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C–H Bond Activation

Iridium-Catalyzed Intermolecular Dehydrogenative Silylation of Polycyclic Aromatic Compounds without Directing Groups

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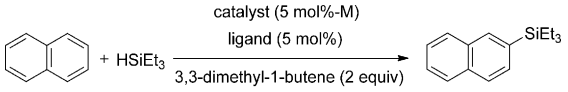
Abstract: This study describes the iridium-catalyzed intermolecular dehydrogenative silylation of C(sp^2)–H bonds of polycyclic aromatic compounds without directing groups. The reaction produced various arylsilanes through both Si–H and C–H bond activation, with hydrogen as the sole byproduct. Reactivity was affected by the electronic nature of the aromatic compounds, and silylation of electron-deficient and polycyclic aromatic compounds proceeded efficiently. Site-selectivity was controlled predominantly by steric factors. Therefore, the current functionalization proceeded with opposite chemo- and site-selectivity compared to that observed for general electrophilic functionalization of aromatic compounds.

Synthesis of functionalized polycyclic aromatic compounds is interesting due to their potential as tools for the construction of complicated aromatic π-systems.[1] Among them, arylsilanes continue to be important because they are key components for new organic functional materials. These compounds can be prepared by the reaction of aryl Grignard or aryl lithium reagents with halosilanes,[2] and transition-metal-catalyzed coupling reaction of aryl halides with hydrosilanes[3] or disilanes.[4] However, dehydrogenative silylation of simple arenes with hydrosilanes through both C–H and Si–H bond activation would be a more direct and attractive because of atom-efficiency and environmental benignity.[5] Pioneering work was done by Chatani and Murai who reported the ruthenium-catalyzed intermolecular dehydrogenative silylation of aromatic compounds using directing groups, such as oxazolyl and pyridyl groups.[6] The intermolecular dehydrogenative C–H silylation of simple aromatic compounds without directing groups still remains challenging. The seminal work by Curtis et al. using Vaska's complex[7a] resulted in several ruthenium, rhodium, and platinum catalysts that are effective for this transformation.[7] However, the reaction had several disadvantages, including the substrate scope, need for a large excess of neat aromatic substrates as solvents (usually more than 50 equiv), and high temperatures. In addition, intermolecular dehydrogenative silylation of polycyclic aromatic compounds has not been reported, because the reaction of fewer substrates in the solvent would be desirable for these solid aromatic compounds.

In our effort to develop dehydrogenative silylation of sp^2 and sp^3 C–H bonds,[8] the unexpected dehydrogenative silylation of naphthalene with silanes occurred in the presence of a catalytic amount of an iridium complex.[9] This observation prompted a more thorough examination of the reaction because of the following: 1) the reaction proceeded efficiently with naphthalene using a slight excess of silanes (~3 equiv); 2) site- and chemoselectivity could be well-controlled (sterically less demanding and electron-deficient aromatic compounds react preferentially), affording mono- and disilylated naphthalenes in good yields; and 3) the major product, β-silylnaphthalene, can be converted easily to β-halonaphthalenes,[10] which are difficult to access by typical electrophilic functionalization with bromine or iodine (Figure 1). Hartwig et al. reported rhodium-catalyzed dehydrogenative silylation of functionalized benzene derivatives during the preparation of this work.[7i,j]

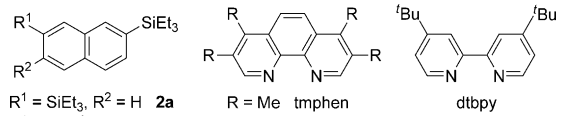
Table 1. Optimization of reaction conditions.



(2 equiv) **1a**

Entry	Catalyst/ligand	Solvent	Yield [%][a]
1	$[RhCl(PPh_3)_3]$	cyclohexane	1
2	$[RhCl(cod)]_2$/tmphen	cyclohexane	1
3	$[IrCl(cod)]_2$/tmphen	cyclohexane	53
4	$[Ir(OMe)(cod)]_2$/tmphen	cyclohexane	71 (70)
5	$[Ir(OMe)(cod)]_2$/tmphen	dioxane	70
6[c]	$[Ir(OMe)(cod)]_2$/tmphen	$(CH_2Cl)_2$	8
7	$[Ir(OMe)(cod)]_2$/dtbpy	cyclohexane	48
8	$[Ir(OMe)(cod)]_2$/1,10-phen	cyclohexane	42
9[b]	$[Ir(OMe)(cod)]_2$/tmphen	cyclohexane	30
10[c]	$[Ir(OMe)(cod)]_2$/tmphen	cyclohexane	62 (59)[d]

[a] Determined by ^1H NMR spectroscopy. The values in parentheses are isolated yields. [b] Cyclohexene was used in place of 3,3-dimethyl-1-butene. [c] Naphthalene/$HSiEt_3$ = 1:3. Yield is based on silane. [d] Mixture of disilylated naphthalenes **2a** and **2a′** were isolated in 13 and 12% yields.



R^1 = $SiEt_3$, R^2 = H **2a**; R^1 = H, R^2 = $SiEt_3$ **2a'**

R = Me tmphen; R = H 1,10-phen; dtbpy

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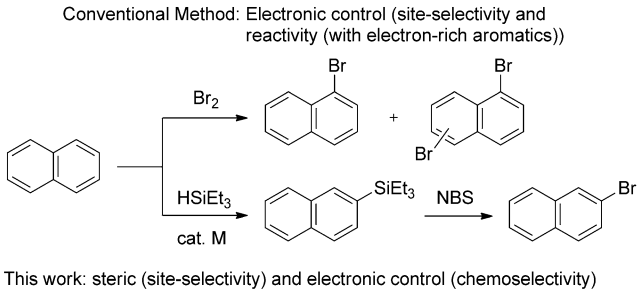


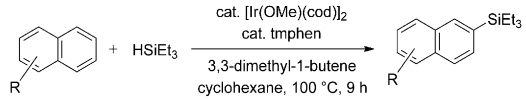
Figure 1. Challenges in the functionalization of polycyclic aromatic compounds. NBS = *N*-bromosuccinimide.

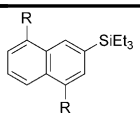
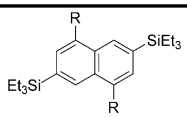
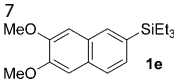
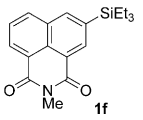
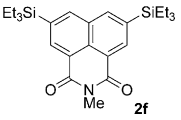
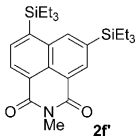
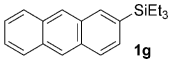
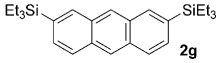
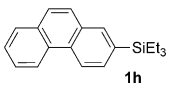
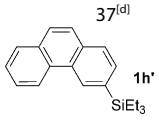
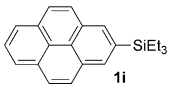
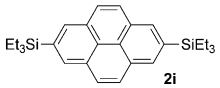
The present study describes the iridium-catalyzed intermolecular dehydrogenative silylation enabling the direct use of polycyclic aromatic compounds without any directing groups as substrates, and the production of hydrogen as the sole byproduct.

Recently, the Wilkinson complex, $[RhCl(PPh_3)_3]$, was found to be effective for the synthesis of 9-silabifluorenes by the intramolecular dehydrogenative silylation of $C(sp^2)$–H bonds.[8a] This successful result encouraged an examination of the intermolecular version of this $C(sp^2)$–H bond silylation. Treatment of naphthalene (2 equiv) with triethylsilane, 3,3-dimethyl-1-butene (2 equiv), and a catalytic amount of $[RhCl(PPh_3)_3]$ in cyclohexane at 100 °C provided 2-silylnaphthalene **1a** albeit in very low yield (Table 1, entry 1). The combination of other rhodium complexes, including $[RhCl(cod)]_2$ (cod = 1,5-cyclooctadiene) and $[Rh(OMe)(cod)]_2$, with a variety of phosphines and phenanthroline-based ligands did not improve the yield of **1a**, and most of the naphthalene was recovered even heated at high temperature for a long reaction time (entry 2). In contrast, dehydrogenative silylation occurred smoothly when iridium complexes were used as catalysts together with phenanthroline-based ligands. For example, 2-silylnaphthalene **1a** was obtained selectively in 53% yield in the presence of a catalytic amount of $[IrCl(cod)]_2$ and 3,4,7,8-tetramethyl-1,10-phenanthroline (referred to as "tmphen") (Table 1, entry 3). Note that the silylation occurred selectively at the β-position to afford **1a** and no formation of its isomer, 1-silyl-naphthalene, was observed under the reaction conditions. Among the iridium and rhodium complexes examined, $[Ir(OMe)(cod)]_2$ was most effective for furnishing **1a** in 70% yield (entry 4). Examination of the solvent indicated that dioxane was as effective as cyclohexane (entries 5 and 6).[11] Next, the effect of ligands was investigated by using $[Ir(OMe)(cod)]_2$ and cyclohexane as the metal complex and solvent, respectively. Other nitrogen ligands, such as 4,4′-di-*tert*-butyl-2,2′-bipyridine (dtbpy), 1,10-phenanthroline (1,10-phen), and 4,7-dimethyl-1,10-phenanthroline also displayed good activity, although none were superior to tmphen (entries 7 and 8). In contrast, phosphine ligands, including PPh_3, PCy_3, dppf, 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (BINAP), and DTBM-SEGPHOS, are completely ineffective, and naphthalene was recovered intact.[7i,j] Note that the reaction proceeded efficiently only when 3,3-dimethyl-1-butene was used as a hydrogen acceptor. Other olefins, such as cyclohexene, cyclooctene, and norbornene, which were identified as optimized hydrogen acceptors in the previous work, were not applicable to the current iridium-catalyzed system due to competitive hydrosilylation (entry 9). When the ratio of naphthalene and hydrosilane employed was changed to 1:3 under the reaction conditions in entry 4, the yield of **1a** was decreased to 59%, and 2,6- and 2,7-disilylnaphthalenes **2a** and **2a′** were obtained in 13 and 12% yields, respectively (entry 10).

Using the optimized reaction conditions, the scope of polycyclic aromatic compounds for dehydrogenative silylation was

Table 2. Ir-catalyzed dehydrogenative silylation of polycyclic aromatic compounds leading to mono- and disilylarenes **1** and **2**.



Entry	Method[a]	Product [%]	
		 **1b** (R = Cl)	 **2b** (R = Cl)
1	A[c]	74	8
2	B	2	94
		1c (R = 4-MeOC$_6$H$_4$)	**2c** (R = 4-MeOC$_6$H$_4$)
3	A[b]	72	0
4	B[b]	31	67
		1d (R = 4-CF$_3$C$_6$H$_4$)	**2d** (R = 4-CF$_3$C$_6$H$_4$)
5	A[b,c]	72	7
6	B[b]	7  **1e**	91
7	B	36  **1f**  **2f**	 **2f′**
8	A[b]	67	7 + 2
9	B[b]	14  **1g**	45 + 23  **2g**
10	A[b]	64	0
11	B[b]	35  **1h**	37[d]  **1h′**
12	A[b]	31  **1i**	31  **2i**
13	A[b]	54	3
14	B[b]	63	20

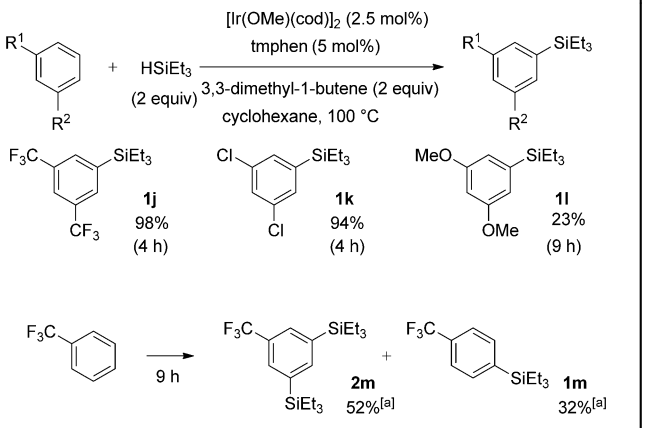
[a] Method A: arene/$HSiEt_3$ = 2:1, $[Ir(OMe)(cod)]_2$ (2.5 mol%), tmphen (5 mol%) 3,3-dimethyl-1-butene (2 equiv). Yields are based on silane. Method B: arene/$HSiEt_3$ = 1:3, $[Ir(OMe)(cod)]_2$ (5.0 mol%), tmphen (10 mol%), 3,3-dimethyl-1-butene (3 equiv). Yields are based on arenes. [b] Dioxane was used as a solvent. [c] For 4 h. [d] Mixture of 2,7- and 2,8-disilylanthracenes (1:1).

investigated (Table 2). The reaction was examined under two different sets of conditions (method A: arene/silane = 2:1, and B: arene/silane = 1:3) for the selective synthesis of mono- and disilylarenes. The reaction of 1,5-dichloronaphthalene gave the monosilylated naphthalene **1b** in 74% yield with method A, and disilylated naphthalene **2b** in 94% yield with method B, respectively (Table 2, entries 1 and 2). In contrast with the previous rhodium-catalyzed system for the silylation of benzene derivatives,[7i] no reductive dechlorination was observed under the present reaction conditions (entry 3). Naphthalene derivatives containing an electron-donating anisyl and an electron-withdrawing trifluoromethylphenyl group were good substrates. The use of dioxane as a solvent to dissolve these naphthalenes was effective, and selective silylation at the β-position of the naphthalene rings furnished **1c**, **1d**, **2c**, and **2d** (entries 3–6). However, dehydrogenative silylation of 2,3-dimethoxynaphthalene was slow and produced **1e** in low yield (entry 7). The current method also can be applied to silylation of the C–H bonds of expanded π-conjugated systems. Monosilylation of benz[*de*]isoquinoline-1,3-(2*H*)-dione using method A provided the expected coupling product **1f** in 67% yield (Table 2, entry 8). Changing the ratio of the two substrates produced a mixture of the mono- and disilylated imides **1f**, **2f**, and **2f′**, which could be separated easily using silica gel column chromatography, in total 82% yield (entry 9). Anthracene, phenanthrene, and pyrene also underwent dehydrogenative silylation to afford the mono- and disilylated products **1g–i** and **2g–i** depending on the reaction conditions (entries 10–14). All of the reactions occurred selectively at the least sterically hindered position of these polycyclic π-conjugated systems.

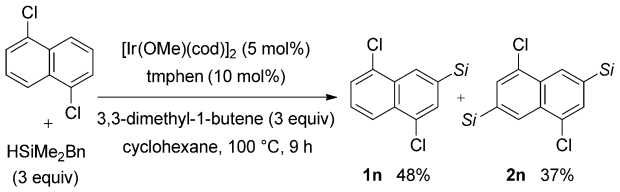
The current catalyst system is also effective for the intermolecular dehydrogenative silylation of functionalized benzenes (Table 3).[7i,j] Electron-deficient 1,3-bis(trifluoromethyl)benzene afforded the corresponding silylarene **1j** in 98% yield. The silylation of 1,3-dichlorobenzene involved high chemoselectivity to provide **1k** in 94% yield without the loss of a chlorine group. In contrast, silylation of an electron-rich aromatic compound, 1,3-dimethoxybenzene, was sluggish. This result is consistent with the reactivity trend demonstrated by the dehydrogenative silylation of 2,3-dimethoxynaphthalene (Table 2, entry 7). Formation of 1,3,5-trisubstituted benzene derivatives were predominant, and their regioisomers were not detected despite the electronic nature of the starting arenes. Trifluoromethylbenzene reacted efficiently to furnish the mono- and disilylated benzene **1m** and **2m** in 32 and 52% yields, respectively. These results demonstrate that electron-deficient arenes **1j** and **1k** were effective substrates for the current dehydrogenative silylation.

Other hydrosilanes can be used as silyl group sources for the current catalytic transformation. When dehydrogenative silylation of 1,5-dichloronaphthalene with benzyldimethylsilane was performed, the expected dehydrogenative coupling products were obtained as a mixture of mono- and disilylated adducts **1n** and **2n** in 85% total yield (Scheme 1). Chlorine groups, which have been used in various cross-coupling reactions, were also well-tolerated. Moreover, because the benzyldimethylsilyl group can be converted easily to aryl groups by Hiyama cross-coupling, this result confirmed the potential utility of the present reaction toward the synthesis of complexed π-conjugated systems.[12]

Table 3. Ir-catalyzed dehydrogenative silylation leading to functionalized benzene derivatives **1** and **2**.



[a] 3 equiv of $HSiEt_3$ and 3,3-dimethyl-1-butene were used.



Scheme 1. Ir-catalyzed dehydrogenative silylation with benzyldimethylsilane (*Si* = $SiMe_2Bn$).

Intermolecular competition experiments (see Table S3 in the Supporting Information for details) using benzene, naphthalene, 1,5-dichloronaphthalene, 1,3-dichloro- and 1,3-dimethoxybenzene revealed that the relative reactivity of these substrates was 1,3-dimethoxybenzene < benzene ≪ naphthalene < 1,3-dichlorobenzene < 1,5-dichloronaphthalene (Figure 2). In addition, intramolecular competition experiments showed that dehydrogenative silylation of naphthalene occurred preferentially over benzene under the present conditions (Scheme 2). Considering that the number of potentially cleavable C–H bonds of naphthalene is less than that of benzene (6 for benzene and 4 for naphthalene), the chemoselectivity of naphthalene over benzene was very high. These results suggest that

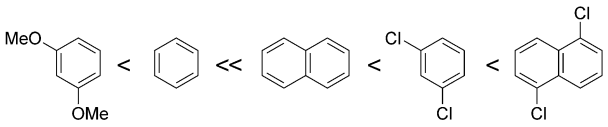
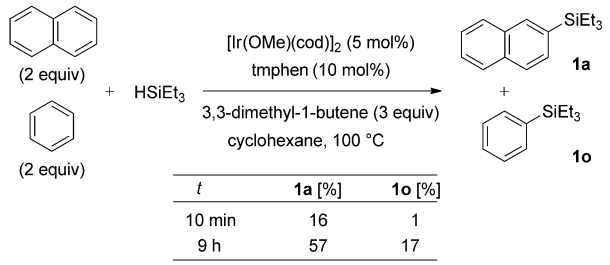


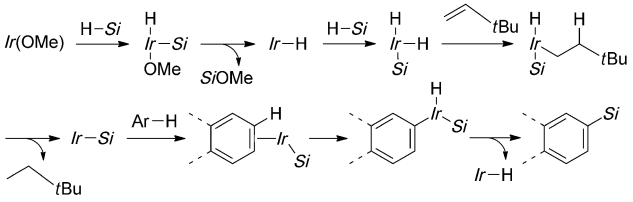
Figure 2. Reactivity of arenes for the current Ir-catalyzed dehydrogenative silylation.



t	1a [%]	1o [%]
10 min	16	1
9 h	57	17

Scheme 2. Selective dehydrogenative silylation of naphthalene in the presence of benzene.

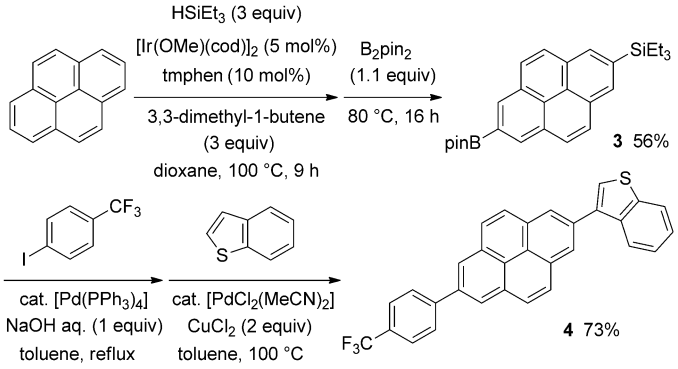
the reactivity order of the aromatic substrates is controlled by their electronic density and efficiency for interaction with an iridium center. Resonance stabilization energy of each benzene ring of polycyclic aromatic hydrocarbons weakens upon fusion of another benzene ring. Therefore, the double bonds tend to behave like a simple alkene, promoting the approach of the catalytically active Ir–Si species through π-coordination (see Scheme 3). Based on these observations, Scheme 3 presents



Scheme 3. Plausible reaction mechanism (tmphen ligand is omitted for clarity. Si indicates SiR_3).

a plausible mechanism for the current intermolecular dehydrogenative silylation. First, Ir–H species was generated by oxidative addition of Ir–OMe to hydrosilane followed by the reductive elimination of Si–OMe.[13] This Ir–H species was subsequently added to hydrosilane, inserted into 3,3-dimethyl-1-butene, and reductively eliminated to convert the Ir–Si species. Next, oxidative addition of the resulting Ir–Si species to the aryl C(sp^2)–H bond generated an Ir–Si intermediate, which then underwent reductive elimination to afford the corresponding arylsilanes along with the regeneration of the Ir–H species.[14,15] Although C–H bond activation without using a directing group is generally difficult,[16] the interaction of the benzene ring in polycyclic aromatic compounds with the Ir–Si intermediate might fix the Ir center near the aryl C–H bond and promote this energetically unfavored step.[17] Steric factors dominated the site-selectivity of this C–H bond activation, which resulted in exclusive formation of the sterically less hindered arylsilanes.

The present reaction can be extended to subsequent C–H silylation and C–H borylation of polycyclic aromatic hydrocarbons. For example, treatment of triethylsilane under the optimized reaction conditions followed by addition of bis(pinacolato)diboron resulted in selective introduction of both silyl and boryl functionalities at the 2- and 7-positions of pyrene, respectively (Scheme 4). The resulting 2-boryl-7-silylpyrene **3**



Scheme 4. One-pot, site-selective silylborylation of pyrene and its synthetic application to donor–acceptor substituted pyrene **4** (See the Supporting Information for detailed reaction conditions).

could be converted to the novel donor–acceptor substituted pyrene **4** by an additional two-step transformation.[18,19] Extension of π-conjugation along the long axis of pyrene is useful for expanding the π-conjugation without generating molecular twist. The absorption in the visible region and strong fluorescence proved the usefulness of **4** as a new component of light-emitting materials and solar cells.

In conclusion, the present report describes the iridium-catalyzed intermolecular dehydrogenative silylation of polycyclic aromatic compounds by activation of both Si–H and C–H bonds. The reaction occurred preferentially for electron-deficient and polycyclic aromatic compounds. Site-selectivity was controlled by steric factors to provide selectively functionalized arenes, which are difficult to access by conventional electrophilic functionalization.

Experimental Section

General procedure for the iridium-catalyzed intermolecular dehydrogenative silylation of polycyclic aromatic compounds (method A)

A mixture of $[Ir(OMe)(cod)]_2$ (3.3 mg, 5.0 μmol), 3,4,7,8-tetramethyl-1,10-phenanthroline (2.4 mg, 10 μmol), and cyclohexane or dioxane (0.25 mL) was stirred at 25 °C for 30 min. The mixture was then added to aromatic compound (0.40 mmol), 3,3-dimethyl-1-butene (33.7 mg, 0.40 mmol), and triethylsilane (23.2 mg, 0.20 mmol), and further stirred at 100 °C for 4 or 9 h. The solvent was removed in vacuo, and the residue was subjected to flash column chromatography on silica gel with hexane/EtOAc as the eluent to afford the corresponding arylsilanes.

Acknowledgements

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Keywords: C–H bond activation · dehydrogenation · iridium · polycyclic aromatic compounds · silylation

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C–H Bond Activation

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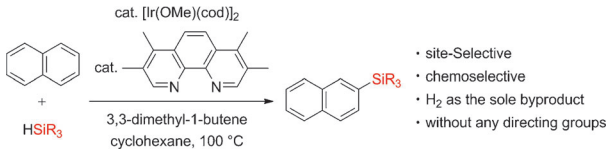
Iridium-Catalyzed Intermolecular Dehydrogenative Silylation of Polycyclic Aromatic Compounds without Directing Groups



Direct silylation: Treatment of aromatic compounds with hydrosilanes in the presence of iridium catalyst afforded silylarenes without any directing groups. The reactivity was affected by the electronic nature of arenes, and silylation of electron-deficient and polycyclic aromatic compounds proceeded more efficiently (see scheme).