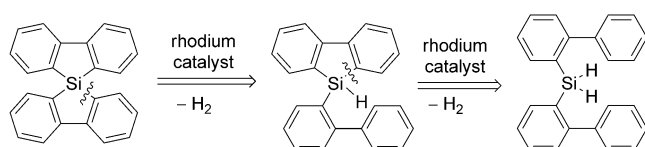


Rhodium-Catalyzed Asymmetric Synthesis of Spirosilabifluorene Derivatives**

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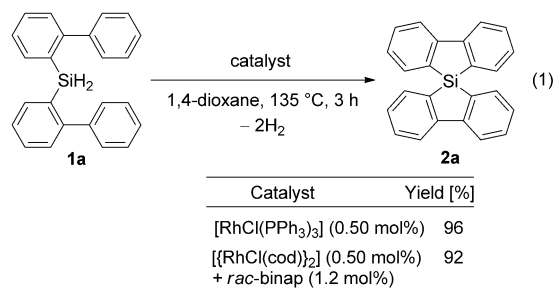
Chiral compounds occupy a large and important area of organic molecules, such as natural products, bioactive compounds, drugs, and functional materials. However, examples of the synthesis of chiral organosilicon compounds are still rare among organic compounds.^[1] It is important to construct a quaternary silicon atom to synthesize chiral organosilicon compounds. Our strategy for the construction of a quaternary silicon atom is a rhodium-catalyzed double dehydrogenative cyclization of bis(biphenyl)silanes through carbon–silicon bond formation (Scheme 1).^[2,3] We report herein the asymmetric synthesis of chiral spirosilabifluorene derivatives from bis(biphenyl)silanes, bearing substituents on the aromatic rings, using a rhodium catalyst with a chiral phosphine ligand.^[4]



Scheme 1. Strategy for the construction of a quaternary silicon atom.

Treatment of the bis(biphenyl)silane **1a** with a catalytic amount of either the rhodium complex $[\text{RhCl}(\text{PPh}_3)_3]$ or a mixture of $[\{\text{RhCl}(\text{cod})\}_2]$ and *rac*-binap, in 1,4-dioxane at 135 °C for 3 hours gave 9,9'-spiro-9-silabifluorene (**2a**) in 96 and 92 % yield, respectively [Eq. (1), binap = 2,2'-bis(diphenylphosphanyl)-1,1'-binaphthyl, cod = cyclo-1,5-octadiene]. In this reaction, dehydrogenative intramolecular cyclization proceeded twice, and a spirocompound with a quaternary silicon atom was produced.^[4,5]

If the reaction is carried out using bis(biphenyl)silanes with two or more substituents on different aromatic rings, the



products are generated as a mixture of enantiomers (racemic mixture). Therefore, chiral spirocompounds must be obtained using rhodium catalysts with a chiral phosphine ligand. Indeed, as a result of the treatment of the bis(methoxybiphenyl)silane **1b** with catalytic amounts of $[\{\text{RhCl}(\text{cod})\}_2]$ and (*R*)-binap, the spirosilabifluorene **2b** was afforded in 95 % yield and 81 % *ee* (Table 1, entry 1).^[6–8] The enantiomers were

Table 1: Synthesis of chiral spirosilabifluorenes **2**.

Entry	R	Yield [%] ^[a]	<i>ee</i> [%] ^[b]	Major enantiomer
1	4-MeO (1b)	95 (2b)	81	(+) <i>S</i>
2	4- <i>t</i> Bu (1c)	94 (2c)	78	(+) <i>S</i> ^[c]
3 ^[d]	4-CF ₃ (1d)	90 (2d)	75	(–) <i>S</i> ^[c]
4	4-Ph (1e)	90 (2e)	70	(+) <i>S</i>
5	2-MeO (1f)	73 (2f)	77	(–) <i>S</i> ^[c]

[a] Yield of isolated product. [b] The *ee* values for the products **2** were determined by HPLC analysis using a chiral stationary phase. [c] Not determined. [d] 115 °C, 2 h.

separated by HPLC methods using a chiral stationary phase, and the structure of the major enantiomer of **2b** was determined by single-crystal X-ray structure analysis to be the *S* form (Figure 1 and the Supporting Information).^[9] The reaction also proceeded well when the bis(biphenyl)silane with *tert*-butyl groups (**1c**) was employed as a substrate (Table 1, entry 2). The corresponding spirosilabifluorene **2d** was afforded in 90 % yield and 75 % *ee* when using the bis(biphenyl)silane having electron-withdrawing groups (**1d**; Table 1, entry 3).^[10] The bis(biphenyl)silane bearing phenyl groups (**1e**) provided the spirosilabifluorene **2e** (Table 1, entry 4).^[11,12] The absolute configuration of the major enan-

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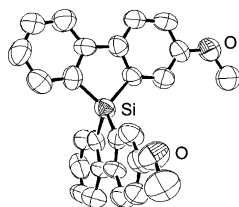
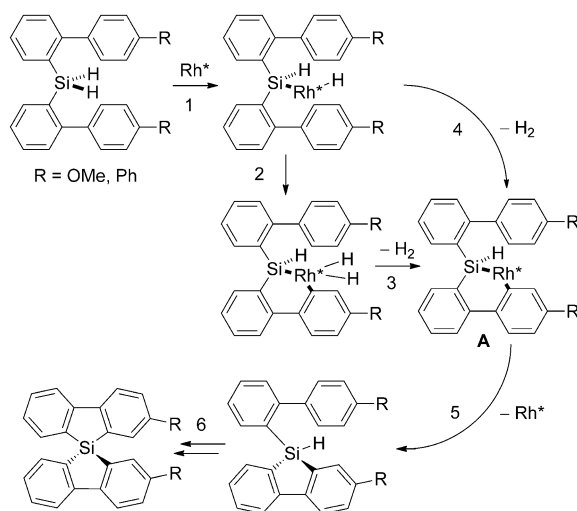


Figure 1. Molecular structure of chiral spirosilabifluorene (S)-**2b**. Thermal ellipsoids set at 50% probability. Hydrogen atoms are omitted for clarity.^[13]

tiomer of **2e** was determined by preparation of **2e** from (S)-**2b** (See the Supporting Information). The retention time of the major enantiomer of **2e** is consistent with the compound derived from (S)-**2b** on a chiral HPLC column. The chiral spirosilabifluorene **2f** was produced when bis(biphenyl)silane with methoxy groups at the 2-position of the phenyl groups (**1f**) was used as a substrate (Table 1, entry 5).

The mechanistic details of the Si–C bond formation reaction are proposed as follows (Scheme 2):^[2]



Scheme 2. Proposed mechanism for the formation of spirosilabifluorene frameworks.

1) oxidative addition of a bis(biphenyl)silane (hydrosilane) to a metal atom (Si–H bond activation), in which the metal atom is oriented close to an aromatic C–H bond; 2) sequential oxidative addition of the aromatic C–H bond to a metal atom (C–H bond activation); 3) elimination of H₂ to give the intermediate **A**. Another possible pathway for the formation of **A** is by step 4: σ -bond metathesis. After the generation of **A**, there is 5) reductive elimination, and then 6) steps 1, 2, 3, and 5 (or 1, 4, and 5) are repeated one more time to give a chiral spirosilabifluorene.

The chirality of the spirosilabifluorenes is determined at the first dehydrogenative cyclization. The conformation of this intermediate is such that steric hindrance between biphenyl groups of the bis(biphenyl)silane and the chiral ligand of the catalyst is avoided. Therefore, the Rh–H species reacts enantioselectively with the biphenyl group closer to the metal atom. After determination of the chirality, the second dehydrogenative cyclization occurs between the remaining Si–H and biphenyl group.

In summary, we have succeeded in the synthesis of a spirosilabifluorene derivative from a bis(biphenyl)silane

by double dehydrogenative cyclization using either the rhodium catalyst [RhCl(PPh₃)₃] or a mixture of [[RhCl(cod)]₂] and *rac*-binap. This reaction is a rare example of the formation of a quaternary silicon atom. This reaction was applied to the synthesis of chiral spirosilabifluorene derivatives using rhodium catalysts with chiral phosphine ligands ([RhCl(cod)]₂ + (R)-binap). The stereochemistry of the major enantiomer of the product was determined by single-crystal X-ray structure analysis, thus confirming this rare example of the synthesis of chiral organosilicon compounds with a quaternary silicon atom. In addition, spirosilabifluorenes are interesting compounds as organic materials.^[4b–e] We hope that this reaction will become a useful method to synthesize chiral spirosilabifluorene derivatives.

Experimental Section

Typical procedure for the synthesis of 2,2'-dimethoxy-9,9'-spiro-9-silabifluorene (**2b**): A mixture of [[RhCl(cod)]₂] (2.5 mg, 0.50 μ mol), (R)-binap (0.75 mg, 1.2 μ mol), and 1,4-dioxane (0.10 mL) was stirred at 25°C for 30 min. The mixture was added to bis(4'-methoxybiphenyl-2-yl)silane (**1b**, 39.6 mg, 0.100 mmol), and the mixture was heated at 135°C for 3 h. After the reaction, the solvent was removed in vacuo. The product was isolated after column chromatography on silica gel (*n*-hexane/ethyl acetate = 50:1) to give 2,2'-dimethoxy-9,9'-spiro-9-silabifluorene (**2b**, 37.4 mg, 0.0952 mmol, 95% yield).

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- [7] Investigation of several chiral phosphine ligands: (*R*)-DM-binap, 72%, 67% *ee* [major: (+)-**2b**]; (*R*)-H8-binap, 95%, 74% *ee* [major: (+)-**2b**]; (*R*)-Tol-binap, 66%, 27% *ee* [major: (+)-**2b**]; (–)-1,2-bis[(2*R*,5*R*)-2,5-diphenylphospholano]ethane, 72%, 35% *ee* [major: (–)-**2b**]; (*R*)-DM-segphos, 95%, 73% *ee* [major: (+)-**2b**]; (–)-1,2-bis[(2*R*,5*R*)-2,5-diethylphosphinano]benzene [(*R,R*)-ethyl-duphos], 61%, 62% *ee* [major: (+)-**2b**]; (2*S*,3*S*)-(–)-bis(diphenylphosphino)butane, 0%, 0% *ee*.
- [8] A reaction of **1b** using (*S*)-binap instead of (*R*)-binap gave (–)-(*R*)-**2b** in 95% yield, 81% *ee*.
- [9] The enantiomers of **2b** could be separated using a chiral HPLC column {Chiralpak IB [LTD., 2.0 cm I.D × 25 cm L, Daicel Chemical Industries; eluent:methanol:H₂O = 95:5; flow rate: 3.2 mL min^{–1}; temp = 25 °C; det. 300 nm (UV); injection: 5.0 mL (ca. 400 mg L^{–1} in eluent)]; time: *R* form, 23 min; *S* form, 24.5 min}.
- [10] Investigation of several combinations of rhodium complexes and phosphine ligands (115 °C, 15 min): [{RhCl(cod)}₂] and (*R*)-binap, 78%, 70% *ee* [major: (–)-**2d**]; [{RhCl(cod)}₂] and (*R*)-DM-binap, 31%, 54% *ee* [major: (–)-**2d**]; [{RhCl(cod)}₂] and (*R*)-H8-binap, 79%, 68% *ee* [major: (–)-**2d**]; [{RhCl(cod)}₂] and (–)-2,3-bis[(2*R*,5*R*)-2,5-dimethylphospholano]maleic anhydride, 18%, 19% *ee* [major: (–)-**2d**]; [{RhCl(cod)}₂] and (–)-1,2-bis[(2*R*,5*R*)-2,5-diphenylphospholano]ethane, 53%, 80% *ee* [major: (+)-**2d**]; [{RhCl(cod)}₂] and (*R*)-(+)-7,7'-bis(diphenylphosphino)-2,2',3,3'-tetrahydro-1,1'-spirobiindene [(*R*)-SDP], 6%, 3% *ee* [major: (–)-**2d**]; (4*S*)-2-[2-(diphenylphosphino)-phenyl]-4,5-dihydro-5,5-dimethyl-4-(1-methylethyl)oxazole, 38%, 50% *ee* [major: (–)-**2d**]; (–)-1,2-bis[(2*R*,5*R*)-2,5-diethylphosphinano]benzene [(*R,R*)-ethyl-duphos], 11%, 27% *ee* [major: (–)-**2d**].
- [11] One of the purposes of the introduction of the phenyl groups is to expand the π-conjugated system. In fact, a stronger purple fluorescence was observed compared with other spiroilabifluorene derivatives when irradiating a either the solid or an ethyl acetate solution of spiroilabifluorene **2e** with λ = 254 nm (UV) light.
- [12] The absolute configuration of **2e** was determined by preparation of (*S*)-**2e** from (*S*)-**2b**. The details of the preparation is described in the Supporting Information.
- [13] CCDC 914745 [(*S*)-**2b**] contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.