Cross-Couplings

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Decarbonylative Silylation of Esters by Combined Nickel and Copper Catalysis for the Synthesis of Arylsilanes and Heteroarylsilanes

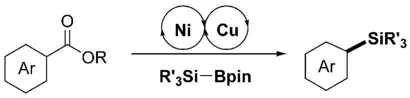
*Lin Guo, Adisak Chatupheeraphat, and Magnus Rueping**

Abstract: *An efficient nickel/copper-catalyzed decarbonylative silylation reaction of carboxylic acid esters with silylboranes is described. This reaction provides access to structurally diverse silanes with high efficiency and excellent functional-group tolerance starting from readily available esters.*

Organosilicon compounds constitute an important class of intermediates in the synthesis of natural products, drug molecules, and functional materials.[1] They have attracted increasing attention in view of their high reactivity as useful synthetic building blocks as well as their unique physical and chemical properties.[2] The synthesis of organosilicon compounds is traditionally based on the addition of Grignard or organolithium reagents to chlorosilanes or cyclosiloxanes.[3] Alternatively, organosilanes can be prepared by transition-metal-catalyzed cross-couplings of organohalides with hydrosilanes[4] or disilanes.[5] Recently, catalytic silylation by C−H bond activation has been achieved. However, the regioselectivity was not always satisfactory or additional directing groups were needed.[6] Therefore, emphasis is directed on research aimed at finding new synthetic routes for the synthesis of organosilicon compounds.

Transition-metal-catalyzed decarboxylative/decarbonylative cross-coupling reactions have recently attracted considerable attention owing to the availability and natural abundance of carboxylic acids and their derivatives as alternatives to halides and organometallic reagents.[7] Unlike the direct decarboxylation of carboxylic acids, decarbonylative couplings can normally be accessed by extrusion of carbon monoxide from acyl–metal species, which can be generated by oxidative addition of carboxylic acid derivatives to metal complexes. Whereas many methods for carbon–carbon bond-forming reactions have been developed by employing different carbonyl precursors, very little is known about carbon–heteroatom, and in particular carbon–silicon, bond-forming reactions by decarbonylative processes. Krafft and co-workers reported a palladium-catalyzed decarbonylative coupling of acyl chlorides with disilanes,[8] and Tsuji and co-workers developed a palladium-catalyzed 1,4-carbosilylation.[9] Hence we wondered whether it would be possible to develop a more convenient approach for building C−Si bonds by a decarbonylative strategy starting from carboxylic acid esters,[10] which, owing to their ubiquitous nature, are more attractive electrophilic coupling partners than the more sensitive and less stable acyl chlorides.

With these considerations in mind, we began to search for potential catalysts and nucleophiles for the decarbonylative silylation of esters. Owing to their air stability, facile synthesis, and environmentally benign nature, silylborane compounds, which serve as efficient silicon nucleophiles in copper-catalyzed transmetalation,[11] have shown high efficiency and remarkable potential in various organic transformations.[12] Herein, we present the discovery of a new method for the nickel-[13] and copper-catalyzed decarbonylative silylation of esters by using silylborane compounds as coupling partners, which also features a wide substrate scope (Scheme 1).



Scheme 1. Nickel/copper-catalyzed decarbonylative silylation of esters.

We started our investigations by examining the reactivity of phenyl 2-naphthoate (**1a**) with silylborane **2a** in the presence of nickel and copper catalysts (Table 1).[14] First, we evaluated various ligands and obtained a promising result when employing tri-*n*-butylphosphine as the ligand and cesium fluoride as the base (entries 1–4). As the nature of the base plays a critical role for the success of the decarbonylative cross-coupling, various bases were evaluated. Replacing cesium fluoride with potassium fluoride under otherwise identical reaction conditions slightly improved the yield (entry 9) whereas the use of other bases or no base gave rather unsatisfying results (entries 5–8). Although different co-catalysts could be utilized (entries 10–12), the best result was obtained with copper(II) fluoride, which confirmed that the copper-based co-catalyst plays a crucial role in activating the Si−B bond.[15] Moreover, a slight increase in temperature gave a dramatic change in reactivity, providing **3a** in 83 % yield (entry 13). Further evaluation resulted in the optimized reaction conditions, which entailed the use of 2.0 equiv of the silylborane nucleophile (entry 14). A control experiment further revealed that the reaction did not occur in the absence of the nickel catalyst (entry 15).

Encouraged by our initial results, we decided to examine a series of aryl esters as electrophiles to determine the scope

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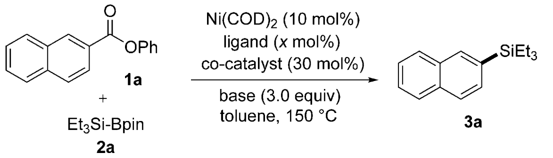
Table 1: Optimization of the decarbonylative silylation of esters.[a]



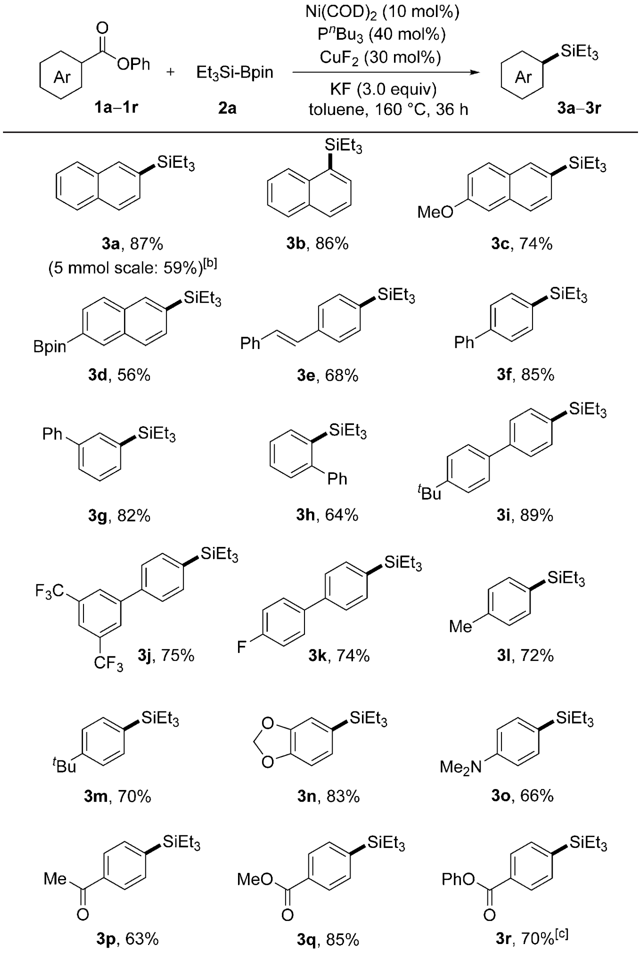
Entry	Ligand (mol%)	Base	Co-catalyst	t [h]	Yield [%][b]
1	PCy_3 (40)	CsF	CuF_2	15	<5
2	dcype (20)	CsF	CuF_2	15	<5
3	P^nBu_3 (40)	CsF	CuF_2	15	18
4	P^nBu_3 (40)	CsF	CuF_2	36	33
5	P^nBu_3 (40)	–	CuF_2	36	16
6	P^nBu_3 (40)	K_3PO_4	CuF_2	36	11
7	P^nBu_3 (40)	Et_3N	CuF_2	36	29
8	P^nBu_3 (40)	Na_2CO_3	CuF_2	36	35
9	P^nBu_3 (40)	KF	CuF_2	36	45
10	P^nBu_3 (40)	KF	–	36	16
11	P^nBu_3 (40)	KF	AgF	36	12
12	P^nBu_3 (40)	KF	ZnF_2	36	13
13[c]	P^nBu_3 (40)	KF	CuF_2	36	83
14[c,d]	**P^nBu_3 (40)**	**KF**	**CuF_2**	**36**	**87**
15[e]	P^nBu_3 (40)	KF	CuF_2	36	0

[a] Reaction conditions: **1a** (0.20 mmol), **2a** (0.30 mmol, 1.5 equiv), Ni(COD)$_2$ (10 mol%), ligand (x mol%), base (3.0 equiv), co-catalyst (30 mol%), toluene (0.2 M), 150°C. [b] Yield of isolated product. [c] 160°C. [d] Et$_3$SiBpin (2.0 equiv). [e] Without Ni(COD)$_2$.

of our decarbonylation method. As shown in Table 2, a wide range of naphthyl (**1a**–**1d**) and phenyl (**1e**–**1r**) esters could be efficiently converted into the corresponding arylsilanes **3a**–**3r** with silylborane **2a** as the coupling partner. Aside from substrate **1e**, which bears a large conjugated system and gave **3e** in 68% yield, *para*, *meta*, and *ortho* substituents were also tolerated, as shown by the formation of aryl silanes **3f**–**3h**. Furthermore, the chemoselectivity profile of this process was nicely illustrated by the fact that functional groups such as methoxy (**3c**), boronic ester (**3d**), alkenyl (**3e**), trifluoromethyl (**3j**), fluoride (**3k**), methyl (**3l**), *tert*-butyl (**3i**, **3m**), dioxole (**3n**), amine (**3o**), and ketone (**3p**) moieties were perfectly tolerated under the reaction conditions. It is notable that substrate **1q** with a methyl ester group was compatible with this method, giving **3q** in 86% yield.[16] Furthermore, substrate **1r**, which contains two phenyl ester moieties, could be substituted selectively in one position (**3r**) with 1.0 equiv of **2a**. Furthermore, to show the synthetic applicability of this process, the reaction of **1a** and **2a** was carried out on a 5 mmol scale with a catalyst loading of 5 mol%, and product **3a** was isolated in 59% yield.

Prompted by our initial results, we next focused our attention on the preparation of various heteroaryl esters. As shown in Table 3, esters of heterocycles such as benzofuran (**4a**), benzothiophene (**4b**), and indole (**4c** and **4d**) were suitable substrate for the decarbonylative silylation reaction. Notably, unprotected indole derivative **4c** could also be converted into the corresponding silane in moderate yield. Likewise, a series of esters with heterocyclic moieties such as quinoline (**4e**), chromone (**4f**), furan (**4g** and **4h**), pyridine (**4i**), and thiophene (**4j** and **4k**) were also tolerated and showed high reactivity.[17]

Table 2: Substrate scope for aryl esters.[a]

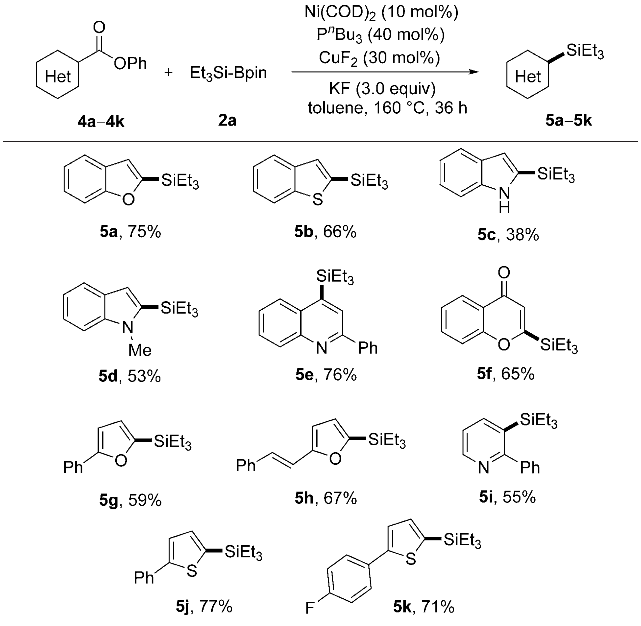


[a] Reaction conditions: **1** (0.20 mmol), **2a** (0.40 mmol, 2.0 equiv), Ni(COD)$_2$ (10 mol%), P^{n}Bu$_3$ (40 mol%), CuF$_2$ (30 mol%), KF (3.0 equiv), toluene (0.2 M), 160°C, 36 h. Yields of isolated products are given. [b] **1a** (5.0 mmol), **2a** (6.0 mmol), Ni(COD)$_2$ (5 mol%), P^{n}Bu$_3$ (20 mol%), CuF$_2$ (30 mol%), KF (3.0 equiv), toluene (20 mL), 160°C, 62 h. [c] **2a** (1.0 equiv).

Furthermore, several different silylboranes were also tested as coupling partners under the optimized reaction conditions. As shown in Table 4, these silylborane nucleophiles also reacted to form the corresponding arylsilanes in good to moderate yields (**3a** and **3s**–**3v**). Overall, the results shown in Tables 2–4 nicely illustrate the high reactivity, wide substrate scope, and excellent chemoselectivity profile of the new Ni/Cu-catalyzed decarbonylative silylation reaction.

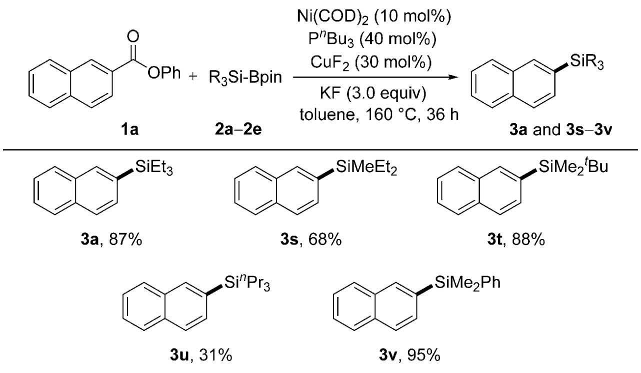
Regarding the reaction mechanism of the decarbonylative silylation (Scheme 2), we propose that in the first step, the C(acyl)−O bond of the ester substrate undergoes oxidative addition to Ni^0 species **A** to form acylnickel(II) complex **B**, which undergoes a transmetalation step facilitated by the in situ generated copper silane complex **C**. Intermediate **D** subsequently undergoes a decarbonylative process to generate complex **E** by extrusion of carbon monoxide. Reductive elimination then releases the organosilane product and regenerates the active Ni^0 species.

Table 3: Substrate scope for heteroaryl esters.[a]



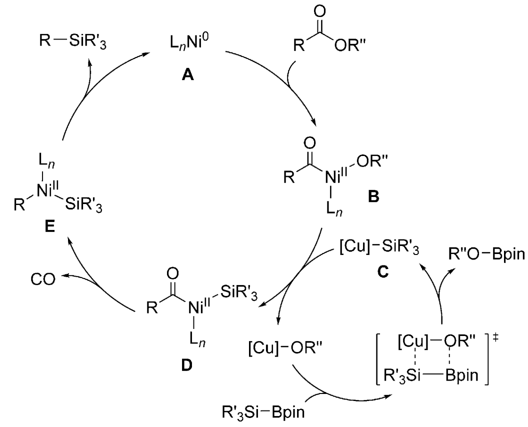
[a] Reaction conditions: **4** (0.20 mmol), **2a** (0.40 mmol, 2.0 equiv), $Ni(COD)_2$ (10 mol%), P^nBu_3 (40 mol%), CuF_2 (30 mol%), KF (3.0 equiv), toluene (0.2 M), 160 °C, 36 h. Yields of isolated products are given.

Table 4: Substrate scope for the silylborane coupling partner.[a]



[a] Reaction conditions: **1a** (0.20 mmol), **2** (0.40 mmol, 2.0 equiv), $Ni(COD)_2$ (10 mol%), P^nBu_3 (40 mol%), CuF_2 (30 mol%), KF (3.0 equiv), toluene (0.2 M), 160 °C, 36 h. Yields of isolated products are given.

In summary, we have developed the first combined nickel and copper catalyzed decarbonylative silylation reaction of carboxylic acid esters with silylboranes as the coupling partners. This ester into silane transformation is characterized by high efficiency, chemoselectivity, and excellent functional-group tolerance, providing a practical and versatile approach to a wide range of aryl and heteroaryl silanes. The mechanism of this process and other related transformations are currently studied in our laboratories.



Scheme 2. Proposed mechanism.

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Keywords: decarbonylative cross-couplings · copper · esters · nickel · silylation

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[17] Primary and even secondary benzylic esters could also be converted into the corresponding silanes under identical reaction conditions albeit with lower yields. See the Supporting Information for details.

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Communications

Cross-Couplings

L. Guo, A. Chatupheeraphat,
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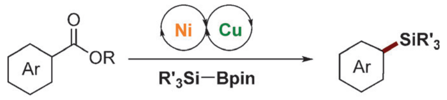
Decarbonylative Silylation of Esters by Combined Nickel and Copper Catalysis for the Synthesis of Arylsilanes and Heteroarylsilanes



- mild reaction conditions
- high chemoselectivity
- broad functional-group tolerance

Copper and nickel: An efficient nickel/copper-catalyzed decarbonylative silylation reaction of carboxylic acid esters with silylboranes is described. This process provides access to structurally diverse aryl- and heteroarylsilanes directly from the corresponding esters and benefits from superior functional-group tolerance.