaction efficiently (Table S1 in SI, entries 1−8). The use of bidentate phosphine ligands resulted in formation of **2b** in moderate to good yield (entries 9−12). Although the typical C_2-symmetric diphosphines, including BINAP[3b,j] and SEGPHOS, were less effective, the yield increased to 96% when (*R*)-(*S*)-BPPFA was used as a ligand even in the absence of a hydrogen-acceptor (entries 13−17).[9] Bulky and electron-rich (*R*)-DTBM-SEGPHOS, which was the best ligand for the enantioselective dehydrogenative silylation in our previous study,[3e,i] produced **2b** in lower yield (entry 15). In contrast, nitrogen-based bidentate ligands, which were useful for a previous intermolecular dehydrogenative silylation of C−H bonds,[10] were less reactive and resulted in recovery of most of precursor **1b**. The combination of other rhodium and iridium precursors, $[Rh(OMe)(cod)]_2$, $[IrCl(cod)]_2$, and $[Ir(OMe)(cod)]_2$, with (*R*)-(*S*)-BPPFA was also tested, but none of them were superior to $[RhCl(cod)]_2$.[11,12]

Several sila[*n*]helicenes (n = 4, 5, and 6) were obtained under the current optimized reaction conditions (Figure 2). With (*R*)-(*S*)-BPPFA as a ligand, the reaction temperature could be decreased to 80 °C while still affording sila[4]helicene **2b** in 93% yield. Similarly, 1-(2-hydrosilylphenyl)naphthalene derivatives were converted to the corresponding sila[4]helicenes **2c** and **2d** in 95% and 90% yields, respectively. Sila[5]- and sila[6]helicenes **2e** and **2f** were also obtained, although a slightly higher temperature (135 °C) was required for the transformations due to the higher steric repulsion compared with that of sila[4]helicenes. The substituents on the silicon center were also variable, and diphenylsilane afforded the corresponding sila[6]-helicene **2g** in slightly lower yield compared with the reaction of dimethylsilane **2f**.

As shown in Table S1 in SI, the current silylative cyclization was greatly facilitated when using (*R*)-(*S*)-BPPFA as a ligand. To investigate this result, a control experiment using 3-hydrosilyl-4-phenylphenanthrene **1e** as a precursor was performed (Table 1). Comparison of reactions using dppf and (*R*)-(*S*)-BPPFA as ligands indicated that the presence of an alkylamino group in the ligand structure promoted the reaction efficiently (entries 1 and 3). This is consistent with the increase in yield in the reaction using dppf as a ligand with triethylamine as an additive (entry 2). A similar trend in reactivity was observed for silylative cyclization

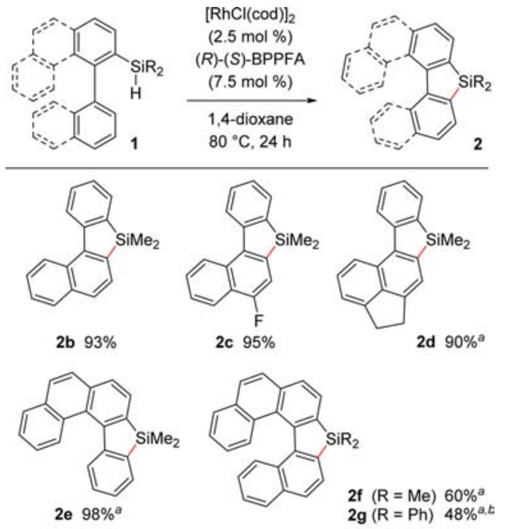
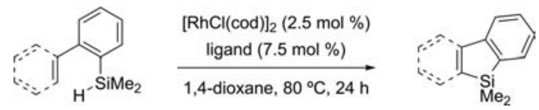
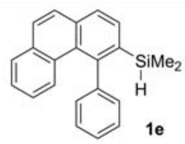
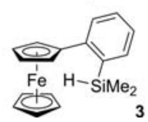


Figure 2. Rhodium-catalyzed dehydrogenative silylation of **1** leading to sila[*n*]helicene derivative **2**. [a] At 135 °C. [b] 29% of the cyclization precursor was recovered.

Table 1. Control experiment to clarify the effect of (*R*)-(*S*)-BPPFA



Entry	Substrate	ligand	Yield[a] / %
1[b]	 **1e**	dppf	87
2[b]		dppf + Et_3N (20 mol%)	93
3[b]		(*R*)-(*S*)-BPPFA	99 (98)
4	 **3**	dppf	72
5		dppf + Et_3N (20 mol%)	77
6		(*R*)-(*S*)-BPPFA	80 (75[c])

[a]Determined by ^{1}H NMR. Isolated yields are in parentheses. [b]At 135 °C. [c](*R*)-8,8-Dimethylbenzosilolo[2,3-*a*]ferrocene was obtained in 26% *ee*.

of hydrosilyl-2-ferrocenylbenzene **3** (entries 4−6).[3e−g] These results can be explained by the facilitation of cleavage and oxidative addition of C−H bonds to the rhodium center by the amino group on (*R*)-(*S*)-BPPFA.

The optical properties of the resulting sila[*n*]helicenes **2b**, **2e**, and **2f** were investigated by UV−vis absorption and fluorescence spectroscopy (Figure 3). The compounds showed a maximum peak around 290−300 nm along with a broad shoulder peak in the region 330−360 nm in dichloromethane. The absorption maximum was red-shifted in the order of silafluorene (286 nm), **2b**, **2e**, and **2f**, which clearly indicates a decreased HOMO−LUMO energy gap due to effective expansion of π-conjugation (see Figure 4 for calculated molecular orbitals). Blue luminescence was observed for dichloromethane solutions of these sila[*n*]helicenes upon excitation at 290 nm. These values are summarized in Table 2 along with the fluorescence quantum yield (Φ), and torsion angles (θ) were estimated from the optimized structure calculated using a DFT (density functional theory) method (Figures 4c and S2 in SI). The relatively high

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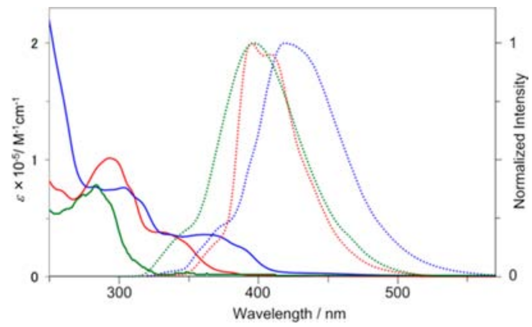


Figure 3. UV−vis absorption (solid line) and fluorescence (dashed line) spectra of sila[*n*]helicenes **2b** (green), **2e** (red), and **2f** (blue) in CH_2Cl_2 (1×10^{-5} M) at 25 °C.

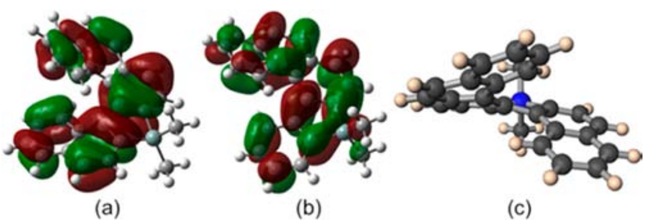


Figure 4. (a) HOMO, (b) LUMO orbitals, and (c) front view of the optimized structure of **2f** calculated by DFT.

Table 2. Optical Data and Torsion Angles for Sila[*n*]helicenes

compd	λ_{abs}/nm ($\varepsilon \times 10^{-4}$/$M^{-1}cm^{-1}$)[a]	λ_{max}^{em}/nm[b]	Φ[c]	θ/deg[d]
2b	288(6.0), 349 (0.31)	397	0.12	16.6
2e	294 (10.2), 333 (3.8)	395, 409	0.15	17.6
2f	304 (7.6), 362 (3.6)	420	0.16	32.4

[a]Absorption in CH_2Cl_2 (1×10^{-5} M). [b]Maximum fluorescence emission in CH_2Cl_2 (1×10^{-6} M). [c]Absolute quantum yield determined by using a calibrated integrating sphere system. [d]Torsion angles estimated for the structure optimized by DFT method at the B3LYP/6-31G(d) level of theory.

fluorescence quantum yield for the silole derivatives was reflected by the rigidity of the helicene backbone.

The optimized structure calculated by DFT clearly indicated that sila[6]helicenes **2f** and **2g** had large overlapping terminal benzene rings (Figure 4c). As expected, a single enantiomer of sila[6]helicene **2f** was obtained by optical resolution using HPLC with a chiral stationary phase at 25 °C. The optical rotation ($[\alpha]_D^{25}$) of enantio-enriched (*M*)-**2f** was −1625 (*c* = 0.09, $CHCl_3$).[13] The racemization rate constant *k*, which obeyed first-order kinetics, was determined at different temperatures (Table S3 and Figure S5 in SI). The activation energy for racemization Δ*E* was estimated from the *k* values to be 28.2 kcal/mol, which was lower than that reported for all benzene-[6]helicenes by 5−10 kcal/mol (Figure S6).[14] Note that **2f** is a rare example of a five-membered ring-fused [6]helicene without any substitutions, which was isolated as a single pure enantiomer. Syntheses and optical resolutions of pyrrole or thiophene-fused [6]helicenes have been previously reported, but the molecules contained substituents on the terminal benzene rings that prevented rapid racemization.[15] The results of the DFT study indicate that the choice of bridging atom significantly affects the torsion angles, and a silicon atom induces a larger overlap of the two terminal benzene rings, which increases the resistance to racemization (Table 3). Due to the high fluorescence quantum yield compared

Table 3. Optimized Torsion Angles (*θ*) for [6]Helicene Derivatives[a]

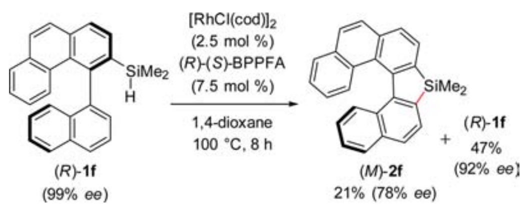
Z	CH_2	NH	O	SiH_2	P(=O)H
∠*C*–*Z*–*C* / degree	102.6	109.4	105.9	91.9	91.4
θ / degree	21.5	18.7	17.0	32.3	29.1

[a]Estimated for the structure optimized by DFT at the B3LYP/6-31G(d) level of theory.

with that of all benzene-[6]helicenes,[16] **2f** can be expected as a novel chiral host molecule applicable to luminescent materials.[6]

Since optically active **1f** was obtained using HPLC with a chiral stationary phase at 25 °C, stereospecific cyclization of **1f** was attempted.[17,18] Treatment of axially chiral atropisomer (*R*)-**1f** (99% *ee*) with a catalytic amount of $[RhCl(cod)]_2$ and (*R*)-(*S*)-BPPFA at 100 °C for 8 h gave (*M*)-**2f** in 21% yield (78% *ee*) with 47% recovery of **1f** (92% *ee*) (Scheme 2).[13,19] This result implies

Scheme 2. Transfer from Axial to Helical Chirality by Stereospecific Cyclization of 1f



that transfer from axial to helical chirality leading to **2f** was achieved during the silylative cyclization of **1f** and that the loss of *ee* occurred after the catalytic reaction due to the competitive racemization of both **1f** and **2f**.[20,21]

In conclusion, a novel catalytic synthesis of sila[*n*]helicene derivatives with an unsymmetical structure was developed via activation of both Si−H and C−H bonds. Due to promotion of the reaction by (*R*)-(*S*)-BPPFA, the current dehydrogenative silylation proceeded under neutral conditions without any oxidants. The resulting sila[6]helicene was a rare example of the five-membered ring-fused [6]helicene, which was isolated as a pure single enantiomer without substituents on the terminal benzene rings. The stereochemical information relay from axial to helical was also attempted.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b02134.

Experimental procedures, spectroscopic data for all new compounds, and copies of ^{1}H and ^{13}C NMR spectra (PDF)

Crystallographic data (CIF)

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Notes

The authors declare no competing financial interest.

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(8) 1,1,3,3-Tetramethyl-1,3-di(2-(1-naphthyl)phenyl)disiloxane (**4**) was obtained as a side product probably due to the competitive oxidation by the dissolved oxygen in dioxane. The structure of this product corresponded to that synthesized by the reaction of 1-(2-lithiophenyl)naphthalene with 1,3-dichloro-1,1,3,3-tetramethyldisiloxane.

(9) Dehydrogenative functionalization without any hydrogen acceptors (oxidants) is rare. For reviews, see: (a) Kuhl, N.; Hopkinson, M. N.; Wencel-Delord, J.; Glorius, F. *Angew. Chem., Int. Ed.* **2012**, *51*, 10236. (b) Mo, J.; Wang, L.; Liu, Y.; Cui, X. *Synthesis* **2015**, *47*, 439. The efficiency of the current silylative cyclization was not improved by addition of hydrogen acceptors, such as 3,3-dimethyl-1-butene, norbornene, cyclohexene, and methyl acrylate, in contrast to the results of our previous study (ref 3a).

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(11) Effect of precatalysts with a catalytic amount of (*R*)-(*S*)-BPPFA at 135 °C in 1,4-dioxane for 24 h: $[Rh(OMe)(cod)]_2$ 89%, $[IrCl(cod)]_2$ 24%, and $[Ir(OMe)(cod)]_2$ 19% of **2b** was obtained, respectively.

(12) Effect of solvents (0.50 M) with a catalytic amount of $[RhCl(cod)]_2$ and (*R*)-(*S*)-BPPFA at 80 °C for 24 h: toluene 84%, 1,2-dichloroethane 82%, MeCN 4%, THF 79%, and DMF 0% of **2b** was obtained, respectively.

(13) The absolute stereochemistry of **2f** was assigned by comparison of experimentally obtained optical rotation with that reported for sila[7]helicene in ref 7f.

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(17) The structure and absolute configuration of **1f** were unambiguously determined by single crystal X-ray crystallography. See Figure S3 and Table S2 in SI for details.

(18) Stereospecific transformation from axial to helical chirality for the synthesis of chiral helicenes is rare. See: (a) Miyasaka, M.; Rajca, A.; Pink, M.; Rajca, S. *J. Am. Chem. Soc.* **2005**, *127*, 13806. (b) Nakano, K.; Hidehira, Y.; Takahashi, K.; Hiyama, T.; Nozaki, K. *Angew. Chem., Int. Ed.* **2005**, *44*, 7136.

(19) The same reaction at 100 °C for 24 h gave **2f** in 30% yield (56% *ee*) with the recovery of **1f** in 20% yield (74% *ee*) and at 135 °C for 12 h gave **2f** in 31% yield (0% *ee*) with the recovery of **1f** in 13% yield (64% *ee*).

(20) Treatment of optically active sila[6]helicene **2f** (99% *ee*) in dioxane at 135 °C for 12 h resulted in complete racemization (0% *ee*). Racemization of the precursor **1f** (99% *ee*) was much slower under the same reaction conditions (**1f** was recovered with 64% *ee*).

(21) The *ee* of the sila[6]helicenes **2f** obtained from silylative cyclization of *rac*-**1f** with (*R*)-(*S*)-BPPFA, (*R*)-BINAP, and (*R*)-DTBM-SEGPHOS at 100 °C for 24 h was less than 5%. The cyclization of **1e** and *rac*-**1g** also gave a similar result due to the rapid racemization of the resulting sila[*n*]helicenes at high temperature. An attempted kinetic resolution of *rac*-**1f** with (*R*)-(*S*)-BPPFA at 100 °C for 8 h gave **2f** in 16% yield (2% *ee*) together with recovery of **1f** in 42% yield (5% *ee*).

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