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Intermolecular Dehydrogenative C−H/Si−H Cross-Coupling for the Synthesis of Arylbenzyl Bis(silanes)

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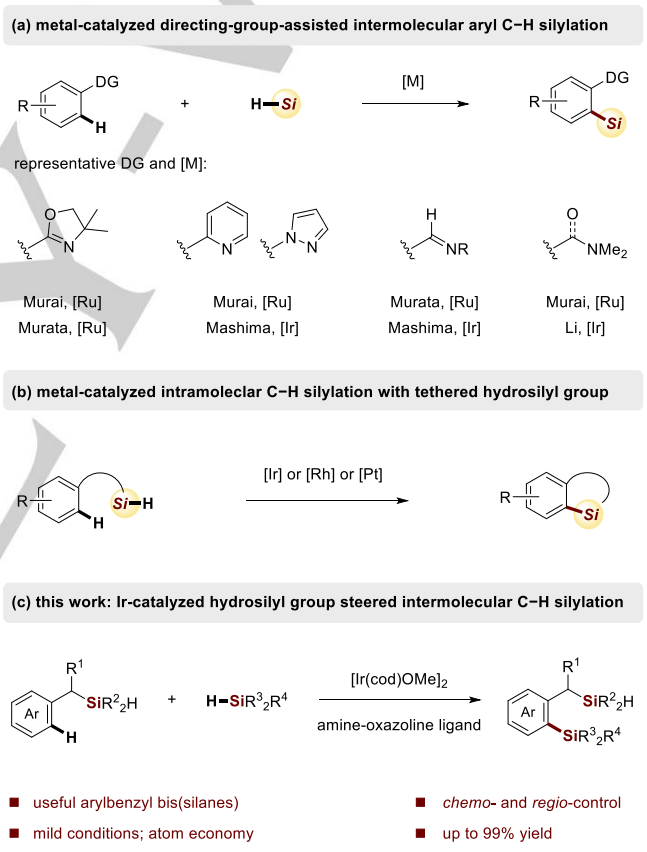
Abstract: An iridium-catalyzed intermolecular dehydrogenative C−H/Si−H cross-coupling reaction for the synthesis of arylbenzyl bis(silanes) is developed. This hydrosilyl group steered intermolecular C−H silylation process features high chemo- and regioselectivity, giving access to a wide range of multi-functionalized organosilanes in good yields from readily available starting materials with atom economy, efficiency, and environmental benignity.

Organosilanes are a class of valuable and versatile compounds with unique chemical, physical, and biological properties, which grant them widespread applications in organic chemistry, agrochemistry, medicinal chemistry, and materials science.[1] Accordingly, substantial efforts have been dedicated to the development of practical and effective approaches for the synthesis of organosilanes from simple silicon-based starting materials. In the past decades, the extraordinary advances achieved by transition-metal-catalyzed C−H bond functionalization have revolutionized the rules for assembling molecules, enabling the rapid construction of functional molecules in a more efficient and straightforward manner.[2] Among them, the silylation of C−H bonds presents a prominent example offering a superior step and atom economic approach to organosilicon compounds.[3] Although with many success, direct intermolecular silylation of aryl C−H bonds using hydrosilanes as the silylation reagents usually required harsh conditions and a large excess of arene substrates.[4] Since 2000, the Murai group reported a series of pioneering works of directing groups assisted ruthenium-catalyzed silylation of aryl C−H bonds with hydrosilanes.[5] The use of directing groups facilitate the proximal C−H bond activation, enabling the facile regioselective C(sp^2)−H silylation. Later, a variety of directing groups such as nitrogen-containing heterocycles, imines, and amides have been introduced in various transition-metal-catalyzed intermolecular aromatic C−H silylation with monohydrosilanes serving as the silicon sources (Scheme 1a).[6] Although these directed C−H silylation reactions are now commonly used, the directing groups must be installed and removed with extra steps if they are not part of the products, which inevitably leads to the formation of nonproduct waste with a significant environmental footprint, and compromises the overall step- and atom-economical nature of C−H functionalization.

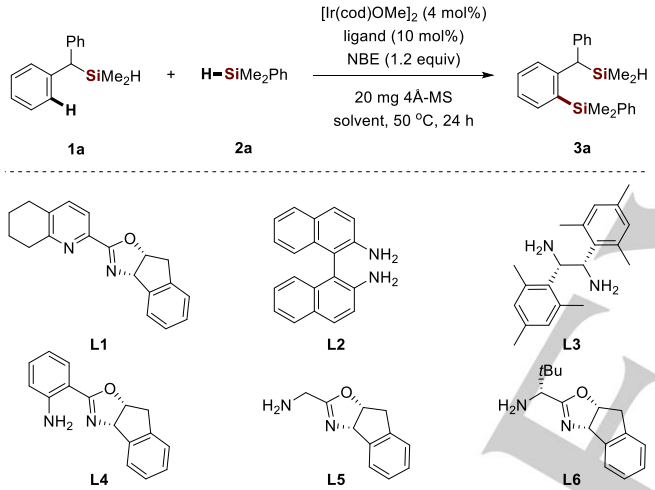


Scheme 1. Metal-catalyzed silylation of aryl C−H bonds.

On the other hand, transition-metal-catalyzed intramolecular aryl C−H silylation has also been extensively studied in recent years.[7] This type of aryl C−H silylation is actually an intramolecular dehydrogenative Si−H/C−H coupling reaction, presumably proceeding via the formation of a cyclometalated species (Scheme 1b). The tethered hydrosilyl group is proposed to initiate the process reacting with metal catalyst, and deliver the metal atom to the proximal C−H bond site allowing the C−H activation, as well as participate the C−Si cyclization reaction.[3c] It is worth mentioning that, a number of enantioselective intramolecular aryl C−H silylation reactions have also been

achieved by using rhodium catalysts ligated with chiral diphosphine ligands or iridium catalysts ligated with chiral pyridinyloxazoline ligands.[7g,7m] With the continued interest in organosilicon chemistry and C−H functionalization,[8] we wondered whether the hydrosilyl group could serve just as a directing group allowing the selective C−H activation;[9] then enable an intermolecular dehydrogenative C−H/Si−H cross-coupling with another hydrosilane partner, generating the bis(silane) compound. Given the versatile convertible property of silyl group, the hydrosilyl group steered C−H silylation process would provide an attractive approach for the assembly of multi-functionalized organosilanes from the viewpoint of economy, efficiency, and environmental benignity. To realize this hypothesis, the precise control of chemo- and regio-selectivity is essential, which could be very challenging. Herein we report the development of an Ir-catalyzed hydrosilyl group steered intermolecular dehydrogenative C−H/Si−H cross-coupling for the synthesis of arylbenzyl bis(silanes) (Scheme 1c).

Table 1. Condition optimization.[a]



Entry	Ligand	Solvent	Yield [%]
1	**L1**	THF	trace
2	**L2**	THF	52
3	**L3**	THF	65
4	**L4**	THF	trace
5	**L5**	THF	76
6	**L6**	THF	81
7[b]	**L6**	DCE	99 (95)
8	**L6**	toluene	trace
9	**L6**	1,4-dioxane	14
10[c]	**L6**	DCE	32

[a] Conditions: **1a** (0.20 mmol), **2a** (0.40 mmol), $[Ir(cod)(OMe)]_2$ (0.0080 mmol), ligand (0.020 mmol), norbornene (0.24 mmol), 4Å molecular sieves (20.0 mg) in 1.0 mL of solvent under argon atmosphere at 50 °C for 24 h. The yield was determined by ^{1}H NMR using 1,1,2,2-tetrachloroethane as internal standard; yield in parentheses was isolated yield. [b] 27% ee was obtained. [c] Room temperature.

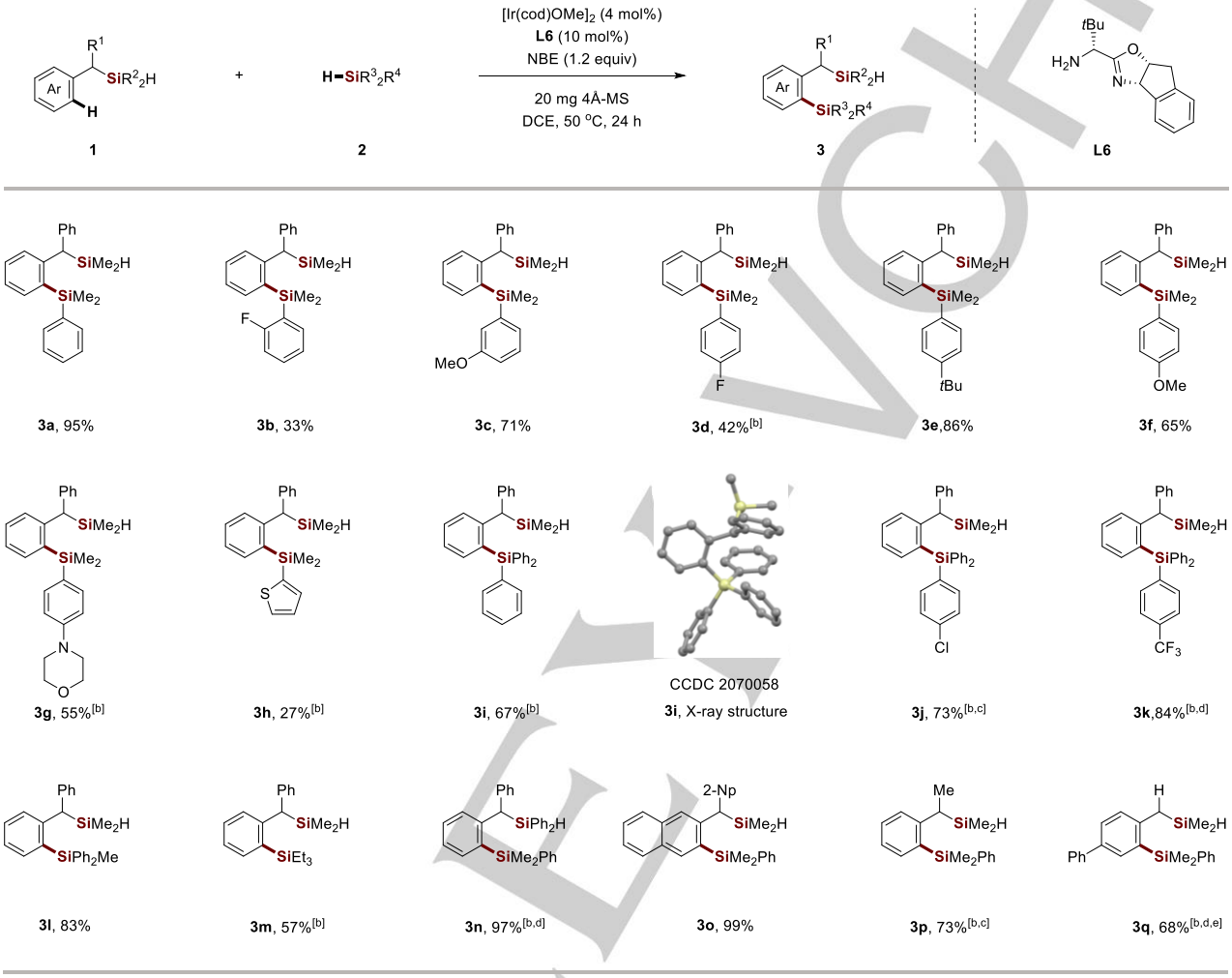
At the outset of our studies, we choosed benzhydryldimethylsilane **1a** bearing appropriate tethered hydrosilyl group as the substrate, and dimethyl(phenyl)silane **2a** as the silylation agent to attempt the intermolecular dehydrogenative Si−H/C−H coupling reaction (Table 1). In the presence of $[Ir(cod)OMe]_2$ catalyst, we first examined the pyridinyl oxazoline ligand (**L1**), which usually performed well in the intramoleclar aryl C−H silylation.[7m] Unfortunately, after many efforts, only trace desired product could be observed (entry 1). Further screening of several bidentated nitrogen ligands disclosed that, diamine (**L2**, **L3**) and amine-oxazoline (**L5**, **L6**) ligands afforded the target cross-coupling arylbenzyl bis(silane) product **3a** in 52−81% yields (entries 2−6). After indentifying amine-oxazoline **L6** as the best ligand with Ir catalyst, additional reaction parameters, including solvent and temperature, were screened. To our delight, the yield of product **3a** could be improved to 99% when the reaction was conducted in the solvent of DCE (1,2-dichloroethane) at 50 °C (entry 7). However, toluene and 1,4-dioxane reduced the yield significantly (entries 8−9). When the reaction was carried out at room temperature, the yield of **3a** decreased to 32% yield (entry 10). It is noteworthy that, at this stage we could obtain 27% *ee* of **3a** when **L6** was used as the ligand (entry 7), which underpins preliminary studies towards enantioselective version of this interesting intermolecular dehydrogenative Si−H/C−H coupling reaction.

With optimized conditions in hand, we next assessed the scope of this dehydrogenative C−Si coupling reaction (Table 2). In general, a wide range of aryldimethylsilane silylation agents **2** bearing different electronically and sterically varied substituents on the aromatic ring all reacted smoothly with **1a**, affording the corresponding arylbenzyl bis(silane) compounds **3a**−**3h** in 27−95% yields. Electron-withdrawing group such as fluoro (**3b**, **3d**), and electron-donating groups such as methoxy (**3c**, **3f**), *tert*-butyl (**3e**) and morpholinyl (**3g**) were well tolerated in the reaction. Thiophene (**3h**) also participated to generate the corresponding product, albeit in a low yield. Moreover, triarylsilanes, methyldiphenylsilane and triethylsilane were found to be competent silylation reagents, giving the desired C−H silylation products **3i**−**3m** in 57−84% yields. The introduction of chloro and trifluoromethyl substituents on the aromatic ring give the bis(silane) products **3j**, **3k** without any problem. For the scope of hydrosilyl group tethered substrate **1**, various benzyl monohydrosilanes could undergo selective ortho C−H silylation with dimethyl(phenyl)silane (**2a**), leading to the corresponding arylbenzyl bis(silane) products **3n**−**3q** in good to outstanding yields (68−99%). It is noteworthy that arylbenzyl bis(silanes) are particularly attractive compounds given their versatile convertible property of the two silyl groups. Traditionally, the access of arylbenzyl bis(silanes) mainly relied on the use of Grignard reagents, *n*BuLi or other strong bases, which displayed poor selectivity and low compatibility with many functional groups.[10] Under the current conditions, the *ee* values of most compounds **3** were low (see Supporting Information for details).

To demonstrate the utility of the arylbenzyl bis(silanes), a sequential substitution reaction showcasing the discrepancy of aryl C−Si bond and benzyl C−Si bond were performed (Scheme 2). The prepared silylation product arylbenzyl bis(silane) **3a** was first subjected to a fluoride-mediated carboxylation at ambient pressure of CO_2, followed by the methylation with

iodomethane.[11] It was interesting to find that the benzylsilyl group fully converted while the arylsilyl group was intact, affording the methyl ester **4a** in 50% yield along with protodesilylation product **4b** in 33% yield (see Supporting Information Page S19). Moreover, the aromatic C−Si moiety could be further transfered into aryl iodide in 35% yield in the presence of iodine monochloride.

Table 2. Scope of arylbenzyl bis(silanes).[a]



[a] Reaction conditions: **1** (0.20 mmol), **2** (0.40 mmol), [Ir(cod)OMe]$_2$ (4.0 mol%), **L6** (10 mol%), norbornene (0.24 mmol), 4Å molecular sieves (20.0 mg) in 1.0 mL of 1,2-dichloroethane under argon atmosphere at 50 °C for 24 h. Isolated yields. The *ee* values of representative compounds **3a**, **3e**, **3f**, **3i**, **3k**, **3l**, **3m**, **3n**, **3o**, and **3p** were determined by chiral HPLC (see Supporting Information for details). [b] 70 °C. [c] 36 h. [d] 48 h. [e] **L3** (10 mol%) was used, in 1.0 mL of toluene. 2-Np = 2-naphthyl.

Scheme 2. Derivatization of the arylbenzyl bis(silanes). [a] **3a** (0.20 mmol), CsF (1.0 mmol), CO_2 (1 atm), DMF (2.0 mL), 100 °C, 2 h, then MeI (0.40 mmol), Cs_2CO_3 (0.40 mmol), rt, 30 min. [b] **4a** (0.10 mmol), ICl (0.60 mmol), CH_2Cl_2 (1.0 mL), 50 °C, 20 h.

In summary, we have developed an efficient intermolecular dehydrogenative C−H/Si−H cross-coupling to access bis(silane) compounds. Under simple and mild conditions, a variety of new functionalized arylbenzyl bis(silane) compounds were obtained in good yields with excellent chemo- and regio-selectivity. Further derivatization of the arylbenzyl bis(silanes) demonstrated the rich chemistry of these multi-functionalized organosilanes, which could be useful as versatile building blocks in synthetic chemistry.

Acknowledgements

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Keywords: organosilanes • arylbenzyl bis(silanes) • C−H functionalization • dehydrogenative cross-coupling • intermolecular C−H silylation

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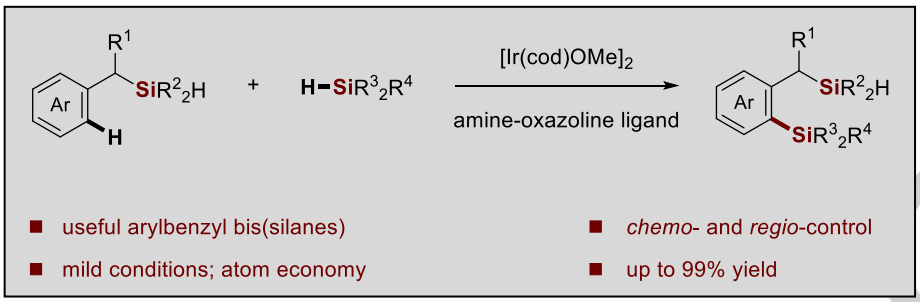
Entry for the Table of Contents

COMMUNICATION



An efficient intermolecular dehydrogenative C−H/Si−H cross-coupling to access bis(silane) compounds is described. Under simple and mild conditions, a variety of new functionalized arylbenzyl bis(silane) compounds were obtained in good yields with excellent chemo- and regio-selectivity from readily available starting materials. Further derivatization of the arylbenzyl bis(silanes) demonstrated the rich chemistry of these multi-functionalized organosilanes, which could be useful as versatile building blocks in synthetic chemistry.