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Palladium/Copper Dual Catalysis for Cross-coupling of Aryl(trialkyl)silanes with Aryl Bromides*

Takeshi Komiyama,[a] Yasunori Minami,*[b] Yuki Furuya,[a] and Tamejiro Hiyama*[b]

Abstract: Although aryl(trialkyl)silanes are apparently ideal organometalic reagents for the cross-coupling reaction due to robustness, low toxicity, solubility, and easy accessibility, they are generally an inert cross-coupling nucleophile. Disclosed herein is that a palladium/copper catalytic system achieves the desired cross-coupling of aryl-$SiMe_3$, -$SiEt_3$, -$SiMe_2(t\text{-Bu})$, and -$Si(i\text{-Pr})_3$ with aryl bromides, allowing application to the sequential C–H and C–Si bond arylation of thiophenes and the synthesis of poly(thiophene-fluorene)s.

The cross-coupling reaction is one of the most general tools for access to biaryl and polyarylenes.[1,2] Among a wide variety of organometallic nucleophiles, simple organo(trialkyl)silanes have ideal characteristics in stability, high solubility in various organic solvents, non-toxicity, easy handling, and high accessibility. Moreover, aryl(triethyl)silanes are easily prepared by catalytic C–H silylation of aromatic hydrocarbons.[3] However, aside from a few exception,[4–7] such silanes are not capable to participate in the cross-coupling. Consequently, they are often converted into aryl halides, -boronic acids, or stannanes (Figure 1, upper) before the coupling reaction.[8] Accordingly, these additional transformations reduce the merit of the silicon reagents.

Direct cross-coupling of aryltrialkylsilanes with iodoarenes is recently made possible by us using a copper(II) catalyst (Figure 1, middle).[9] Although this finding is a great step for green chemistry, harsh conditions and use of iodoarenes has remained yet to be modified for large-scale synthesis.[10] These issues are also obstacle to operate a cross-coupling polymerization. To solve them, herein we found that a Pd/Cu catalytic system accomplished a practical cross-coupling reaction of aryl(trialkyl)silanes including $SiMe_3$, $SiEt_3$, $SiMe_2(t\text{-Bu})$, and even $Si(i\text{-Pr})_3$ groups with bromoarenes (Figure 1, lower).

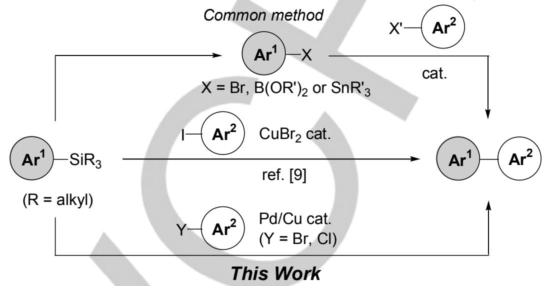
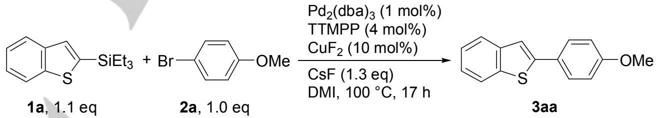


Figure 1. Cross-coupling Strategy Using Simple Aryl(trialkyl)silanes

In light of examples which employ a copper cocatalyst to promote palladium-catalyzed cross-coupling using well-designed organosilicon reagents,[11] we examined the reaction of **1a** with **2a** employing Pd/Cu catalysts. After investigating a wide array of reaction conditions, we found that the reaction gave desired biaryl **3aa** in excellent yield with $Pd_2(dba)_3$/tris(2,4,6-trimethoxyphenyl)phosphine (TTMPP) and CuF_2 catalysts and CsF in DMI at 100 °C (Table 1, Run 1). When we replaced the $SiEt_3$ group with other trialkylsilyl groups such as $SiMe_3$, $SiMe_2(t\text{-Bu})$, and $Si(i\text{-Pr})_3$, **3aa** was obtained in comparable yields (Runs 2-4). It is noteworthy that this is the first example of cross-coupling using a much sterically bulky $Si(i\text{-Pr})_3$ group (Run 4). Control experiments showed that the combination of palladium and CuF_2 was crucial for this reaction (Runs 5 and 6). Other ligands such as PPh_3, PCy_3, $P[2,6\text{-}(MeO)_2C_6H_3]_3$, $P(2,4,6\text{-}Me_3C_6H_2)_3$, and (di-*tert*-butylphosphino)biphenyl (JohnPhos), or the absence of ligands exhibited lower or null yields (Runs 7-13). Of note, a comparable yield was observed at both lower concentration and lower temperature (Runs 11 and 12). CuI and $CuBr_2$ led to lower yields (Runs 14 and 15).

Table 1: Pd/Cu-catalyzed Reaction of **1a** with **2a** [a]



Run	Variation from the standard conditions	**3aa** (%)[b]
1	none	92[c]
2	$SiMe_3$ instead of $SiEt_3$	96
3	$SiMe_2(t\text{-Bu})$ instead of $SiEt_3$	94
4	$Si(i\text{-Pr})_3$ instead of $SiEt_3$	91
5	without CuF_2	6
6	without $Pd_2(dba)_3$	trace
7	PPh_3 instead of TTMPP	67
8	PCy_3 instead of TTMPP	trace
9	$P[2,6\text{-}(MeO)_2C_6H_3]_3$ instead of TTMPP	77
10	$P(2,4,6\text{-}Me_3C_6H_2)_3$ instead of TTMPP	14
11[d]	JohnPhos instead of TTMPP	78
12[d,e]	JohnPhos instead of TTMPP	76
13	without TTMPP	13
14	CuI instead of CuF_2	14
15	$CuBr_2$ instead of CuF_2	35

[a] Unless otherwise noted, a mixture of **1a** (1.1 eq), **2a** (0.3 mmol), $Pd_2(dba)_3$ (1 mol%), TTMPP (4 mol%), CuF_2 (10 mol%), and CsF (1.3 eq) in DMI (2 M) was heated at 100 °C for 17 h. The purity of the employed CuF_2 is 99.5%. The purities of the employed CuI and $CuBr_2$ are both 99.999%. [b] NMR yields. [c] Isolated yield. [d] 30 h. [e] DMI (1 M) at 90 °C.

The scope of substrates is summarized in Table 2. Initially, we examined a range of aryltriethylsilanes with **2a**. 2-Thienylsilanes having an aryl group at the 5-position, **1b**, **1c** and 5-methyl-3,4-ethylenedioxy-2-silylthiophene **1d**, gave products **3ba**, **3ca**, and **3da** in good yields, respectively. 2-Benzofurylsilane **1e** underwent the reaction to form the product **3ea**. 2-Pyridylsilane **1f** and 2-pyradylsilane **1g** proved to be effective nucleophiles with $PPh_2(2\text{-}NMe_2C_6H_4)$ as a ligand at 120 °C. Perfluorophenyl(triethyl)silane **1h** coupled readily using the 2-dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl (XPhos) ligand to form **3ha**. In addition, 2,6-

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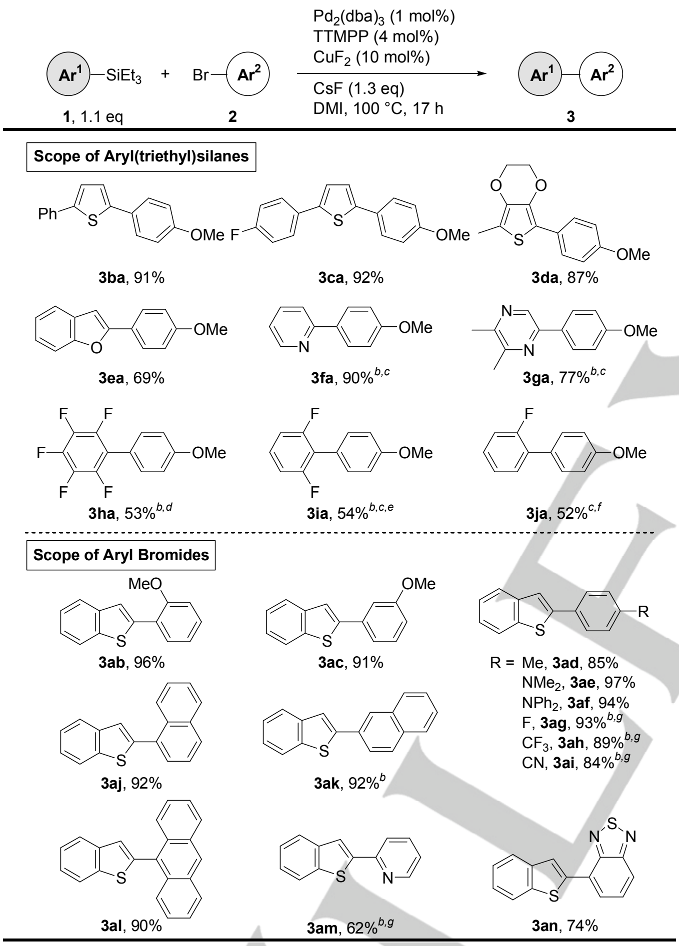
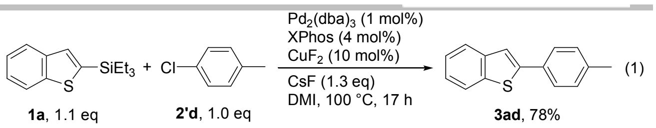
difluoro- and 2-fluorophenylsilanes **1i** and **1j** gave **3ia** and **3ja**, respectively, in the presence of PPh$_2$(2-NMe$_2$C$_6$H$_4$) at higher temperatures. The coupling was also applicable to a variety of aryl bromides. *meta*- and *ortho*-Bromoanisoles **2b** and **2c** coupled smoothly with **1a** to produce **3ab** and **3ac** in excellent yields. The reaction worked with various aryl bromides having other electron-donating and electron-withdrawing groups at the *para*-position, giving corresponding products **3ad**-**3ai**. In the case of electron-deficient bromoarenes, conditions using JohnPhos ligand at a higher temperature were required to promote the coupling. Cross-coupling using 1- and 2-bromonaphthalenes and 9-bromoanthracene gave **3aj**, **3ak**, and **3al** in excellent yields. Such heteroaryl bromides as 2-bromopyridine (**2l**) afforded coupled product **3am**. 4-Bromobenzothiadiazole, which plays important roles in material science,[12] gave coupled product **3an** in good yield.

Table 2: Scope of Substrates [a]



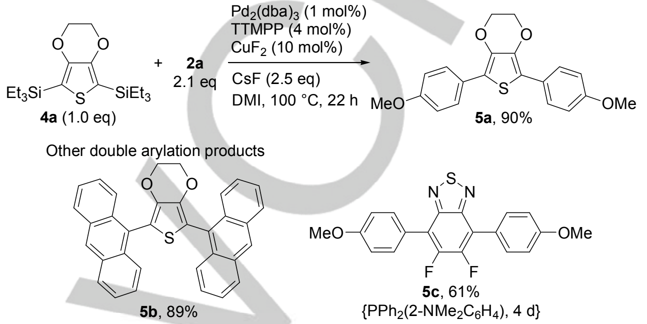
[a] Unless otherwise noted, a mixture of **1** (1.1 eq), **2** (0.3 mmol), Pd$_2$(dba)$_3$ (1 mol%), TTMPP (4 mol%), CuF$_2$ (10 mol%), and CsF (1.3 eq) in DMI (0.15 mL) was heated at 100 °C for 17 h. All described yields are isolated ones. The purity of the employed CuF$_2$ is 99.5%. [b] 120 °C. [c] PPh$_2$(2-NMe$_2$C$_6$H$_4$) was used instead of TTMPP. [d] XPhos was used instead of TTMPP and heated at 120 °C. [e] 3 d. [f] 140 °C for 24 h. [g] JohnPhos was used instead of TTMPP.

The present Pd/Cu(II) dual catalysis is shown to be applicable to a less reactive aryl chloride. The reaction of **1a** with *p*-chlorotoluene (**2'd**) using XPhos ligand to give **3ad** in 78% yield [Eq. (1)].[13]



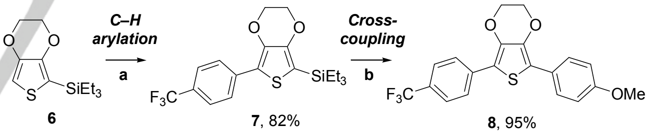
(1)

With the success of the mono-coupling in hand, double-coupling was examined using 2,5-disilyl-3,4-ethylenedioxythiophene **4a** and **2a** under the standard conditions, providing double arylation product **5a** in 90% yield (Scheme 1). Similarly, **4a** coupled with 9-bromoanthracene **2l** to give **5b** in 89% yield, showing that sterically hindered aryl groups can be incorporated without significant loss in yield. In addition, 4,7-bis(triethyl)silyl-5,6-difluorobenzothiadiazole (**4b**) was found to react with **2a** giving **5c** in 61% yield in the presence of PPh$_2$(2-NMe$_2$C$_6$H$_4$) instead of TTMPP.



Scheme 1. Double Coupling Using Disilylarenes

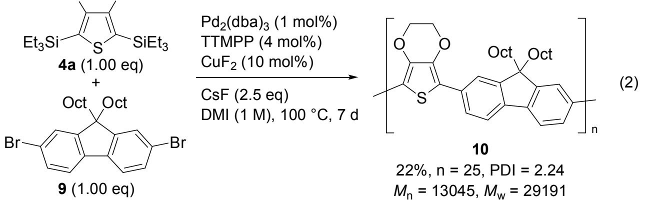
As mentioned above, trialkylsilyl groups are stable under various conditions. This fundamental feature makes the sequential functionalization of monosilyl substrates possible. Thus, we examined a combination of catalytic C–H arylation and the present coupling (Scheme 2). As a result, Pd-catalyzed C–H arylation of 2-triethylsilylthiophene **6** with *p*-bromobenzotrifluoride (**2h**) gave a monoarylated silylthiophene **7** without loss of the TES group.[14] Subsequently, **7** coupled with **2a** under the Pd/Cu-conditions and produced unsymmetrical diarylthiophene **8** in excellent yield.



Reagents and conditions: (a) **6** (1.0 eq), **2h** (1.1 eq), Pd(OAc)$_2$ (5 mol%), dppb (5 mol%), Cs$_2$CO$_3$ (1.2 eq), toluene, 110 °C, 24 h; (b) **7** (1,1 eq), **2a** (1.0 eq), Pd$_2$(dba)$_3$ (1 mol%), TTMPP (4 mol%), CuF$_2$ (10 mol%), CsF, (1.3 eq), DMI, 100 °C, 17 h.

Scheme 2. Sequential Arylation via C–H/C–Si Activation

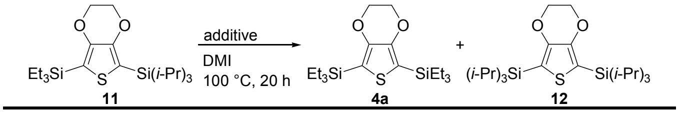
The present cross-coupling was applicable to the synthesis of polyarylenes.[15] Indeed, **4a** and 2,7-dibromo-9,9-dioctyl-fluorene (**9**) underwent cross-coupling polymerization to produce a copolymer **10**, poly(ethylenedioxythiophene-fluorene),[16] with M_n = 13045 and PDI = 2.24 in 22% yield after reprecipitation [Eq. (2)].[17]



(2)

To obtain information on the C–Si bond activation, we treated disilyl thiophene **11** having $SiEt_3$ and $Si(i\text{-}Pr)_3$ groups with a stoichiometric amount of CsF, and observed silicon scrambling to form **4a** and **12** (Table 3). Use of CuF_2 (10 mol%) instead of CsF did not induce the silicon scrambling at all. These results may mean that arylsilanes react first with CsF to proceed an aryl exchange via aryl(trialkyl)fluorosilicates.[18] This exchange may be attributed to aryl-bridged silicate dimer,[19] wherein an interaction between silicates and silanes takes place in a manner similar to that observed with tri-/tetracoordinate system,[20] and/or arylcesium reversibly. On the other hand, addition of CuF_2 or CuF_2/TTMPP to the mixture of **11** and CsF did not affect the yields of **4a** and **12**.[21] Of note, in cases using CuF_2, homo-coupled products, bithiophenes, were not observed at all, suggesting that formation of Ar-Cu^I complexes may be excluded.[22] Although the behavior of CuF_2 is unclear yet,[23] it may be asumed to assist transmetalation between silicates and a palladium complex via reversible formation of Ar-CuX_2 or Ar-CuX.[24]

Table 3: Reactivity of C–Si Bond



additive	recovered **11** (%)	**4a** (%)	**12** (%)
CsF (1.3 eq)	37	18	19
CuF_2 (10 mol%)	>99	<1	<1
CuF_2 (10 mol%), CsF (1.3 eq)	34	18	14
CuF_2 / TTMPP (10 mol%), CsF (1.3 eq)	29	15	15

In conclusion, we have demonstrated that the Pd/Cu dual catalysis undergoes the cross-coupling of aryl(trialkyl)silanes with bromoarenes under mild conditions. A wide variety of silyl groups such as $SiMe_3$, $SiEt_3$, $SiMe_2(t\text{-Bu})$, and $Si(i\text{-}Pr)_3$ are found to be applicable to the dual catalytic system as well as various aryl groups in both coupling partners. The stability of trialkylsilyl groups permits sequential C–H arylation/present cross-coupling using a monosilylthiophene, leading to a unsymmetrical diarylthiophene. Moreover, the present cross-coupling is applicable to the polyarylene synthesis. We are now focusing on extension of the arylsilanes, especially those containing electron-rich and -neutral aryl groups and elucidation of the reaction mechanism.

Keywords: arene • copper • cross-coupling • palladium • silanes

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[18] To check the generation of arylsilicates, we treated **1a** with CsF in DMF-d_7. As a result, benzothiophene by hydrodesilylation was only observed with **1a**. During this NMR study, no signal in ^{19}F NMR was detected.

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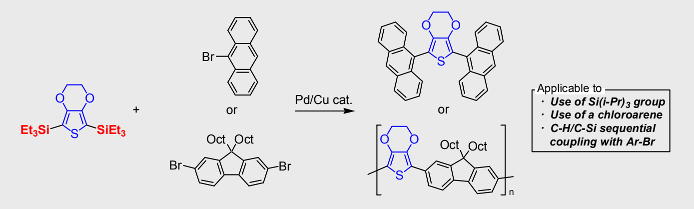
Layout 2:

COMMUNICATION



Under palladium/copper catalysis, aryl(trialkyl)silanes are demonstrated to undergo practical cross-coupling with haloarenes, giving biaryls and teraryls. Various trialkylsilyl groups including stable and bulky triisopropylsilyl are applicable to this reaction. This high reactivity permits the cross-coupling polymerization as well as sequential C–H arylation/the present Pd/Cu-catalyzed cross-coupling is achieved.

Takeshi Komiyama, Yasunori Minami, Yuki Furuya, and Tamejiro Hiyama**

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Palladium/Copper Dual Catalysis for Cross-coupling of Aryl(trialkyl)silanes with Aryl Bromides