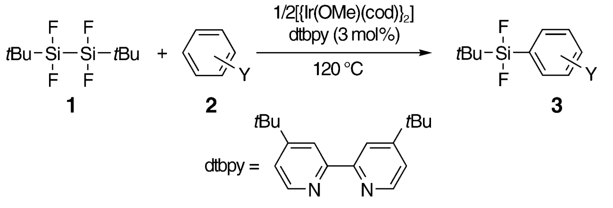
Ir-Catalyzed Silylation of Arenes

Direct Synthesis of Aryl Halosilanes through Iridium(I)-Catalyzed Aromatic C−H Silylation by Disilanes[**]

Tatsuo Ishiyama,[*] Kazuaki Sato, Yukihiro Nishio, and Norio Miyaura[*]

Aryl halosilanes and their hypervalent derivatives are versatile reagents for carbon–carbon[1–2] and carbon–heteroatom[3] bond formation in modern organic synthesis. Although they have been prepared by arylation of halosilanes with aryl magnesium or aryl lithium reagents,[4] and by Pd-catalyzed cross-coupling of halogenated disilanes with aryl electrophiles,[5] direct silylation of arenes through C−H bond activation would provide a more attractive route from the viewpoints of economy, efficiency, and environmental benignity. Indeed, aromatic C−H silylation by disilanes[6] or hydrosilanes[6a,7] catalyzed by a transition-metal complex has been developed by several research groups. However, the application of this protocol has been limited to the synthesis of aryl triorganosilanes. On the other hand, we recently found that Ir^I complexes generated from 1/2[{IrCl(cod)}$_2$] (cod = 1,5-cyclooctadiene) or 1/2[{Ir(OMe)(cod)}$_2$] and 2,2′-bipyridine (bpy) or 4,4′-di-*tert*-butyl-2,2′-bipyridine (dtbpy) are excellent catalysts for aromatic C−H borylation by bis(pinacolato)diboron.[8] These results prompted us to extend the methodology to the aromatic C−H silylation of arenes (**2**) by 1,2-di-*tert*-butyl-1,1,2,2-tetrafluorodisilane (tBuF$_2$Si)$_2$ (**1**) in the presence of a 1/2[{Ir(OMe)(cod)}$_2$]-dtbpy catalyst. This process enables, for the first time, the direct synthesis of aryl halosilanes (**3**) through aromatic C−H bond activation (Scheme 1).



Scheme 1. Aromatic C−H silylation.

Our initial investigation focused on the effects of substituents on the disilanes on the reaction. The reactions were carried out at 80 °C for 16 h in a resealable Schlenk tube by using disilanes (1.0 mmol), benzene (60 mmol), [{Ir(OMe)(cod)}$_2$] (0.015 mmol), and dtbpy (0.03 mmol). Among the disilanes examined, **1** exhibited the highest reactivity to produce the corresponding phenylsilane in 28 % yield with 28 % conversion of **1**. The use of tetrafluorodisilanes is critical as (Me$_2$FSi)$_2$ gave the corresponding arylsilane in 9 % yield, and (tBuCl$_2$Si)$_2$ or (Me$_3$Si)$_2$ led to no reaction. The structures of alkyl substituents also had significant effects on silylation. For example, (sBuF$_2$Si)$_2$ and (nBuF$_2$Si)$_2$ formed no silylated product.

The reaction of *o*-xylene with **1** was carried out at 120 °C to optimize catalyst precursors and ligands. Of the precursors and ligands examined, the combination of 1/2[{Ir(OMe)(cod)}$_2$] and dtbpy was found to be the best catalyst to provide isomerically pure 4-silyl-1,2-dimethylbenzene in 99 % yield based on the molar amount of **1**. Although the substrate has weaker benzylic C−H bonds,[9] the reaction selectively occurred at the aromatic C−H bonds. The combination of dtbpy and either 1/2[{IrCl(cod)}$_2$] or [{Ir(cod)$_2$}BF$_4$] produced silylated products in 82 % and 78 % yield, respectively, but [Ni(acac)$_2$]–nBuLi (acac = acetylacetonato), 1/2[{RhCl(cod)}$_2$], 1/3[Ru$_3$(CO)$_{12}$], and [Pt(dba)$_2$] (dba = dibenzylideneacetone) with or without a dtbpy ligand formed no silylated product. Reactions with 1/2[{Ir(OMe)(cod)}$_2$] as a catalyst precursor were markedly affected by steric and electronic properties of bipyridine ligands. Bpy, 4,4′-di-Me-bpy, 5,5′-di-Me-bpy, and even 6,6′-di-Me-bpy displayed moderate reactivity (49–55 % yields), while 3,3′-di-Me-bpy showed little activity (8 % yield) owing to the importance of a parallel arrangement of two pyridine rings. Electronic effects of bpy derivatives were perplexing as electron-rich or -poor derivatives of bpy resulted in low yields, for example, 4,4′-di-Me$_2$N-bpy (1 %); 4,4′-di-MeO-bpy (34 %); 4,4′-di-Cl-bpy (2 %); and 4,4′-di-O$_2$N-bpy (0 %).

Reactions of **1** with representative arenes **2** catalyzed by the combination of 1/2[{Ir(OMe)(cod)}$_2$] and dtbpy at 120 °C are summarized in Table 1. Under optimized conditions, benzene produced phenylsilane in 97 % yield (entry 1). The orientation can be controlled by steric effects of substituents. Reactions occurred at C−H bonds located *meta* or *para* to a substituent in preference to those of *ortho* positions. Thus, *o*- and *m*-xylenes gave a single product (entries 2 and 3), but *p*-xylene resulted in no reaction because of steric hindrance. Bicyclic **2** such as tetralin and indan yielded silylated products (entries 4 and 5); indan gave a mixture of 5- and 4-silyl derivatives owing to only a small steric hindrance of the five-membered ring. Compounds **2** in which the rings were electron-rich or electron-poor participated in silylation reactions (entries 6 and 7). The reactions of 1,3-dialkylated **2** selectively occurred only at the common *meta* position; therefore, isomerically pure compounds of **3** were obtained even with two distinct substituents on **2** (entry 8), whereas analogous substrates of **2** that have less bulky substituents such as a MeO or Cl group produced a regioisomeric mixture of **3** (entries 9 and 10).

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[*] Prof. T. Ishiyama, Prof. N. Miyaura, K. Sato, Y. Nishio
Division of Molecular Chemistry
Graduate School of Engineering
Hokkaido University
Sapporo, 060-8628 (Japan)
Fax: (+81) 11-706-6562
E-mail: ishiyama@org-mc.eng.hokudai.ac.jp
miyaura@org-mc.eng.hokudai.ac.jp

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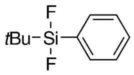
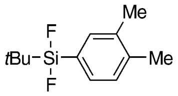
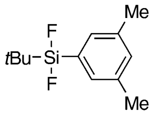
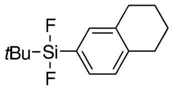
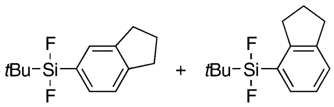
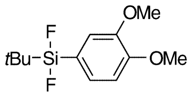
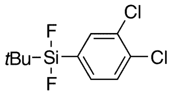
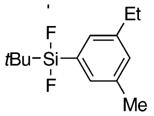
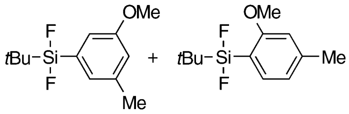
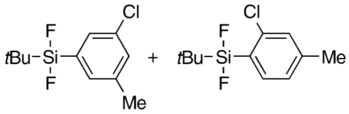
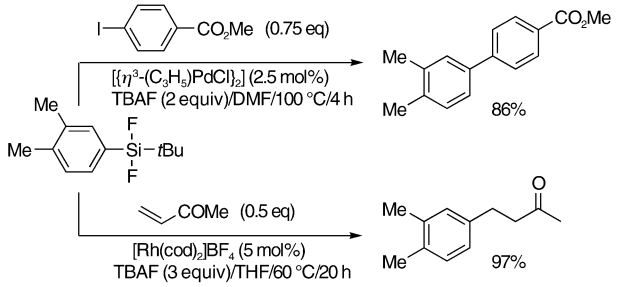
Table 1: Synthesis of arylsilanes **3** (Scheme 1).[a]

Entry	Arylsilane **3**	Yield [%][b]
1		97
2		99
3		97
4		96
5		98 (82:18)
6		73
7		46
8		75
9		79 (66:34)
10		72 (87:13)

[a] A mixture of $(t\mathrm{BuF_2Si})_2$ **1** (1.0 mmol), arene **2** (60 mmol), $[\{\mathrm{Ir(OMe)(cod)}\}_2]$ (0.015 mmol), and dtbpy (0.03 mmol) was stirred at 120 °C for 16 h. [b] GC yields based on **1**.

Although we have not investigated the reaction mechanism yet, the present C–H silylation may proceed through: (a) the generation of a (silyl)iridium intermediate (**4**) by the reaction of **1** with an iridium(I) complex; (b) oxidative addition of an aromatic C–H bond to **4** followed by reductive elimination of an arylsilane **3** or direct σ-bond metathesis between an Ir–Si bond of **4** and an aromatic H–C bond to form an iridium hydride complex (**5**); (c) oxidative addition of **1** to **5** followed by reductive elimination of a hydrosilane or direct σ-bond metathesis between **1** and **5** to regenerate a (silyl)iridium intermediate **4**. It is unclear at this moment whether the mechanism involves a mono(silyl)iridium(I) or a tris(silyl)iridium(III) intermediate, and why two of the silyl groups in **1** do not participate in the reaction.



Scheme 2. Synthetic utility of **3**.

Arylsilanes **3** thus obtained are useful reagents for carbon–carbon bond-formation reactions (Scheme 2). For example, **3** cross-coupled with aryl halides in the presence of a palladium catalyst and a fluoride-ion source in dimethylformamide (DMF) to produce the corresponding unsymmetrical biaryls in high yields.[1] Also, **3** participated in 1,4-addition to α,β-unsaturated ketones in the presence of a rhodium catalyst and a fluoride-ion source in THF to give β-arylketones in excellent yields.[2]

In summary, iridium complexes composed of $1/2[\{\mathrm{Ir(OMe)(cod)}\}_2]$ and 4,4′-di-*tert*-butyl-2,2′-bipyridine were found to be efficient catalysts for the aromatic C-H silylation by 1,2-di-*tert*-butyl-1,1,2,2-tetrafluorodisilane, thus enabling the first direct synthesis of arylhalosilanes from arenes in high yields. Further investigations to survey the scope and limitation of this C–H silylation, including that of monosubstituted arenes, heteroarenes, alkenes, and alkanes, as well as the application of this catalyst system to other types of C–H functionalization are in progress.

Experimental Section

A representative procedure for **3**: A resealable Schlenk tube containing $[\{\mathrm{Ir(OMe)(cod)}\}_2]$[10] (0.015 mmol) and dtbpy (0.03 mmol) was flushed with nitrogen, then charged with *o*-xylene (60 mmol) and $(t\mathrm{BuF_2Si})_2$[11] **1** (1.0 mmol). The tube was sealed with a Teflon screwcap, and the mixture was stirred at 120 °C for 16 h. The product was isolated by Kugelrohr distillation to give an analytically pure sample: ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$, 25 °C, TMS): $\delta = 1.07$ (t, $J = 1.0$ Hz, 9H), 2.29 (s, 3H), 2.30 (s, 3H), 7.21 (d, $J = 7.3$ Hz, 1H), 7.40 (d, $J = 9.8$ Hz, 1H), 7.42 ppm (s, 1H); ^{13}C NMR (100 MHz, $\mathrm{CDCl_3}$, 25 °C, TMS): $\delta = 17.87$ (t, $J = 15.3$ Hz), 19.67, 20.00, 24.83, 124.45 (t, $J = 16.5$ Hz), 129.55, 132.02, 135.41, 136.52, 140.68 ppm; HRMS calcd for $\mathrm{C_{12}H_{18}F_2Si}$: 228.1145; found: 228.1140.

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Keywords: arenes · C-H activation · homogeneous catalysis · iridium · silicon

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