

Rhodium-Catalyzed Synthesis of Silafluorene Derivatives via Cleavage of Silicon–Hydrogen and Carbon–Hydrogen Bonds

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Abstract: The rhodium-catalyzed synthesis of silafluorenes from biarylhydrosilanes is described. This highly efficient reaction proceeds via both Si–H and C–H bond activation, producing only H₂ as a side product. Using this method, a ladder-type bis-silicon-bridged *p*-terphenyl could also be synthesized.

Silafluorene derivatives have recently received much attention because they are useful in organic materials, such as organic electroluminescent compounds.¹ There have been several reports on the synthesis of silafluorenes,² including iridium-catalyzed [2 + 2 + 2] cycloaddition of silicon-bridged diynes and alkynes,³ palladium-catalyzed intramolecular coupling of 2-(arylsilyl)aryl triflate,⁴ rhodium-catalyzed coupling of 2-silaphenylboronic acids with alkynes via carbon–silicon bond cleavage,⁵ and palladium-catalyzed reactions between 2,2'-diiodobiaryls and dihydrosilanes.⁶ As a novel strategy for the synthesis of silafluorenes, we employed a method based on metal-catalyzed double activation of Si–H and C–H bonds with dehydrogenation (Figure 1).

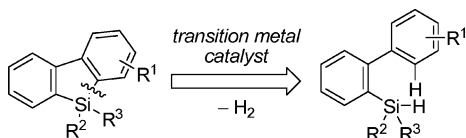
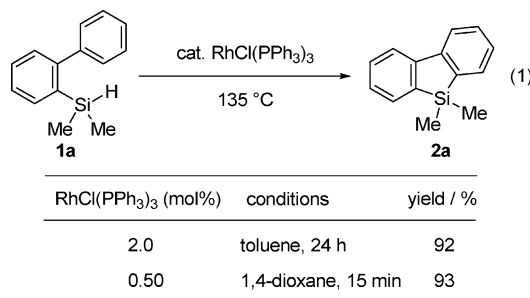


Figure 1. Retrosynthesis for the formation of silafluorenes.

To synthesize silafluorenes via dehydrogenation, we screened several transition metal complexes that can catalyze transformations starting from Si–H or C–H bond activation in toluene. First, transition metal complexes that can promote Si–H bond cleavage such as hydrosilylation were investigated (eq 1). Among those examined, a rhodium complex, RhCl(PPh₃)₃, showed high catalytic activity, and **2a** was obtained in 92% yield.^{7–10} Other rhodium complexes, [RhCl(cod)]₂, [Rh(OAc)₂]₂, and Rh₄(CO)₁₂ also provided **2a** in 72%, 41%, and 18% yields, respectively. Ruthenium complexes, Ru₃(CO)₁₂ (53%) and RuHCl(CO)(PPh₃)₃ (19%); an iridium complex, Ir₄(CO)₁₂ (21%); and a rhenium complex, ReCl(CO)₅ (21%),¹¹ also promoted both Si–H and C–H bond activation and produced silafluorene **2a**.

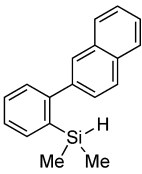
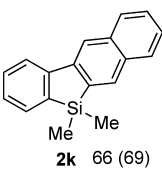
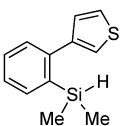
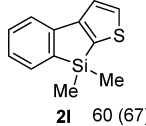
Using RhCl(PPh₃)₃, which gave the highest yield of **2a**, we investigated the best reaction conditions (eq 1). By changing the solvent, the amount of RhCl(PPh₃)₃ could be decreased (0.50 mol %) and the reaction time could be shortened (15 min). This method is highly efficient because the only side product is H₂.



The scope of substrates was examined with the rhodium catalyst in 1,4-dioxane (Table 1). Biarylhydrosilanes bearing an electron-withdrawing group, **1b** and **1c**, gave silafluorenes **2b** and **2c**, respectively, in 95% yields (entries 1 and 2). The corresponding silafluorene derivative **2d** and its dechlorinated product **2a** were afforded in 72% and 11% yields, respectively (entry 3).¹² This result enables the construction of further derivatives based on cross-coupling reactions. Silafluorenes having an electron-donating group, **2e** and **2f**, were obtained from the corresponding biarylhydrosilanes **1e** and **1f**; however, the yields were decreased and the reaction times were longer compared to **2b** and **2c** (entries 4 and 6). To improve the yields of **2e** and **2f** and to shorten the reaction times, 3,3-dimethyl-1-butene was added as a hydrogen acceptor, and **2e** and **2f** were produced in 91% and 83% yields, respectively (entries 5 and 7). When a biarylhydrosilane with a methyl group at the *meta*-position, **1g**, was used, only silafluorene derivative **2g** was produced regioselectively in 96% yield (entry 8). The reaction was not inhibited by a substituent at the *ortho*-position, and the corresponding silafluorene **2h** was afforded in 93% yield (entry 9).¹³ Biphenylhydrosilanes with two ethyl groups on the silyl group, **1i**, or with methyl and phenyl groups on the silyl group, **1j**, also afforded silafluorene derivatives **2i** and **2j** in 94% and 84% yields, respectively (entries 10 and 11).¹⁴ To expand the π -conjugated system, 2-(2'-naphthyl)phenylhydrosilane **1k** was employed as a substrate. As a result, the corresponding silafluorene derivative **2k** was generated in 66% yield (entry 12).¹⁵ The yield of **2k** was increased to 90% upon addition of 3,3-dimethyl-1-butene (entry 13). The corresponding silafluorene **2l** was produced regioselectively when hydrosilane with a 3-thiophenyl group, **1l**, was employed as a substrate (entry 14). Using (2-ethenylphenyl)dimethylsilane, intramolecular hydrosilylation proceeded, and the corresponding dihydrobenzosilole was formed in 90% yield, but the desired benzosilole was not obtained (not shown).¹⁶

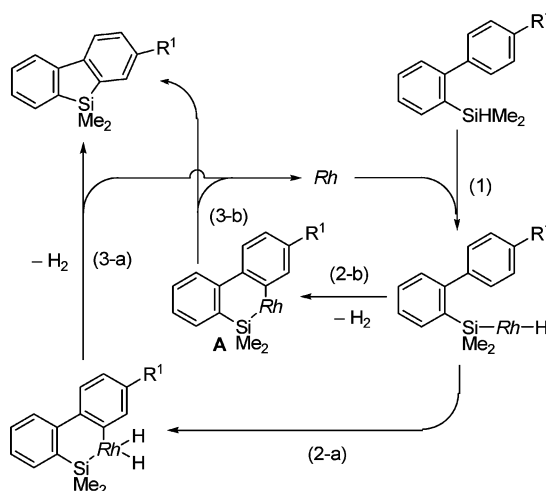
Since biarylhydrosilanes bearing an electron-withdrawing group have higher reactivities compared to biarylhydrosilanes with an electron-donating group, this reaction should not proceed by a Friedel–Crafts-type reaction. The proposed mechanism is as follows (Scheme 1): (1) oxidative addition of a hydrosilane to a metal center (Si–H bond activation; the metal center is oriented close to an

Table 1. Investigation of Several Biarylhydrosilanes

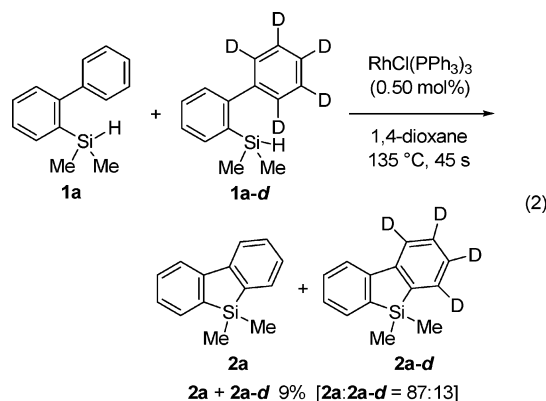
entry	R ¹	R ²	R ³	yield / % ^a
1	4-CF ₃	Me	Me	1b 2b 95 (98)
2	4-F	Me	Me	1c 2c 95 (97)
3 ^{b,c}	4-Cl	Me	Me	1d 2d 72 (74)
4 ^d	4-MeO	Me	Me	1e 2e 60 (63)
5 ^{c,e}	1e			2e 91 (95)
6 ^d	4- ^t Bu	Me	Me	1f 2f 87 (90)
7 ^{e,f}	1f			2f 83 (86)
8 ^d				
	3-Me	Me	Me	1g 2g 96 (98)
9 ^{c,e}	2-MeO	Me	Me	1h 2h 93 (96)
10 ^{e,g}	H	Et	Et	1i 2i 94 (96)
11 ^h	H	Ph	Me	1j 2j 84 (92)
12 ^d				
				1k 2k 66 (69)
13 ^{e,i}	1k			2k 90 (94)
14 ^d				
				1l 2l 60 (67)

^a Isolated yield. Yield determined by ¹H NMR is reported in parentheses. ^b RhCl(PPh₃)₃ (1.0 mol %). **2a** was formed in 11% yield as a side product. ^c 1 h. ^d 24 h. ^e 3,3-Dimethyl-1-butene (5.0 equiv) was used as a hydrogen acceptor. ^f 30 min. ^g 7 h. ^h 6 h. ⁱ 2 h.

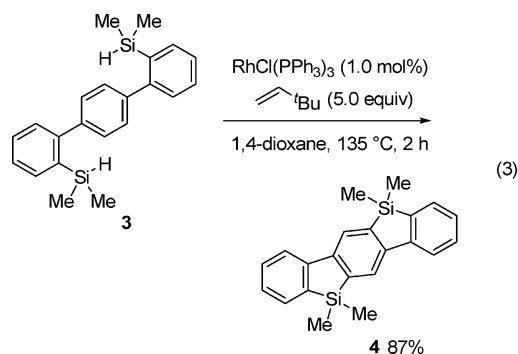
aromatic C–H bond);¹⁷ (2-a) sequential oxidative addition of the aromatic C–H bond to a metal center (C–H bond activation);¹⁸ and (3-a) reductive elimination to give silafluorene **2**. Another possible pathway is (2-b) the formation of intermediate **A** via σ -bond metathesis (C–H bond activation); (3-b) reductive elimination to give silafluorene **2**. In step (2-a) or (2-b), it is important that the position of the Si–Rh–H moiety is close to the C–H bond because intramolecular C–H bond activation proceeds more easily than intermolecular C–H bond activation. In addition, such C–H bond transformation occurs regioselectively.

Scheme 1. Proposed Mechanism for the Formation of Silafluorenes **2**

Next, we performed a deuterium labeling experiment to elucidate the rate-determining step for the formation of the silafluorenes. If the C–H bond activation is the rate-determining step, a kinetic isotope effect (KIE) should be observed using a mixture of biarylhydrosilane **1a** and its pentadeuterated substrate **1a-d**. Treatment of a mixture of **1a** and **1a-d** with a catalytic amount of RhCl(PPh₃)₃, at 135 °C for 45 s, gave silafluorenes **2a** and **2a-d** in 9% yield (**2a**:**2a-d** = 87:13, KIE = 6.8) (eq 2). This result shows that C–H bond activation of a phenyl group is the rate-determining step in the formation of silafluorenes.



This reaction could be applied to the synthesis of ladder-type bis-silicon-bridged *p*-terphenyl **4** (eq 3).^{2d,19} After a mixture of **3**, 3,3-dimethyl-1-butene, RhCl(PPh₃)₃, and 1,4-dioxane was heated, double cyclization occurred and ladder-type silafluorene **4** was obtained in 87% yield.²⁰



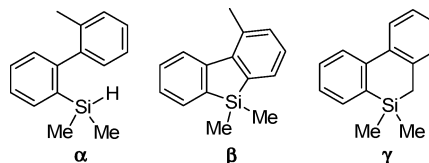
In summary, we have succeeded in the synthesis of silafluorenes from biarylhydrosilanes. This reaction proceeds by double activation of Si–H and C–H bonds via dehydrogenation. The dehydrogenation reaction does not require oxidants, such as molecular oxygen. Using this method, a ladder-type bis-silicon-bridged *p*-terphenyl was also synthesized. We hope that this reaction will become a useful method to synthesize silafluorenes.

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Supporting Information Available: General experimental procedure and characterization data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (7) Investigation of several transition metal complexes (metal: 2.0 mol%): RhCl(CO)(PPh₃)₂, 9%; the following complexes did not give silafluorene **2a**: Cr(CO)₆, Mo(CO)₆, W(CO)₆, ReCl₃, ReCl₃(PMe₂Ph)₃, ReOCl₃(PPh₃)₂, MeReO₃, Fe₃(CO)₁₂, Co₂(CO)₈, CoCl(PPh₃)₃, [RhCl(CO)₂]₂, RhCl₃·3H₂O, Rh(acac)₃, PtO₂, PtH₂Cl₆·6H₂O.
- (8) Investigation of several rhodium catalytic systems by mixing of [RhCl(cod)]₂ with a phosphine ligand: ([RhCl(cod)]₂/monodentate phosphine ligand = 1:6; [RhCl(cod)]₂/bidentate phosphine ligand = 1:3): none, 44%; PMe₃, 57%; PCy₃, 97%; PPh₃, 58%; 1,2-bis(diphenylphosphino)ethane (dppe), trace; 1,3-bis(diphenylphosphino)propane (dppp), 52%; 1,4-bis(diphenylphosphino)butane (dppb), 45%; (*R*)-BINAP, 87%.
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- (13) In the case of using a biarylhydrosilane with a methyl group at the *ortho*-position, **α**, a mixture of silafluorene **β** and 9,10-dihydro-9-silaphenanthrene **γ**, which was formed by intramolecular dehydrogenative coupling between the hydrosilyl moiety and methyl group on the aromatic ring, was produced in 19% and 47% yields, respectively (RhCl(PPh₃)₃, 5.0 mol%; 24 h). The silafluorene **β** could not be separated from **γ** by silica gel column chromatography or GPC.



- (14) Although the corresponding silafluorene was formed using biphenylhydrosilanes bearing two isopropyl groups on the silicon atom, the yield was only 12% (3,3-dimethyl-1-butene: 5.0 equiv, 180 °C, 24 h; not shown).
- (15) A purple fluorescence was observed when irradiating 254 nm UV light on a hexane solution of **2k** or solid sample of **2k**.
- (16) In the case of (2-ethenylphenyl)dimethylsilane, intramolecular hydrosilylation occurred easily. Therefore, to compare the reaction rates between the formation of silafluorenes and intermolecular hydrosilylation, a mixture of 2-(dimethylsilyl)biphenyl (**1a**) and styrene was heated in the presence of a catalytic amount of RhCl(PPh₃)₃. Intermolecular hydrosilylation did not occur, and only silafluorene **2a** was obtained in 93% yield. This result shows that only the formation of silafluorenes occurred even in the presence of styrene, which is an excellent substrate for hydrosilylation.
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- (20) A purple fluorescence was observed when irradiating 254 nm UV light on a hexane solution of **4** or solid sample of **4**. See ref 19.

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