Fluorescent Heterocycles

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Palladium-Catalyzed C–H Fluorosilylation of 2-Phenylpyridines: Synthesis of Silafluorene Equivalents**

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Abstract: *Treatment of 2-phenylpyridines with amino(1,3,2-dioxaborolan-2-yl)diphenylsilane produced fluorosilylated 2-phenylpyridines in good to excellent yields under palladium catalysis. This reaction is the first example of C–H fluorosilylation. Single-crystal X-ray structure analysis revealed a Lewis acid–base interaction between the silicon and nitrogen atoms, and the obtained fluorosilylated products are silafluorene equivalents. The fluorosilylated products showed stronger fluorescence than the corresponding silafluorene derivative.*

π-Conjugated molecules with silicon atom(s) such as silafluorenes (dibenzosiloles) are important organic functional materials, as are their basic structures.[1] Several methods have been developed to synthesize silafluorenes. The most general method is dilithiation of 2,2′-dihalobiaryls and successive treatment of the formed 2,2′-dilithiobiaryls with dichlorosilanes.[2] In silafluorene structures, π-conjugated biaryl moieties and a silicon atom are connected by two Si–C covalent bonds (Figure 1 a). Our design for a new category of original π-conjugated molecules is a silafluorene equivalent in which one of the two Si–C covalent bonds is replaced with a Si···N Lewis acid–base interaction (Figure 1 b).[3] This molecular design is based on the characteristics of silicon atoms bearing electron-withdrawing group(s), so that hypervalent structures can be formed as a result of the high Lewis acidity of silicon atoms.[4,5]

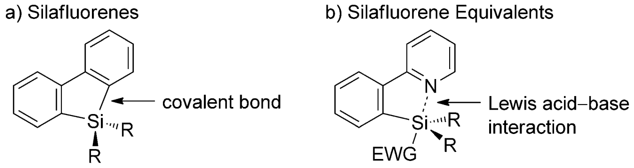
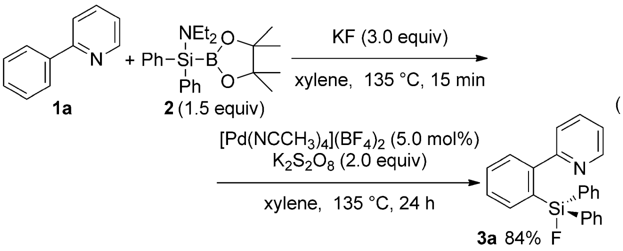


Figure 1. Comparison of the structures of silafluorenes and their proposed equivalents. EWG = electron-withdrawing group.

To synthesize the designed structures (Figure 1 b), we planned to use directing-group-assisted (pyridyl group), transition-metal-catalyzed direct C–H silylation. Such transformations are highly efficient and atom economical compared with previous methods such as the lithiation/transmetallation sequence. Previously, one of the authors succeeded in synthesizing silafluorenes by rhodium-catalyzed direct intramolecular C–H silylation.[6,7] Because pyridyl groups can be used as an effective directing group of transition-metal catalysts, several methods for intermolecular direct C–H silylation at the *ortho* position of 2-phenylpyridines have been reported,[8] however, coordination of the directing groups to the introduced silicon atom was not detected in the products, and is presumably a result of the low Lewis acidity of the silicon atoms introduced by the previous C–H silylations (trialkyl- or triarylsilyl groups).[8–11] If electron-deficient silyl groups can be introduced, the designed silafluorene equivalents (Figure 1 b) comprising intramolecular Si···N interactions can be obtained from 2-phenylpyridines in only one step. Herein we describe the successful development of the first aromatic C–H fluorosilylationm and the products are fluorescent in solution, similar to silafluorenes.

Based on recent studies by the group of Suginome, we selected a palladium complex and *N*,*N*-diethyl-1,1-diphenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)silanamine (**2**)[12] as the catalyst and silicon source, respectively. Treatment of 2-phenylpyridine (**1a**) with **2** in the presence of a palladium catalyst [Pd(MeCN)$_4$](BF$_4$)$_2$ (6.0 mol%) in toluene at 100 °C for 24 hours did not lead to formation of the assumed hydrosilane, but rather, the *ortho*-fluorosilylated product **3a** was obtained in 10% yield [for structure see Eq. (1)]. The origin of the fluorine atom of **3a** must be the BF$_4$ anion of the palladium catalyst, thus KF was added as a fluorine source and the reaction conditions were optimized.[13–20] As a result, the yield of **3a** increased to 74%. In addition, the order of the addition of **1a**, **2**, [Pd(MeCN)$_4$](BF$_4$)$_2$, KF, and K$_2$S$_2$O$_8$ was altered, that is, a mixture of **1a** and **2** was treated with KF before addition of the palladium catalyst and oxidant, and thus improved the yield of **3a** to 84% [Eq. (1)].



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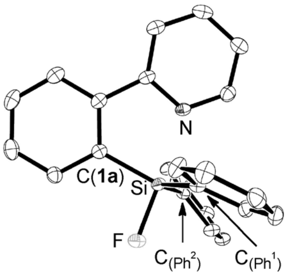


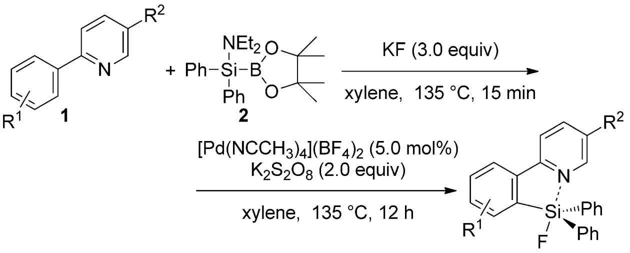
Figure 2. Single-crystal X-ray structure of **3a**. The ellipsoids are shown at 50% probability. Hydrogen atoms are omitted for clarity. Selected distances [Å]: Si-N 2.2068(15), Si−F 1.6674(12), Si−C(**1a**) 1.8748(19), Si−C(Ph^1) 1.8779(19), Si−C(Ph^2) 1.871(2). Selected angles [°]: C(**1a**)-Si-C(Ph^1) 118.16(9), C(Ph^1)-Si-C(Ph^2) 123.28(8), C(Ph^2)-Si-C(**1a**) 115.17(8), C(**1a**)-Si-N 79.00(7), C(Ph^1)-Si-N 84.72(7), C(Ph^2)-Si-N 87.64(7), C(**1a**)-Si-F 98.05(7), C(Ph^1)-Si-F 95.18(7), C(Ph^2)-Si-F 95.29(8).

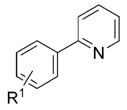
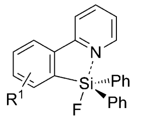
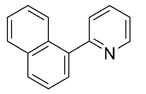
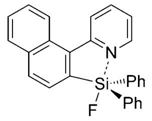
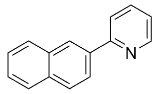
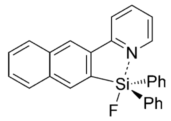
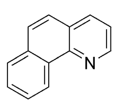
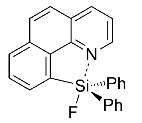
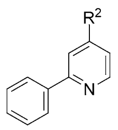
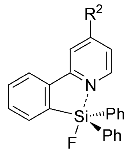
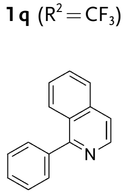
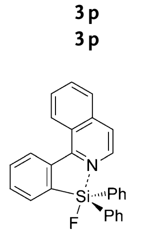
The structure of **3a** was determined by single-crystal X-ray structure analysis (Figure 2). The findings indicated that the nitrogen atom of the pyridyl group coordinated to the silicon atom and **3a** was a pentacoordinated silicon compound (trigonal-bipyramidal geometry). In fact, the length between the nitrogen and silicon atoms was 2.2068(15) Å, thus supporting the existence of a Lewis acid–base interaction.[4a,b,21] The arrangement of N-Si-F was almost linear (176.5°). The dihedral angle of N-C$_{(py)}$-C$_{(benzene)}$-C$_{(\mathbf{1a})}$ was 4.8°, and the sum of the three angles of C$_{(\mathbf{1a})}$-Si-C$_{(Ph^1)}$, C$_{(Ph^1)}$-Si-C$_{(Ph^2)}$, and C$_{(Ph^2)}$-Si-C$_{(\mathbf{1a})}$ was 356.6°. These findings indicate that the pyridine and benzene rings, and Si, C$_{(\mathbf{1a})}$, C$_{(Ph^1)}$, and C$_{(Ph^2)}$ atoms existed in almost the same planes, perpendicular to each other.

Next, we investigated the substrate scope and limitations (Table 1). Fluorosilylation proceeded in good to excellent yields using the 2-phenylpyridines **1b–g**, having an electron-donating or electron-withdrawing group, a chlorine, or an ethoxycarbonyl group at the 4-position, without loss of the functional groups (entries 1–6). Although two possible regioisomers might be formed when a substituent exists at the 3-position, only a single isomer, with the silicon atom introduced at the less hindered site, was formed (entries 7 and 8). The silylation reaction was not inhibited by steric hindrance from a substituent at the 2-position (entries 9–11). The corresponding silylated products, such as the pyridylnaphthalenes **3m** and **3n**, and benzo[*h*]quinoline **3o**, were produced in 62–88% yields (entries 12–14). An electron-donating or electron-withdrawing substituent on the pyridine ring was also tolerated in this fluorosilylation reaction (entries 15 and 16). A quinoline group also worked as a directing group, and the corresponding fluorosilylated product **3r** was obtained in 76% yield (entry 17). Other directing groups, however, such as pyrazolyl and N-methylimidazolyl groups, were not effective for the fluorosilylation.

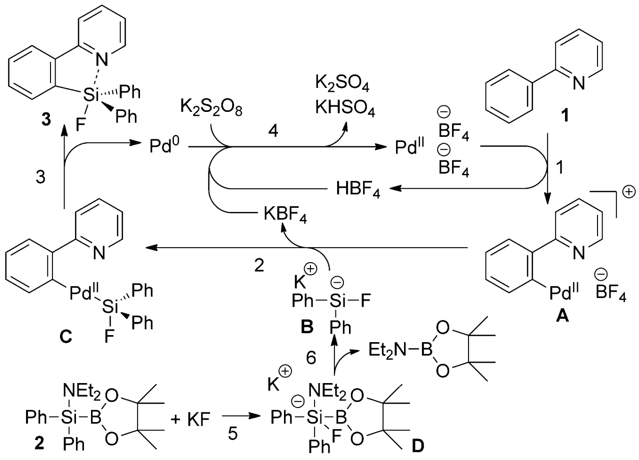
The proposed mechanism for the fluorosilylation is shown in Scheme 1. The reaction would proceed through the following four key steps: 1) formation of an *ortho*-palladated intermediate **A** (C−H bond activation); 2) formation of the fluorosilyl palladium intermediate **C** from **A** and **B**; 3) reductive elimination of **C** to give the fluorosilylated product **3** and

Table 1: Investigation of several 2-phenylpyridines and their derivatives (**1**).[a]



Entry	1	3	Yield [%]
			
1	**1b** (R^1 = 4-MeO)	**3b**	74
2	**1c** (R^1 = 4-Me)	**3c**	82
3	**1d** (R^1 = 4-CF$_3$)	**3d**	58
4	**1e** (R^1 = 4-CO$_2$Et)	**3e**	57
5	**1f** (R^1 = 4-F)	**3f**	84
6	**1g** (R^1 = 4-Cl)	**3g**	75
7	**1h** (R^1 = 3-MeO)	**3h**	88
8	**1i** (R^1 = 3-Ph)	**3i**	75
9	**1j** (R^1 = 2-MeO)	**3j**	78
10	**1k** (R^1 = 2-Me)	**3k**	66
11	**1l** (R^1 = 2-Ph)	**3l**	77
			
12	**1m**	**3m**	62
			
13	**1n**	**3n**	64
			
14	**1o**	**3o**	88
			
15	**1p** (R^2 = OMe)	**3p**	75
16	**1q** (R^2 = CF$_3$)	**3p**	68
			
17	**1r**	**3r**	76

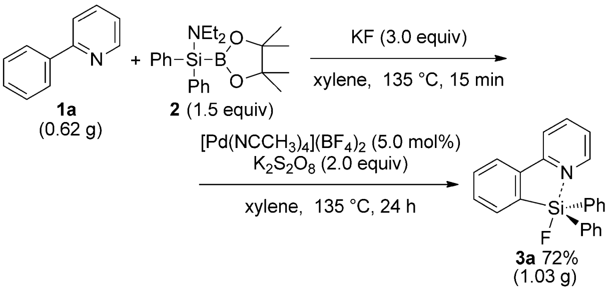
[a] **2** (1.5 equiv).



Scheme 1. Proposed mechanism for the formation of 2-fluorosilylated 2-phenylpyridines and their derivatives.

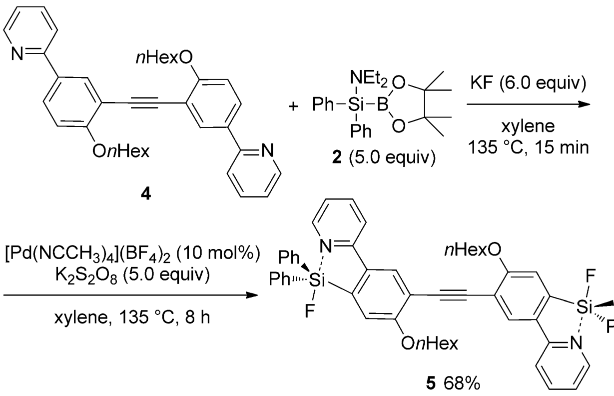
a palladium(0) species; and 4) oxidation of the palladium(0) species by $K_2S_2O_8$ to regenerate the palladium(II) catalyst. The intermediate **B** could be formed by the formation of the silicate **D** from **2** and KF (5), and elimination of Et_2N-Bpin from **D** (6).

The reaction can be performed on a gram scale. The reaction of 0.62 g of **1a** with a fluorine source, KF, and successive treatment with a catalytic amount of $[Pd(NCCH_3)_4](BF_4)_2$ and the oxidant $K_2S_2O_8$ produced 1.03 g of **3a** in 72 % yield [Eq. (2)].



(2)

To expand the π-conjugated system, we investigated double fluorosilylation [Eq. (3)]. Treatment of a mixture of 1,2-bis(2-hexyloxy-5-(2-pyridinyl)phenyl)ethyne (**4**) and **2** with KF, and successive treatment with a palladium catalyst and $K_2S_2O_8$ afforded the double-fluorosilylated product **5** in 68 % yield.



(3)

As we expected, the fluorosilylated 2-phenylpyridines **3** were fluorescent. For expression of the fluorescence, both nitrogen and fluorine atoms are indispensable because the quantum yields of 2-(2-(methyldiphenylsilyl)phenyl)pyridine (**6**) and 2-fluorosilylbiphenyl **7** are quite low (Figure 3). Interestingly, the quantum yield of **3a** was much higher than that of the corresponding silafluorene **8** (dibenzosilole).[22] The double-fluorosilylated product **5** showed blue fluorescence ($\lambda_{em} = 435$ nm) and had a high quantum yield ($\Phi_F = 0.60$).

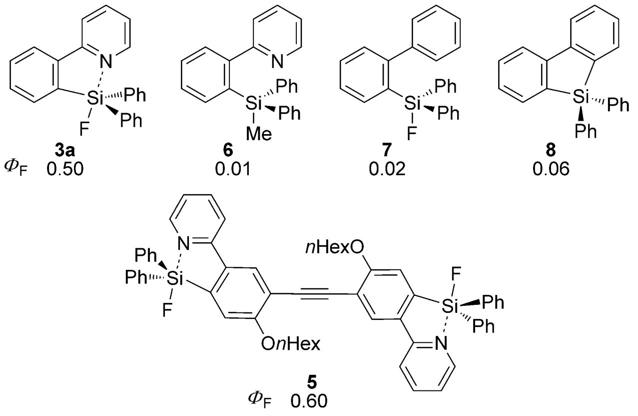


Figure 3. Comparison of fluorescent quantum yields in THF.

According to the density functional theory (DFT) calculations at the B3LYP/6-31 + G* level of theory, the HOMO orbitals of **3a** and **8** differed considerably, whereas the LUMO orbitals were almost the same (Figure 4). The HOMO orbital of **3a** is located mainly on one of the phenyl

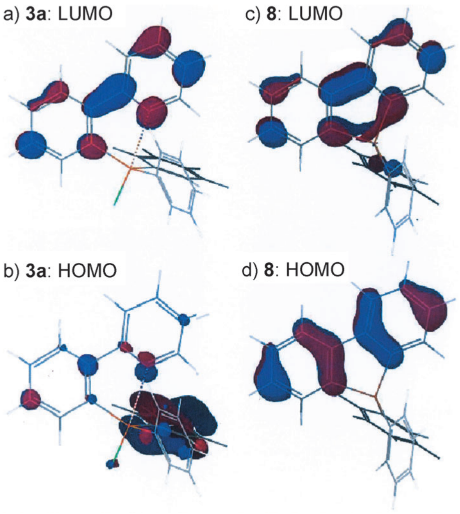


Figure 4. LUMO and HOMO orbitals of 2-(2-fluorosilylated)phenylpyridine (**3a**) and the silafluorene **8**.

groups on the silicon atom, while the LUMO orbital delocalizes on the 2-phenylpyridine moiety. The time-dependent DFT calculation at the same level of theory indicated that the emission of **3a** occurred from an excited state generated by the intramolecular charge-transfer transition from the HOMO to LUMO.

In summary, we successfully developed a one-step synthesis of silafluorene (dibenzosilole) equivalents (**3**) by developing a palladium-catalyzed regioselective C–H fluorosilylation of 2-phenylpyridines and their related compounds. The silafluorene equivalents comprise a pentacoordinated silicon atom through an intramolecular Lewis acid–base interaction (noncovalent bond) between the fluorosilyl and pyridyl groups because of the high Lewis acidity of the fluorinated silicon atom. The pyridyl group acts as both a directing group to promote C–H fluorosilylation and a component of the silafluorene equivalents. This reaction is useful and practical because the fluorosilylation reaction has high functional-group tolerance and proceeds in good to excellent yields, even on gram scale. The fluorosilylated 2-phenylpyridines and their derivatives are fluorescent, and the Lewis acid–base interaction between the silicon and nitrogen atoms is critical for the fluorescence emission because of the expansion of the π-conjugated system through the interaction. In addition, the quantum yield of *ortho*-fluorosilylated 2-phenylpyridine was much higher than that of the corresponding silafluorene. The time-dependent DFT calculations indicate that the emission of fluorosilylated products occurs from an excited state generated by the intramolecular charge-transfer transition from the HOMO to the LUMO. We hope that this result will contribute to a novel category of functional materials based on noncovalent bond(s).

Experimental Section

Typical procedure for the reaction of 2-phenylpyridine (**1a**) with amino(1,3,2-dioxaborolan-2-yl)diphenylsilane (**2**): Under an argon atmosphere (or in a glove box), **1a** (621 mg, 4.00 mmol), **2** (2.29 g, 6.00 mmol), and KF (697 mg, 12.0 mmol) were added to xylene (12 mL). The mixture was then stirred at 135 °C for 15 min. At the same time, $K_2S_2O_8$ (3.24 g, 12.0 mmol) and $[Pd(MeCN)_4](BF_4)_2$ (88.8 mg, 0.200 mmol) was added into the reaction system. The mixture was then stirred at 135 °C for 24 h. Upon completion of the reaction, the crude product was purified by column chromatography (*n*-hexane/EtOAc 10:1) to afford pure **3a** as a white solid (1.03 g, 72 %).

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[14] Investigation of several F^- sources ($[Pd(NCCH_3)_4](BF_4)_2$ (5.0 mol %), $K_2S_2O_8$ (2.0 equiv), toluene, 100 °C): CsF: trace, KHF_2: trace, KBF_4: 11 %, KF: 36 %, Bu_4NF: trace, $Et_4NF\cdot3HF$: 0 %.

[15] Investigation of several oxidants ($[Pd(NCCH_3)_4](BF_4)_2$ (5.0 mol %), KF (3.0 equiv), toluene, 100 °C): benzoquinone: 0 %, 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ): 0 %, $K_2S_2O_8$: 36 %, $Cu(OAc)_2$: 0 %, AgOAc: 0 %, $AgBF_4$: 0 %.

[16] Investigation of several solvents ($[Pd(NCCH_3)_4](BF_4)_2$ (5.0 mol %), KF (3.0 equiv), $K_2S_2O_8$ (2.0 equiv), 100 °C): hexane: 25 %, 1,4-dioxane: 16 %, toluene: 36 %, THF: trace, dichloromethane: 7 %, *N,N*-dimethylformamide: 0 %, acetonitrile: trace.

[17] Investigation of the amount of $K_2S_2O_8$ ($[Pd(NCCH_3)_4](BF_4)_2$ (5.0 mol %), KF (3.0 equiv), toluene; 100 °C): 2.0 equiv: 36 %, 3.0 equiv: 36 %, 5.0 equiv: 32 %.

[18] Investigation of several temperatures ($[Pd(NCCH_3)_4](BF_4)_2$ (5.0 mol %), xylene, KF (3.0 equiv), $K_2S_2O_8$ (2.0 equiv)): 100 °C: 36 %, 135 °C: 60 %, 150 °C: 59 %.

[19] Second investigation of several solvents ($[Pd(NCCH_3)_4](BF_4)_2$ (5.0 mol %), KF (3.0 equiv), $K_2S_2O_8$ (2.0 equiv), 135 °C): octane: 55 %, 1,4-dioxane: 22 %, xylene: 60 %, chlorobenzene: 32 %, THF: 12 %, 1,2-dichloroethane: 21 %, *N,N*-dimethylformamide: 0 %, acetonitrile: trace.

[20] Investigation of several concentrations ($[Pd(NCCH_3)_4](BF_4)_2$ (5.0 mol %), KF (3.0 equiv), $K_2S_2O_8$ (2.0 equiv), 135 °C): 0.20 M: 61 %, 0.33 M: 74 %, 0.50 M: 68 %.

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