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Lewis Acid-Catalyzed Synthesis of Silafluorene Derivatives from Biphenyls and Dihydrosilanes via Double Sila-Friedel-Crafts Reaction

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The synthesis of silafluorene derivatives from aminobiphenyl compounds and dihydrosilanes via a double sila-Friedel-Crafts reaction using a borane catalyst has been achieved. This method is applicable toward the synthesis of a variety of silafluorene derivatives, such as multisubstituted silafluorenes, spiro-silafluorenes, and silicon-bridged terphenyl compounds, which are not readily obtained using conventional synthetic methods. In addition, we have demonstrated the transformation of the amino groups in these silafluorene derivatives into other substituents.

Introduction

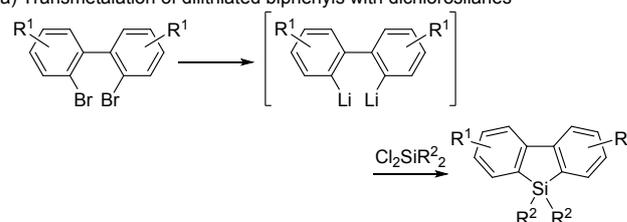
Silafluorenes (dibenzosiloles) derivatives are one of the most important compounds applied as organic functional materials, such as organic electroluminescent compounds,¹ light emitting materials,² field effect transistors,³ and photovoltaics.⁴ Therefore, several useful methods for the synthesis of silafluorene derivatives have been developed. As the conventional method, dilithiation of 2,2'-dibromobiphenyls and successive transmetalation of the dilithiated biphenyls with dichlorosilanes is well known (Scheme 1a).⁵ Although this method is useful, it has some drawbacks including: (1) multiple reaction steps are required to synthesize the target silafluorene derivatives, (2) it is difficult to synthesize silafluorene derivatives with functional group(s), which react with organolithium reagents, and (3) the synthesis of multisubstituted silafluorene derivatives is difficult because the

preparation of their multisubstituted dibromobiphenyl precursors is troublesome. Hence, a straightforward synthetic method for the preparation of multisubstituted silafluorenes is still desirable.

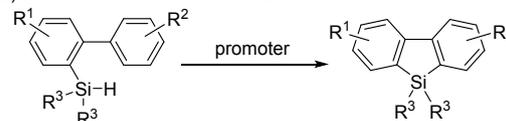
Recently, the synthesis of silafluorene derivatives using an intramolecular sila-Friedel-Crafts reaction of biphenylhydrosilanes has been reported (Scheme 1b).⁶⁻⁸ In addition, we have successfully prepared a variety of silafluorene derivatives via a rhodium-catalyzed intramolecular C-H silylation of biphenylhydrosilanes (Scheme 1c).⁹⁻¹¹ Several transition metal-catalyzed synthetic methods to prepare silafluorenes have also been reported by other research groups.¹²

Based on the above-mentioned synthetic strategies, the reaction between biphenyl compounds and dihydrosilanes is a

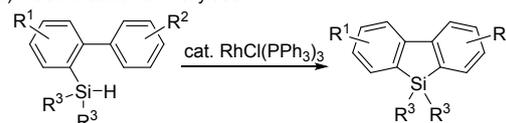
(a) Transmetalation of dilithiated biphenyls with dichlorosilanes



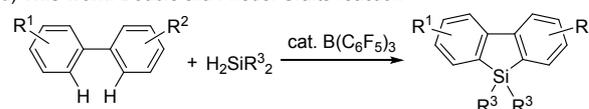
(b) Intramolecular sila-Friedel-Crafts reaction



(c) Intramolecular C-H silylation



(d) This work: Double sila-Friedel-Crafts reaction



Scheme 1. Several Synthetic Methods of Silafluorene Derivatives.

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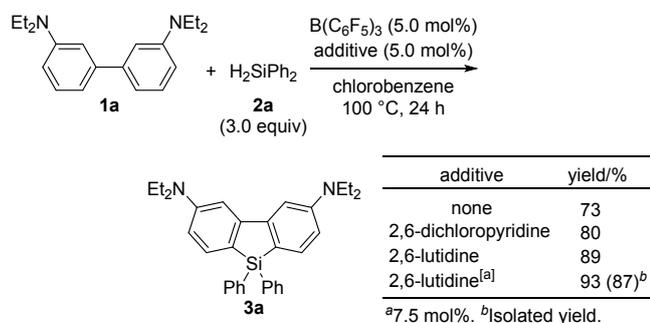
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more ideal and promising approach to synthesize silafluorene derivatives. Recently, Ingleson^{7b} and Hou¹³ independently reported an effective borane-catalyzed C-H silylation of aromatic compounds via intra- and intermolecular sila-Friedel-Crafts reactions.¹⁴ We then considered that the synthesis of silafluorene derivatives was feasible based on a double sila-Friedel-Crafts reaction. Although a ruthenium-catalyzed reaction between 2-phenylindoles and dihydrosilanes via sequential C-H silylation was reported, there is no example of the synthesis of silafluorenes.¹⁵ Herein, we report a direct borane-catalyzed synthesis of silafluorene derivatives from biphenyls and dihydrosilanes (Scheme 1d). This is the first example of the synthesis of silafluorene derivatives from biphenyls and dihydrosilanes via a double C-H silylation reaction.

Results and discussion

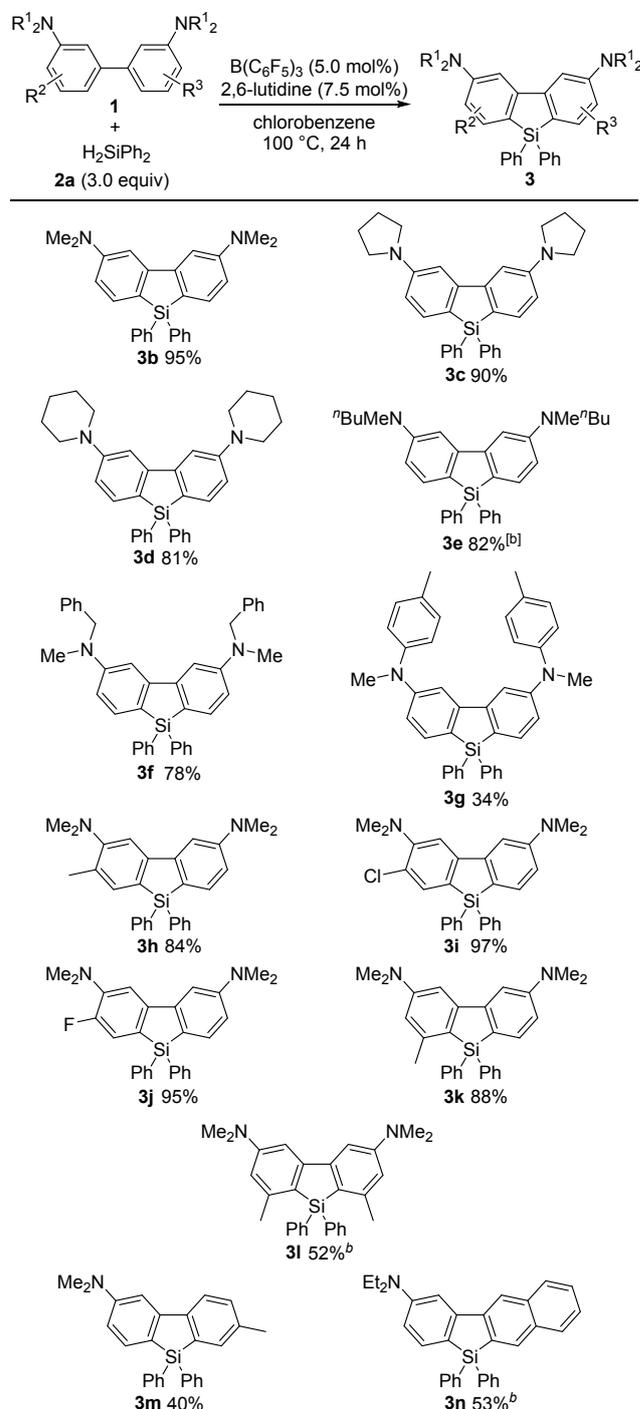
We initially investigated the feasibility of our synthetic approach using diaminobiphenyl **1a** and dihydrodiphenylsilane **2a** as model substrates (Scheme 2). As a result, the double sila-Friedel-Crafts reaction of **1a** with **2a** in the presence of a catalytic amount of B(C₆F₅)₃ in chlorobenzene heated at 100 °C for 24 h afforded silafluorene **3a** in 73% yield. Ingleson reported that 2,6-dichloropyridine is crucial during the catalytic cycle of the intramolecular sila-Friedel-Crafts reaction of biphenylhydrosilanes. 2,6-Dichloropyridine is probably effective for the deprotonation of the silylated arenium cation.^{7b} Therefore, we investigated several additives as a base. The yield of **3a** was improved to 80% in the presence of 5.0 mol% 2,6-dichloropyridine and **3a** was obtained in 93% yield (87% isolated yield) using 7.5 mol% 2,6-lutidine.



Scheme 2. Synthesis of Silafluorene Derivative **3a** from Diaminobiphenyl **1a** and Dihydrodiphenylsilane (**2a**).

We then investigated the scope of the biaryl compounds used in the reaction (Scheme 3). Biphenyls bearing acyclic or cyclic *N,N*-dialkylamino groups **1b–e** gave their corresponding silafluorene derivatives (**3b–e**) in 81–95% yield.¹⁶ Silafluorenes **3f** and **3g** were formed using *N*-benzyl-*N*-methylamino and *N*-aryl-*N*-methylamino group-substituted biphenyls **1f** and **1g**, respectively. The previous synthetic methods used to prepare multisubstituted silafluorene derivatives have drawbacks due to the difficulties preparing their multisubstituted starting materials. In contrast, trisubstituted silafluorene derivatives

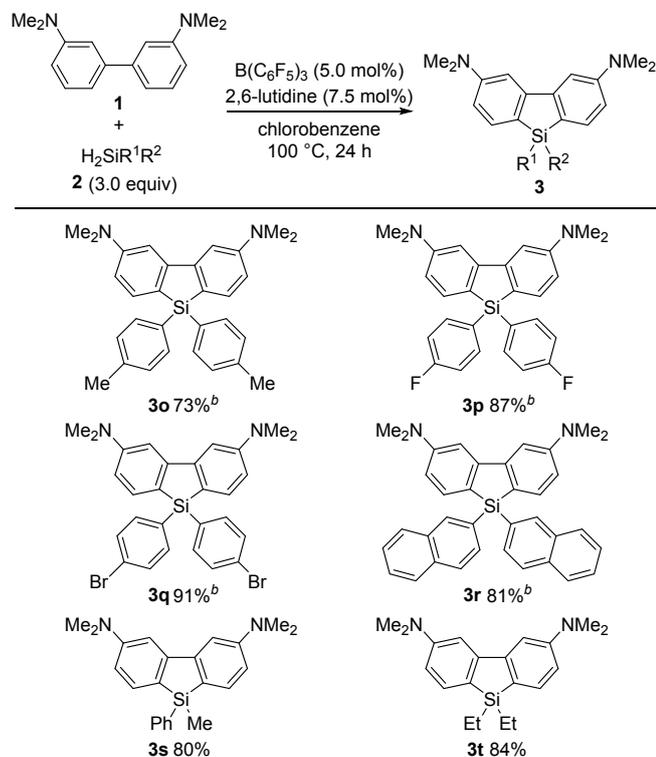
3h–k were obtained in good to excellent yield from their corresponding biphenyls (**1h–k**), which can be readily synthesized. Notably, tetrasubstituted silafluorene **3l** can be obtained in 52% yield. The reaction system is also applicable to mono-aminobiphenyls **1m** and **1n**, which gave their corresponding silafluorenes **3m** and **3n** in 40 and 53% yields, respectively.



^a Isolated yield. ^b 140 °C.

Scheme 3. Substrate Scope of Biaryls **1**.

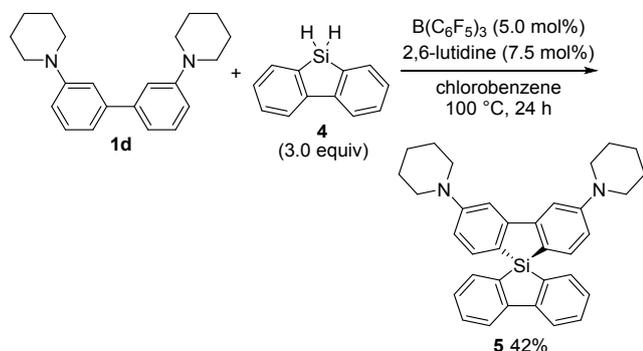
Subsequently, the scope of the dihydrosilane substrate (**2**) was investigated (Scheme 4). Diaryldihydrosilanes bearing electron-donating and electron-withdrawing groups gave silafluorene derivatives **3o**, **3p**, and **3q** in 73, 87, and 91% yield, respectively. Silafluorene **3r** was obtained using di(2-naphthyl)silane (**2e**) in high yield. Phenylmethylsilane and diethyldihydrosilane were also transformed into silafluorene derivatives **3s** and **3t** in high yield.



^a Isolated yield. ^b 140°C .

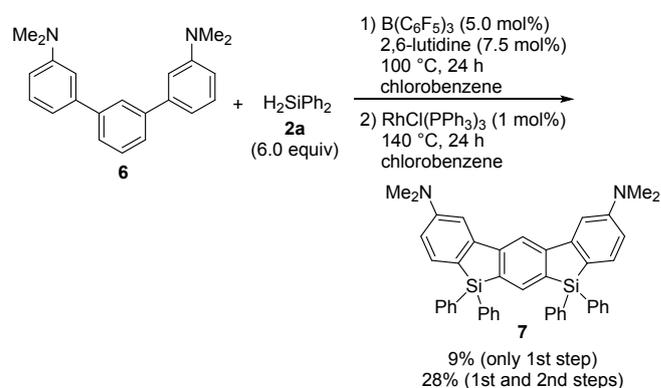
Scheme 4. Substrate Scope of Dihydrosilanes **2**.^a

Spirosilabifluorenes are an attractive scaffold for organic optoelectronic materials due to their decreased HOMO–LUMO energy gap and fluorescent properties.^{9b,12a,17} It is notable that spiroilabifluorene derivative **5** was obtained from biphenyl **1d** and 9,9-dihydro-5-silafluorene (**4**) in 42% yield (Scheme 5).



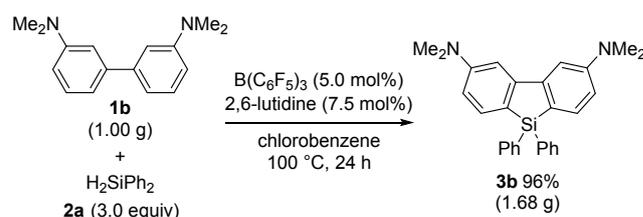
Scheme 5. Synthesis of Spirosilabifluorene Derivative **5**.

Silicon-bridged terphenyl compounds have attracted a lot of attention due to their optoelectronic properties. Although silicon-bridged *para*-terphenyl compounds are well known,^{7a,9a,12a,17e,18} examples of the synthesis of silicon-bridged *meta*-terphenyl compounds are quite rare.¹⁹ Hence, we investigated the synthesis of a silicon-bridged *meta*-terphenyl compound using our synthetic method. A quadruple sila-Friedel-Crafts reaction of *meta*-terphenyl derivative **6** with diphenylsilane (**2a**) afforded silicon-bridged *meta*-terphenyl compound **7** in only 9% yield (Scheme 6). After the reaction, a mixture of biphenylhydrosilanes was observed using ^1H NMR spectroscopy. This result indicates that the intramolecular sila-Friedel-Crafts reaction on the central benzene ring did not proceed effectively. Therefore, after the intermolecular borane-catalyzed sila-Friedel-Crafts reaction, a successive rhodium-catalyzed intramolecular C–H silylation⁹ was carried out. As a result, the yield of **7** was improved to 28% (Scheme 5).



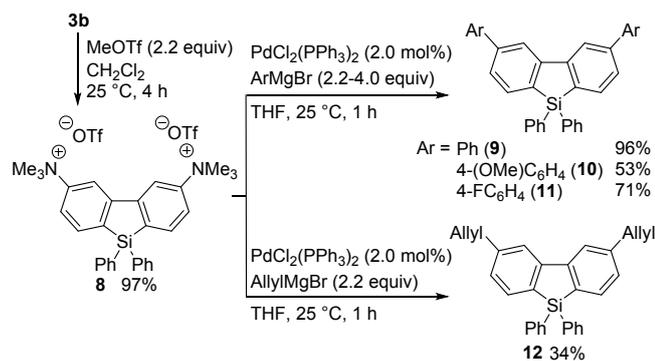
Scheme 6. Synthesis of Silicon-bridged Terphenyl Molecule **7**.

Silafluorene **3b** was obtained in good yield, even on a gram-scale (Scheme 7). Treating 1.00 g of biphenyl **1b** with 2.33 g of dihydrodiphenylsilane (**2a**) in the presence of catalytic amounts of $\text{B}(\text{C}_6\text{F}_5)_3$ and 2,6-lutidine in chlorobenzene afforded 1.68 g of silafluorene **3b** (96% yield).



Scheme 7. Gram-scale Synthesis of Silafluorene Derivative **3b**.

The amino groups on the silafluorene derivatives can be converted into other functional groups (Scheme 8).²⁰ Initially, the amino groups in **3b** were converted into their ammonium salts upon treatment with MeOTf and gave **8** in 97% yield. Ammonium salt **8** was then treated with a Grignard reagent (PhMgBr) in the presence of a palladium catalyst ($\text{PdCl}_2(\text{PPh}_3)_2$) to give the cross-coupling product (**9**) in 96% yield. Other Grignard reagents including 4-(MeO) $\text{C}_6\text{H}_4\text{MgBr}$, 4- $\text{FC}_6\text{H}_4\text{MgBr}$ and ($\text{CH}_2=\text{CH}-\text{CH}_2$) MgBr also gave their corresponding silafluorenes (**10–12**) in moderate to good yield.



Scheme 8. Conversions of Amino Groups.

Conclusions

In summary, we have successfully prepared a variety of silafluorene derivatives from electron-rich biaryls and dihydrosilanes using a double sila-Friedel-Crafts reaction. The silafluorene derivatives were obtained in good to excellent yield, even on a gram-scale. Multisubstituted silafluorene derivatives were afforded from their corresponding biphenyl derivatives, which can be readily prepared. This new method is also applicable toward the synthesis of spiro-silafluorenones and silicon-bridged terphenyl derivatives. In addition, we have demonstrated the transformation of the amino groups in the silafluorene derivatives into several other substituents. We hope that the developed reaction will become a useful and effective protocol to synthesize a variety of silafluorene derivatives.

Conflicts of interest

There are no conflicts to declare.

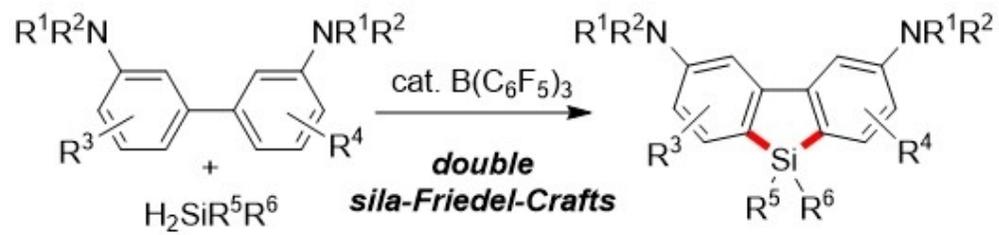
Acknowledgement

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