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Palladium-catalyzed cleavage of the Me–Si bond in *ortho*-trimethylsilyl aryltriflates: synthesis of benzosilole derivatives from *ortho*-trimethylsilyl aryltriflates and alkynes†

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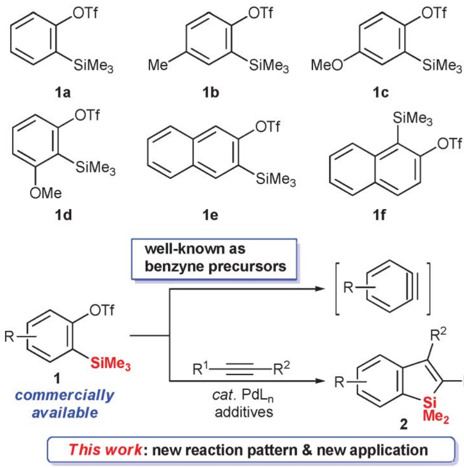
An efficient Pd-catalyzed cleavage of the Me–Si bond in *ortho*-trimethylsilyl aryltriflates was realized and synthetically applied. Most of the commercially available *ortho*-trimethylsilyl aryltriflates could undergo the Pd-catalyzed intermolecular coupling with alkynes *via* cleavage of the Me–Si bond, which represents a new reaction pattern of *ortho*-trimethylsilyl aryltriflates. Potassium bromide (KBr) was found effective for this process. A variety of benzosilole derivatives were thus generated in high yields.

Transition metal-catalyzed selective cleavage of the Me–Si bond in a $SiMe_3$ group and its synthetic applications have attracted much recent interest.[1–7] However, although remarkable achievements have been made, this research area is still at a very early stage, with much limitation in the diversity of suitable $SiMe_3$-substituted substrates and reaction types. Further development of the transition-metal-catalyzed coupling accompanied by a selective cleavage of the $C(sp^3)$–Si bond would lead to useful protocols for the synthesis of substituted siloles and derivatives, which are very important organic materials in electronic and optoelectronic devices.[8,9]

Commercially available *ortho*-silyl aryltriflates **1** have been frequently used as benzyne precursors in organic synthesis.[10] As our continued interest in the search of suitable $SiMe_3$-containing substrates for the catalytic synthetic application of their Me–Si bonds,[7] we turned our attention to those commercially available *ortho*-silyl aryltriflates **1** and envisioned that such compounds could be good substrates. Thus, in this paper, we report a new reaction pattern of *ortho*-silyl aryltriflates **1**, which undergo efficient Pd-catalyzed intermolecular coupling with alkynes *via* cleavage of the Me–Si bond to provide a novel synthetic method for benzosilole derivatives **2** (Scheme 1).

Initially, as given in Table 1, we tested the reaction of *o*-(trimethylsilyl)phenyl triflate **1a** with diphenylacetylene as a model example. The expected benzosilole derivative **2a** could be generated under certain reaction conditions. Notably, in addition to the remarkable effect of different catalysts and ligands, the base was found to be very sensitive for this transformation.[11] When LiO*t*-Bu was used as the base, the triflate **1a** was partially changed to its corresponding 2-trimethylsilylphenyl *t*-butyl ether (entries 1–3). The base K_2CO_3 could mediate the reaction to afford the product **2a** in 41% GC yield (entry 6). LiOEt was found to be the most effective base, while most other bases such as NaO*t*-Bu, KO*t*-Bu, Li_2CO_3, Na_2CO_3, Cs_2CO_3, NaOEt, LiOAc, NaOAc, KOAc afforded very low yields of products or no product at all. Meanwhile, the addition of KBr was found to remarkably promote the catalytic process and increase the yield of the product **2a** from



Scheme 1 Commercially available *ortho*-silyl aryltriflates **1a–f** and transition metal-catalyzed cleavage of the Me–Si bonds in **1** and subsequent intermolecular coupling with alkynes for the synthesis of benzosiloles **2**.

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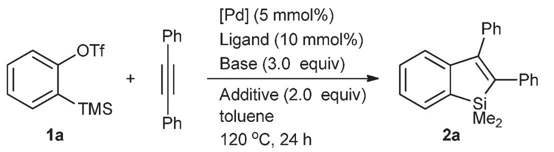
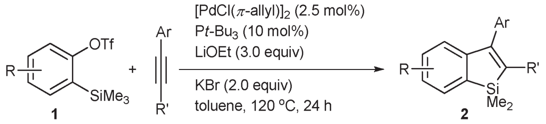
Table 1 Optimization of reaction conditions for the reaction of **1a** with diphenylacetylene (see ESI† for details)

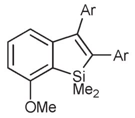


Entry	[Pd]	Ligand	Base	Additive	Yield of 2a (%)[a]
1	$[Pd(\pi\text{-allyl})Cl]_2$	P*t*-Bu$_3$	LiO*t*-Bu	—	15
2	$[Pd(\pi\text{-allyl})Cl]_2$	P*t*-Bu$_3$	LiO*t*-Bu	KI	trace
3	$[Pd(\pi\text{-allyl})Cl]_2$	P*t*-Bu$_3$	LiO*t*-Bu	KBr	32
4	$[Pd(\pi\text{-allyl})Cl]_2$	P*t*-Bu$_3$	Li_2CO_3	KBr	NR
5	$[Pd(\pi\text{-allyl})Cl]_2$	P*t*-Bu$_3$	Na_2CO_3	KBr	10
6	$[Pd(\pi\text{-allyl})Cl]_2$	P*t*-Bu$_3$	K_2CO_3	KBr	41
7	$[Pd(\pi\text{-allyl})Cl]_2$	P*t*-Bu$_3$	Cs_2CO_3	KBr	12
8	$[Pd(\pi\text{-allyl})Cl]_2$	P*t*-Bu$_3$	LiOEt	—	16
9	$[Pd(\pi\text{-allyl})Cl]_2$	P*t*-Bu$_3$	LiOEt	KBr	84 (80)
10	$[Pd(\pi\text{-allyl})Cl]_2$	P*t*-Bu$_3$	NaOEt	KBr	—[b]
11	$[Pd(\pi\text{-allyl})Cl]_2$	P*t*-Bu$_3$	LiOAc	KBr	NR
12	$[Pd(\pi\text{-allyl})Cl]_2$	P*t*-Bu$_3$	NaOAc	KBr	22
13	$[Pd(\pi\text{-allyl})Cl]_2$	P*t*-Bu$_3$	KOAc	KBr	18
14	$[Pd(\pi\text{-allyl})Cl]_2$	P*t*-Bu$_3$	NaO*t*-Bu	KBr	—[b]
15	$[Pd(\pi\text{-allyl})Cl]_2$	P*t*-Bu$_3$	KO*t*-Bu	KBr	—[b]

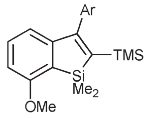
[a] GC yields. Isolated yields are given in parenthesis. [b] The substrate decomposed.

Table 2 Formation of benzosiloles **2** from **1** and aromatic alkynes

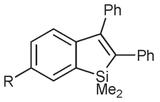




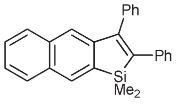
2b: Ar = Ph, 86%
2c: Ar = 4-Tol, 64%
2d: Ar = 1-Naph, 67%
2e: Ar = 4-FC$_6$H$_4$, 59%
2f: Ar = 2-Thenyl, 73%



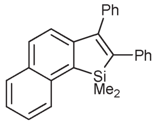
2g: Ar = Ph, 65%
2h: Ar = 4-Tol, 53%
2i: Ar = 1-Naph, 56%
2j: Ar = 2-Thenyl, 51%



2k: R = Me, 56%
2l: R = OMe, 63%



2m: 58%



2n: 84%

15% (entry 1) to 32% (entry 3). When LiOEt was used as the base, the yield of product **2a** was increased from 16% (entry 8) to 84% in the presence of two equivalents of KBr (entry 9). Detailed investigation into the effect of additives was summarized and provided in the ESI.† An optimal reaction condition was realized as follows: $[PdCl(\pi\text{-allyl})]_2$ (2.5 mol%), P*t*-Bu$_3$ (10 mol%), LiOEt (3.0 equiv), KBr (2.0 equiv), in toluene, 120 °C, 24 h.

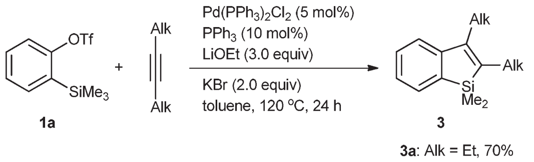
Under the optimized reaction condition, the benzosilole derivatives **2b–n** were obtained in 51% to 86% isolated yields (Table 2). Aromatic alkynes substituted with electron-withdrawing groups generally afforded moderate to good yields of their corresponding products. Those alkynes with electron-donating groups gave the products in slightly lower yields. Unsymmetrically substituted alkynes with a TMS group and an aromatic group afforded their products in moderate yields, regioselectively with the TMS group at the 2-position of the benzosiloles (**2g–j**). When **1b** (R′ = Me) and **1c** (R′ = OMe) were treated with diphenylacetylene, their corresponding products **2k** and **2l** were also obtained. Similarly, as given in Table 2, the naphthyl derivatives **1e** and **1f** could afford their corresponding benzosiloles **2m** and **2n** in 58% and 84% isolated yields, respectively.

When an aliphatic alkyne, such as 3-hexyne or 4-octyne, was subjected to the optimal reaction condition for the reaction of aromatic alkynes, the expected products **3a** and **3b** were formed in very low yields (Scheme 2). Most of the starting materials **1** decomposed. Optimization of reaction conditions for the reaction of **1a** with 4-octyne was provided in the ESI.† Again, the addition of KBr was proved to be necessary and LiOEt was found to be the most effective base. The optimal reaction condition for the reaction of **1** with aliphatic alkynes is as follows: $Pd(PPh_3)_2Cl_2$ (5 mol%), PPh$_3$ (10 mol%), KBr (2 equiv), LiOEt (3 equiv), in toluene, 120 °C, 24 h (Scheme 2). The 2,3-bisalkyl-substituted benzosiloles **3a–c** could be obtained in moderate to good isolated yields.

Several experiments were carried out to investigate the reaction mechanism. (1) There are several examples of palladium-catalyzed conversion of aryl and vinyl triflates to their corresponding bromides in the presence of KBr or LiBr.[12] However, as given in Scheme 3, under our palladium-catalyzed condition, no formation of its corresponding bromide **4** was observed.

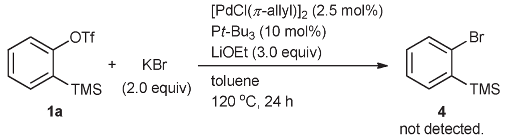
(2) When the 2-silylarylbromide **4** was subjected to the optimal reaction condition for **1**, the product **2a** was obtained in 60% yield, along with 30% of the six-membered silacycle **5** (Scheme 4).[13] These results indicate that the 2-silylarylbromide **4** may not be directly involved in this current reaction.

(3) The gas composition of the reaction was analyzed by using GC-MS analysis. Experimental results showed that when KBr was

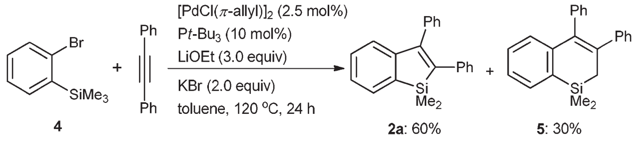


3a: Alk = Et, 70%
3b: Alk = Pr, 76%
3c: Alk = Bu, 53%

Scheme 2 Formation of benzosiloles **3** from **1a** and aliphatic alkynes.



Scheme 3 Control experiment: palladium-catalyzed conversion of aryl triflates to bromides.

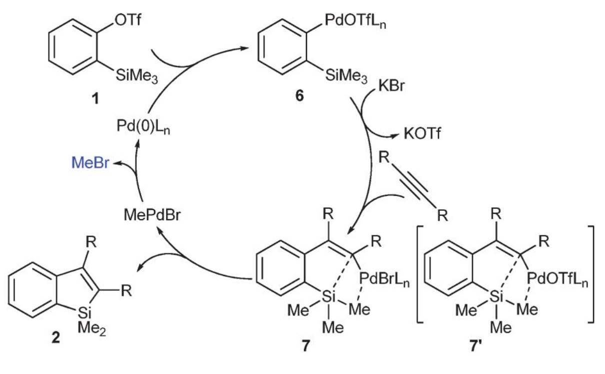


Scheme 4 Comparison of reactivity between 2-silylaryl bromide **4** with *o*-(trimethylsilyl)phenyl triflate **1a**.

introduced, the formation of MeBr was obviously observed. On the contrary, no MeBr was detected in the absence of KBr, and most of the starting compound **1a** was decomposed.

Based on all the above preliminary experimental results, a plausible mechanism for this process is proposed in Scheme 5. The intermediate **6** would be first generated *via* oxidative addition of **1** to Pd(0). When KBr was added, a nucleophilic substitution reaction of the *in situ* generated **6** with KBr, and subsequent intermolecular carbopalladation of an aromatic alkyne would form the intermediate **7**.[14] Then, a nucleophilic attack from the C–Pd bond to the silicon center would generate the product silole **2** along with the MePdBr species *via* cleavage of the Me–Si bond.[15] Reductive elimination of the MePdBr would then release MeBr and regenerate the active Pd(0) species for the catalytic cycle. Alternatively, the nucleophilic substitution reaction with KBr may take place at the species **7′**.

In summary, an efficient Pd-catalyzed cleavage of the Me–Si bond in *ortho*-trimethylsilyl aryltriflates was realized and synthetically applied. Most commercially available *ortho*-trimethylsilyl aryltriflates could undergo the Pd-catalyzed intermolecular coupling with alkynes *via* cleavage of the Me–Si bond, affording a variety of benzosilole derivatives. A new reaction pattern of *ortho*-trimethylsilyl aryltriflates was thus developed. The addition of potassium bromide (KBr) was found to be very effective for this reaction.



Scheme 5 A proposed reaction mechanism.

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