C–H Activation

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Palladium-Catalyzed C–H Silylation through Palladacycles Generated from Aryl Halides

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Abstract: *A highly efficient palladium-catalyzed disilylation reaction of aryl halides through C–H activation has been developed for the first time. The reaction has broad substrate scope. A variety of aryl halides can be disilylated by three types of C–H activation, including C(sp^2)–H, C(sp^3)–H, and remote C–H activation. In particular, the reactions are also unusually efficient. The yields are essentially quantitative in many cases, even in the presence of less than 1 mol% catalyst and 1 equivalent of the silylating reagent under relatively mild conditions. The disilylated biphenyls can be converted into disiloxane-bridged biphenyls.*

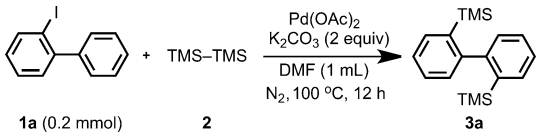
The past few decades have witnessed noticeable progress in the development of transition-metal-catalyzed C–H functionalization.[1] In this context, palladium catalysis is particularly attractive, and a number of palladium-catalyzed reactions have been developed.[2] However, the majority of palladium-catalyzed C–H functionalization reactions suffer from high catalyst loading, limited substrate scope, and imperfect yields. For intermolecular reactions, excess reactant is often needed to achieve satisfactory yields. These issues restrict application of these methods in organic synthesis. Therefore, it is highly desirable to develop innovative C–H functionalization protocols that provide excellent yields with broad substrate scope using low catalyst loading and 1 equivalent of each of the reaction partners.

Organosilicon compounds are widely used in organic synthesis[3] and materials science,[4] and have also found applications in medicinal chemistry.[5] Therefore, the development of new methods for the formation of C–Si bonds has been the topic of extensive investigation. Although the C–H functionalization strategy has been exploited to introduce silyl groups into organic molecules,[6] it is much less developed than the borylation of C–H bonds, and the application of the silylation of C–H bonds to synthetic chemistry has been limited by the inefficiency of the silylation reaction.[6a] In particular, palladium-catalyzed C–H silylation reactions are rare and remain to be developed. Although several excellent reactions have been developed, primarily by using bidentate directing groups,[7] they generally require an excess of the silylating reagent hexamethyldisilane, use high catalyst loading, and provide only moderate yields in the majority of substrates.

Transition-metal-enabled C–H functionalization reactions often rely on the use of directing groups.[8] This strategy restricts the scope of accessible products. Therefore, the development of transient directing groups has attracted considerable interest.[9] Notably, halogens have been exploited as transient directing groups to activate C–H bonds. For palladium-catalyzed reactions of this type, the reactions form palladacycles as intermediates. Most of the current reactions involve intramolecular cyclization,[10] and intermolecular reactions are quite rare.[11] Our group has been interested in this type of palladacycle[12] because they may exhibit novel reactivity, and the two Pd–C bonds offer opportunities to develop innovative reactions. Herein, we report extremely efficient reactions of such palladacycles with hexamethyldisilane. This mode of reactivity allows efficient formation of disilylated products in quantitative yields, very low catalyst loading, 1 equivalent of reactant, and broad substrate scope.

We commenced our study by investigating the reaction of 2-iodobiphenyl (**1a**) with hexamethyldisilane (**2**). Surprisingly, the disilylated product **3a** was formed almost quantitatively when the reaction was carried out using 2 equivalents of **2** and 10 mol% of $Pd(OAc)_2$ (Table 1, entry 1). In transition-metal-catalyzed C–H silylation reactions with **2**, only one of the silyl groups is typically incorporated into products, and the other one ultimately becomes byproduct. In the present reaction, both of the silyl groups are incorporated, so it not only provides a new disilylating method, but also represents a highly atom-economic example of C–H functionalization. Gratifyingly, the yield was nearly quantitative, even when using 1 mol% of $Pd(OAc)_2$ and 1 equivalent of **2**

Table 1: Optimization of reaction conditions for the disilylation of 2-iodobiphenyl.



1a (0.2 mmol) **2** **3a**

Entry	Solvent	$Pd(OAc)_2$ (mol%)	**2** (equiv)	Yield [%][a]
1	DMF	10	2	98
2	DMF	1	1	97 (94[b])
3	DMF	0.1	1	96[b,c]

[a] The yields were determined by ^{1}H NMR analysis of the crude reaction mixture. [b] Yield of the isolated product. [c] 3.0 mmol of **1a**, 0.1 mol% of $Pd(OAc)_2$, 24 h. DMF = *N*,*N*-dimethylformamide, TMS = trimethylsilyl.

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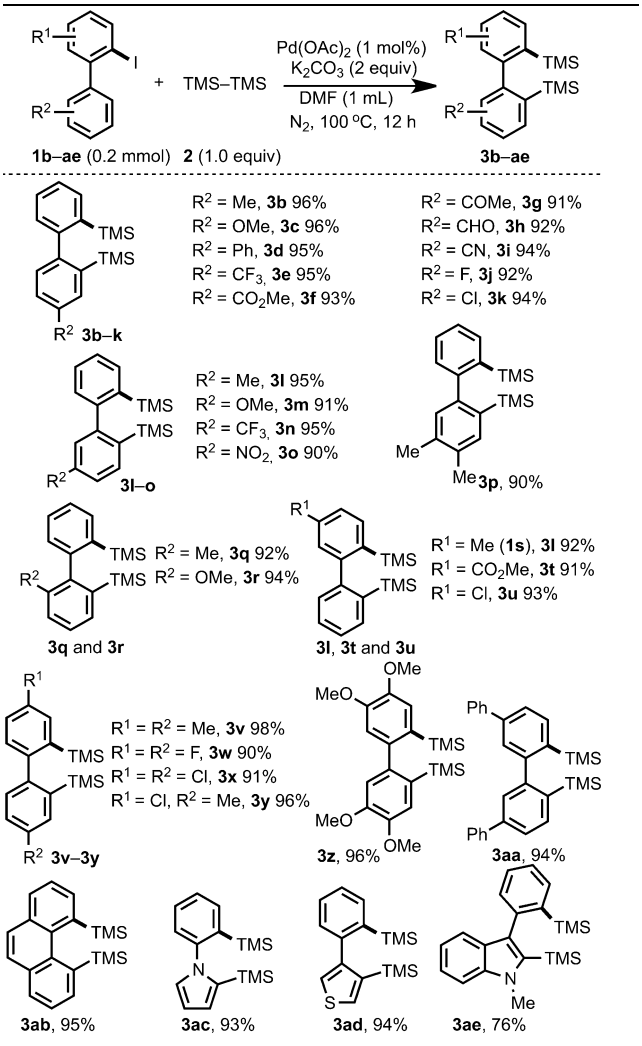
(entry 2), which indicates that the disilylation reaction is extremely efficient. Notably, a yield of 96% was still obtained even when the catalyst loading was lowered to 0.1 mol% and the reaction was scaled up to 3.0 mmol (entry 3; for the detailed optimization tables see the Supporting Information).

Next, we investigated the substrate scope of the disilylation protocol. We first examined the compatibility of various functional groups by investigating the reactions of 4′-substituted 2-iodobiphenyls. As shown in Table 2, the yields were essentially quantitative for a range of functional groups, including electron-donating and electron-withdrawing substituents (**3b–k**). The performance of 2-iodobiphenyls bearing substituents at other positions was also examined. Substituents at 3′- or even 2′-positions did not affect the high yields of the disilylation protocol (**3l–r**). A range of substrates with substituents on the iodo-bearing benzene ring or both of the benzene rings could be disilylated with excellent yields (**3t–ab**). Substrates containing either a pyrrole or thiophene ring also exhibited very high reactivity (**3ac** and **3ad**), and an indole ring was also suitable (**3ae**).

Table 2: Disilylation of 2-iodobiphenyl derivatives.[a]

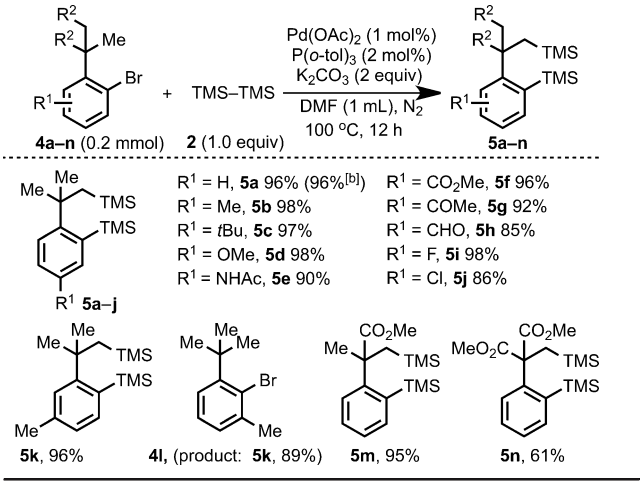


[a] All yields are those of the the isolated products.

C(sp^3)–H bonds can also be activated by utilizing halogens as transient directing groups, and the reactions form palladacycles consisting of a C(sp^2)-Pd-C(sp^3) bonding motif. Likewise, most examples in the literature involve intramolecular cyclization.[10e–h] Intermolecular reactions are comparatively underdeveloped.[11d–f] Encouraged by the disilylation reaction of 2-iodobiphenyls, we set out to investigate the intermolecular reactions of palladacycles obtained by C(sp^3)–H activation with **2**. Therefore, 1-(*tert*-butyl)-2-iodobenzene was subjected to the above standard reaction conditions. Gratefully, the expected disilylated product **5a** (for structure see Table 3) was obtained in 93% yield. 1-(*tert*-Butyl)-2-bromobenzene (**4a**) was also reactive, but the yield was very low (16%). The yield was dramatically improved to 96% when 2 mol% of P(*o*-tol)$_3$ was added.

The substrate scope of the C(sp^3)–H silylation protocol was then examined (Table 3). Various electron-donating and electron-withdrawing functional groups were compatible (**5b–h**), and fluoro and chloro groups were well-tolerated

Table 3: Disilylation of 1-(*tert*-butyl)-2-bromobenzene derivatives.[a]



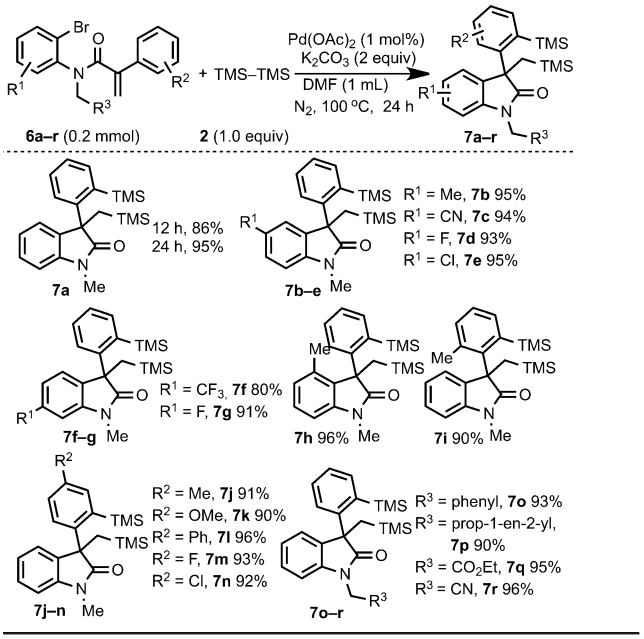
[a] All yields are those of the isolated products. [b] 2.5 mmol of **4a**, 0.1 mol% of Pd(OAc)$_2$, 0.2 mol% of P(*o*-tol)$_3$, 24 h.

(**5i** and **5j**). All the reactions were high-yielding, with most being quantitative. For the sterically hindered substrate **4l**, **5k** was formed as the final product (for the mechanism of this transformation see the Supporting Information). The ester derivatives of **4b** were suitable, although the yield of the substrate containing one methyl group was low (**5m** and **5n**). It should be noted that the disilylation of **4a** was also scalable and that the yield remained quantitative even when using 0.1 mol% of Pd(OAc)$_2$.

Recently, remote C–H activation initiated by an intramolecular Heck-type cyclization has attracted considerable interest because the strategy represents a means of expanding the substrate scope of C–H functionalization.[13] This type of reaction involves formation of spiropalladacycle intermediates, which can undergo either intramolecular cyclization[14] or intermolecular functionalization.[15] We envisioned that the spiropalladacycles formed by remote C–H activation could also be captured by **2**. Therefore, the 2-phenylacrylamide **6a**

was reacted with **2** under the standard conditions for the disilylation of 2-iodobiphenyl (Table 4). Although the desired disilylated product **7a** was formed in 86% yield, the yield was improved to 95% when the reaction time was extended to

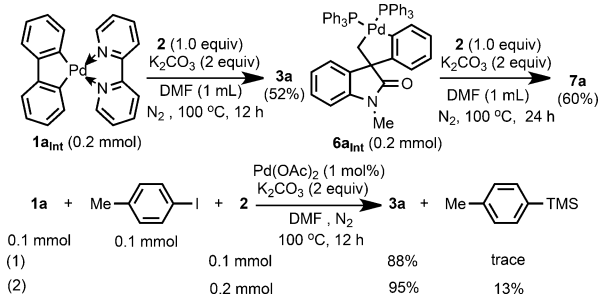
Table 4: Disilylation of 2-phenylacrylamide derivatives.[a]



[a] All yields are those of the isolated products.

24 hours. Subsequently, we examined the performance of various derivatives of acrylamides. A range of 2-phenylacrylamides bearing various groups on the benzene rings with the bromo group were reactive (**7b**–**h**), and the yields were excellent for most of the substrates. Substrates with different substituents on the aryl ring linked to the double bond also underwent the disilylation reaction in excellent yields (**7i**–**n**). Finally, changing the *N*-substituents did not affect the high reactivity of the acrylamides (**7o**–**r**).

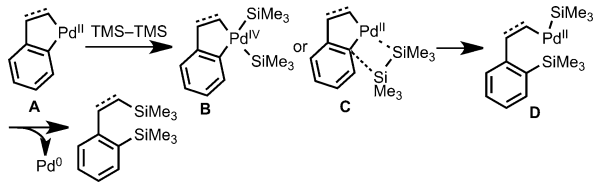
To gain insights into the mechanism of the disilylation reactions, we prepared palladacycles derived from **1a** (**1a**$_{Int}$) and **6a** (**6a**$_{Int}$; Scheme 1). Both **1a**$_{Int}$ and **6a**$_{Int}$ reacted with **2**, thus affording the disilylated products **3a** and **7a**, respectively. It is noted that **6a** was also disilylated to give **7a** in 95% yield by using 1 mol% of **6a**$_{Int}$ as the catalyst. Moreover, when equivalent amounts of **1a** and 4-iodotoluene were treated



Scheme 1. Mechanistic studies.

with 0.5 or 1 equivalents of **2**, **1a** was still transformed into **3a** in high yields, whereas only trace amounts of 4-trimethylsilyltoluene were obtained. Furthermore, 4-trimethylsiyltoluene was obtained in 9% yield when only 4-iodotoluene was subjected to the standard reaction conditions. These experimental results indicate that the disilylation reactions should proceed through palladacycle intermediates. In particular, the palladacycles have far higher reactivity towards **2** than a simple open-chain arylpalladium species and should be responsible for the high efficiency of these disilylation reactions. The kinetic isotope effect in the reaction was investigated. Whereas the intermolecular KIE value was 1.0, the intramolecular KIE value was 5.7. Furthermore, parallel reactions of **1a** and 2′,3′,4′,5′,6′-pentadeuterated 2-iodobiphenyl with **2** were carried out, and the KIE value was 1.02. These results indicate that the turnover-limiting step of the catalytic disilylation reaction did not involve C–H bond activation (for the detailed mechanistic studies see the Supporting Information.)

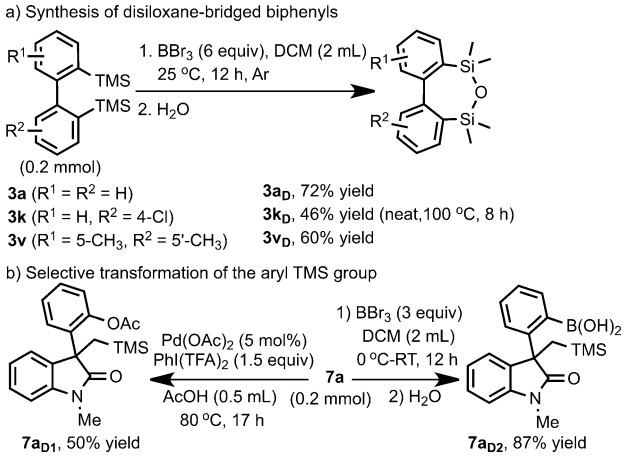
On the basis of the products formed in the reactions, the above mechanistic studies, and previous reports,[7,16] we propose a tentative mechanism for the palladium-catalyzed disilylation reactions. As shown in Scheme 2, the palladacycle



Scheme 2. Proposed mechanism for the disilylation reactions.

A, which is formed through intramolecular C–H activation from aryl halides, reacts with **2** by oxidative addition to afford the Pd^{IV} species **B**. The intermediate **B** then undergoes reductive elimination to yield **D**. An alternative metathesis pathway cannot be excluded for the formation of **D**. Finally, a second reductive elimination gives the disilylated product and releases the Pd^0 species. For palladacycles consisting of a C(sp^2)-Pd-C(sp^3) bonding motif, it remains to be investigated which C–Si bond [C(sp^2)-Si or C(sp^3)-Si] is first formed (for the detailed mechanism of all the three reactions see the Supporting Information).

It should be noted that disilylated arenes have potential applications in materials science[17] and medicinal chemistry.[18] We also explored other synthetic applications of the disilylated products (Scheme 3). When **3a** was treated with BBr_3, the disiloxane **3a**$_D$ was formed. Other derivatives such as **3k** and **3v** also underwent this transformation. It should be noted that silicon-bridged π-conjugated compounds including disiloxane-bridged biphenyls are widely studied as OLED materials.[19] Currently, disiloxane-bridged biphenyls are usually synthesized with disilane derivatives, which are prepared from 2,2′-diiodobiphenyls with *t*BuLi. Herein, we have developed a facile synthetic strategy starting from 2-iodobiphenyls. Moreover, the aryl TMS group in the products can be manipulated selectively. As shown in Scheme 3, the aryl TMS group was transformed into either the acetoxy or boronic acid



Scheme 3. Transformation of the synthetic products. DCM = dichloromethane, TFA = trifluoroacetate.

group with the alkyl TMS group intact,[20] which demonstrates the potential utility of the products in organic synthesis.

In conclusion, we have developed a novel protocol for palladium-catalyzed C–H silylation. The palladacycles obtained through various C–H activations act as the key intermediates and are disilylated with hexamethyldisilane. The modular protocol has broad substrate scope and is highly efficient. The disilylated biphenyls can be converted into disiloxane-bridged biphenyls, and the aryl TMS group can be transformed selectively. Further studies towards understanding the detailed mechanism (in particular the origins of the unusually high efficiency) and exploring this type of C–H functionalization reaction are underway in our lab.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: biaryls · C–H activation · palladacycles · palladium · reaction mechanism

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