DOI: 10.1002/anie.201105636

Scandium-Catalyzed Silylation of Aromatic C–H Bonds**

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Exploring the potential of untapped elements is an important strategy for the development of more efficient, selective catalysts for useful chemical transformations. The direct silylation of aromatic C–H bonds is an efficient, straightforward method for the preparation of silyl-substituted arenes[1–8]—a family of useful intermediates in modern organic synthesis and materials science.[9–11] The catalysts reported so far for this transformation have largely relied on late transition metals such as Ru,[1,3] Rh,[3,5] Ir,[2,6] Ni,[7] and Pt.[4,8] In contrast, rare-earth-metal catalysts for the C–H silylation of arenes have hardly been explored, despite many examples of stoichiometric C–H bond activation by rare-earth complexes.[12] A scandium metallocene complex was reported for the catalytic silylation of methane, but it could not be applied to the catalytic silylation of arenes.[13]

We report herein that half-sandwich scandium alkyls can serve as excellent catalyst precursors for the *ortho*-regioselective C–H silylation of alkoxy-substituted benzene derivatives. Some active intermediate species in the present catalyst system have been isolated and structurally characterized, thus offering important insight into the mechanistic aspects of the catalytic process. The regioselective, catalytic C–H silylation of alkoxyarenes has not been reported previously. It usually difficult to use an alkoxy moiety as a directing group in late-transition-metal-catalyzed C–H silylation reactions because the interaction between an ether group and a late-transition-metal center is too weak.

The *ortho*-metalation of anisole (**2a**) by the half-sandwich yttrium and lutetium alkyl complexes **1a** and **1b** (Figure 1) took place smoothly at room temperature in benzene.[12i,p,14]

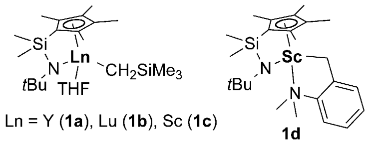
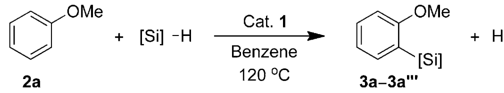


Figure 1. Half-sandwich rare-earth-metal alkyl complexes.

Table 1: *ortho*-C–H silylation of anisole with hydrosilanes under various conditions.[a]



Run	Catalyst	[Si]–H	Product	Yield [%][b]
1	**1a**	$PhSiH_3$	**3a**	(3)
2	**1b**	$PhSiH_3$	**3a**	(3)
3	**1c**	$PhSiH_3$	**3a**	(37)
4	**1d**	$PhSiH_3$	**3a**	(64)
5	**1d**	$PhSiH_3$	**3a**	(1)[c]
6	**1d**	$PhSiH_3$	**3a**	(23)[d]
7	**1d**	$PhSiH_3$	**3a**	(85)[e]
8	**1d**	$PhSiH_3$	**3a**	88 (92)[f]
9	**1d**	$PhSiH_3$	**3a**	89 (93)[f,g]
10	**1d**	$PhCH_2SiH_3$	**3a′**	75[f]
11	**1d**	$n\text{C}_8H_{17}SiH_3$	**3a″**	46[f]
12	**1d**	Ph_2SiH_2	**3a‴**	36[f]

[a] Reaction conditions: catalyst (0.02 mmol), anisole (**2a**) (3 mmol), hydrosilane (1 mmol), benzene (1 mL), 120 °C, 36 h. [b] Yield of isolated product based on hydrosilane. Yields measured by GC analysis are given in parentheses. [c] THF was used instead of benzene. [d] **2a** (1 mmol), $PhSiH_3$ (3 mmol). The yield was based on **2a**. [e] **1d** (0.04 mmol). [f] **1d** (0.04 mmol), **2a** (10 mmol), 6 h. [g] No solvent.

However, the catalytic silylation reaction did not occur either at room or at high temperatures (up to 120 °C) in the presence of excess anisole and $PhSiH_3$ (Table 1, runs 1 and 2). In contrast, the scandium analogue **1c** showed considerable catalytic activity to give the *ortho*-silylation product 2-phenylsilylanisole (**3a**) in 37 % yield (based on $PhSiH_3$) when a mixture of anisole and $PhSiH_3$ (3:1) was heated in the presence of 2 mol % **1c** at 120 °C for 36 h (Table 1, run 3). The aminobenzyl scandium complex **1d**, which is more thermally stable than its trimethylsilylmethyl analogue **1c**, afforded **3a** in 64 % yield under the same reaction conditions (Table 1, run 4).

Complex **1d** was then further examined under various conditions. The use of THF as a solvent severely hampered the reaction, probably owing to the coordination of the Lewis base THF molecule to the metal center (Table 1, run 5). The use of a lower amount of anisole to $PhSiH_3$ (1:3) resulted in a decrease of the product yield (23 %) (Table 1, run 6). An increase of the catalyst loading from 2 to 4 mol % led to an increase of the product yield from 64 % to 85 % (Table 1, runs 4 and 7). When the molar ratio of anisole to $PhSiH_3$ was raised to 10:1, the product yield reached 92 % in 6 h (Table 1, run 8). The C–H silylation reaction selectively proceeded even in the absence of a solvent (Table 1, run 9). Benzylsilane, *n*-octylsilane, and diphenylsilane could also be used as a silicon source for this reaction, albeit giving a lower yield under the same reaction conditions (Table 1, runs 10–12).

The silylation of various alkoxy-substituted benzene derivatives by phenylsilane was then examined by use of **1d** as a catalyst. Some representative results are summarized in Table 2. 4-Methylanisole (**2b**) could be silylated similarly to

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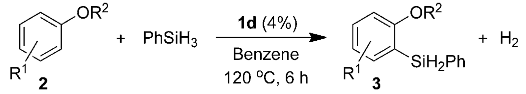
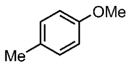
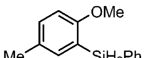
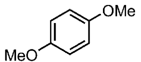
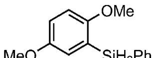
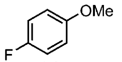
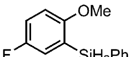
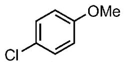
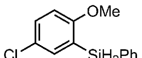
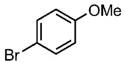
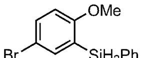
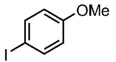
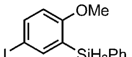
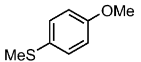
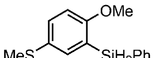
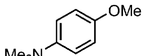
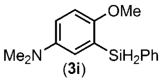
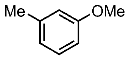
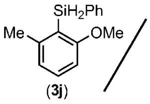
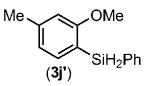
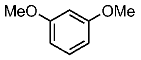
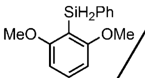
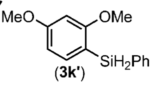
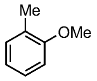
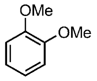
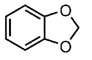
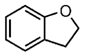
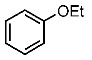
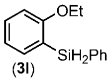
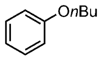
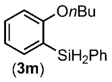
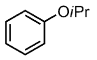
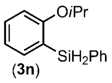
[**] This work was partly supported by a Grant-in-Aid for Scientific Research (S) from JSPS (No. 21225004).

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201105636.

Table 2: Scandium-catalyzed silylation of alkoxy-substituted benzene derivatives with phenylsilane.[a]



Run	Substrate	Product	Yield [%][b]
1[c]	 **(2b)**	 **(3b)**	89 (89)
2	 **(2c)**	 **(3c)**	90 (94)[d]
3	 **(2d)**	 **(3d)**	79 (84)
4[c]	 **(2e)**	 **(3e)**	88 (94)
5	 **(2f)**	 **(3f)**	68 (88)
6	 **(2g)**	 **(3g)**	51 (57)
7	 **(2h)**	 **(3h)**	76 (84)
8	 **(2i)**	 **(3i)**	67 (75)
9	 **(2j)**	 **(3j)**  **(3j')**	72 [1/6][e]
10	 **(2k)**	 **(3k)**  **(3k')**	83 [1.8/1][e]
11			n.r.[f]
12			n.r.[f]
13			n.r.[f]
14			trace
15	 **(2l)**	 **(3l)**	69 (72)
16	 **(2m)**	 **(3m)**	70 (72)
17	 **(2n)**	 **(3n)**	17

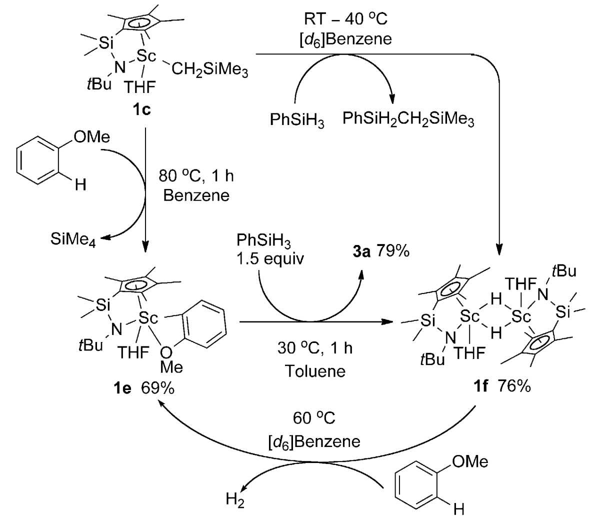
[a] Reaction conditions: **1d** (0.04 mmol), substrate **2** (10 mmol), $PhSiH_3$ (1 mmol), benzene (1 mL), 120 °C, 6 h, unless otherwise noted.
[b] Yields of isolated product based on $PhSiH_3$. Yields measured by GC analysis are given in parentheses. [c] No solvent was used. [d] 2,5-Bis(phenylsilyl)-1,4-dimethoxybenzene (**4**) was also formed in approximately 2% yield. [e] Product ratio given in brackets was determined by ^1H NMR spectroscopy. [f] No reaction was observed.

anisole (Table 2, run 1). In the case of 1,4-dimethoxybenzene (**2c**), the monosilylated product **3c** was obtained predominantly in 94% yield, although a small amount of the bis-silylated product **4** (ca. 2%) was also observed (Table 2, run 2). Aromatic carbon–halogen (F, Cl, Br, I) bonds could survive the reaction conditions to give the corresponding halogenated *ortho*-phenylsilylanisoles (Table 2, runs 3–6). In the case of 4-methylthioanisole (**2h**) and 4-dimethylamino-anisole (**2i**), the silylation took place selectively at the position *ortho* to the methoxy group, in agreement with the strong oxophilicity of a scandium ion (Table 2, runs 7 and 8). In the case of 3-methylanisole (**2j**), the silylation at the less sterically demanding position is significantly favored in a 6:1 ratio (**3j'**/**3j**) (Table 2, run 9), whereas in the case of 1,3-dimethoxybenzene, the silylation at the more crowded position is slightly favored in a 1.8:1 ratio (**3k**/**3k'**), probably because this position can be activated with two *ortho*-methoxy groups (Table 2, run 10). *ortho*-Substituted anisole derivatives, such as 2-methylanisole, 1,2-dimethoxybenzene, 1,2-methylenedioxybenzene, and 2,3-dihydrobenzofuran, are not applicable to the catalytic silylation under the same reaction conditions (Table 2, runs 11–14), possibly owing to the steric hindrance of the *ortho* substituents (see below).

In addition to a methoxy unit, the ethoxy and *n*-butoxy moieties can also be used as a directing group (Table 2, runs 15 and 16). However, the more sterically demanding *iso*-propoxy group is less effective apparently owing to steric hindrance (Table 2, run 17).

It is also noteworthy that the present catalytic C–H silylation reaction does not require a hydrogen acceptor, which is in contrast with most late-transition-metal catalysts, which usually required the addition of an equimolar amount of a hydrogen acceptor, such as an alkene, to achieve high conversion.[1–3]

To gain information on the mechanistic aspects of the catalytic *ortho* C–H silylation reaction, some stoichiometric reactions were carried out. At room temperature, no reaction between **1c** or **1d** with anisole was observed. However, rapid *ortho*-metalation of anisole was observed at high temperatures. The reaction of **1c** with 20 equivalents of anisole in benzene at 80 °C afforded the 2-anisyl complex **1e** in 69% yield within 1 h (Scheme 1). An X-ray diffraction study revealed that the anisyl unit in **1e** is bonded to the Sc atom in a chelating fashion through both the methoxy group and the *ortho* carbon atom (Figure 2, left). The CH_3 group of the methoxy unit is directed away from the metal center and towards the hydrogen atom H3 on the *ortho*-carbon atom C3 (H3···C7: 2.529(3) Å). The reaction of the anisyl complex **1e** with 1.5 equivalents of $PhSiH_3$ at 30 °C afforded rapidly the hydride complex **1f** in 76% yield with concomitant formation of the *ortho*-silylation product **3a** (Scheme 1). Alternatively, the hydride complex **1f** could also be obtained easily by the reaction of the alkyl complex **1c** with $PhSiH_3$.[15] An X-ray diffraction study established that **1f** adopts a dimeric structure through two bridging hydride ligands (Figure 2).[16] The reaction of the hydride complex **1f** with anisole took place at 60 °C to give **1e** with release of H_2. However, this reaction could not be completed probably owing to a possible reverse reaction (hydrogenation of **1e** to give **1f** and anisole).



Scheme 1. Isolation and reactions of some active Sc intermediates.

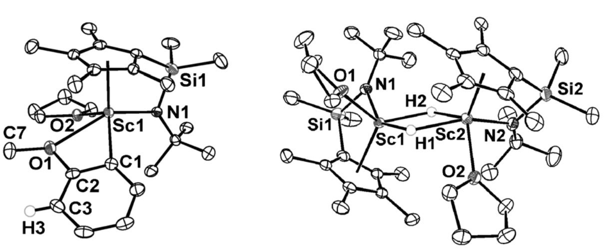
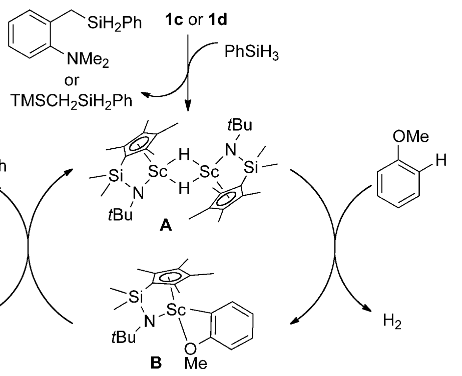


Figure 2. ORTEP drawings of **1e** (left) and **1f** (right) with 30% probability thermal ellipsoids. Hydrogen atoms except for H3 in **1e** and hydride ligands on Sc in **1f** have been omitted for clarity. Selected bond lengths [Å] and angles [°]; **1e**: Sc1–C1 2.271(3), Sc1–N1 2.064(2), Sc1–O1 2.575(2), Sc1–O2 2.225(2); C1-C2-O1 110.9(3). **1f**: Sc1–N1 2.096(3), Sc1–O1 2.247(2), Sc1–H1 1.99(3), Sc1–H2 1.95(4); H1-Sc1-H2 61.0(13).

Nevertheless, both the anisyl complex **1e** and the hydride complex **1f** exhibited almost equally high activity for the catalytic silylation of anisole with PhSiH$_3$ to give **3a** in 88% yield under the conditions described in Table 1, run 8, suggesting that **1e** and **1f** are true active catalyst species.

The C–H activation reaction of 2,3-dihydrobenzofuran with **1c** was much slower than that of anisole under the same conditions, as monitored by ^{1}H NMR spectroscopy, probably owing to the rigidity of its cyclic ether structure, which could make it more difficult to form a chelating aryl species analogous to **1e**. The silylation of the resulting metalated species by PhSiH$_3$ was possible, but the catalytic silylation of 2,3-dihydrobenzofuran was not observed in the presence of excess amounts of PhSiH$_3$ and 2,3-dihydrobenzofuran. The metalation reaction of 2-methylanisole with **1c** did not occur under the same conditions, probably because of the steric repulsion between the *ortho*-CH$_3$ group and the CH$_3$ group of the methoxy unit in the metalation species analogous to **1e** (see Figure 2). These results demonstrate again the importance of the coordination of an alkoxy group to the catalyst metal center in the present catalytic silylation reactions.

The ^{1}H NMR spectroscopic monitoring of the reaction of anisole with PhSiH$_3$ by use of **1c** as a catalyst precursor showed the formation (presence) of the hydride species **1f** (in addition to the silylation product **3a**) in the reaction mixture, suggesting that **1f** might be a catalyst resting state in the present catalytic reaction. The catalytic silylation of 2-deuterio-4-methylanisole with PhSiH$_3$ showed no kinetic isotope effect ($k_H/k_D = 1.0$). This result suggests that C–H activation is not the rate-determining step in the present catalytic reaction. The kinetic study of the reaction of **1c** with anisole gave the activation parameters $\Delta H^{\neq} = 76.3\ \mathrm{kJ\,mol^{-1}}$ and $\Delta S^{\neq} = -80.2\ \mathrm{J\,K^{-1}\,mol^{-1}}$. The large negative $\Delta S^{\neq}$ value suggests that the rate-determining step should be the coordination of anisole to the metal center of the catalyst species. These results are in agreement with the observation that an excess amount of anisole is needed to achieve high yield of the silylation product.



Scheme 2. A possible mechanism for the catalytic silylation reaction.

On the basis of the above experimental results, a possible mechanism for the catalytic silylation reaction is shown in Scheme 2. The reaction of **1c** or **1d** with phenylsilane would easily give the hydride complex **A**.[17] The *ortho* C–H bond activation of an anisole compound through assistance of the interaction between the methoxy group and the Sc atom in **A** could afford the 2-anisyl complex **B** with release of H$_2$. The σ-bond metathesis reaction between **B** and phenylsilane would yield the silylation product and regenerate **A**. The coordination of anisole to the metal center of the hydride species such **A** could be the rate-determining step of this catalytic process. The isolation and structural characterization of the anisyl complex **1e** and the hydride complex **1f**, together with the kinetic studies, strongly support this mechanism.

In summary, we have demonstrated that the half-sandwich scandium alkyl complexes, such as **1d**, can serve as a unique catalyst for the *ortho*-selective C–H silylation of various alkoxy-substituted benzene derivatives without the requirement for a hydrogen acceptor to achieve high conversion. Aromatic C–X bonds (X = Cl, Br, I, SMe, NMe$_2$) can survive the reaction conditions. The successful isolation and structural characterization of the anisyl complex **1e** and the hydride complex **1f** have offered important insight into the mechanistic aspects of the catalytic process. Studies on other functionalization reactions of aromatic C–H bonds by rare-earth-based catalysts are in progress.

Received: August 9, 2011

Keywords: anisoles · C–H activation · hydrosilanes · scandium · silylation

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