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Oxidative Homocoupling Reaction of Aryltrimethylsilanes by Pd/*o*-chloranil Catalysis

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Oxidative Homocoupling Reaction of Aryltrimethylsilanes by Pd/*o*-chloranil Catalysis

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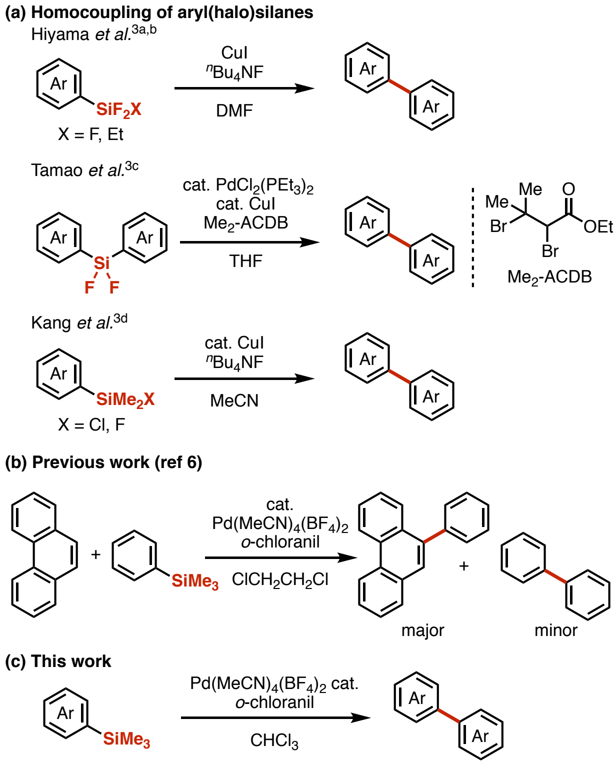
A practical oxidative homocoupling reaction of aryltrimethylsilanes has been achieved by Pd/*o*-chloranil catalytic system. The reaction shows the good functional group tolerability toward bromo, fluoro, ester and methoxy groups to give a series of biaryls bearing electron-withdrawing and donating groups. The boronate group is also retained on biaryls without any Ar–B bond cleavage, which is highly advantageous for orthogonal coupling.

Transition metal-catalyzed homocoupling reaction of aryl halides or arylmetal reagents represents the fundamental organic transformation for obtaining biaryls which are key structural components of functional molecules.[1] For examples, reductive homocoupling reactions such as Cu(0)-mediated Ullman coupling and Ni(0)-mediated Yamamoto coupling of aryl halides have been widely employed in the synthesis of oligo- and polyarylated compounds, precursors of nanographenes, graphene nanoribbons, carbon nanorings, and carbon nanobelt.[2] In the oxidative homocoupling reactions, various transition metal-catalyzed reactions have been achieved by using arylmetal reagents such as aryllithium, arylmagnesiums, arylzincs, arylstannanes, and arylborans.[1] Comparing to these reactions, only few examples of oxidative homocoupling reaction using arylsilanes have been reported (Scheme 1a).[3] In addition, reported homocoupling of arylsilanes are limited to the examples using reactive aryl(halo)silanes[3a–d] or alkoxy(aryl)silane[3e,f] which are air- and moisture-sensitive (Scheme 1a). On the other hand, homocoupling of aryltrimethylsilanes,[4] which are abundant, stable and easy-to-synthesize compounds, has not been established yet. To the best of our knowledge, only limited examples regarding to Pd- or Au-catalyzed undesirable formation of biaryls as side-products have been reported.[4] Development of efficient and catalytic homocoupling reaction of aryltrimethylsilanes is expected to provide novel synthetic tool for the synthesis of functional biaryls and enable late-stage functionalizations and orthogonal coupling reactions.

Recently, we have reported the palladium-catalyzed C–H arylations of unfunctionalized polycyclic aromatic hydrocarbons (PAHs) with arylboroxins and aryltrimethylsilanes (Scheme 1b) or dibenzosilole derivatives in the presence of *o*-chloranil.[5,6] Our mechanistic study on the C–H arylation of phenanthrene with trimehtylphenylsilane revealed that the reaction is likely initiated by the unprecedented transmetalation of inactive trimehtylphenylsilane with cationic Pd(II), and *o*-chloranil plays an important role as a ligand, an oxidant and a base for the stabilization of each intermediates and the diminution of activation energies.[6] On the course of this study, we found that biphenyl is generated as a side-product to some extent. We envisaged that various biaryls can be obtained from inactive aryltrimethylsilanes. Here, we report a novel oxidative homocoupling reaction of aryltrimethylsilanes by Pd/*o*-chloranil catalytic system (Scheme 1c).


(a) Homocoupling of aryl(halo)silanes

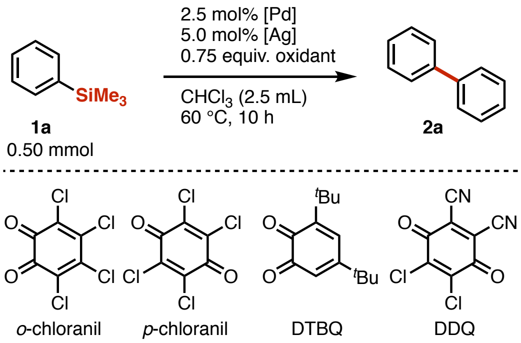
(b) Previous work (ref 6)

(c) This work

Scheme 1. (a) Cu- and Pd-promoted homocoupling of aryl(halo)silanes. (b) Previously developed Pd-catalyzed C–H arylation of phenanthrene with trimethylphenylsilane and *o*-chloranil. (c) This work.

We began by optimizing the reaction conditions using palladium catalysts (2.5 mol%), silver salts (5 mol%), trimethylphenylsilane (**1**) (0.50 mmol, 1.0 equiv.) and *o*-chloranil (0.75 equiv.) in $CHCl_3$ (2.5 mL) at 60 °C (Table 1). The reaction with $PdCl_2$ gave biphenyl (**2a**) in 26% yield (Table 1, entry 1). The use of $Pd(OAc)_2$ increased the yield of **2a** to 38% (entry 2), and the use of $Pd(OCOCF_3)_2$ resulted in quantitative formation of **2a** (99%, entry 3). The combination of $Pd(OAc)_2$ and $AgOCOCF_3$ was also found to be effective (entry 4). From a viewpoint of high reproducibility and easy handleability, we decided to use Pd(MeCN)$_4$(BF$_4$)$_2$ as a standard Pd catalyst for the homocoupling (entry 5). Next, we investigated the effect of oxidants (entries 6–11). Comparing to *o*-chloranil, the use of *p*-chloranil dramatically decreased the yield of **2a** (26%, entry 6), while other oxidants such as 3,5-di-*tert*-butylbenzoquinone (DTBQ), 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ), *N*-fluorobenzenesulfonimide (NFSI), and inorganic oxidants showed lower efficiency or no reaction (entries 7–11). This tendency is almost similar to the previously reported Pd-catalyzed C–H arylation of PAHs and heteroaromatics (for the effect of solvent, see table S1 in Supporting Information).[5,6]

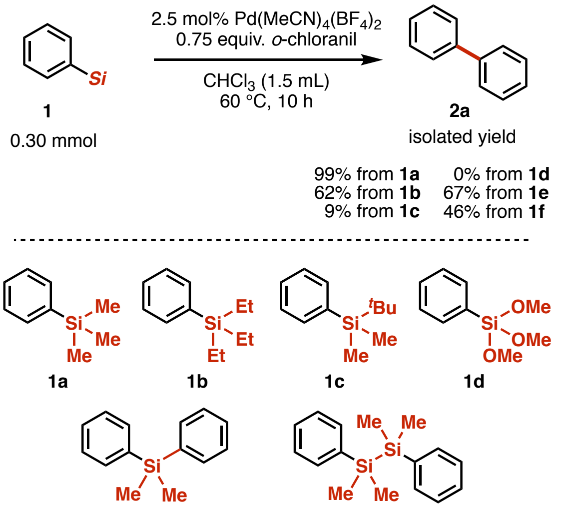
Table 1. Optimization of reaction conditions.



Entry	[Pd]/[Ag]	Oxidants	GC Yield, %
1	PdCl$_2$	*o*-chloranil	26
2	Pd(OAc)$_2$	*o*-chloranil	38
3	Pd(OCOCF$_3$)$_2$	*o*-chloranil	>99
4	Pd(OAc)$_2$/AgOCOCF$_3$	*o*-chloranil	>99
5	Pd(MeCN)$_4$(BF$_4$)$_2$	*o*-chloranil	>99 (99)[a]
6	Pd(MeCN)$_4$(BF$_4$)$_2$	*p*-chloranil	26
7	Pd(MeCN)$_4$(BF$_4$)$_2$	DTBQ	0
8	Pd(MeCN)$_4$(BF$_4$)$_2$	DDQ	0
9	Pd(MeCN)$_4$(BF$_4$)$_2$	NFSI	0
10	Pd(MeCN)$_4$(BF$_4$)$_2$	K$_2$S$_2$O$_8$	0
11	Pd(MeCN)$_4$(BF$_4$)$_2$	CuCl$_2$	10

[a] Isolated yield in the parenthesis. NFSI = *N*-fluorbenzenesulfonimide.

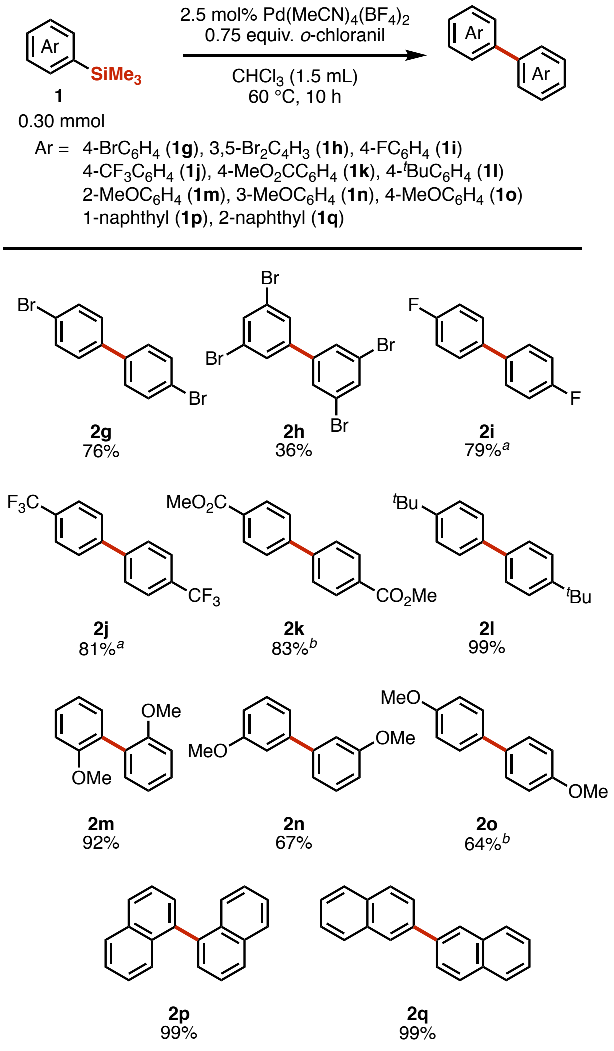
We further tested the reactivity of various alkylsilanes and alkoxysilanes under the optimized reaction conditions (Scheme 2). Triethylphenylsilane (**1b**) showed moderate reactivity toward the homocoupling, resulting in the formation of **2a** in 62%. However, the reaction of more bulky *tert*-butyldimethylphenylsilane (**1c**) gave a very small amount of **2a**, with almost all the starting material remained unchanged after the reaction for 10 hours. Trimethoxyphenylsilane (**1d**), which is sometimes employed in Hiyama cross-coupling reaction[7] as a reactive coupling reagent, resulted only in the consumption of **1d** without any formation of **2a**. Dimethyldiphenylsilane (**1e**) showed the same reactivity as **1b**, and disilane **1f** was found to be also reactive to some extent. As a result, sterically less hindered and stable alkylphenylsilanes are the favorable substrates for the current homocoupling reaction.



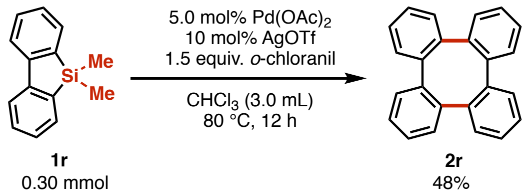
Scheme 2. Effect of substituents on a silicon atom.

Next we explored the scope of aryltrimethylsilanes (Table 2). The present homocoupling reaction shows good functional group tolerability toward electron-withdrawing and -donating groups. 4-Bromo, 4-fluoro, 4-trifluoromethyl and 4-methoxycarbonyl groups are well tolerated in this reaction to afford 4,4'-disubstituted biphenyls **2g**, **2i**, **2j** and **2k** in good yields. The reaction of (3,5-dibromophenyl)trimethylsilane (**1h**) gave tetrabromobiphenyl **2h** in 36% yield which can be an useful structure motif for the further extension to oligoarylated compounds by the conventional coupling reactions. (4-*tert*-Butylphenyl)trimethylsilane (**1l**) shows excellent reactivity toward homocoupling to give the corresponding biphenyl **2l** quantitatively. The reactions of electron-rich methoxylphenylsilanes **2m**, **2n** and **2o** also gave homocoupling products **2m**, **2n** and **2q** in excellent to good yields. 1,1'-Binaphthyl (**2p**) and 2,2'-binaphthyl (**2q**) were quantitatively obtained from trimethyl(1-naphth-yl)silane (**1p**) and trimethyl(2-naphthyl)silane (**1q**). When 5,5-dimethyldibenzosilole (**1r**) was employed with the slight modification using 5 mol% of Pd(OAc)$_2$ and 10 mol% of AgOTf for the reaction, intermolecular annulative homocoupling occurred to form tetraphenylene (**2r**) in 48% yield (Scheme 3).

Table 2. Substrate scope of Pd/o-chloranil-catalyzed homocoupling of aryltrimethylsilanes.

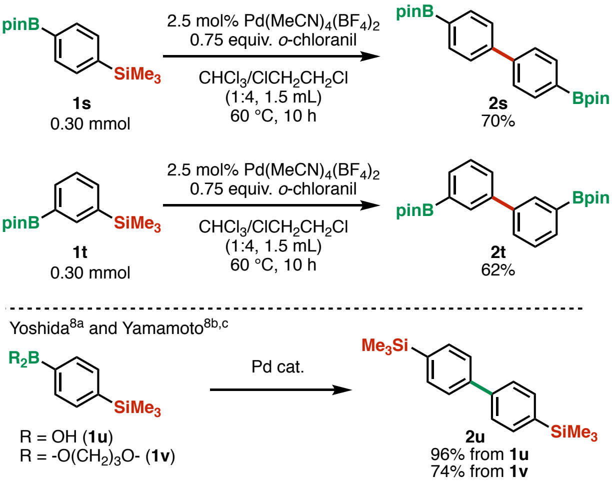


[a] $ClCH_2CH_2Cl$ (2.5 mL) was used as solvent. [b] $CHCl_3$ (0.50 mL) and $ClCH_2CH_2Cl$ (2.0 mL) were used as solvent.



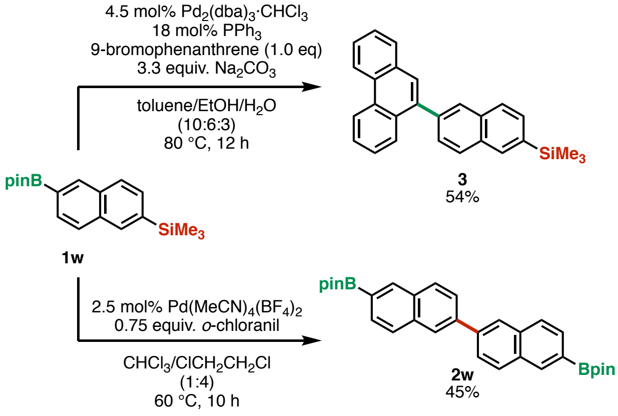
Scheme 3. Annulative homocoupling of dibenzosilole **1r**.

We further tested the functional group tolerability of present homocoupling reaction by using boronate-substituted aryltrimethylsilanes (Scheme 4). In the reported Pd-catalyzed homocoupling reactions of arylboronates or arylboronic acids, trimethylsilyl group is intact and Ar–B bond is selectively cleaved. For example, Yoshida[8a] and Yamamoto[8b,c] reported the selective formation of 4,4'-bis(trimethylsilyl)-1,1'-biphenyl (**2u**) from Pd-catalyzed homocoupling reactions of (4-trimetylsilyl)phenylboronic acid (**1u**) or its propylene glycol ester (**1v**). On the stark contrast, our catalytic system using cationic Pd and *o*-chloranil showed remarkable and selective Ar–Si bond-cleaving ability toward (trimethylsilyl)phenylboronic acid pinacol esters **1s** and **1t** with good tolerability toward boronate groups, forming biphenyl diboronic acid esters **2s** and **2t** in 70% and 62% yields, respectively (Scheme 4). These results are complementary to the previously reported Pd-catalyzed homocoupling reactions.



Scheme 4. Boronate-tolerable homocoupling of aryltrimethylsilanes.

Furthermore, we demonstrated the orthogonal coupling reactions using 2-trimethysilyl-6-boraneylnaphthalene (**1w**) (Scheme 5). The Suzuki–Miyaura cross-coupling of **1w** with 9-bormophenanthrene was possible under typical Pd-catalyzed conditions to give the coupling product **3** in 54% yield without significant loss of trimethylsilyl group. On the other hand, the employment of our newly developed homocoupling reaction with cationic Pd(II) catalyst/*o*-chloranil furnished 2,2'-binaphthyl bearing two boronate groups (**2w**) in 45% yield, whose structure is otherwise difficult to be constructed by the conventional coupling reactions.



Scheme 5. Orthogonal coupling reactions of boronate-substituted trimethylsilylnaphthalene **1w**.

The reaction mechanism of present homocoupling reaction of aryltrimethylsilanes is considered as general transmetalation/reductive elimination mechanism.

Successive transmetalation of arytrimethylsilane with Pd(II) afford monoaryl and diaryl Pd(II) intermediates, and the latter would easily release biaryls through reductive elimination. In the present homocoupling reaction, we presume that *o*-chlorail works as the effective bidentate ligand and oxidant in the transmetalations, reductive elimination and reoxidation, facilitating the otherwise difficult homocoupling of inactive aryltrimethylsilanes. The clarification of detailed reaction mechanism and the crucial role of *o*-chloranil are now under investigation.

In summary, we have developed a practical oxidative homocoupling of inactive aryltrimethylsilanes by cationic palladium/*o*-chloranil catalytic system. This catalytic system enabled selective Ar–SiMe$_3$, Ph–SiEt$_3$ and Ph–SiMe$_2$Ph bond cleavages to afford various biaryls bearing bromo, fluoro, CF$_3$, CO$_2$Me, ^{t}Bu and OMe groups. In particular, boronate group remained unreacted to furnish the bis-boronate-substituted biaryls, which is otherwise difficult to synthesize. We believe that the newly developed homocoupling reaction of aryltrimethylsilanes will provide alternative strategies for the synthesis of functionalized oligoaryl fragments.

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This paper is dedicated to the late Professor Yoshihiko Ito on the occasion of the 10th anniversary of his sudden death.

Supporting Information is available on http://dx.doi.org/10.1246/cl.******.

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