CHEMISTRY
AN ASIAN JOURNAL

DOI: 10.1002/asia.200800090

Rhodium-Catalyzed Silylation of Aromatic Carbon–Hydrogen Bonds in 2-Arylpyridines with Disilane

Mamoru Tobisu,*[a] Yusuke Ano,[b] and Naoto Chatani*[b]

Dedicated to Professor Ryoji Noyori on the occasion of his 70th birthday

Abstract: The rhodium(I)-catalyzed regioselective silylation of the *ortho* carbon–hydrogen bond in 2-arylpyridines with disilane is described. For example, the reaction of 2-(2-methylphenyl)pyridine with 2 equivalents of hexamethyldisilane in the presence of 5 mol% $[RhCl(cod)]_2$ (cod = 1,5-cyclooctadiene) in *o*-xylene at 130 °C for 15 h gave 2-[2-methyl-6-(trimethylsilyl)phenyl]pyridine in 86% yield. In contrast to silylation with hydrosilanes, hydrogen acceptors are not required to achieve high conversion. A variety of substituents, including alkoxy, amine, ester, and fluorinated groups, are compatible with this catalysis. When substrates containing two *ortho* C–H bonds are used, monosilylated products are obtained selectively by utilizing the 3-methyl-2-pyridyl group as a directing group.

Keywords: C–H activation · disilanes · homogeneous catalysis · regioselectivity · silylation

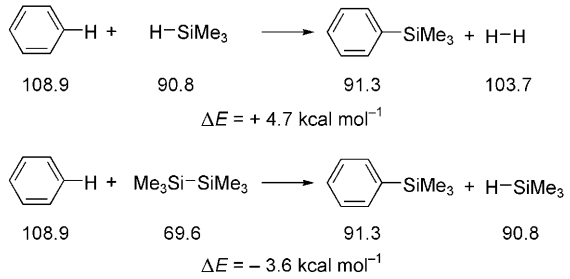
Introduction

Over the past few years, catalytic functionalization of C–H bonds has become one of the most important frontiers in exploratory research of synthetic organic chemistry, as the direct transformation of C–H bonds, which are ubiquitous in organic molecules, does not require the preparation of the reactive intermediates (e.g., halides or triflates).[1] In this context, the silylation of aromatic C–H bonds represents a valuable method for the preparation of arylsilanes, which are versatile intermediates in organic synthesis.[2] Moreover, demand for this type of silylation reaction has increased in the field of materials chemistry.[3] Most of the C–H silylation reactions reported to date involved hydrosilanes as the silicon source.[4] These reactions require the addition of alkenes as hydrogen acceptors to achieve high conversion. Although one catalytic system that does not require a hydrogen acceptor has been reported, it is intrinsically nonregioselective when applied to substituted benzene derivatives.[5] Kakiuchi, Murai, and co-workers reported that vinyl silanes can also serve as silicon sources for the silylation of C–H bonds, although applicable substrates are limited to heteroarenes.[6] On the other hand, the catalytic silylation of C–H bonds also proceeds with disilanes.[7–10] In this reaction, the addition of alkenes to trap the co-produced hydrosilanes is not required. The difference in reactivity between hydrosilane and disilane in C–H silylation reactions can be attributed to the different thermodynanic properties of these reactions (Scheme 1). On the basis of DFT analysis, the silylation reaction of benzene with hydrosilane is thermodynamically unfavorable by 4.7 kcal mol^{-1}. Thus, to make this process feasible, integration with a more exothermic process, such as hydrogenation of alkenes, is required. In contrast, the corresponding reaction with disilane is exothermic by 3.6 kcal mol^{-1}, arising, in part, from the smaller bond-dissociation energy of the silicon–silicon bond relative to the silicon–hydrogen bond. In spite of this energetic advantage, the C–H silylation reactions with disilanes reported so far have many drawbacks, such as the photochemical conditions required,[7] the use of strained disilanes[8] and excess amounts of arenes (>5 equiv),[9] and the formation of a mixture of mono- and disilylated products.[10] In this article, we describe a rhodi-

[a] Dr. M. Tobisu
Frontier Research Base for Young Researchers
Graduate School of Engineering, Osaka University
Suita, Osaka 565-0871 (Japan)
Fax: (+81) 6-6879-7396
E-mail: tobisu@chem.eng.osaka-u.ac.jp

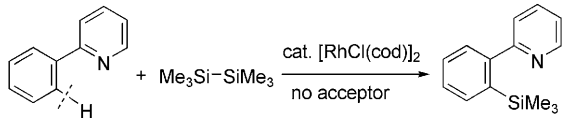
[b] Y. Ano, Prof. Dr. N. Chatani
Department of Applied Chemistry
Faculty of Engineering, Osaka University
Suita, Osaka 565-0871 (Japan)
Fax: (+81) 6-6879-7396
E-mail: chatani@chem.eng.osaka-u.ac.jp

Supporting information for this article is available on the WWW under http://www.chemasianj.org or from the author.



Scheme 1. Thermodynamic profiles of carbon–hydrogen bond silylation reactions based on bond-dissociation energies. The values under each compound refer to the bond-dissociation energies (kcal mol^{-1}) of the indicated bonds.

um-catalyzed silylation of the aromatic C−H bond in 2-arylpyridines with hexamethyldisilane, which affords monosilylated products in a regioselective manner (Scheme 2).

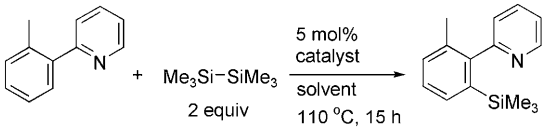


Scheme 2. Rhodium-catalyzed silylation of C−H bonds in 2-phenylpyridines with disilane.

Results and Discussion

We recently reported the rhodium(I)-catalyzed silylation of benzonitrile derivatives with disilanes.[11] In this reaction system, the carbon–cyano bond is cleaved by rhodium–silyl species generated in situ by the deinsertion of silyl isocyanide. Intrigued by the unique reactivity of this postulated species toward C–CN bonds, we investigated the silylation of other unreactive bonds in the presence of a rhodium catalyst and disilanes. To our delight, the reaction of 2-(2-methylphenyl)pyridine (**1**) with hexamethyldisilane (**2**) in the presence of a catalytic amount of $[RhCl(cod)]_2$ in toluene under reflux furnished *ortho*-silylated product **3** in 86% yield (Table 1, entry 1). Notably, the introduction of a trimethylsilyl group has never been demonstrated in C–H silylation with hydrosilane owing to the gaseous nature of trimethylsilane (b.p. = 6.7 °C). Thus, the advantage of using disilanes is reinforced. As the silylation of toluene, which was used as the solvent, was not observed, a directing group was required for the C–H silylation reaction to proceed. The reaction temperature has a significant impact on the catalysis. Almost no silylated product was observed even at slightly lower temperature (90 °C; Table 1, entry 2). With regard to the solvent, the use of dioxane was comparably effective, whereas DMF and an alcoholic solvent completely prevented the silylation reaction (Table 1, entries 4 and 5). Other transition-metal complexes, including $[Rh(cod)_2]BF_4$, $[Rh(OMe)(cod)]_2$, and $[IrCl(cod)]_2$, exhibited much less or no catalytic activity for this C–H silylation reaction (Table 1, entries 6–9). Some metal complexes, such as $[Ru_3(CO)_{12}]$, $[RuCl_2(cod)]_n$, and $Cu(OAc)_2$, were totally inactive. Addition of phosphine led to a complete loss of catalytic activity (Table 1, entry 10).

Table 1. Optimization of reaction conditions.[a]



1 2 3

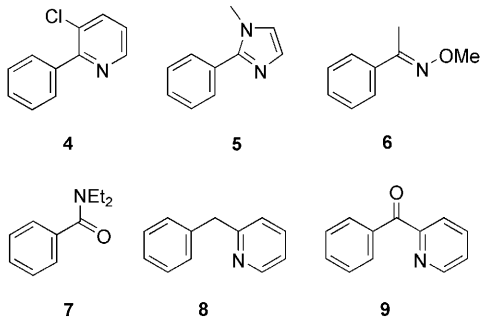
Entry	Catalyst	Solvent	Yield [%][b]
1	$[RhCl(cod)]_2$	toluene	91 (86)[c]
2[d]	$[RhCl(cod)]_2$	toluene	trace
3	$[RhCl(cod)]_2$	dioxane	91
4	$[RhCl(cod)]_2$	DMF	0
5	$[RhCl(cod)]_2$	*tert*-amyl alcohol	0
6	$[RhCl(CO)]_2$	toluene	0
7[e]	$[Rh(cod)_2]^+BF_4^-$	toluene	0
8	$[Rh(OMe)(cod)]_2$	toluene	66
9	$[IrCl(cod)]_2$	toluene	0
10[f]	$[RhCl(cod)]_2$	toluene	0

[a] Reaction conditions: 2-arylpyridine (1.0 mmol), hexamethyldisilane (2.0 mmol), and catalyst (0.05 mmol) in solvent (1 mL) at 110 °C, 15 h. [b] Determined by GC. [c] Yield of isolated **3**. [d] The reaction was conducted at 90 °C. [e] 0.10 mmol of catalyst was used. [f] PPh_3 (0.10 mmol) was added. cod = 1,5-cyclooctadiene, DMF = *N*,*N*-dimethylformamide.

Chelation assistance by a 2-pyridyl group was crucial in this Rh-catalyzed C–H silylation to achieve a reasonable reaction rate and regioselectivity. We also examined other coordinating groups for their ability to promote the silylation reaction (Scheme 3). Pyridine **4**, which contains an electron-withdrawing group, imidazole **5**, oxime **6**, and amide **7** did not serve as directing groups at all. Furthermore, no silylation occurred with substrates extended by one carbon atom, as in **8** and **9**, thus indicating the importance of the formation of a five-membered metallacycle intermediate (see below). Among the substrates we examined, oxazoline **10**

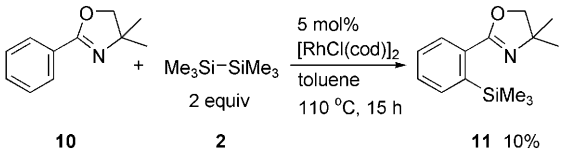
Abstract in Japanese:
ロジウム触媒によるジシランをケイ素源とする 2-フェニルピリジンのオルト位炭素－水素結合のシリル化反応について報告する。一般に、ヒドロシランをケイ素源とする炭素－水素結合のシリル化反応では、副生する水素 を捕捉するために、化学量論量以上のオレフィンなどの存在下で反応を行う 必要がある。これに対し、このロジウム触媒によるジシランを用いる反応では、副生するヒドロシランを捕捉する必要がなく、高い転化率が得られる。本反応は高い官能基許容性を示すとともに、配向基として 3-メチル-2-ピリジル基を用いることで、反応点が２つある基質を用いた場合でもモノシリル化体を 選択的に得ることができる。

CHEMISTRY
AN ASIAN JOURNAL



Scheme 3. Failed directing groups.

was the only directing group that afforded the silylated product, although the yield was significantly lower than that of the corresponding pyridine-based substrate (Scheme 4).

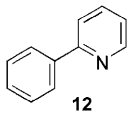
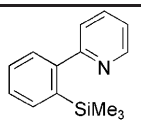
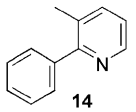
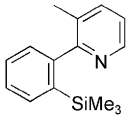
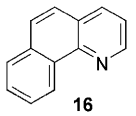
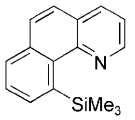
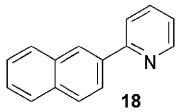
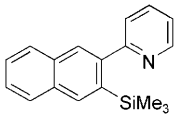
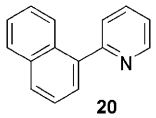
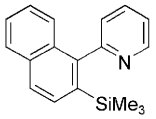
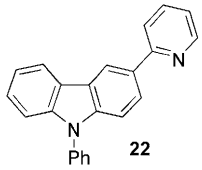
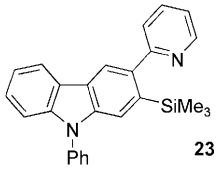
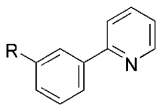
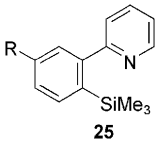
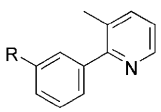
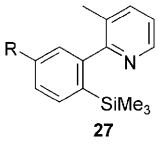


Scheme 4. Rhodium-catalyzed silylation of 2-phenyloxazoline **10**.

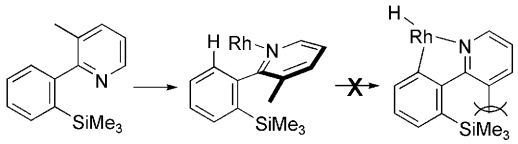
With the optimized conditions in hand, we next examined the scope of this reaction with respect to disilanes. The use of other disilanes, such as $(PhMe_2Si)_2$, $(tBuMe_2Si)_2$, and $(Et_3Si)_2$, did not afford any silylated products under the reaction conditions used in this study. The unsuccessful result with $(PhMe_2Si)_2$ was slightly unexpected, as it furnished a silylated product in a C–CN bond silylation reaction under almost-identical conditions.[11] This indicates that the postulated rhodium–silyl species is generated even in the case of $(PhMe_2Si)_2$, but that subsequent events, such as C−H bond activation or C–Si bond formation, presumably proceed with difficulty with this silyl group.

We next explored the scope of the Rh^I-catalyzed silylation by using a diverse collection of 2-arylpyridines with **2** (Table 2). Mono- and disilylated products were obtained in a 1:1.1 ratio in the reaction of 2-phenylpyridine (**12**). However, exclusive formation of the monosilylated product was achieved by employing the bulkier 3-methyl-2-pyridyl directing group (Table 2, entry 2). This group impedes the formation of the metallacycle intermediate required for the second *ortho* silylation owing to steric congestion between the 3-methyl group and the silyl group already added (Scheme 5).[12] Benzo[*h*]quinoline (**16**), in which the pyridine moiety is fixed to be coplanar with the benzene ring to be silylated, also serves as a good substrate (Table 2, entry 3), although the rate of the reaction was slower than that with conformationally flexible substrate **14**. Pyridine-directed silylation is also applicable to substrates containing extended π systems, such as naphthalene (Table 2, entries 4 and 5) and carbazole (Table 2, entry 6). Functional-group compatibility of this reaction was examined by using 2-phenylpyridines bearing a substituent at the *meta* position (Table 2, entries 7–14). Ether (Table 2, entries 8, 9, and 13), amine

Table 2. Rh-catalyzed silylation of 2-arylpyridines with disilane **2**.[a]

Entry	2-Arylpyridine	Product	Yield [%][b]
1	 **12**	 **13**	69 (1:1.1)[c]
2	 **14**	 **15**	84
3	 **16**	 **17**	77[d,e]
4	 **18**	 **19**	72[d,e]
5	 **20**	 **21**	86
6	 **22**	 **23**	56
7	 **24**	 **25**	**a**: R = Me 75
8			**b**: R = OMe 56 (8.3:1)[c]
9			**c**: R = O*i*Pr 69 (6.7:1)[c]
10			**d**: R = NMe_2 75[f]
11			**e**: R = CO_2Et 51[d]
12			**f**: R = CF_3 51[e]
13	 **26**	 **27**	**a**: R = OMe 70[f]
14			**b**: R = CF_3 82

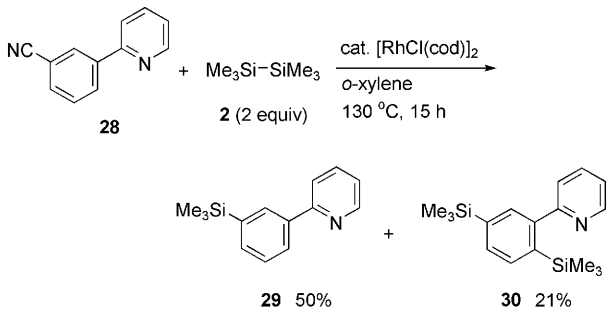
[a] Reaction conditions: 2-arylpyridine (1.0 mmol), hexamethyldisilane (2.0 mmol), and $[RhCl(cod)]_2$ (0.05 mmol) in *o*-xylene (0.5 mL) at 130 °C, 15 h. [b] Yield of isolated monosilylated product unless otherwise noted. [c] Combined yield of isolated mono- and disilylated products. The ratio in the parentheses refers to that of mono- to disilylated product, determined by ^1H NMR spectroscopy. [d] Carried out with 4.0 mmol of disilane for 45 h. [e] Carried out in *o*-xylene (1 mL). [f] Carried out with 0.10 mmol of $[RhCl(cod)]_2$.



Scheme 5. Steric repulsion by a 3-methyl-2-pyridyl group in the second silylation.

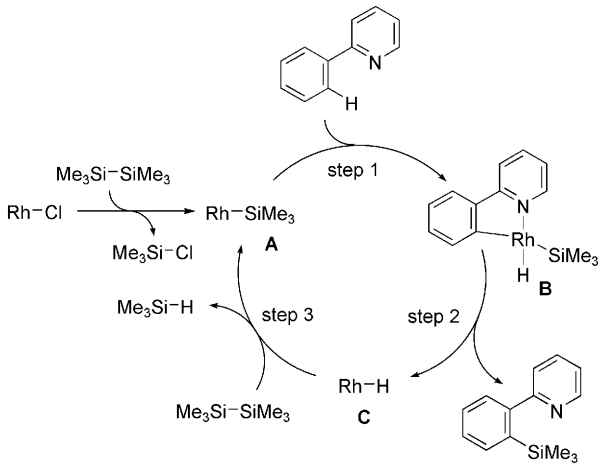
(Table 2, entry 10), ester (Table 2, entry 11), and fluoroalkyl (Table 2, entries 12 and 14) groups were all tolerated under the reaction conditions. In this series of substrates, silylation occurred specifically at the less-hindered site, with the exception of alkoxy-substituted substrates **24b** and **24c**, which afforded a small amount of disilylated product (Table 2, entries 8 and 9).[13] The amount of disilylated product was not significantly affected by the steric bulk of the substituent on the oxygen atom of the alkoxy group (Table 2, entry 8 vs. 9). However, exclusive formation of the monosilylated product was achieved by introduction of a methyl group on the pyridine ring (Table 2, entry 13), as was the case for the substrate with no *meta* substituent (Table 2, entry 2). As such, unlike the Pt-catalyzed system,[10] substrates with a wide variety of substituents efficiently furnished the corresponding monosilylated products.

Our success in the carbon–cyano bond cleavage reaction[11] led us to examine 2-(3-cyanophenyl)pyridine (**28**) to determine the relative reactivity of carbon–cyano and carbon–hydrogen bonds in the present catalytic system. As a result, monosilylated product **29**, in which the CN group is replaced by a trimethylsilyl (TMS) group, was obtained in 50% yield, along with disilylated product **30** (21% yield). This result indicates that the cyano group has a higher reactivity toward the rhodium–silyl species than the *ortho* C–H bond of 2-arylpyridines (Scheme 6).



Scheme 6. Silylation of a 2-phenylpyridine containing a CN group.

Although the detailed mechanism remains elusive, a possible catalytic cycle is depicted in Scheme 7. The catalytically active rhodium–silyl species **A** is initially generated by the reaction of $[RhCl(cod)]_2$ with hexamethyldisilane (**2**). For simplicity, Rh^{I}–$SiMe_3$ is shown in Scheme 7, although Rh^{III}–$(SiMe_3)_3$ is also a possible competent species.[9] The rhodium–silyl species **A** then activates the *ortho* C–H bond of the 2-arylpyridine with the aid of coordination of the pyridine ring. Although several modes of C–H bond activation are possible,[14] the exact activation mechanism in our catalysis is currently unclear. Activation through oxidative addition of the C–H bond (i.e., step 1) is one plausible pathway. Complex **B** affords the silylated product through C–Si bond-forming reductive elimination, along with the formation of rhodium hydride **C** (step 2). The catalytic cycle is completed by the reaction of hydride **C** with disilane, which generates

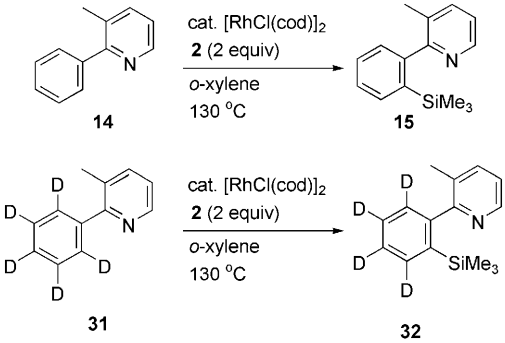


Scheme 7. Possible mechanism for the rhodium-catalyzed silylation of 2-arylpyridines with disilane.

the active rhodium–silyl species **A** and $HSiMe_3$ (step 3). The role of co-produced $HSiMe_3$ as a silylating agent in this catalysis is likely to be less significant owing to unfavorable energetics in the absence of a hydrogen acceptor (see Scheme 1).[15]

To probe the mechanism of C–H bond activation in our system, we next examined the kinetic isotope effect of this reaction. Thus, the rhodium-catalyzed silylation reactions of 2-phenylpyridine **14** and its deuterium-labeled counterpart **31** were performed in a different batch under identical reaction conditions, and the yield of the product in each reaction was monitored by GC analysis (Table 3).[16] The yield of the deuterated compound **32** was found to be slightly higher than that of **15** at a conversion of 15–65%. These results clearly indicate that the cleavage of the C–H bond of 2-arylpyridines is not involved in the rate-limiting step of this rho-

Table 3. Kinetic isotope effect.[a]



Time [h]	0.5	1.0	2.0	3.0
Yield of **15** [%][b]	15	35	50	51
Yield of **32** [%][b]	22	50	56	65
15/**32**	0.70	0.70	0.89	0.78

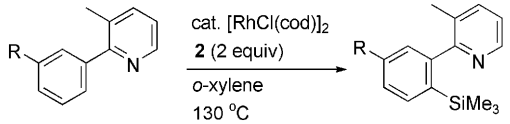
[a] Reaction conditions: 2-arylpyridine (1.0 mmol), hexamethyldisilane (2.0 mmol), and $[RhCl(cod)]_2$ (0.05 mmol) in *o*-xylene (0.5 mL) at 130 °C, 15 h. [b] Yield determined by GC. The values given are the average of three runs.

CHEMISTRY
AN ASIAN JOURNAL

dium-catalyzed silylation reaction. Although the origin of the inverse kinetic isotope effect in our catalysis is a subject for future study, a similar isotope effect has been observed in several organometallic processes that involve the cleavage of C–H bonds.[17]

To gain further insight into the reaction mechanism, the reactivity of an electronically different set of 2-arylpyridines was examined (Table 4). Under the catalytic conditions used

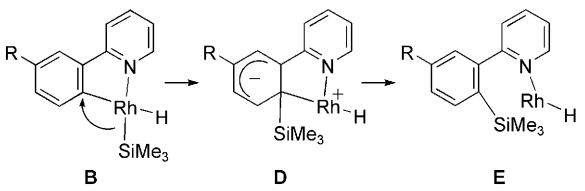
Table 4. Substituent effect.[a]



Entry	R	Yield [%][b]	
		10 h[c]	15 h[c]
1	CF_3	76	82
2	H	55	84
3	OMe	24	43

[a] Reaction conditions: 2-arylpyridine (1.0 mmol), hexamethyldisilane (2.0 mmol), and $[RhCl(cod)]_2$ (0.05 mmol) in *o*-xylene (0.5 mL) at 130 °C, 15 h. [b] Yield of isolated product. [c] Reaction time.

in this study, an electron-deficient C–H bond was silylated slightly faster than a 2-arylpyridine with no substituent at the *meta* position (Table 4, entry 1 vs. 2). On the other hand, the yield decreased significantly when an electron-donating group was introduced (Table 4, entry 3). Thus, the order of reactivity in this catalysis is as follows: $CF_3 > H > OMe$. This order of reactivity probably reflects the susceptibility of the rate-limiting step to the electronic nature of the substrate. As the oxidative addition of the C–H bond (i.e., step 1 in Scheme 7) is unlikely to be rate-limiting on the basis of the kinetic isotope effect observed above, reductive elimination (i.e., step 2 in Scheme 7) is the only possible step that can be affected by the substituent of the 2-arylpyridine; thus, reductive elimination is presumed to be the rate-limiting step of the catalytic cycle. The rate acceleration by an electron-withdrawing group might be rationalized by a rate-limiting C–Si bond-forming reductive elimination via Meisenheimer-type intermediate **D**, which could be stablized by an electron-withdrawing group at the *meta* position (σ–π coupling mechanism; Scheme 8). This σ–π coupling mechanism was also proposed in ruthenium-catalyzed chelation-assisted C–H bond alkylation, in which C–C bond-forming reductive elimination is rate-limiting.[18]



Scheme 8. Possible mechanism for the C–Si bond-forming reductive elimination.

Conclusions

We have developed a rhodium-based catalytic system for the regioselective silylation of aromatic C–H bonds of 2-arylpyridines with hexamethyldisilane. In sharp contrast to C–H silylation with hydrosilanes, no additive is required to trap the co-product (i.e., hydrosilane) in the present system. A variety of functional groups, such as ethers, esters, fluorides and amines, are tolerated under the reaction conditions to furnish monosilylated products. As no primary kinetic isotope effect was observed, the cleavage of the *ortho* C–H bond is not involved in the rate-limiting step of this catalysis. On the basis of the substituent and the kinetic isotope effect observed, we currently consider that the C–Si bond-forming reductive elimination is rate-limiting. Ongoing work seeks to explore a catalytic system that can effect the cleavage of other unreactive bonds.

Experimental Section

General

^1H and ^{13}C NMR spectra were recorded on a JEOL JMN-270 or JEOL JMTC-400/54/ss spectrometer in $CDCl_3$ with $CHCl_3$ as the internal standard. Data are reported as follows: chemical shifts in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant (Hz), integration. Infrared (IR) spectra were obtained on a Horiba FT-700 spectrometer. Mass spectra were obtained on a Shimadzu GCMS-QP 5000 or GCMS-QP 2010 instrument with ionization voltages of 70 eV. Elemental analysis was performed by the Elemental Analysis Section of Osaka University. High-resolution mass spectrometry (HRMS) was performed on a JEOL JMS-DX303 spectrometer. Column chromatography was performed with SiO_2 (Merck silica gel 60 (230–400 mesh)).

Materials

Commercially available materials were used as received unless otherwise noted. Toluene and *o*-xylene were distilled from CaH_2. $[RhCl(cod)]_2$ and **16** were purchased from Wako Chemicals. Disilane **2** was purchased from Tokyo Chemical Industry Ltd. Compounds **10** and **12** were purchased from Aldrich. Compounds **18**, **22**, **24e**, and **28** were prepared from the Pd-catalyzed cross-coupling reaction of 2-bromopyridine with the corresponding aryl boronic acid.[19] Compound **24d** was obtained according to a previously published method.[20] Other substituted 2-arylpyridines were prepared from the Ni-catalyzed cross-coupling reaction of 2-bromopyridine with the corresponding aryl magnesium bromide.[21]

Synthesis and Experimental Data

24c: Colorless oil. $R_f = 0.19$ (hexane/EtOAc = 10:1); b.p.: 85 °C (0.5 mmHg); IR (neat): $\tilde{\nu} = 3074, 2978, 2931, 1585, 1564, 1493, 1385, 1290, 1213, 1117, 995, 966, 883, 771, 744, 694, 640, 615\ cm^{-1}$; ^1H NMR ($CDCl_3$, 270.05 MHz): $\delta = 1.37$ (d, $J = 5.9$ Hz, 6H), 4.68 (sept, $J = 4.68$ Hz, 1H), 6.95 (dd, $J = 7.8$, 1.9 Hz, 1H), 7.23–7.26 (m, 1H), 7.37 (t, $J = 7.8$ Hz, 1H), 7.52–7.57 (m, 2H), 7.69–7.78 (m, 2H), 8.68 ppm (d, $J = 4.9$ Hz, 1H); ^{13}C NMR ($CDCl_3$, 67.80 MHz): $\delta = 22.2$, 70.0, 114.3, 116.7, 119.1, 120.5, 122.1, 129.6, 136.6, 140.7, 149.4, 157.2, 158.2 ppm; MS (70 eV, EI): *m*/*z* (%) = 213 (28) $[M]^+$, 171 (100); elemental analysis: calcd (%) for $C_{14}H_{15}NO$: C 78.84, H 7.09, N 6.57; found: C 78.63, H 7.08, N 6.40.

General procedure for the rhodium-catalyzed silylation of 2-arylpyridines with disilane: $[RhCl(cod)]_2$ (0.05 mmol), 2-arylpyridine (1.0 mmol), hexamethyldisilane (2.0 mmol), and *o*-xylene (0.5 mL) were added to an oven-dried 10-mL two-necked flask under a gentle stream of nitrogen. The mixture was stirred for 15 h at 130 °C under N_2 atmosphere. The product was isolated by silica-gel column chromatography.

3: Colorless oil. R_f=0.21 (hexane/EtOAc=5:1); b.p.: 130°C (2.0 mmHg); IR (neat): $\tilde{\nu}$=3074, 2954, 2897, 1587, 1564, 1473, 1410, 1248, 1194, 1149, 1097, 1053, 1026, 993, 877, 837, 791, 762, 690, 623, 569 cm^{-1}; ^1H NMR ($CDCl_3$, 270.05 MHz): δ=−0.13 (s, 9H), 1.99 (s, 3H), 7.18–7.23 (m, 3H), 7.42 (dd, J=6.9, 2.1 Hz, 1H), 7.65 (td, J=7.6, 2.1 Hz, 1H), 8.61–8.64 ppm (m, 1H); ^{13}C NMR ($CDCl_3$, 67.80 MHz): δ=0.2, 20.4, 121.8, 124.9, 127.2, 130.7, 132.0, 135.0, 135.6, 138.4, 146.3, 148.9, 160.9 ppm; MS (70 eV, EI): m/z (%)=241 (3) $[M]^+$, 226 (100); elemental analysis: calcd (%) for $C_{15}H_{19}NSi$: C 74.63, H 7.93, N 5.80; found: C 74.39, H 7.69, N 5.77.

11: Colorless oil. R_f=0.31 (hexane/EtOAc=5:1); b.p.: 80°C (2.0 mmHg); IR (neat): $\tilde{\nu}$=3057, 2968, 2895, 1657, 1462, 1435, 1352, 1309, 1282, 1246, 1213, 1190, 1128, 1095, 1059, 1041, 991, 968, 926, 845, 781, 733, 690, 621 cm^{-1}; ^1H NMR ($CDCl_3$, 270.05 MHz): δ=0.32 (s, 9H), 1.41 (s, 6H), 4.12 (s, 2H), 7.36–7.45 (m, 2H), 7.63 (dd, J=6.4, 2.6 Hz, 1H), 7.90 ppm (d, J=6.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ=0.6, 28.4, 67.4, 79.4, 128.8, 129.9, 130.1, 135.2, 140.4, 164.4 ppm; MS (70 eV, EI): m/z (%)=247 (16) $[M]^+$, 232 (100); HRMS: m/z calcd for $C_{14}H_{21}NOSi$: 247.1392; found: 247.1385.

13: Obtained as a mixture of mono- and disilylated products. R_f=0.23 (hexane/EtOAc=15:1); IR (neat): $\tilde{\nu}$=3049, 2952, 2897, 1587, 1562, 1475, 1427, 1390, 1248, 1147, 1124, 1099, 1051, 1022, 991, 856, 839, 800, 771, 752, 729, 688, 621, 463 cm^{-1}; ^1H NMR ($CDCl_3$, 270.05 MHz): δ=−0.09 (s, disilylated product), 0.08 (s, monosilylated product), 7.24–7.51 (m), 7.63–7.77 (m), 8.64–8.68 ppm (m); ^{13}C NMR ($CDCl_3$, 67.80 MHz): δ=0.4, 0.9, 121.8, 122.4, 122.9, 125.6, 126.3, 127.3, 128.5, 128.6, 135.1, 135.3, 135.3, 136.2, 138.0, 139.2, 146.8, 148.3, 148.4, 152.9, 161.2, 162.9 ppm; MS (70 eV, EI): monosilylated product: m/z (%)=226 (4) $[M-H]^+$, 212 (100); disilylated product: m/z (%)=298 (1) $[M-H]^+$, (100); HRMS: monosilylated product: m/z calcd for $C_{14}H_{17}NSi$: 227.1130; found: 227.1104; disilylated product: m/z calcd for $C_{17}H_{25}NSi_2$: 299.1526; found: 299.1486.

15: Colorless oil. R_f=0.26 (hexane/EtOAc=5:1); b.p.: 130°C (1.5 mmHg); IR (neat): $\tilde{\nu}$=3051, 2952, 2897, 1583, 1570, 1458, 1442, 1419, 1250, 1126, 1092, 849, 841, 795, 758, 731 cm^{-1}; ^1H NMR ($CDCl_3$, 270.05 MHz): δ=−0.05 (s, 9H), 2.15 (s, 3H), 7.18–7.23 (m, 2H), 7.34–7.41 (m, 2H), 7.55 (d, J=7.8 Hz, 2H), 7.65–7.68 (m, 1H), 8.47 ppm (d, J=4.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 67.80 MHz): δ=−0.1, 19.7, 122.3, 126.8, 128.3, 128.3, 131.4, 134.9, 137.5, 138.4, 145.8, 146.4, 161.0 ppm; MS (70 eV, EI): m/z (%)=240 (2) $[M-H]^+$, 226 (100); elemental analysis: calcd (%) for $C_{15}H_{19}NSi$: C 74.63, H 7.93, N 5.80; found: C 74.51, H 7.76, N 5.74.

17: White solid. R_f=0.40 (hexane/EtOAc=25:1); m.p.: 110–111°C; IR (KBr): $\tilde{\nu}$=3043, 3016, 2951, 2935, 2897, 1502, 1406, 1240, 1107, 933, 829, 773, 746, 721, 663, 619 cm^{-1}; ^1H NMR ($CDCl_3$, 270.05 MHz): δ=0.46 (s, 9H), 7.53 (dd, J=7.8, 4.3 Hz, 1H), 7.67–7.23 (m, 2H), 7.86 (d, J=8.6 Hz, 1H), 7.95 (d, J=7.6 Hz, 1H), 8.12 (d, J=7.3 Hz, 1H), 8.20 (d, J=7.8 Hz, 1H), 8.90 ppm (d, J=4.3 Hz, 1H); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ=3.3, 121.3, 124.6, 126.5, 127.3, 128.7, 129.2, 133.5, 135.2, 135.7, 135.9, 138.6, 145.4, 146.4 ppm; MS (70 eV, EI): m/z (%)=250 (1) $[M-H]^+$, 236 (100); elemental analysis: calcd (%) for $C_{16}H_{17}NSi$: C 76.44, H 6.82, N 5.57; found: C 76.33, H 6.77, N 5.52.

19: Colorless oil. R_f=0.34 (hexane/EtOAc=10:1); b.p.: 130°C (0.5 mmHg); IR (neat): $\tilde{\nu}$=3053, 2951, 2897, 1587, 1566, 1477, 1423, 1284, 1243, 1082, 975, 889, 841, 787, 769, 746, 685, 476 cm^{-1}; ^1H NMR ($CDCl_3$, 270.05 MHz): δ=0.17 (s, 9H), 7.26–7.32 (m, 1H), 7.48–7.54 (m, 2H), 7.64 (d, J=7.6, 1H), 7.79–7.94 (m, 4H), 8.2 (s, 1H), 8.68 ppm (d, J=4.1 Hz, 1H); ^{13}C NMR ($CDCl_3$, 67.80 MHz): δ=1.2, 121.8, 122.9, 126.2, 126.6, 127.4, 127.6, 127.8, 132.3, 133.1, 136.3, 136.4, 137.2, 143.5, 148.3, 161.1 ppm; MS (70 eV, EI): m/z (%)=263 (6) $[M-14]^+$, 262 (100) $[M-Me]^+$; elemental analysis: calcd (%) for $C_{18}H_{19}NSi$: C 77.93, H 6.90, N 5.05; found: C 77.93, H 6.95 N 5.10.

21: Colorless oil. R_f=0.23 (hexane/EtOAc=5:1); b.p.: 150°C (2.5 mmHg); IR (neat): $\tilde{\nu}$=3051, 2952, 2895, 1585, 1562, 1502, 1471, 1427, 1377, 1248, 1149, 1105, 1026, 995, 876, 841, 816, 783, 760, 652 cm^{-1}; ^1H NMR ($CDCl_3$, 270.05 MHz): δ=0.01 (s, 9H), 7.33–7.49 (m, 5H), 7.72–7.91 (m, 4H), 8.79 ppm (d, J=4.3 Hz, 1H); ^{13}C NMR ($CDCl_3$, 67.80 MHz): δ=0.2, 122.3, 125.8, 125.9, 126.0, 126.1, 127.1, 127.7, 130.3, 131.8, 133.5, 135.6, 136.2, 145.0, 149.2, 160.1 ppm; MS (70 eV, EI): m/z (%)=277 (2) $[M]^+$, 262 (100); elemental analysis: calcd (%) for $C_{18}H_{19}NSi$: C 77.93, H 6.90, N 5.05; found: C 77.80, H 6.85, N 5.09.

23: Yellow solid. R_f=0.19 (hexane/EtOAc=5:1); m.p.: 116–117°C; IR (KBr): $\tilde{\nu}$=3060, 3010, 2949, 2895, 1585, 1545, 1500, 1454, 1425, 1406, 1362, 1329, 1227, 1151, 1082, 837, 791, 762, 744, 698, 663 cm^{-1}; ^1H NMR ($CDCl_3$, 270.05 MHz): δ=0.10 (s, 9H), 7.20–7.34 (m, 2H), 7.39–7.52 (m, 3H), 7.59–7.70 (m, 5H), 7.75–7.77 (m, 2H), 8.15 (d, J=7.6 Hz, 1H), 8.27 (s, 1H), 8.65 ppm (d, J=4.3 Hz, 1H); ^{13}C NMR ($CDCl_3$, 67.80 MHz): δ=1.4, 108.3, 109.9, 110.0, 116.8, 119.9, 120.4, 120.6, 121.4, 122.9, 123.2, 126.2, 126.9, 127.3, 129.8, 136.3, 136.3, 137.4, 137.4, 140.1, 141.3, 148.1, 161.6 ppm; MS (70 eV, EI): m/z (%)=392 (2) $[M]^+$, 378 (32), 377 (100), 189 (18); HRMS: m/z calcd for $C_{26}H_{24}N_2Si$: 392.1709; found: 392.1713.

25a: Colorless oil. R_f=0.32 (hexane/EtOAc=5:1); b.p.: 130°C (2.0 mmHg); IR (neat): $\tilde{\nu}$=3051, 3012, 2952, 2897, 1587, 1568, 1475, 1425, 1248, 1149, 1099, 1051, 995, 881, 839, 791, 768, 748, 682, 648, 584, 472 cm^{-1}; ^1H NMR ($CDCl_3$, 270.05 MHz): δ=0.06 (s, 9H), 2.40 (s, 3H), 7.21–7.29 (m, 3H), 7.48 (d, J=7.6 Hz, 1H), 7.60 (d, J=7.6 Hz, 1H), 7.73 (td, J=7.6, 1,6 Hz, 1H), 8.63 ppm (d, J=4.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 67.80 MHz): δ=0.9, 21.3, 121.8, 122.9, 128.1, 129.4, 135.4, 135.6, 136.1, 138.5, 147.0, 148.3, 161.3 ppm; MS (70 eV, EI): m/z (%)=240 (3) $[M-H]^+$, 226 (100); HRMS: m/z calcd for $C_{15}H_{19}NSi$: 241.1287; found: 241.1244.

25b: White solid. R_f=0.30 (hexane/EtOAc=5:1); m.p.: 53–54°C; IR (KBr): $\tilde{\nu}$=3051, 3005, 2960, 2947, 2897, 2835, 1589, 1554, 1473, 1423, 1404, 1304, 1277, 1252, 1215, 1180, 1151, 1103, 1053, 1030, 879, 841, 831, 793, 762, 762, 754, 727, 681 cm^{-1}; ^1H NMR ($CDCl_3$, 270.05 MHz): δ=0.05 (s, 9H), 3.85 (s, 3H), 6.95 (dd, J=8.1, 2.4 Hz, 1H), 7.02 (d, J=2.4 Hz, 1H), 7.24–7.26 (m, 1H), 7.48 (d, J=7.6 Hz, 1H), 7.62 (d, J=8.1 Hz, 1H), 7.75 (td, J=7.6, 1.6 Hz, 1H), 8.65 ppm (d, J=4.3 Hz, 1H); ^{13}C NMR ($CDCl_3$, 67.80 MHz): δ=1.0, 55.2, 112.9, 114.6, 122.0, 122.9, 130.2, 136.2, 136.8, 148.3, 148.5, 159.8, 161.0 ppm; MS (70 eV, EI): m/z (%)=256 (1) $[M-H]^+$, 242 (100); elemental analysis: calcd (%) for $C_{15}H_{19}NOSi$: C 69.99, H 7.44, N 5.44; found: C 69.98, H 7.28, N 5.42.

25c: Colorless oil. R_f=0.30 (hexane/EtOAc=10:1); b.p.: 130°C (1.5 mmHg); IR (neat): $\tilde{\nu}$=3060, 2978, 2951, 2897, 1591, 1552, 1471, 1425, 1383, 1302, 1248, 1209, 1107, 1051, 1032, 995, 968, 839, 793, 768, 748, 685, 615 cm^{-}; ^1H NMR ($CDCl_3$, 270.05 MHz): δ=0.04 (s, 9H), 1.35 (d, J=5.9 Hz, 6H), 4.62 (sept, J=5.9 Hz, 1H), 6.92 (dd, J=8.1, 2.4 Hz, 1H), 7.00 (d, J=2.4 Hz, 1H), 7.24–7.29 (m, 1H), 7.47 (d, J=7.6 Hz, 1H), 7.59 (d, J=8.1 Hz, 1H), 7.74 (td, J=7.6, 1.6 Hz, 1H), 8.64 ppm (d, J=4.1 Hz, 1H); ^{13}C NMR ($CDCl_3$, 67.80 MHz): δ=1.1, 22.2, 69.7, 114.5, 116.4, 121.9, 122.8, 129.9, 136.2, 136.8, 148.2, 148.4, 158.2, 161.0 ppm; MS (70 eV, EI): m/z (%)=270 (89) $[M-Me]^+$, 228 (100); HRMS: m/z calcd for $C_{17}H_{23}NOSi$: 285.1549; found: 286.1636.

25d: White solid. R_f=0.20 (hexane/EtOAc=5:1); m.p.: 109–110°C; IR (KBr): $\tilde{\nu}$=3078, 3047, 2954, 2893, 1603, 1585, 1537, 1427, 1363, 1250, 1227, 1107, 854, 835, 795, 758 cm^{-1}; ^1H NMR ($CDCl_3$, 270.05 MHz): δ=0.04 (s, 9H), 3.00 (s, 6H), 6.77–6.81 (m, 2H), 7.24–7.28 (m, 1H), 7.49 (d, J=7.8 Hz, 1H), 7.56 (d, J=7.8 Hz, 1H), 7.73 (td, J=7.6, 1.6 Hz, 1H), 8.65 ppm (d, J=4.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 67.80 MHz): δ=1.0, 40.4, 111.4, 113.0, 121.7, 123.1, 124.5, 136.0, 136.3, 148.1, 148.3, 150.5, 162.1 ppm; MS (70 eV, EI): m/z (%)=270 (1) $[M]^+$, 255 (100); elemental analysis: calcd (%) for $C_{16}H_{22}N_2Si$: C 71.06, H 8.20, N 10.36; found: C 71.01, H 8.09, N 10.34.

25e: Colorless oil. R_f=0.24 (hexane/EtOAc=10:1); b.p.: 175°C (1.5 mmHg); IR (neat): $\tilde{\nu}$=3059, 2981, 2954, 2898, 1720, 1587, 1568, 1477, 1427, 1398, 1367, 1309, 1246, 1124, 1095, 1084, 843, 795, 756 cm^{-1}; ^1H NMR ($CDCl_3$, 270.05 MHz): δ=0.10 (s, 9H), 1.39 (t, J=7.0 Hz, 3H), 4.39 (q, J=7.0 Hz, 2H), 7.28 (dd, J=6.5, 4.6 Hz 1H), 7.55 (d, J=8.1 Hz, 1H), 7.73–7.81 (m, 2H), 8.04 (dd, J=7.6, 1.4 Hz, 1H), 8.13 (s, 1H), 8.64 ppm (d, J=4.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 67.80 MHz): δ=0.8, 14.4, 61.0, 122.2, 122.8, 127.8, 128.9, 130.5, 135.5, 136.4, 145.5, 146.9, 148.3, 160.2, 166.3 ppm; MS (70 eV, EI): m/z (%)=298 (3) $[M-H]^+$, 284 (100); elemental analysis: calcd (%) for $C_{17}H_{21}NO_2Si$: C 68.19, H 7.07, N 4.68; found: C 68.16, H 6.91, N 4.70.

25f: Colorless oil. R_f=0.34 (hexane/EtOAc=20:1); b.p.: 115°C (2.0 mmHg); IR (neat): $\tilde{\nu}$=3066, 3020, 2954, 2898, 1589, 1570, 1477, 1400, 1338, 1281, 1252, 1171, 1128, 1066, 993, 904, 854, 837, 793, 771, 748, 690,

658, 621, 484 cm^{-1}; ^1H NMR ($CDCl_3$, 270.05 MHz): $\delta = 0.11$ (s, 9H), 7.32 (dd, $J = 7.3$, 5.1 Hz, 1H), 7.53 (d, $J = 8.1$ Hz, 1H), 7.63 (d, $J = 7.8$ Hz, H), 7.70 (s, 1H), 7.76–7.85 (m, 2H), 8.67 ppm (d, $J = 4.9$ Hz, 1H); ^{13}C NMR ($CDCl_3$, 67.80 MHz): $\delta = 0.7$, 122.5, 122.8, 123.6 (q, $J = 3.9$ Hz), 124.0 (q, $J = 271.1$ Hz), 124.8 (q, $J = 3.9$ Hz), 130.7 (q, $J = 32.3$ Hz), 135.8, 136.5, 144.3, 147.4, 148.5, 159.8 ppm; MS (70 eV, EI): m/z (%) = 294 (4) $[M-H]^+$, 280 (100); elemental analysis: calcd (%) for $C_{15}H_{16}F_3NSi$: C 60.99, H 5.46, N 4.74; found: C 60.83, H 5.57, N 4.72.

27a: Colorless oil. $R_f = 0.17$ (hexane/EtOAc = 5:1); b.p.: 155 °C (3.5 mmHg); IR (KBr): $\tilde{\nu} = 3066$, 2958, 2898, 1597, 1581, 1556, 1462, 1427, 1302, 1248, 1213, 1174, 1117, 1097, 1059, 1034, 883, 837, 808, 761, 748, 731, 700, 683, 594 cm^{-1}; ^1H NMR ($CDCl_3$, 270.05 MHz): $\delta = -0.08$ (s, 9H), 2.16 (s, 3H), 3.81 (s, 3H), 6.74 (d, $J = 2.4$ Hz, 1H), 6.92 (dd, $J = 8.1$, 2.4 Hz, 1H), 7.21 (dd, $J = 7.6$, 4.9 Hz, 1H), 7.54–7.59 (m, 2H), 8.47 ppm (d, $J = 3.8$ Hz, 1H); ^{13}C NMR ($CDCl_3$, 67.80 MHz): $\delta = 0.0$, 19.7, 55.2, 112.7, 114.2, 122.5, 129.5, 131.5, 136.4, 137.7, 145.7, 147.8, 159.6, 160.6 ppm; MS (70 eV, EI): m/z (%) = 257 (21) $[M-14]^+$, 256 (100) $[M-Me]^+$; elemental analysis: calcd (%) for $C_{16}H_{21}NOSi$: C 70.80, H 7.80, N 5.16; found: C 70.90, H 7.74, N 5.17.

27b: Colorless oil. $R_f = 0.36$ (hexane/EtOAc = 5:1); b.p.: 130 °C (2.0 mmHg); IR (neat): $\tilde{\nu} = 3053$, 2954, 2898, 1585, 1572, 1446, 1392, 1336, 1281, 1252, 1169, 1068, 1057, 860, 843, 800, 791, 771, 758, 737, 721, 683, 633 cm^{-1}; ^1H NMR ($CDCl_3$, 270.05 MHz): $\delta = 0.02$ (s, 9H), 2.15 (s, 3H), 7.22–7.27 (m, 1H), 7.46 (s, 1H), 7.58–7.63 (m, 2H), 7.80 (d, $J = 7.8$ Hz, 1H), 8.49 ppm (d, $J = 4.3$ Hz, 1H); ^{13}C NMR ($CDCl_3$, 67.80 MHz): $\delta = -0.3$, 16.6, 122.9, 123.3 (q, $J = 3.9$ Hz), 124.0 (q, $J = 271.1$ Hz), 124.9 (q, $J = 3.9$ Hz), 130.4 (q, $J = 32.3$ Hz), 131.4, 135.5, 137.9, 143.8, 146.1, 147.0, 159.6 ppm; MS (70 eV, EI): m/z (%) = 308 (2) $[M-H]^+$, 294 (100); elemental analysis: calcd (%) for $C_{16}H_{18}F_3NSi$: C 62.11, H 5.86, N 4.53; found: C 61.88, H 5.90, N 4.58.

29: Colorless oil. $R_f = 0.37$ (hexane/EtOAc = 5:1); b.p.: 110 °C (2.0 mmHg); IR (neat): $\tilde{\nu} = 3084$, 3051, 3006, 2954, 2897, 1587, 1564, 1460, 1431, 1389, 1282, 1250, 1174, 1153, 1120, 1095, 1041, 991, 858, 838, 771, 754, 694, 638, 620 cm^{-1}; ^1H NMR ($CDCl_3$, 270.05 MHz): $\delta = 0.32$ (s, 9H), 7.22–7.26 (m, 2H), 7.47 (t, $J = 7.6$ Hz, 1H), 7.59 (d, $J = 7.6$ Hz, 1H), 7.72–7.80 (m, 2H), 7.95 (d, $J = 8.1$ Hz, 1H), 8.12 (s, 1H), 8.71 ppm (d, $J = 4.6$ Hz, 1H); ^{13}C NMR (67.80 MHz): $\delta = -0.9$, 120.7, 121.9, 127.4, 128.0, 131.7, 133.9, 136.6, 138.5, 140.9, 157.8 ppm; MS (70 eV, EI): m/z (%) = 227 (27) $[M]^+$, 212 (100); elemental analysis: calcd (%) for $C_{14}H_{17}NSi$: C 73.95, H 7.54, N 6.16; found: C 74.06, H 7.32, N 6.36.

30: Colorless oil. $R_f = 0.14$ (hexane/EtOAc = 20:1); b.p.: 120 °C (2.0 mmHg); IR (neat): $\tilde{\nu} = 3051$, 3010, 2954, 2897, 1587, 1566, 1475, 1425, 1367, 1250, 1157, 1130, 1038, 993, 841, 793, 752, 694, 636, 586, 480, 445 cm^{-1}; ^1H NMR ($CDCl_3$, 270.05 MHz): $\delta = 0.07$ (s, 9H), 0.29 (s, 9H), 7.26–7.30 (m, 1H), 7.48–7.57 (m, 3H), 7.68–7.79 (m, 2H), 8.65 ppm (d, $J = 4.3$ Hz, 1H); ^{13}C NMR ($CDCl_3$, 67.80 MHz): $\delta = -1.1$, 0.8, 121.8, 123.1, 132.2, 133.3, 133.6, 134.5, 136.2, 139.7, 141.0, 148.4, 161.6 ppm; MS (70 eV, EI): m/z (%) = 298 (2) $[M-H]^+$, 284 (100); elemental analysis: calcd (%) for $C_{17}H_{25}NSi_2$: C 68.16, H 8.41, N 4.68; found: C 68.43, H 8.19, N 4.90.

Acknowledgements

This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas "Advanced Molecular Transformations of Carbon Resources" and by the Program of Promotion of Environmental Improvement to Enhance Young Researchers' Independence of the Special Coordination Funds for Promoting Science and Technology from the Ministry of Education, Culture, Sports, Science, and Technology, Japan. M.T. also acknowledges the Sumitomo Foundation and the Kurata Memorial Hitachi Science and Technology Foundation. We also thank the Instrumental Analysis Center, Faculty of Engineering, Osaka University for assistance with MS, HRMS, and elemental analysis.

[1] For recent reviews, see: a) F. Kakiuchi, N. Chatani, *Adv. Synth. Catal.* **2003**, *345*, 1077; b) A. R. Dick, M. S. Sanford, *Tetrahedron* **2006**, *62*, 2439; c) K. Godula, D. Sames, *Science* **2006**, *312*, 67; d) D. Alberico, M. E. Scott, M. Lautens, *Chem. Rev.* **2007**, *107*, 174; e) L.-C. Campeau, D. R. Stuart, K. Fagnou, *Aldrichimica Acta* **2007**, *40*, 35; f) *Topics in Organometallic Chemistry*, *Vol. 24* (Ed.: N. Chatani), Springer, Berlin, **2007**.

[2] E. W. Colvin, *Silicon Reagents in Organic Synthesis*, Academic Press, London, **1988**.

[3] The introduction of main-group elements into π-conjugated molecules has become a promising design strategy for organic optoelectronic materials; see: M. Elbing, G. C. Bazan, *Angew. Chem.* **2008**, *120*, 846; *Angew. Chem. Int. Ed.* **2008**, *47*, 834.

[4] For selected reports, see: a) K. Ezbiansky, P. I. Djurovich, M. LaForest, D. J. Sinning, R. Zayes, D. H. Berry, *Organometallics* **1998**, *17*, 1455; b) F. Kakiuchi, M. Matsumoto, K. Tsuchiya, K. Igi, T. Hayamizu, N. Chatani, S. Murai, *J. Organomet. Chem.* **2003**, *686*, 134.

[5] a) N. Tsukada, J. F. Hartwig, *J. Am. Chem. Soc.* **2005**, *127*, 5022; b) M. Murata, N. Fukuyama, J.-i. Wada, S. Watanabe, Y. Masuda, *Chem. Lett.* **2007**, 910.

[6] F. Kakiuchi, M. Matsumoto, M. Sonoda, T. Fukuyama, N. Chatani, S. Murai, N. Furukawa, Y. Seki, *Chem. Lett.* **2000**, 750.

[7] T. Sakakura, Y. Tokunaga, T. Sodeyama, M. Tanaka, *Chem. Lett.* **1987**, 2375.

[8] a) M. Ishikawa, S. Okazaki, A. Naka, H. Sakamoto, *Organometallics* **1992**, *11*, 4135; b) M. Ishikawa, A. Naka, J. Ohshita, *Organometallics* **1993**, *12*, 4987; c) A. Naka, K. K. Lee, K. Yoshizawa, T. Yamabe, M. Ishikawa, *Organometallics* **1999**, *18*, 4524.

[9] a) T. Ishiyama, K. Sato, Y. Nishio, N. Miyaura, *Angew. Chem.* **2003**, *115*, 5504; *Angew. Chem. Int. Ed.* **2003**, *42*, 5346; b) T. Ishiyama, K. Sato, Y. Nishio, N. Miyaura, *Chem. Commun.* **2005**, 5065; c) T. Saiki, Y. Nishio, T. Ishiyama, N. Miyaura, *Organometallics* **2006**, *25*, 6068.

[10] a) N. A. Williams, Y. Uchimaru, M. Tanaka, *J. Chem. Soc. Chem. Commun.* **1995**, 1129; b) N. A. Williams, Y. Uchimaru, M. Tanaka, *Dalton Trans.* **2003**, 236.

[11] M. Tobisu, Y. Kita, N. Chatani, *J. Am. Chem. Soc.* **2006**, *128*, 8152.

[12] N. Chatani, Y. Ie, F. Kakiuchi, S. Murai, *J. Org. Chem.* **1997**, *62*, 2604.

[13] A similar trend in selectivity toward mono/difunctionalization was observed; see: Y. Ie, N. Chatani, T. Ogo, D. R. Marshall, T. Fukuyama, F. Kakiuchi, S. Murai, *J. Org. Chem.* **2000**, *65*, 1475.

[14] A. D. Ryabov, *Chem. Rev.* **1990**, *90*, 403; see also Ref. [1d].

[15] When a mixture of 2-phenylpyridine **1** and Et_3SiH was subjected to the catalytic conditions, the corresponding silylated product was obtained in only 10% yield.

[16] Competition experiments would give us more insight into the mechanism for the C–H bond cleavage. Indeed, we examined an intramolecular competition experiment by using 2-(2-deuteriophenyl)pyridine. However, the kinetic isotope effect of the reaction cannot be determined accurately owing to H/D scrambling between the starting material and the co-produced hydrosilane.

[17] W. D. Jones, *Acc. Chem. Res.* **2003**, *36*, 140.

[18] F. Kakiuchi, S. Murai, *Acc. Chem. Res.* **2002**, *35*, 826.

[19] A. Ford, E. Sinn, S. Woodward, *J. Organomet. Chem.* **1995**, *493*, 215.

[20] D. Kalyani, A. R. Dick, W. Q. Anani, M. S. Sanford, *Tetrahedron* **2006**, *62*, 11483.

[21] B. M. Holligan, J. C. Jeffery, M. K. Norgett, E. Schatz, M. D. Ward, *J. Chem. Soc. Dalton Trans.* **1992**, 3345.

Received: March 12, 2008
Published online: May 21, 2008

