$C(sp^3)$–Si Activation

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Palladium-Catalyzed Intermolecular Coupling of 2-Silylaryl Bromides with Alkynes: Synthesis of Benzosiloles and Heteroarene-Fused Siloles by Catalytic Cleavage of the $C(sp^3)$–Si Bond**

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Siloles, including benzosiloles and heteroarene-fused siloles, have become ever more attractive in recent years, because they have practical applications as organic materials in electronic and optoelectronic devices.[1] As a consequence, much interest has been paid to the development of synthetic methods toward siloles.[1–4] In the meantime, the cleavage of Si–C bonds is an important process in synthetic chemistry for the construction of new C–C or C–X bonds (X = heteroatom).[5–7] The $C(sp^3)$–Si bond in trialkylsilyl groups, such as $SiMe_3$, is among the most frequently encountered C–Si bonds, because many compounds are substituted with trialkylsilyl groups. Thus, the development of a transition-metal-catalyzed coupling reaction that is accompanied by a selective cleavage of the $C(sp^3)$–Si bonds would lead to a useful protocol for the synthesis of differently substituted siloles and derivatives.

However, in contrast to many reports on the cleavage of the $C(sp^3)$–Si bonds through stoichiometric reactions[8,9] or through transition-metal-catalyzed reactions of activated $C(sp^3)$–Si bonds,[3c,4b–d,10] little is known about the transition-metal-catalyzed cleavage of unactivated $C(sp^3)$–Si bonds.[11–15] Rauf and Brown reported the cleavage of a $C(sp^3)$–Si bond in an $SiMe_3$ group by using the $SiMe_3$ group as a methyl source in a Pd-catalyzed oxidative methylation of olefins.[11] Nakao et al. demonstrated that 2-(2-hydroxyprop-2-yl)phenyl-substituted alkylsilanes selectively transfer an alkyl group to facilitate the alkylation of aryl halides by cleavage of the $C(sp^3)$–Si bond.[12] Chatani and co-workers developed a Rh-catalyzed intermolecular coupling of 2-trimethylsilylphenylboronic acids with alkynes by cleavage of the $C(sp^3)$–Si bond.[13] So far, this latter example has been the only report of the synthesis of siloles by a transition-metal-catalyzed intermolecular coupling accompanied by the cleavage of the $C(sp^3)$–Si bonds. Recently, we reported a Pd-catalyzed selective cleavage of the $C(sp^3)$–Si bond in a trialkylsilyl group and a subsequent intramolecular $C(sp^2)$–Si bond-forming process, which resulted in the efficient synthesis of benzosilolo[2,3-*b*]indoles.[15] Remarkably, the addition of an aldehyde promoted the efficiency of the catalytic process.

Herein, we report a facile Pd-catalyzed synthesis of siloles **2** from 2-silylaryl bromides **1** and alkynes by an intermolecular coupling reaction that is accompanied by the selective cleavage of the three $C(sp^3)$–Si bonds. Compared to the pioneering work by Chatani and co-workers,[13] our method has the following features: 1) bromides **1** are used instead of boronic acids as starting materials (the boronic acids used by Chatani and co-workers were prepared from the corresponding bromides **1** in low yields that ranged from 10 % to 30 %); 2) the transition-metal catalyst that is used is based on Pd instead of Rh; 3) wider substitution patterns of **1** can be applied; and 4) differently substituted siloles and derivatives are obtained.

Initially, we tested the reaction of 2-trimethylsilylphenyl bromide **1a** with diphenylacetylene as a model example (Table 1). The expected benzosilole derivative **2a** could be generated under certain reaction conditions. When NaO*t*Bu and KO*t*Bu were used as base, bromide **1a** was completely transformed to its corresponding 2-trimethylsilylphenyl *tert*-butyl ether (entries 5 and 6). The base LiO*t*Bu could mediate the reaction to afford **2a** in 57 % yield (entry 8). In this reaction, the addition of an aldehyde again promoted the catalytic process, and the yield of **2a** was increased from 57 % to 93 % (entries 8 and 12, respectively). The yield of **2a** was increased from 35 % to 65 % (entries 4 and 7, respectively) when K_2CO_3 was used as the base in the presence of one equivalent of 4-nitrobenzaldehyde. Aromatic aldehydes with electron-withdrawing groups gave better results than those with electron-donating substituents. The addition of water resulted in a slightly decreased yield of **2a**, while the addition of alcohols, such as *t*BuOH, slightly increased the yield. A detailed investigation into the effect of additives is provided in the Supporting Information. Optimized reaction conditions include: $[PdCl(\pi\text{-allyl})]_2$ (2.5 mol %), $P\mathit{t}Bu_3$ (10 mol %), LiO*t*Bu (3 equiv), 4-nitrobenzaldehyde (1 equiv), toluene, 120 °C, 24 hours.

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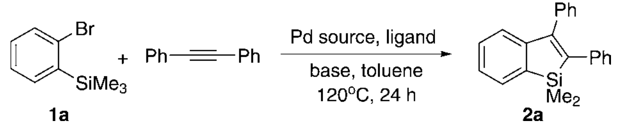
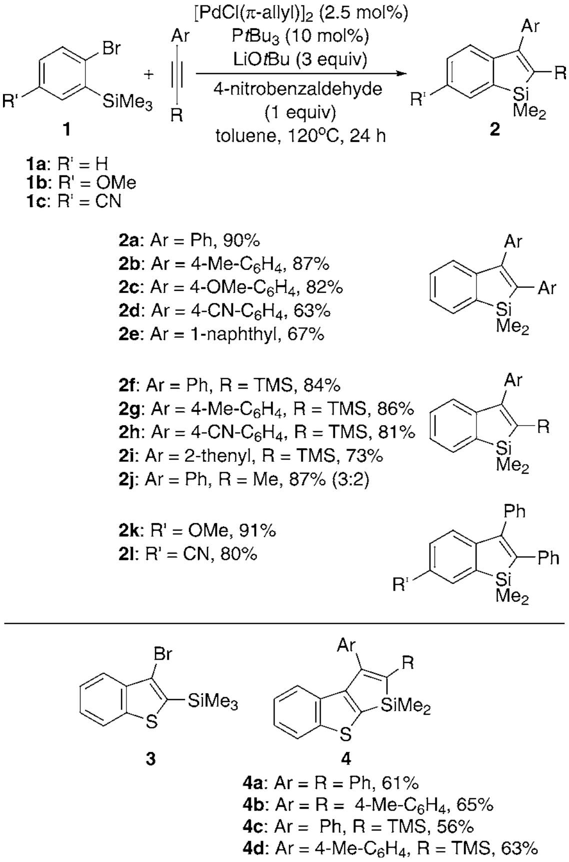
Table 1: Optimization of reaction conditions for the reaction of 2-silylaryl bromide **1a** with diphenylacetylene.[a]

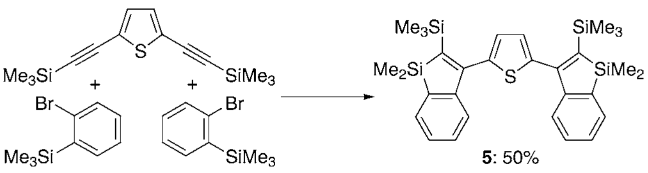


Entry	Pd source (2.5 mol%)	Ligand	Base	Yield [%][b]
1	$Pd(OAc)_2$	$PtBu_3$	LiO*t*Bu	30[c]
2	$[Pd_2(dba)_3]$	$PtBu_3$	LiO*t*Bu	32
3	$[Pd(PPh_3)_4]$	–	K_2CO_3	10[c]
4	$[PdCl(\pi\text{-allyl})]_2$	$PtBu_3$	K_2CO_3	35
5	$[PdCl(\pi\text{-allyl})]_2$	$PtBu_3$	NaO*t*Bu	0[d]
6	$[PdCl(\pi\text{-allyl})]_2$	$PtBu_3$	KO*t*Bu	0[d]
7	$[PdCl(\pi\text{-allyl})]_2$	$PtBu_3$	K_2CO_3	65[e]
8	$[PdCl(\pi\text{-allyl})]_2$	$PtBu_3$	LiO*t*Bu	57
9	$[PdCl(\pi\text{-allyl})]_2$	PCy_3	LiO*t*Bu	22
10	$[PdCl(\pi\text{-allyl})]_2$	P(2-tol)$_3$	LiO*t*Bu	44
11	$[PdCl(\pi\text{-allyl})]_2$	$PtBu_3$	LiO*t*Bu	27
12	$[PdCl(\pi\text{-allyl})]_2$	$PtBu_3$	LiO*t*Bu	93 (90)[e]
13	$[PdCl(\pi\text{-allyl})]_2$	$PtBu_3$	LiO*t*Bu	76 (73)[f]

[a] Reaction conditions: **1a** (0.36 mmol), PhCCPh (0.3 mmol), Pd catalyst ([Pd] = 2.5 mol%), ligand (10 mol%), base (0.9 mmol), toluene (2 mL). [b] Yields determined by GC analysis. Yields of isolated products given in parenthesis. [c] [Pd] = 5 mmol%. [d] 2-Trimethylsilylphenyl *tert*-butyl ether was obtained quantitatively. [e] 4-Nitrobenzaldehyde (1 equiv). [f] 4-Nitrobenzaldehyde (0.5 equiv). Cy = cyclohexyl, dba = *trans,trans*-dibenzylidene acetone, 2-tol = 2-tolyl.



Scheme 1. Formation of benzosiloles from 2-silylaryl bromides **1** and various aromatic alkynes. Yields of isolated products given. TMS = trimethylsilyl.



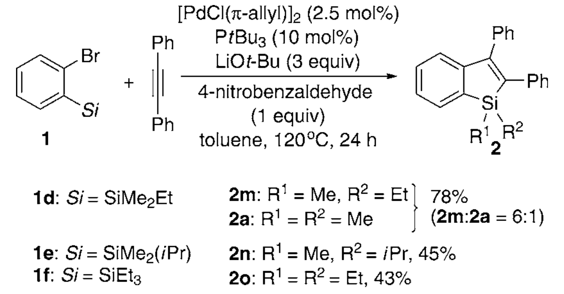
Scheme 2. One-pot synthesis of compound **5** with an extended π-conjugated system by using the reaction conditions shown in Scheme 1.

Scheme 1 shows the results obtained with the optimized reaction conditions. Aromatic alkynes that were substituted with electron-donating groups generally afforded the corresponding products in high yields. Alkynes with electron-withdrawing groups gave the corresponding products in slightly lower yields. Alkynes that were unsymmetrically substituted with a TMS group and an aromatic group afforded the corresponding products in high yields and regioselectively with the TMS group at the 2-position of the benzosiloles (**2f**–**i**). When 1-phenyl-1-propyne was used, the corresponding product **2j** was obtained as a 3:2 mixture of regioisomers. When **1b** (R′ = MeO) and **1c** (R′ = CN) were treated with diphenylacetylene, the corresponding products **2k** and **2l** were also obtained in excellent yields.

In recent years, benzothiophene-fused siloles have been the subject of growing interest as organic materials.[16] Our synthetic protocol could also be applied to the coupling reaction of benzothiophene derivative **3** with aromatic alkynes. Benzothiophene-fused silole derivatives **4** (Scheme 1) were obtained in good yields, both from symmetrically substituted aromatic alkynes (**4a**,**b**) and from alkynes that were unsymmetrically substituted with a TMS group and an aromatic group (**4c**,**d**). Such benzothiophene-fused silole skeletons are very rare.[3b] As a further demonstration of the application of the above-mentioned protocol, the thiophene-bridged 2,5-bisbenzosilole **5** with its extended π-conjugated system was obtained in 50% yield when the thiophene-bridged diyne was treated with two equivalents of **1a** under the optimized reaction conditions in a one-pot synthesis (Scheme 2).[2b,17]

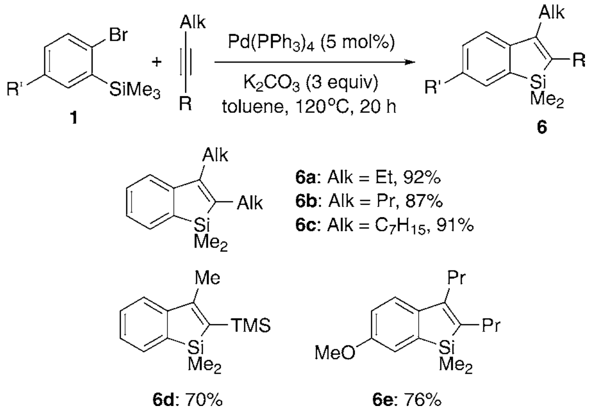
We then investigated the effect of different substituents at the silicon center, and expected the chemoselective cleavage of one of the C(sp^3)–Si bonds.[13,15] In $SiMe_2Et$ and SiMe$_2$*i*Pr, mainly the C(Me)–Si bond was cleaved, probably because of a steric effect (Scheme 3). The reaction of $SiEt_3$ (**1f**) afforded **2o** in a much lower yield, again suggesting a steric effect.

Surprisingly, when aliphatic alkynes, such as 3-hexyne and 4-octyne, were subjected to the previously optimized reaction conditions for aromatic alkynes (see Scheme 1), the expected products **6a** and **6b** were formed in very low yields (≈30–40%), regardless of whether the aldehyde was added or not. A mixture of other products was obtained, including desilylated and debrominated derivatives of starting materials **1**. The formation of 2-trimethylsilylphenyl *tert*-butyl ether was also observed. The optimization of the reaction conditions for the reaction of **1a** with 4-octyne is provided in the Supporting Information. Optimized reaction conditions for the reaction



Scheme 3. Investigation into the reactivity of the substituents on the silicon center.

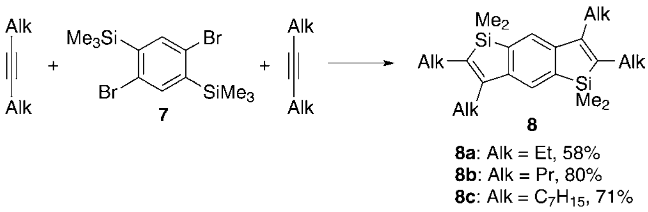
of **1** with aliphatic alkynes include: [Pd(PPh$_3$)$_4$] (5 mol %), K$_2$CO$_3$ (3 equiv), toluene, 120 °C, 20 hours (Scheme 4). 2,3-Bisalkyl-substituted benzosiloles **6** could be obtained in high yields.



Scheme 4. Formation of benzosiloles **6** from **1** and various aliphatic alkynes.

Ladder-type π-conjugated molecules have received considerable attention because of the effective conjugation that is achieved by their rigid coplanar structures.[2c,4f,18] Fortunately, the above-mentioned Pd-catalyzed intermolecular coupling reaction of aliphatic alkynes could be successfully applied to the preparation of the ladder-type π-conjugated molecules **8**, which were obtained in good yields from the doubly functionalized starting material **7** and two equivalents of an aliphatic alkyne (Scheme 5).

The reaction mechanism is not clear yet. For the coupling reaction involving aromatic alkynes, which was improved remarkably by the addition of aldehydes, we assume that a similar mechanism to the one we proposed previously might be operating.[15] The presence of an aldehyde in the reaction system would change the intermediate from the MePdBr species to the MePdH species.[19] Since reductive elimination of MePdH is more facile than that of MePdBr,[19,20] the yields of products are remarkably increased by the addition of an aldehyde. A discussion of this proposed reaction mechanism is provided in the Supporting Information. For the coupling reaction involving aliphatic alkynes, it should be mentioned that addition of P*t*Bu$_3$, which is an electron-rich ligand, dramatically decreased the yield of products **6** (see the Supporting Information). This observation indicated that the coupling reaction of the C−Si bond might be suppressed when electron-rich ligand P*t*Bu$_3$ is coordinated to the palladium center. Furthermore, the addition of aldehydes also decreased the yields of the products **6**, which again suggested that the reaction pathway for the coupling reaction with aromatic alkynes might be different from that with aliphatic alkynes.



Scheme 5. Formation of ladder-type π-conjugated molecules from **7** and aliphatic alkynes by using the reaction conditions shown in Scheme 4.

Further investigations into the reaction mechanism, including the reason for the different optimized coupling conditions for aromatic and aliphatic alkynes, and into further applications of this synthetic method are in progress.

In summary, we developed an intermolecular coupling reaction of 2-silylaryl bromides with alkynes accompanied by a Pd-catalyzed cleavage of the C(sp^3)−Si bond to obtain benzosiloles and heteroarene-fused siloles. This methodology conveniently affords silole-containing π-conjugated systems, which have great potentials as organic materials in electronic and optoelectronic devices.

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Keywords: cleavage reactions · C−Si activation · intermolecular coupling · palladium · trialkylsilyl group

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