Available online at www.sciencedirect.com

ScienceDirect

ELSEVIER

Tetrahedron

Tetrahedron 63 (2007) 4087–4094

Synthesis of aryltriethoxysilanes via rhodium(I)-catalyzed cross-coupling of aryl electrophiles with triethoxysilane

Miki Murata,* Hiyoruki Yamasaki, Tsukasa Ueta, Masayuki Nagata, Masanori Ishikura, Shinji Watanabe and Yuzuru Masuda

Department of Materials Science, Kitami Institute of Technology, 165 Koencho, Kitami 090-8507, Japan

Received 19 January 2007; revised 22 February 2007; accepted 23 February 2007
Available online 25 February 2007

Abstract—The general and efficient silylation of aryl halides has been developed utilizing triethoxysilane and a rhodium catalyst. The substrate scope is broad and includes *ortho*-, *meta*-, and *para*-substituted electron-rich and -deficient aryl iodides. In addition, the silylation of aryl bromides and fluoroalkanesulfonates proceeded in the presence of tetra-*n*-butylammonium iodide.

---

1. Introduction

Arylsiloxanes and their hypervalent derivatives are versatile reagents for carbon–carbon[1–6] and carbon–heteroatom bond formation,[7] and provide an alternative to the reaction of organotin or -boron compounds. Much attention has been focused on the use of aryltrialkoxysilanes in palladium-catalyzed aryl–aryl coupling with aryl halides[1,2] and palladium-[3] or rhodium-catalyzed conjugate addition to α,β-unsaturated carbonyl compounds.[4,5] The 1,2-addition to aldehydes[5] and the Heck-type reaction[6] are also important methods for carbon–carbon bond formation. Therefore, the supply of various functionalized aryltrialkoxysilanes has become more and more necessary for modern organic synthesis. The most common method for the synthesis of aryltriethoxysilanes is based on the reaction of tetraalkyl orthosilicate with aryl Grignard or lithium reagent (Fig. 1, Route A).[8] However, the protocol has lacked the wide applicability to polyfunctionalized substrates and is difficult to suppress competing formation of di- and triarylsilanes.

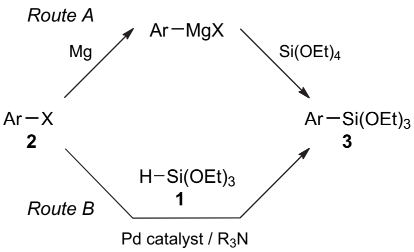


Figure 1. Synthesis of aryltriethoxysilanes.

The palladium(0)-catalyzed cross-coupling reaction of metalloid hydride with organic halides has emerged as a powerful and atom-economical method for the synthesis of organometalloids. The metalations of organic halides using various metalloid hydrides, including silicon,[9–11] germanium,[12] tin,[13] and boron compounds,[14] have been extensively studied. In 1997, we demonstrated the first examples of the silylation of aryl halides **2** with triethoxysilane **1** to provide aryltriethoxysilanes **3** (Route B).[9a] Although the reaction conditions were mild to permit the synthesis of functionalized arylsiloxanes **3**, the electronic and steric characteristics of substrates had a significant impact on the reactions; i.e., the starting halides were restricted to aryl iodides having electron-donating groups at *para*-position. Thereafter, the palladium(0)-catalyzed silylation using **1** has been extended to aryl bromides and chlorides by other groups,[9b,c] but there was no example of the efficient silylation of *ortho*-substituted or electron-deficient aryl halides, that is to say, the above problems were invincible. Further, in the palladium(0)-catalyzed silylation of other hydrosilanes, similar limitation was pointed out.[10]

As a consequence of our reinvestigation of the silylation of aryl halides **2** using triethoxysilane **1**, we found that a rhodium(I) complex was one of the efficient catalysts.[15,16] Herein, we present a full report of the rhodium(I)-catalyzed silylation of aryl halides that enables the synthesis of *ortho*-, *meta*-, and *para*-substituted electron-rich and -poor arylsiloxanes **3**, and successful application of facile aryl fluoroalkanesulfonates to this reaction. Our present method overcomes a number of limitations of the

---

Keywords: Arylsilanes; Hydrosilane; Silylation; Rhodium catalyst.

* Corresponding author. Tel.: +81 157 26 9438; fax: +81 157 26 4973; e-mail: muratamk@mail.kitami-it.ac.jp

doi:10.1016/j.tet.2007.02.103

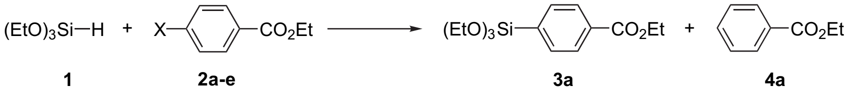
palladium(0)-catalyzed silylation and is the most general system that is available to date.

2. Results and discussion

In our initial screening experiments, triethoxysilane **1** and ethyl 4-iodobenzoate **2a** were used as substrates for discovery of suitable reaction conditions. The results of screening of catalyst systems are summarized in Table 1. Treatment of **2a** (1.0 equiv) with **1** (2 equiv) and triethylamine (3 equiv) in the presence of a rhodium(I) catalyst (3 mol % of rhodium metal) in DMF at 80 °C was found to lead to the desired ethyl 4-(triethoxysilyl)benzoate **3a**. The formation of ethyl benzoate **4a** by reduction of the starting **2a** was the major side reaction. As we reported previously, the palladium-catalyzed reaction of such electron-deficient aryl iodide gave only 23% yield of the silylated product **3a** due to a strong tendency to produce **4a**. $[RhCl(cod)]_2$ was found to exhibit catalytic activity, although the yield was moderate (entry 1). Compared with the chloride complex, cationic $[Rh(cod)(MeCN)_2]BF_4$ and acetylacetonato rhodium complexes, Rh(acac)(cod) and $Rh(acac)(CO)_2$, showed much higher catalytic activity affording the product **3a** in ca. 90% yield (entries 2–4). While these phosphine-free rhodium complexes proved to be effective catalysts for the silylation of **2a**, phosphine-containing $RhCl(PPh_3)_3$ did not show good catalytic activity (entry 5). Other conditions in the silylation of **2a** were then examined using $[RhCl(cod)]_2$ as a catalyst. For the present reaction of **2a**, tertiary amines were found to be effective as bases analogous to the previous palladium-catalyzed silylation (entry 6); however, K_2CO_3 decreased the yield and selectivity (entry 8), and pyridine and KOAc completely inhibited the silylation (entries 7 and 9). Several solvents were tested, and DMF proved to be the most effective solvent, while the use of other solvents resulted in slower conversion to product **3a** (entries 10–13). Under similar reaction condition to that used for the above silylation of **2a**, replacing the leaving group of aryl halides with the corresponding bromide **2b** gave lower yields of the desired arylsilane **3a** accompanied by a considerable amount of ethyl benzoate **4a** (entry 14). We then examined a treatment with an additional equal amount of tetra-*n*-butylammonium iodide (TBAI), and the silylation proceeded selectively (entry 15).[10d] Unfortunately, aryl chloride did not have enough reactivity; i.e., the reaction of **2c** resulted in only 19% conversion and 9% GC yield of product (entry 16). From the synthetic point of view, the use of aryl fluoroalkanesulfonates, such as aryl triflates ($X{=}OSO_2CF_3$, OTf) and nonaflates ($X{=}OSO_2(CF_2)_3CF_3$, ONf), as aryl electrophiles **2** have some advantages, in part due to the easy access from phenols.[17,18] Although we have failed in all attempts at the silylation of aryl fluoroalkanesulfonates using the previous palladium catalyst system, the rhodium(I)-catalyzed silylation of aryl triflate **2d** and nonaflate **2e** could be carried out in good yield when an additional iodide ion and a reaction temperature of 100 °C were required (entries 17 and 20). While Rh(acac)(cod) was found to be effective catalyst for the reactions of **2d**, $[Rh(cod)(MeCN)_2]BF_4$ was ineffective (entry 19).[19]

The results obtained with representative aryl halides and triflates **2** are listed in Table 2. The presence of functional groups, such as CO_2Et (entry 1), COMe (entries 2–4), and CN (entry 18), in the starting **2** did not interfere with the

Table 1. Reaction of aryl electrophiles **2a–e** with triethoxysilane **1** under various conditions[a]



Entry	**2**, X=	Catalyst	Base	Solvent	Yield[b] (%) **3a**	Yield[b] (%) **4a**
1	**2a**, X=I	$[RhCl(cod)]_2$	Et_3N	DMF	76	16
2		$[Rh(cod)(MeCN)_2]BF_4$	Et_3N	DMF	88	12
3		Rh(acac)(cod)	Et_3N	DMF	92	4
4		$Rh(acac)(CO)_2$	Et_3N	DMF	90	3
5		$RhCl(PPh_3)_3$	Et_3N	DMF	15	35
6		$[RhCl(cod)]_2$	$i\text{-}Pr_2NEt$	DMF	75	15
7		$[RhCl(cod)]_2$	Pyridine	DMF	0	6
8		$[RhCl(cod)]_2$	K_2CO_3	DMF	22	19
9		$[RhCl(cod)]_2$	KOAc	DMF	0	57
10		$[RhCl(cod)]_2$	Et_3N	NMP	30	46
11		$[RhCl(cod)]_2$	Et_3N	MeCN	28	17
12		$[RhCl(cod)]_2$	Et_3N	Dioxane	0	20
13		$[RhCl(cod)]_2$	Et_3N	Toluene	0	15
14	**2b**, X=Br	$[Rh(cod)(MeCN)_2]BF_4$	Et_3N	DMF	40	49
15[c]		$[Rh(cod)(MeCN)_2]BF_4$	Et_3N	DMF	90	6
16[c,d]	**2c**, X=Cl	$[Rh(cod)(MeCN)_2]BF_4$	Et_3N	DMF	9	10
17[c,d]	**2d**, X=OTf	Rh(acac)(cod)	Et_3N	DMF	92	3
18[d]		Rh(acac)(cod)	Et_3N	DMF	6	12
19[c,d]		$[Rh(cod)(MeCN)_2]BF_4$	Et_3N	DMF	0	6
20[c,d]	**2e**, X=ONf	Rh(acac)(cod)	Et_3N	DMF	90	4

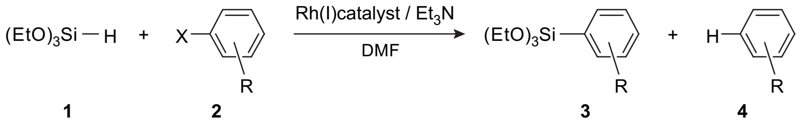
[a] Reactions of **2** (0.25 mmol) with **1** (0.50 mmol) were carried out at 80 °C for 1 h in 1 mL of solvent by using a catalyst (3 mol % of rhodium metal) and a base (0.75 mmol).

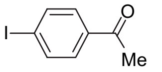
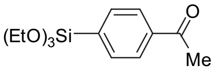
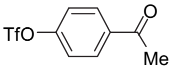
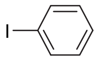
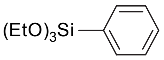
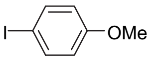
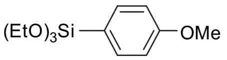
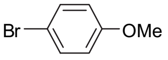
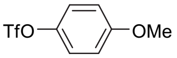
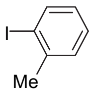
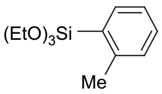
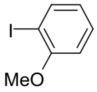
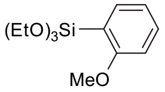
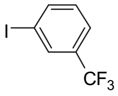
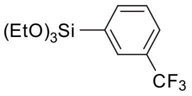
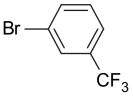
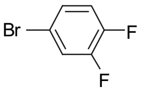
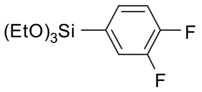
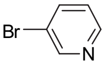
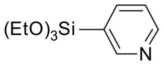
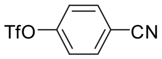
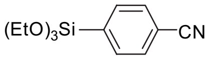
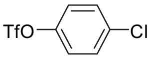
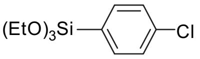
[b] GLC yields are based on **2**.

[c] The reaction was performed in the presence of $n\text{-}Bu_4NI$ (0.25 mmol).

[d] At 100 °C for 16 h.

Table 2. Silylation of various aryl electrophiles **2** with triethoxysilane **1**[a]



Entry	Aryl electrophiles **2**	Product **3**	Catalyst[b]	Condition	Yield[c] (%)
1	**2b**	**3a**	A	80 °C, 1 h[d]	78
2	 **2f**	 **3f**	A	80 °C, 2 h	75
3	**2f**	**3f**	B	80 °C, 2 h	84
4	 **2g**	**3f**	B	100 °C, 16 h[d]	76
5	 **2h**	 **3h**	A	80 °C, 2 h	86
6	 **2i**	 **3i**	A	80 °C, 2 h	90
7	 **2j**	**3i**	B	100 °C, 16 h[d]	(9)
8	 **2k**	**3i**	B	100 °C, 16 h[d]	(3)
9	 **2l**	 **3l**	A	80 °C, 2 h	81
10	 **2m**	 **3m**	A	80 °C, 2 h	87
11	 **2n**	 **3n**	A	80 °C, 2 h	72
12	**2n**	**3n**	B	80 °C, 2 h	92
13	 **2o**	**3n**	A	80 °C, 2 h[d]	70
14	**2o**	**3n**	B	80 °C, 2 h[d]	89
15	 **2p**	 **3p**	A	80 °C, 16 h[d]	76
16	**2p**	**3p**	B	80 °C, 16 h[d]	85
17	 **2q**	 **3q**	A	80 °C, 2 h[d]	80
18	 **2r**	 **3r**	B	100 °C, 16 h[d]	88
19	 **2s**	 **3s**	B	100 °C, 16 h[d]	71

[a] All reactions of **2** with **1** (2 equiv) were carried out in DMF by using 3 mol % of the rhodium complex and Et_3N (3 equiv).

[b] A: $[Rh(cod)(MeCN)_2]BF_4$. B: Rh(acac)(cod).

[c] Isolated yields are based on **2**. Those in parentheses are GLC yields.

[d] The reaction was performed in the presence of *n*-Bu_4NI (1 equiv).

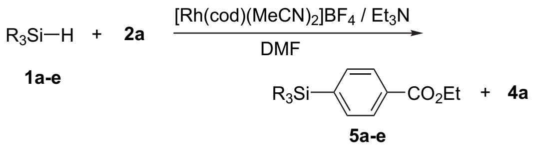
outcome of the present reaction. The previous methods via Grignard reagents or organolithiums should require the protection of functional groups frequently.[8] Furthermore, in contrast to the previous palladium-catalyzed silylation,[9,10] both the yield and the selectivity in the reaction of aryl iodides **2** (X=I) were almost independent of the electronic and steric requirement. In fact, the differences in the yields and on the selectivity among aryl iodides having electron-donating (entry 6) or -withdrawing groups (entry 2, 3, 11, and 12) were not particularly large. Additionally, sterically hindered **2l** and **2m** (entries 9 and 10) were also coupled with **1** without any difficulty. On the other hand, the silylation of heteroaryl bromides **2q** (entry 17) and electron-deficient **2b**, **2o**, and **2p** (entries 1 and 13–16) proceeded smoothly in the presence of TBAI; however, the coupling of electron-rich 4-bromoanisole **2j** was problematic and starting aryl bromide was recovered (entry 7). Similarly, in the case of aryl triflate **2** (X=OTf), the silylation of electron-deficient substrates could be accomplished (entries 4, 18, and 19); however, the presence of the electron-donating substituent remarkably decreased the yield of **3** (entry 8). Compared with the cationic $[Rh(cod)(MeCN)_2]BF_4$, Rh(acac)(cod) showed much higher catalytic activity (entries 3, 12, 14, and 16). As a whole, the desired products **3** were contaminated with small amounts of the reduced by-products **4** in any case, but their isolation was very easy; i.e., the desired **3** and reduced arenes **4** were purely separated by bulb-to-bulb distillation. Accordingly, the present reaction provides a simple and widely available procedure for synthesizing aryltriethoxysilanes **3**.

To verify the feasibility of the reaction on a common laboratory scale, the silylation of **2a** was repeated on a 10 mmol scale (see Section 4). In this case, the amounts of triethoxysilane **1**, the catalyst, and the solvent were lowered. Reducing the amount of the reagents would be desirable to limit the amount of waste generation from this procedure, especially if the silylation was performed on a preparative scale. Actually, the present system was applied to the larger scale synthesis of **3a** without any difficulty.

Finally, we examined the effect of other hydrosilanes under our optimized conditions. These results are summarized in Table 3. The use of **1a–c** induced lowering of the selectivity and prevented the formation of the desired arylsilanes **5a–c** (entries 1–5). Additionally, no coupling occurred with halosilanes **1d–e** and the starting aryl iodide **2a** was recovered (entries 6 and 7). The present study demonstrates that triethoxysilane **1** selectively acted as a silicon source for the coupling of aryl electrophiles **2**.

A plausible reaction pathway is shown in Figure 2, although there is no clear experimental evidence. Initially, triethoxysilane **1** would add to the rhodium(I) catalyst to give a silyl hydrido species **6**,[20] followed by reductive elimination of hydrogen halide HX, giving a silyl rhodium(I) complex **7**. As the deprotonation of silyl hydrido complexes in the presence of a base has been known,[21] the reductive elimination of HX may occur with the aid of triethylamine. Then, oxidative addition of the aryl halide **2** would furnish an arylrhodium(III) intermediate **8**, and subsequent reductive elimination would lead to the product **3** along with regeneration of the catalyst. Bearing in mind the quite recently described result, however, it seems also possible that aryl halide **2** added oxidatively to the silyl hydrido species **6**.[11b] At present, the mechanism involving the Rh(V) intermediate cannot necessarily be ruled out.

Table 3. Effect of other hydrosilanes [a]



Entry	Hydrosilane	Catalyst[b]	Yield[c] (%)	
			5	4a
1	$(MeO)_2MeSi–H$ (**1a**)	A	40	19
2		B	18	59
3	$Et_3Si–H$ (**1b**)	A	53	47
4		B	5	39
5	$(Me_2N)_3Si–H$ (**1c**)	A	16	20
6	$Cl_3Si–H$ (**1d**)	A	0	Trace
7	$Cl_2MeSi–H$ (**1e**)	A	0	Trace

[a] Reactions of **2a** (0.25 mmol) with hydrosilane (0.50 mmol) were carried out at 80 °C for 4 h in 1 mL of DMF by using 3 mol % of the rhodium complex and Et_3N (0.75 mmol).

[b] A: $[Rh(cod)(MeCN)_2]BF_4$. B: Rh(acac)(cod).

[c] GLC yields are based on **2a**.

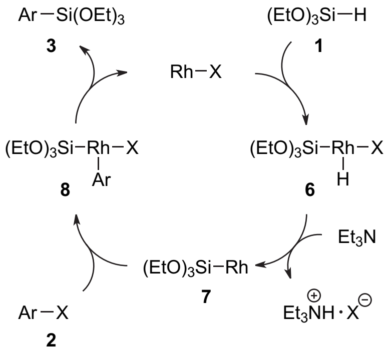


Figure 2. Plausible catalytic cycle for silylation of **2** with **1**.

Hydrogenolysis of **2**, affording a reduced by-product **4**, would occur in the case that reductive elimination of halosilane $(EtO)_3SiX$ from **6** or **8** proceeded. The effect of iodide ion on the reaction of aryl bromide and triflate can be understood in terms of the ligand exchange between iodide ion and X of the rhodium(III) halide **6** or **8**. Recently, Osakada and co-workers have reported that $RhI(H)[Si(OEt)_3](PPh_3)_2$ did not undergo coupling of their iodo and silyl ligands, whereas the formation of $(EtO)_3SiCl$ from analogous $RhCl(H)[Si(OEt)_3](PPh_3)_2$ took place rapidly.[20b] In addition, bearing in mind the previously described result, in which iodosilane added oxidatively to a transition metal even in the presence of triethylamine,[22] silyl(hydrido)rhodium(III) iodide (**6**, X=I) may be more favorable for preventing reductive elimination of halosilane $(EtO)_3SiX$.

3. Conclusion

We have developed a general method for the silylation of aryl halides using triethoxysilane as a silylating reagent. The cross-coupling of aryl iodides with triethoxysilane in the presence of triethylamine and a catalytic amount of [Rh(cod)(MeCN)$_2$]BF$_4$ or Rh(acac)(cod) provides the corresponding aryltriethoxysilanes in high yield. The substrate scope is significantly broader than previous palladium-catalyzed silylation, and includes electron-deficient and *ortho*-substituted aryl iodides. In the case of aryl bromides, the efficient silylation proceeded by a treatment with an additional equal amount of tetra-*n*-butylammonium iodide. Additionally, in the presence of Rh(acac)(cod) catalyst and iodide anion, the silylation of aryl fluoroalkanesulfonates was achieved.

4. Experimental

4.1. General information

All the experiments were carried out under an argon atmosphere using oven-dried (120 °C) glassware. IR spectra were taken with a Perkin–Elmer System 2000 FTIR spectrometer. NMR spectra were recorded on a JNM-A500 spectrometer (^{1}H, 500 MHz; ^{13}C, 125 MHz). Chemical shifts of ^{1}H NMR and ^{13}C NMR signals reported δ parts per million referenced to CHCl$_3$ (7.26 and 77.0) or an internal SiMe$_4$. Mass spectra were obtained at an ionization potential of 70 eV with a JEOL JMS-SX102 spectrometer. GLC analyses were carried out with a Shimadzu GC-14B equipped with a glass column (OV-17 on Chromosorb W, 2 m). GLC yields were determined using suitable hydrocarbons as internal standards.

4.2. Materials

N,*N*-Dimethylformamide (DMF) was distilled from CaH$_2$ before use. Hydrosilanes, aryl halides, triethylamine, and tetra-*n*-butylammonium iodide (TBAI) were purchased from commercial sources, and used without purification. Aryl triflates were obtained from the corresponding phenols and trifluoromethanesulfonic anhydride.[17] All rhodium complexes were commercial products except for [Rh(cod)-(MeCN)$_2$]BF$_4$, which was prepared by the known method.[23]

4.3. Synthesis of aryltriethoxysilane: typical procedure

[Rh(cod)(MeCN)$_2$]BF$_4$ (0.03 mmol), aryl electrophile **2** (1.0 mmol) (if a solid), and TBAI (1 mmol) (when aryl bromide or triflate was used as **2**) were placed in a test tube capped with a septum rubber. The tube was evacuated and backfilled with argon, and then charged with DMF (4 mL). Triethylamine (3 mmol), **2** (1.0 mmol) (if a liquid), and triethoxysilane **1** (2 mmol) were added by a syringe through the septum rubber. The reaction mixture was then stirred at 80–100 °C. After the reaction, the mixture was diluted with ether, washed three times with H$_2$O to remove DMF, and dried over Na$_2$SO$_4$. The solvent was removed under reduced pressure, and the residue was purified by Kugelrohr distillation to give the desired aryltriethoxysilane **3**.

4.3.1. Ethyl 4-(triethoxysilyl)benzoate (3a).[9a] The typical procedure was followed using **2b** (229.1 mg, 1.00 mmol) and TBAI (1.0 mmol). The product was purified by distillation to afford 243.1 mg (78% yield) as a colorless oil. IR (neat): 2977, 2928, 2361, 1720, 1558, 1445, 1391, 1367, 1279, 1101 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ=1.24 (t, *J*=7.0 Hz, 9H), 1.47 (t, *J*=7.0 Hz, 3H), 3.88 (q, *J*=7.0 Hz, 6H), 4.39 (q, *J*=7.0 Hz, 2H), 7.74 (d, *J*=8.2 Hz, 2H), 8.04 (d, *J*=8.2 Hz, 2H). ^{13}C NMR (CDCl$_3$): δ=10.29, 14.16, 54.84, 56.96, 124.55, 128.05, 130.70, 132.94, 162.63. EIMS: *m*/*z* (%)=312 (5, [M^{+}]), 267 (100), 253 (15), 239 (61), 223 (16), 195 (22), 183 (17), 163 (25), 147 (20). HRMS (EI): *m*/*z* calcd for $C_{15}H_{24}O_5Si$ [M^{+}]: 312.1393; found: 312.1392.

4.3.2. 4-(Triethoxysilyl)acetophenone (3f).[9b] Following the typical procedure, **3f** was prepared starting from **2f** (60.7 mg, 0.247 mmol) as a colorless oil. The product was purified by distillation to afford 52.5 mg (75% yield). The reaction of **2f** (124.3 mg, 0.505 mmol) using Rh(acac)(cod) catalyst instead of [Rh(cod)(MeCN)$_2$]BF$_4$ gave 120.4 mg (84% yield) of the title compound. Also, the silylation of **2g** (270.0 mg, 1.01 mmol) was carried out at 100 °C using Rh(acac)(cod) (0.03 mmol) and TBAI (1.0 mmol) to afford 214.8 mg (76% yield) of **3f**. IR (neat): 2977, 2928, 2890, 1689, 1390, 1359, 1265, 1078 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ=1.25 (t, *J*=7.0 Hz, 9H), 2.62 (s, 3H), 3.88 (q, *J*=7.0 Hz, 6H), 7.78 (d, *J*=8.3 Hz, 1H), 7.94 (d, *J*=8.3 Hz, 1H). ^{13}C NMR (CDCl$_3$): δ=18.19, 26.69, 58.88, 127.28, 135.02, 137.29, 138.31, 198.41. EIMS: *m*/*z* (%)=282 (9, [M^{+}]), 267 (100), 238 (69), 223 (18), 209 (14). HRMS (EI): *m*/*z* calcd for $C_{14}H_{22}O_4Si$ [M^{+}]: 282.1287; found: 282.1284.

4.3.3. Phenyltriethoxysilane (3h).[8b] Following the typical procedure, **3h** was prepared starting from **2h** (203.8 mg, 1.00 mmol). The product was purified by distillation to afford 206.8 mg (86% yield) as a colorless oil. IR (neat): 2976, 2928, 2886, 1594, 1483, 1431, 1391, 1295, 1168, 1129, 1103, 1080 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ=1.25 (t, *J*=7.0 Hz, 9H), 3.88 (q, *J*=7.0 Hz, 6H), 7.3–7.5 (m, 3H), 7.6–7.8 (m, 2H). ^{13}C NMR (CDCl$_3$): δ=18.12, 58.68, 127.78, 130.22, 131.08, 134.74. EIMS: *m*/*z* (%)=240 (16, [M^{+}]), 195 (38), 181 (13), 162 (28), 147 (100), 139 (33), 135 (33). HRMS (EI): *m*/*z* calcd for $C_{12}H_{20}O_3Si$ [M^{+}]: 240.1182; found: 240.1141.

4.3.4. 4-(Triethoxysilyl)anisole (3i).[8b] Following the typical procedure, **3i** was prepared starting from **2i** (57.7 mg, 0.247 mmol). The product was purified by distillation to afford 59.9 mg (90% yield) as a colorless oil. IR (neat): 2975, 2360, 1598, 1567, 1506, 1459, 1390, 1282, 1250 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ=1.24 (t, *J*=7.0 Hz, 9H), 3.82 (s, 3H), 3.85 (q, *J*=7.0 Hz, 6H), 6.92 (d, *J*=8.5 Hz, 2H), 7.61 (d, *J*=8.5 Hz, 2H). ^{13}C NMR (CDCl$_3$): δ=18.12, 54.89, 58.55, 113.57, 122.00, 136.37, 161.37. EIMS: *m*/*z* (%)=270 (52, [M^{+}]), 255 (53), 225 (38), 211 (25), 181 (28), 169 (27), 149 (22), 147 (100), 135 (32). HRMS (EI): *m*/*z* calcd for $C_{13}H_{22}O_4Si$ [M^{+}]: 270.1287; found: 270.1261.

4.3.5. 2-Tolyltriethoxysilane (3l).[8b] Following the typical procedure, **3l** was prepared starting from **2l** (54.1 mg, 0.248 mmol). The product was purified by distillation to afford 51.1 mg (81% yield) as a colorless oil. IR (neat): 2975, 2928, 2886, 1594, 1442, 1391, 1285, 1167, 1138, 1103, 1079 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ=1.25 (t, *J*=7.0 Hz, 9H), 2.51 (s, 3H), 3.86 (q, *J*=7.0 Hz, 6H), 7.1–7.2 (m, 2H), 7.32 (t, *J*=7.3 Hz, 1H), 7.72 (d, *J*=7.3 Hz, 1H). ^{13}C NMR (CDCl$_3$): δ=18.17, 22.39, 58.48, 124.64, 129.69, 129.82, 130.46, 136.46, 144.51. EIMS: *m*/*z* (%)=254 (68, [M^{+}]), 209 (65), 195 (25), 181 (22), 162 (74), 147 (100), 135 (50), 119 (67). HRMS (EI): *m/z* calcd for $C_{13}H_{22}O_3Si$ [M$^+$]: 254.1338; found: 254.1323.

4.3.6. 2-(Triethoxysilyl)anisole (3m).[8b] Following the typical procedure, **3m** was prepared starting from **2m** (231.0 mg, 0.987 mmol). The product was purified by distillation to afford 231.6 mg (87% yield) as a colorless oil. IR (neat): 2975, 2928, 2891, 1592, 1573, 1476, 1429, 1391, 1244, 1168, 1104, 1081 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ=1.23 (t, J=7.0 Hz, 9H), 3.83 (s, 3H), 3.88 (q, J=7.0 Hz, 6H), 6.85 (d, J=8.2 Hz, 1H), 6.96 (dd, J=7.0, 7.0 Hz, 1H), 7.40 (dd, J=8.2, 7.0 Hz, 1H), 7.65 (d, J=7.0 Hz, 1H). ^{13}C NMR (CDCl$_3$): δ=18.20, 55.09, 58.65, 109.62, 119.30, 120.48, 132.14, 137.54, 164.37. EIMS: *m/z* (%)=270 (42, [M$^+$]), 255 (33), 181 (42), 151 (33), 147 (100), 139 (40). HRMS (EI): *m/z* calcd for $C_{13}H_{22}O_4Si$ [M$^+$]: 270.1287; found: 270.1274.

4.3.7. 3-(Triethoxysilyl)benzotrifluoride (3n). Following the typical procedure, **3n** was prepared starting from **2n** (137.4 mg, 0.505 mmol). The product was purified by distillation to afford 111.6 mg (72% yield) as a colorless oil. The reaction of **2n** (136.7 mg, 0.503 mmol) using Rh(acac)(cod) catalyst instead of [Rh(cod)(MeCN)$_2$]BF$_4$ gave 143.4 mg (92% yield) of the title compound. Also, the silylation of **2o** (227.1 mg, 1.01 mmol) was carried out at 80 °C using TBAI (1.0 mmol) to afford 218.8 mg (70% yield) of **3n**, and the reaction of **2o** (113.7 mg, 0.505 mmol) using Rh(acac)(cod) catalyst gave 139.5 mg (89% yield) of **3n**. IR (neat): 2978, 2930, 2892, 1607, 1511, 1393, 1329, 1275, 1169, 1131, 1078 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ=1.26 (t, J=7.0 Hz, 9H), 3.89 (q, J=7.0 Hz, 6H), 7.50 (t, J=7.6 Hz, 1H), 7.68 (d, J=7.6 Hz, 1H), 7.85 (d, J=7.6 Hz, 1H), 7.92 (s, 1H). ^{13}C NMR (CDCl$_3$): δ=17.86, 58.71, 124.17 (q, J=272.4 Hz), 126.71 (q, J=4.1 Hz), 127.97, 129.94 (q, J=32.1 Hz), 131.08 (q, J=2.1 Hz), 132.68, 137.89. EIMS: *m/z* (%)=308 (2, [M$^+$]), 293 (15), 263 (100), 249 (38), 235 (15), 219 (26), 207 (49), 191 (24), 181 (56), 163 (18), 154 (24), 147 (26). HRMS (EI): *m/z* calcd for $C_{13}H_{19}F_3O_3Si$ [M$^+$]: 308.1056; found: 308.1083.

4.3.8. 3,4-Difluorophenyltriethoxysilane (3p). The typical procedure was followed using **2p** (47.5 mg, 0.246 mmol) and TBAI (0.25 mmol). The product was purified by distillation to afford 51.4 mg (76% yield) as a colorless oil. Also, the reaction of **2p** (97.1 mg, 0.503 mmol) using Rh(acac)(cod) catalyst instead of [Rh(cod)(MeCN)$_2$]BF$_4$ gave 117.7 mg (85% yield) of the title compound. IR (neat): 2978, 2929, 2891, 1607, 1511, 1392, 1275, 1168, 1089 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ=1.25 (t, J=7.0 Hz, 9H), 3.86 (q, J=7.0 Hz, 6H), 7.18 (dt, J=10.3, 7.9 Hz, 1H), 7.39 (br s, 1H), 7.46 (t, J=10.3 Hz, 1H). ^{13}C NMR (CDCl$_3$): δ=18.29, 59.05, 117.42 (d, J=15.5 Hz), 123.60 (dd, J=18.5, 2.1 Hz), 131.4 (d, J=4.1 Hz), 131.5 (d, J=4.1 Hz), 150.47 (dd, J=250.3, 12.4 Hz), 152.18 (dd, J=251.4, 12.4 Hz). EIMS: *m/z* (%)=276 (15, [M$^+$]), 261 (17), 231 (100), 217 (31), 203 (16), 187 (27), 175 (53), 162 (55), 147 (71). HRMS (EI): *m/z* calcd for $C_{12}H_{18}F_2O_3Si$ [M$^+$]: 276.0994; found: 276.0980.

4.3.9. 3-Pyridyltriethoxysilane (3q).[9a] The typical procedure was followed using **2q** (39.5 mg, 0.250 mmol) and TBAI (0.25 mmol). The product was purified by distillation to afford 46.9 mg (80% yield) as a colorless oil. IR (neat): 2977, 2929, 2890, 1578, 1561, 1395, 1167, 1138, 1080 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ=1.26 (t, J=7.0 Hz, 9H), 3.89 (q, J=7.0 Hz, 6H), 7.29 (dd, J=7.4, 4.9 Hz, 1H), 7.95 (d, J=7.4 Hz, 1H), 8.65 (d, J=4.9 Hz, 1H), 8.83 (s, 1H). ^{13}C NMR (CDCl$_3$): δ=18.04, 58.80, 123.07, 126.55, 142.36, 151.05, 154.99. EIMS: *m/z* (%)=241 (54, [M$^+$]), 240 (100), 226 (18), 212 (27), 196 (88), 147 (29), 182 (25). HRMS (EI): *m/z* calcd for $C_{11}H_{19}O_3NSi$ [M$^+$]: 241.1134; found: 241.1112.

4.3.10. 4-(Triethoxysilyl)benzonitrile (3r).[9a] Following the typical procedure, the silylation of **2r** (248.2 mg, 0.988 mmol) was carried out at 100 °C using Rh(acac)(cod) (0.03 mmol) and TBAI (1.0 mmol) to afford 230.0 mg (88% yield) of **3r** as a colorless oil. IR (neat): 2977, 2231, 1444, 1390, 1296 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ=1.25 (t, J=7.0 Hz, 9H), 3.88 (q, J=7.0 Hz, 6H), 7.65 (d, J=8.3 Hz, 2H), 7.78 (d, J=8.3 Hz, 2H). ^{13}C NMR (CDCl$_3$): δ=18.16, 59.04, 113.93, 131.12, 135.23, 137.88, 159.74. EIMS: *m/z* (%)=265 (43, [M$^+$]), 250 (17), 220 (100), 206 (46), 192 (20), 176 (34), 164 (62). HRMS (EI): *m/z* calcd for $C_{13}H_{19}O_3NSi$ [M$^+$]: 265.1134, found: 265.1144.

4.3.11. 4-Chloro(triethoxysilyl)benzene (3s).[9a] Following the typical procedure, the silylation of **2s** (257.6 mg, 0.937 mmol) was carried out at 100 °C using Rh(acac)(cod) (0.03 mmol) and TBAI (1.0 mmol) to afford 174.2 mg (71% yield) of **3s** as a colorless oil. IR (neat): 2975, 2888, 2360, 1699, 1583, 1557, 1485, 1443, 1389, 1296, 1261 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ=1.17 (t, J=7.0 Hz, 9H), 3.79 (q, J=7.0 Hz, 6H), 7.28 (d, J=8.5 Hz, 2H), 7.54 (d, J=8.5 Hz, 2H). ^{13}C NMR (CDCl$_3$): δ=18.12, 58.75, 128.06, 129.53, 136.13, 136.70. EIMS: *m/z* (%)=274 (3, [M$^+$]), 239 (27), 229 (44), 185 (15), 173 (25), 162 (31), 147 (100), 135 (9). HRMS (EI): *m/z* calcd for $C_{12}H_{19}O_3ClSi$ [M$^+$]: 274.0792; found: 274.0792.

4.3.12. Ethyl 4-(methyldimethoxysilyl)benzoate (5a). The typical procedure was followed using **1a** as a silicon source and aryl iodide **2a**. IR (neat): 2978, 2838, 1720, 1391, 1280, 1090 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ=0.40 (s, 3H), 1.40 (t, J=7.3 Hz, 3H), 3.57 (s, 6H), 4.39 (q, J=6.8 Hz, 2H), 7.70 (d, J=7.9 Hz, 2H), 8.05 (d, J=7.9 Hz, 2H). ^{13}C NMR (CDCl$_3$): δ=−5.21, 14.31, 50.59, 61.03, 128.66, 131.86, 133.95, 139.49, 166.61. EIMS: *m/z* (%)=254 (7, [M$^+$]), 239 (100), 209 (20), 181 (10), 119 (7), 105(35). HRMS (EI): *m/z* calcd for $C_{12}H_{18}O_4Si$ [M$^+$]: 254.0974, found: 254.1003.

4.3.13. Ethyl 4-(triethylsilyl)benzoate (5b). The typical procedure was followed using **1b** as a silicon source and aryl iodide **2a**. IR (neat): 2955, 1721, 1599, 1588, 1557, 1463, 1416, 1389, 1367, 1278 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ=0.81 (q, J=7.7 Hz, 6H), 0.96 (t, J=7.6 Hz, 9H), 1.39 (t, J=7.3 Hz, 3H), 4.38 (q, J=7.1 Hz, 2H), 7.56 (d, J=7.9 Hz, 2H), 8.00 (d, J=7.9 Hz, 2H). ^{13}C NMR (CDCl$_3$): δ=3.17, 7.30, 14.34, 60.86, 128.34, 130.58, 134.11, 143.88, 166.86. EIMS: *m/z* (%)=264 (3, [M$^+$]), 235 (85), 207 (100), 133 (8), 115 (3), 104 (45), 57 (4). HRMS (EI): *m/z* calcd for $C_{15}H_{24}O_2Si$ [M$^+$]: 264.1546, found: 264.1523.

4.3.14. Ethyl 4-tris(dimethylamino)silylbenzoate (5c). The typical procedure was followed using **1d** as a silicon source and aryl iodide **2a**. IR (neat): 3545, 2838, 1722, 1464, 1279, 1176, 1091 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ=1.39 (t, J=7.0 Hz, 3H), 2.52 (s, 18H), 4.38 (q, J=7.1 Hz, 2H), 7.63 (d, J=7.9 Hz, 2H), 7.99 (d, J=7.9 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ=14.33, 38.01, 60.80, 128.17, 130.53, 135.17, 142.83, 166.93. EIMS: m/z (%)=309 (53, $[M^+]$), 265 (100), 264 (25), 221 (33), 148 (15), 72 (16). HRMS (EI): m/z calcd for $C_{15}H_{27}O_2N_3Si$ $[M^+]$: 309.1873, found: 309.1904.

4.4. Procedure for the large-scale preparation of aryltriethoxysilane

A flask with a septum inlet was charged with Rh(acac)(cod) (62 mg, 0.2 mmol) and a magnetic stirring bar, and then flushed with nitrogen. DMF (10 mL), Et_3N (4.2 mL, 30 mmol), **2a** (2.82 g, 10 mmol), and **1** (2.8 mL, 15 mmol) were added by syringe. After being stirred for 16 h at 80 °C, the mixture was extracted with ether (20 mL). The extract was washed with H_2O (10 mL), dried over Na_2SO_4, and concentrated. The residue was purified by Kugelrohr distillation to give 2.38 g (78% yield) of **3a**.

Acknowledgements

This work was partially supported by a Grant-in-Aid for Encouragement of Young Scientists (B) from the Ministry of Education, Culture, Sports, Science and Technology, Japan (No. 16750069).

References and notes

1. For examples of fluoride-induced biaryl coupling, see: (a) Shibata, K.; Miyazawa, K.; Goto, Y. *Chem. Commun.* **1997**, 1309; (b) Mowery, M. E.; DeShong, P. *J. Org. Chem.* **1999**, *64*, 1684; (c) Mowery, M. E.; DeShong, P. *Org. Lett.* **1999**, *1*, 2137; (d) DeShong, P.; Handy, C. J.; Mowery, M. *Pure Appl. Chem.* **2000**, *72*, 1655; (e) Lee, H. M.; Nolan, S. P. *Org. Lett.* **2000**, *2*, 2053; (f) Seganish, W. M.; DeShong, P. *J. Org. Chem.* **2004**, *69*, 6790; (g) Li, J.-H.; Deng, C.-L.; Liu, W.-J.; Xie, Y.-X. *Synthesis* **2005**, 3039; (h) Murata, M.; Yoshida, S.; Nirei, S.-i.; Watanabe, S.; Masuda, Y. *Synlett* **2006**, 118.
2. Aqueous NaOH can be used as an activator in place of fluoride ion. See: (a) Murata, M.; Shimazaki, R.; Watanabe, S.; Masuda, Y. *Synthesis* **2001**, 2231; (b) Wolf, C.; Lerebours, R. *Org. Lett.* **2004**, *6*, 1147; (c) Lerebours, R.; Wolf, C. *Synthesis* **2005**, 2287.
3. (a) Denmark, S. E.; Amishiro, N. *J. Org. Chem.* **2003**, *68*, 6997; (b) Nishikata, T.; Yamamoto, Y.; Miyaura, N. *Chem. Lett.* **2003**, *32*, 752; (c) Nishikata, T.; Yamamoto, Y.; Miyaura, N. *Organometallics* **2004**, *23*, 4317.
4. (a) Oi, S.; Honma, Y.; Inoue, Y. *Org. Lett.* **2002**, *4*, 667; (b) Oi, S.; Taira, A.; Honma, Y.; Inoue, Y. *Org. Lett.* **2003**, *5*, 97.
5. Murata, M.; Shimazaki, R.; Ishikura, M.; Watanabe, S.; Masuda, Y. *Synthesis* **2002**, 717.
6. Koike, T.; Du, X.; Sanada, T.; Danda, Y.; Mori, A. *Angew. Chem., Int. Ed.* **2003**, *42*, 89.
7. (a) Lam, P. Y. S.; Deudon, S.; Averill, K. M.; Li, R.; He, M. Y.; DeShong, P.; Clark, C. G. *J. Am. Chem. Soc.* **2000**, *122*, 7600; (b) Lam, P. Y. S.; Deudon, S.; Hauptman, E.; Clark, C. G. *Tetrahedron Lett.* **2001**, *42*, 2427.
8. (a) Selin, T. G.; West, R. *J. Am. Chem. Soc.* **1962**, *84*, 1856; (b) Manoso, A. S.; Ahn, C.; Soheili, A.; Handy, C. J.; Correia, R.; Seganish, W. M.; DeShong, P. *J. Org. Chem.* **2004**, *69*, 8305; (c) Lee, A. S.-Y.; Chang, Y.-T.; Chu, S.-F.; Tsao, K.-W. *Tetrahedron Lett.* **2006**, *47*, 7085.
9. For the synthesis of aryltrialkoxysilanes, see: (a) Murata, M.; Suzuki, K.; Watanabe, S.; Masuda, Y. *J. Org. Chem.* **1997**, *62*, 8569; (b) Manoso, A. S.; DeShong, P. *J. Org. Chem.* **2001**, *66*, 7455; (c) Komuro, K.; Ishizaki, K.; Suzuki, H. *Touagousei-kenkyu-nenpo* **2003**, *6*, 24.
10. For other examples of the palladium(0)-catalyzed silylation of organic halides, see: (a) Murata, M.; Watanabe, S.; Masuda, Y. *Tetrahedron Lett.* **1999**, *40*, 9255; (b) Denmark, S. E.; Kallemeyn, J. M. *Org. Lett.* **2003**, *5*, 3483; (c) Yamanoi, Y. *J. Org. Chem.* **2005**, *70*, 9607; (d) Murata, M.; Ohara, H.; Oiwa, R.; Watanabe, S.; Masuda, Y. *Synthesis* **2006**, 1771.
11. Quite recently, platinum- and rhodium-catalyzed silylations using Et_3SiH have been reported: (a) Hamze, A.; Provot, O.; Alami, M.; Brion, J.-D. *Org. Lett.* **2006**, *8*, 931; (b) Karshtedt, D.; Bell, A. T.; Tilley, T. D. *Organometallics* **2006**, *25*, 4471; (c) Yamanoi, Y.; Nishihara, H. *Tetrahedron Lett.* **2006**, *47*, 7157.
12. Nakamura, T.; Kinoshita, H.; Shinokubo, H.; Oshima, K. *Org. Lett.* **2002**, *4*, 3165.
13. Murata, M.; Watanabe, S.; Masuda, Y. *Synlett* **2000**, 1043.
14. (a) Murata, M.; Watanabe, S.; Masuda, Y. *J. Org. Chem.* **1997**, *62*, 6458; (b) Murata, M.; Oyama, T.; Watanabe, S.; Masuda, Y. *J. Org. Chem.* **2000**, *65*, 164; (c) Murata, M.; Oyama, T.; Watanabe, S.; Masuda, Y. *Synthesis* **2000**, 778; (d) Baudoin, O.; Guénard, D.; Guéritte, F. *J. Org. Chem.* **2000**, *65*, 9268; (e) Murata, M.; Oyama, T.; Watanabe, S.; Masuda, Y. *Synth. Commun.* **2002**, *32*, 2513; (f) Broutin, P.-E.; Čerña, I.; Campaniello, M.; Leroux, F.; Colobert, F. *Org. Lett.* **2004**, *6*, 4419; (g) Murata, M.; Sambommatsu, T.; Watanabe, S.; Masuda, Y. *Synlett* **2006**, 1867.
15. The preliminary communication of this work has been reported: Murata, M.; Ishikura, M.; Nagata, M.; Watanabe, S.; Masuda, Y. *Org. Lett.* **2002**, *4*, 1843.
16. Berry has reported on a rhodium-catalyzed dehydrogenative coupling of arenes with triethylsilane: Ezbiansky, K.; Djurovich, P. I.; LaForest, M.; Sinning, D. J.; Zayes, R.; Berry, D. H. *Organometallics* **1998**, *17*, 1457. In the reaction of chlorobenzene, the formation of $Et_3SiC_6H_5$ was observed. However, it is difficult to distinguish direct silylation of the C–Cl bond from subsequent reduction of $Et_3Si(C_6H_4Cl)$.
17. For a review, see: Stang, P. J.; Hanack, M.; Subramanian, L. R. *Synthesis* **1982**, 85.
18. For examples of coupling reactions of aryl nonaflates, see: (a) Rottlander, M.; Knochel, P. *J. Org. Chem.* **1998**, *63*, 203; (b) Anderson, K. W.; Mendez-Perez, M.; Priego, J.; Buchwald, S. L. *J. Org. Chem.* **2003**, *68*, 9563.
19. Very recently, the $[Rh(cod)(MeCN)_2]BF_4$-catalyzed silylation of 2,6-bis(trifluoromethanesulfonyl)-anthracene with **1** in the presence of TBAI has been reported: Shimada, T.; Tanaka, N.; Goto, Y.; Inagaki, S. Abstract of the 86th Annual Meeting of Chemical Society of Japan, Chiba; March 2006, 3PB-191. However, no example of other aryl triflates was provided.
20. For examples, see: (a) Muir, K. W.; Ibers, J. A. *Inorg. Chem.* **1970**, *9*, 440; (b) Nishihara, Y.; Takemura, M.; Osakada, K. *Organometallics* **2002**, *21*, 825 For a recent review, see: (c) Corey, J. Y.; Braddock-Wilking, J. *Chem. Rev.* **1999**, *99*, 175.

21. (a) Knorr, M.; Schubert, U. *J. Organomet. Chem.* **1989**, *365*, 151; (b) Seebald, S.; Mayer, B.; Schubert, U. *J. Organomet. Chem.* **1993**, *462*, 225; (c) Schubert, U.; Seebald, S. *J. Organomet. Chem.* **1994**, *472*, C15; (d) Schubert, U. *Organosilicon Chemistry—From Molecules to Materials*; Auner, N., Weis, J., Eds.; VCH: Weinheim, 1993; p 205.
22. (a) Yamasita, H.; Hayashi, T.; Kobayashi, T.-a.; Tanaka, M.; Goto, M. *J. Am. Chem. Soc.* **1988**, *110*, 4417; (b) Yamasita, H.; Kobayashi, T.-a.; Hayashi, T.; Tanaka, M. *Chem. Lett.* **1990**, *19*, 1447; (c) Yamasita, H.; Kobayashi, T.-a.; Hayashi, T.; Tanaka, M. *Chem. Lett.* **1991**, *20*, 761.
23. Green, M.; Kuc, T. A.; Taylor, S. H. *J. Chem. Soc. A* **1971**, 2334.