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Novel Carbon–Carbon Bond Formation through Mizoroki–Heck Type Reaction of Silanols and Organotin Compounds

Kazunori Hirabayashi, Jun-ichi Ando, Jun Kawashima, Yasushi Nishihara, Atsunori Mori,* and Tamejiro Hiyama#

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Nagatsuta, Yokohama 226-8503

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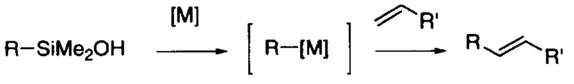
The reaction of dimethyl(phenyl)silanol with butyl acrylate in the presence of a stoichiometric amount of $Pd(OAc)_2$ or by a combined use of 0.1 molar amount of $Pd(OAc)_2$ and $Cu(OAc)_2$/LiOAc (molar ratio 3/2) gave butyl cinnamate in 76% or 57% yield, respectively. The similar reaction with tributyl(phenyl)tin also proceeded in 77% yield. The organotin compound was shown to react faster than the silanol, although the tin reagent sometimes induced undesirable homo-coupling, while the reaction with silanol did not give such by-product.

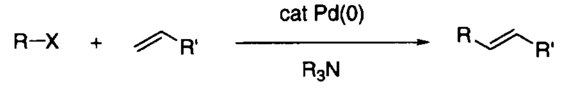
Although a wide variety of synthetic organic reactions have been developed using organosilicon reagents,[1] silanols have remained unexplored as a practical tool for organic syntheses. Few efforts have been devoted to the synthetic utilization of silanols due mainly to the synthetic difficulties, since silanols are considered unstable to moisture, heat, acids, and bases. However, we have recently reported that silanols can be easily prepared by alkylative cleavage of cyclic siloxanes with organolithium reagents.[2—4] We have also found that the hydroxy group of silanols allows us to achieve Simmons–Smith cyclopropanation of alkenylsilanols.[3,5] The related hydroxy-assisted transformations of alkenylsilanols are realized in the reactions of epoxidation,[6] halo-cyclization,[7] and reactions of dilithiated allyl- and alkynylsilanol with electrophiles.[8]

We then focused on the activation of a carbon–silicon bond of silanols for a carbon–carbon bond-forming reaction. Although carbon–carbon bond-forming reactions with aryl- and alkenylsilanes have already been realized by the palladium-catalyzed cross-coupling reaction, an additional fluoride ion activator is required to effect the reaction.[9] Moreover, carbon–silicon bonds are generally inferior in reactivity to related carbon–boron or carbon–tin bonds. However, enhancement of the reactivity of organosilicon compounds comparable to the boron and tin reagents by the introduction of a hydroxy group into the silicon atom, if possible, would open a new area of organosilicon chemistry.

We envisaged that the hydroxy group of silanols might assist the reaction with a transition metal catalyst to achieve a carbon–carbon bond-forming reaction without using the fluoride ion. The organic moiety of silanols would readily migrate to a metallic center to complete transmetalation. The migrated organic group on the metal center would be able to react with various electrophiles to form a variety of carbon–carbon bonds. For example, a possible reaction with an olefin via an addition-elimination process might complete the Mizoroki–Heck (MH) type reaction (Eq. 1). The Mizoroki–Heck reaction is the reaction of an aryl or alkenyl halide with an olefin to give aryl- or alkenyl-substituted olefins by use of a palladium(0) catalyst and a tertiary amine via the addition-elimination, as shown in Eq. 2.[10] In lieu of halides, organometallic compounds have rarely been employed.[11—16]



(1)



(2)

We herein report that aryl- and alkenylsilanols and aryltin reagents undergo the MH type reaction in the presence of palladium(II) acetate and we discuss the relative reactivity between the two reagents.[17]

Results and Discussion

When dimethyl(phenyl)silanol (**1a**) was treated with methyl vinyl ketone (**2a**) in the presence of a stoichiometric amount of palladium(II) acetate in dimethoxyethane (DME) at 60 °C for 21 h, 4-phenyl-3-buten-2-one (**3a**) was obtained in 67% yield. In the absence of the $Pd(OAc)_2$, no reaction took place. We examined the reaction of **1a** with **2a** using other palladium species in DME at 60 °C; the results are shown in Table 1. The reaction with 0.2 molar amount of palladium(II) acetate afforded **3a** in 18% yield, showing the dependency of the stoichiometry of the palladium species (Entries 1 and 3). Palladium(II) chloride was partly effective to give **3a** (37% yield; Entry 4). Triphenylphosphine com-

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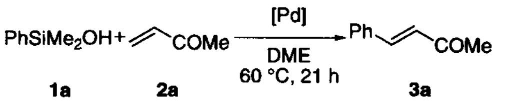
Present address: Department of Material Chemistry, Graduate School of Engineering, Kyoto University, Yoshida, Sakyo-ku, Kyoto 606-8501, Japan.

Table 1. MH Type Reaction with Various Palladium Spieces[a)]



Entry	[Pd]	Yield/%
1	$Pd(OAc)_2$	67
2	—	NR
3	$Pd(OAc)_2$ (0.04 mmol)	18
4	$PdCl_2$	37
5	$Pd(OAc)_2 + PPh_3$ (0.04 mmol)	NR
6	$Pd(PPh)_4$	NR
7	$Pd_2(dba)_3 \cdot CHCl_3$	NR
8	Pd/C	NR

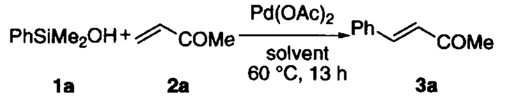
a) The reaction was carried out using **1a** (0.3 mmol), **2a** (0.3 mmol), [Pd] (0.3 mmol) in DME (2 mL) at 60 °C for 21 h.

pletely inhibited the reaction (Entry 5). Palladium(0) species such as $Pd(PPh_3)_4$, $Pd_2(dba)_3 \cdot CHCl_3$, and Pd/C were totally ineffective (Entries 6, 7, and 8).

We then investigated solvent effect using palladium(II) acetate under similar conditions (60 °C, 13 h). The results are summarized in Table 2. The reaction proceeded in a variety of solvents in moderate to excellent yields. It was noteworthy that the reaction occurred in a nonpolar solvent, hexane, as well as in a protic solvent, AcOH (Entries 6 and 8).

We next examined the substituent on silicon applicable to the reaction and the results are summarized in Table 3. All silanols **1a**—**1d** afforded coupling product **3a** in good yields (Entries 1, 2, 3, and 4). Methoxy(dimethyl)(phenyl)silane (**1e**) also gave **3a**, though in a slightly lower yield (Entry 5). On the contrary, no reaction occurred with pentamethyl(phenyl)disiloxane (**1f**) or trimethyl(phenyl)silane (**1g**) (Entry 6 or 7, respectively). These results clearly show that the hydroxy group plays a significant role in the promotion of the reaction. We also examined fluorosilanes **1h**—**1j**. Although trifluoro(phenyl)silane (**1h**) afforded the corresponding product in 79% yield, the reaction with the difluoro or monofluoro derivative (**1i** or **1j**) was less effective. These results indicate that the reactivity of silanols (**1a**—**1d**) is comparable to that of **1h**, which was shown to be an excellent organosilicon reagent for the successful cross-coupling reaction.[9]

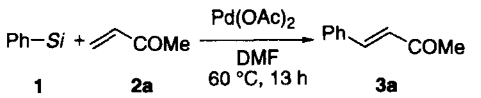
Table 2. Solvent Effect of the MH Type Reaction[a)]



Entry	Solvent	Yield%[b)]
1	1,2-Dimethoxyethane (DME)	64
2	THF	45
3	CH_3CN	66
4	Dimethyl sulfoxide (DMSO)	62
5	Dimethylformamide (DMF)	71
6	Hexane	38
7	Toluene	55
8	AcOH	77

a) The reaction was carried out using **1a** (0.3 mmol), **2a** (0.3 mmol), $Pd(OAc)_2$ (0.3 mmol), in a solvent at 60 °C for 13 h. b) Determined by ^1H NMR with $CCl_2{=}CHCl$ as an internal standard.

Table 3. Substituent Effect on Silicon[a)]



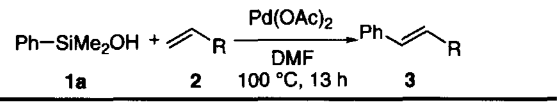
Entry	Si		Yield/%[b)]
1	$SiMe_2OH$	(**1a**)	64
2	$SiEt_2OH$	(**1b**)	66
3	SiPhMeOH	(**1c**)	80
4	$SiPh_2OH$	(**1d**)	57
5	$SiMe_2(OMe)$	(**1e**)	47
6	$SiMe_2OSiMe_3$	(**1f**)	NR
7	$SiMe_3$	(**1g**)	Trace
8	SiF_3	(**1h**)	79
9	$SiMeF_2$	(**1i**)	32
10	$SiMe_2F$	(**1j**)	Trace
11	$SiMe_2Cl$	(**1k**)	6

a) The reaction was carried out using **1** (0.3 mmol), **2a** (0.3 mmol), $Pd(OAc)_2$ (0.3 mmol), DME (2 mL). b) Determined by ^1H NMR with $CCl_2{=}CHCl$ as an internal standard.

The reactions of **1a** with various olefins **2** were studied and the results are shown in Table 4. An olefin substituted with an electron-withdrawing group gave the corresponding products smoothly in high yields, whereas styrene (**2e**) did not react with **1a** (Entry 5).

Since the product in the reaction of silanols with olefins appears similar to that of the MH reaction, the mechanism of the silanol reaction should also be similar, despite the use of a different reaction system (catalytic Pd(0) with a tertiary amine vs equimolar Pd(II)). The initial step of the MH reaction is considered to be oxidative addition of Pd(0) to a carbon–halogen bond of RX to give R–Pd(II)–X. Insertion of an olefin, followed by β-elimination, leads to a substituted olefin along with the formation of Pd(0) and HX.[10] Based on this mechanism, we consider that the mechanism shown in Fig. 1 is plausible. In contrast to the oxidative addition of palladium(0) towards RX, the oxidative addition

Table 4. Reaction with Olefin in the Presence of Equimolar Amount of $Pd(OAc)_2$[a)]



Entry	R		Yield/%
1	COMe	(**2a**)	80
2	CO_2Bu	(**2b**)	76
3	CHO	(**2c**)	83
4	CN	(**2d**)	86
5	Ph	(**2e**)	NR

a) Conditions: A mixture of **1a** (0.3 mmol), **2** (0.3 mmol), and $Pd(OAc)_2$ (0.3 mmol) in DMF (2 mL) was stirred at 100 °C for 13 h.

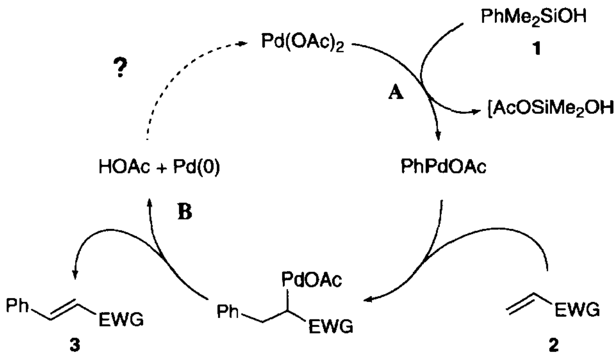
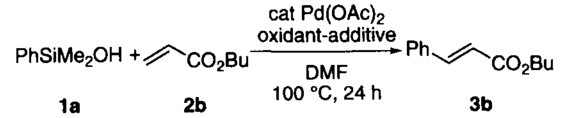


Fig. 1. The MH type reaction mechanism of a silanol.

of palladium(0) to the carbon–silicon bond of silanols would be less plausible. Indeed, the MH type reaction of **1a** with **2a** in the presence of palladium(0) did not take place (Table 1). Hence, the active palladium species responsible for the initial reaction should be palladium(II). Thus, we may assume transmetalation of the phenyl group on **1** to palladium(II) acetate, as illustrated in step **A** in Fig. 1. Subsequent reactions are followed in the manner of the MH reaction. Thus, the reaction finally affords substituted olefins along with the formation of palladium(0) species (step **B**).

In light of the above mechanistic discussion, it is obvious that, if the produced palladium(0) is oxidized to regenerate palladium(II), a catalytic version would be viable. Various oxidants were surveyed and a combination of copper(II) acetate and lithium acetate was found to realize the catalytic reaction successfully. As summarized in Table 5, copper(II) acetate or lithium acetate alone was ineffective (Entries 2 and 3). Lithium acetate probably enhances the solubility of copper(II) acetate. In place of LiOAc, $NaOCOCF_3$ (Entry 4), NaOAc (Entry 5), or LiCl (Entry 6) was also effective, although the yield was slightly inferior. The highest yield was achieved by the use of 3 molar amounts of copper(II) acetate and 2 molar amounts of lithium acetate (Entry 10). The reaction using $CuCl_2$–LiOAc (Entry 11) lowered the yield to 22%. The use of $CuCl_2$–LiCl (Entry 12) system resulted in no reaction. Benzoquinone as an oxidant did not effect the reaction (Entry 13).

Table 5. The Effect of Additives in the MH Type Reactions with a Catalytic Amount of $Pd(OAc)_2$[a)]



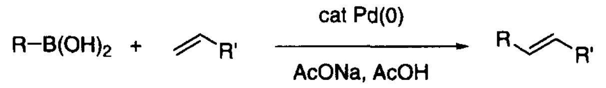
Entry	Oxidant		Additive		Yield/%[b)]
1	$Cu(OAc)_2$	(2)	LiOAc	(2)	78
2	$Cu(OAc)_2$	(2)	—		NR
3	—		LiOAc	(2)	NR
4	$Cu(OAc)_2$	(2)	$NaOCOCF_3$	(2)	70
5		(2)	NaOAc	(2)	66
6		(2)	LiCl	(2)	78
7		(2)	LiOAc	(1)	58
8		(2)		(3)	44
9		(1)		(2)	61
10		(3)		(2)	>99
11[c)]	$CuCl_2$	(3)		(2)	22
12[c)]		(3)	LiCl	(2)	NR
13[c)]	Benzoquinone	(3)	LiOAc	(2)	NR

a) The reaction was carried out usig **1a** (0.3 mmol), **2b** (0.3 mmol), $Pd(OAc)_2$ (0.03 mmol) in DMF (2 mL) at 100 °C for 24 h. b) GC yield with decane as an internal standard are given. c) Reaction time was 12 h.

The reaction of silanols **1** with various olefins **2** using palladium(II) acetate (0.1 mmol), copper(II) acetate (3 mmol), and lithium acetate (2 mmol) was studied in DMF at 100 °C; the results are summarized in Table 6. Monosubstituted ethenes gave the corresponding olefinic products in moderate yields. Although styrene (**2e**) failed to react under the stoichiometric conditions (Entry 5, Table 4), the catalytic system was applicable (Entry 6).[18] Note that (*E*)-ethyl crotonate (**2g**) gave product **3g** in 55% yield as a 9 : 1 mixture of (*E*) and (*Z*)-isomers, whereas diethyl fumarate (**2h**) gave solely (*Z*)-isomer **3h** in 49% yield. Methyl 3-methylbutenoate (**2i**) gave a complex mixture. Dimethyl(phenyl)(vinyl)silane (**2j**) also reacted with **1a** in 57% yield. Even *ortho*-substituted arylsilanols (**4d**) could undergo the reaction. Alkenylsilanols such as **6a** and **6b** also reacted with **2f** to give 2,4-pentadienoates **7a** and **7b**, respectively.

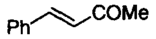
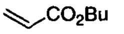
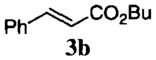
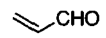
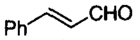
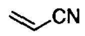
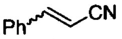
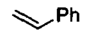
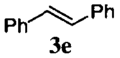
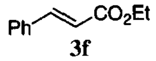
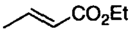
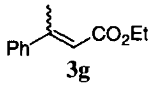
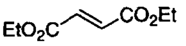
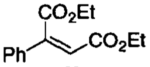
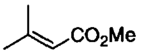
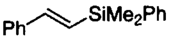
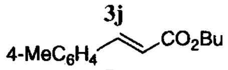
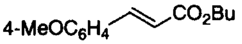
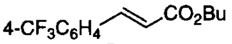
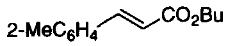
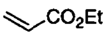
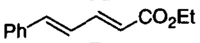
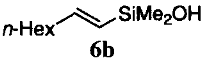
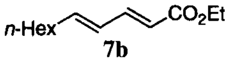
It should be pointed out that the reaction of silanols with olefins affords products similar to those of the MH reaction that uses organic halides as a coupling partner. Although metallic reagents of methyllithium,[11] Grignard reagents,[12] dihydroxyboranes,[13] organolead,[14] organopentafluoro silicates ($RSiF_5{}^{2-}$),[15] diarylmercuries,[16] and tetraaryltins[16] have been used for the MH reaction, there have been no reports on the use of neutral tetravalent organosilicon compounds. The example of the MH type carbon–carbon bond-forming reaction using neutral organosilicon compound is thus realized for the first time by the silanol. Although trifluoro- and difluoroarylsilanes also effect the MH type reaction, it is remarkable that a single substitution with a hydroxy group on silicon is as effective as two or three fluorine substituents, which generally increase the electrophilicity of a silicon center.[9] In addition, it is especially noteworthy that the reaction proceeds without any nucleophilic additive such as a fluoride ion that is necessary for the cross-coupling reaction of organosilicon compounds.

We then explored a possibility of the MH type reaction using a trialkyl(aryl)tin,[19] since organotin compounds are often compared with organosilicon and -boron compounds in the cross-coupling reactions.[20] Uemura reported a similar reaction using dihydroxy(phenyl)borane. The reaction, in contrast to our results, proceeds with a palladium(0) catalyst probably via oxidative addition to a carbon–boron bond (Eq. 3).[13] We have therefore focused on the possibility of organotin compounds undergoing oxidative addition[21] or transmetalation.[22]



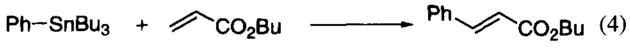
(3)

Table 6. Reactions of Organosilanols with Olefins in the Presence of $Pd(OAc)_2$[a]

Entry	Silanol	Olefin	Products	Yield/%
1	Ph-$SiMe_2OH$ **1a**	 **2a**	 **3a**	48
2[b]		 **2b**		57
3			**3b**	69
4		 **2c**	 **3c**	37
5		 **2d**	 **3d**	34[c]
6		 **2e**	 **3e**	63
7		 **2f**	 **3f**	56
8[d]		 **2g**	 **3g**	55[e]
9		 **2h**	 **3h**	49
10[f]		 **2i**	Complex mixture	
11		 **2j**	 **3j**	57
12	4-MeC_6H_4-$SiMe_2OH$ **4a**	 **2b**	 **5a**	54
13	4-$MeOC_6H_4$-$SiMe_2OH$ **4b**		 **5b**	55
14	4-$CF_3C_6H_4$-$SiMe_2OH$ **4c**		 **5c**	65
15	2-MeC_6H_4-$SiMe_2OH$ **4d**		 **5d**	54
16[g]	 **6a**	 **2f**	 **7a**	41
17[g]	 **6b**		 **7b**	52

a) Unless otherwise noted, all the reaction was carried out in DMF (3 mL), using a silanol (0.5 mmol), an olefin (0.5 mmol), $Pd(OAc)_2$ (0.05 mmol), $Cu(OAc)_2$ (1.5 mmol), and LiOAc (1.0 mmol) at 100 °C for 24 h. b) Reaction was carried out at r.t. for 48 h. c) E/Z = ca. 2/1 by ^{1}H NMR. d) Reaction time was 48 h. e) E/Z = ca. 9/1 by ^{1}H NMR. f) Reaction time was 72 h. g) Reaction time was 44 h.

We first examined the reaction of tributyl(phenyl)tin (**8a**) with **2b** under the conditions for silanols (Eq. 4). The reaction proceeded in the presence of a stoichiometric amount of palladium(II) acetate to afford **3b** in 60% yield. The catalytic conditions with $Pd(OAc)_2/Cu(OAc)_2$/LiOAc also gave **3b** in 80% yield, whereas **3b** was not produced under the Uemura conditions. These results suggest that organotin compounds undergo the MH type reaction through a mechanism similar to silanols, namely, a transmetalation sequence. We next studied the scope of organotin compounds **8** and olefins **2**. The results are summarized in Table 7. The tin reagents **8** gave products in comparable or better yields than silanols. Although some homo-coupling products accompanied the desired products, the homo-coupling was, to some extent, suppressed when the reactions were carried out under an argon atmosphere.[23] Nevertheless, the reaction of tributyl(styryl)tin (**9**) with **2b** afforded homo-coupled product **10** in 51% yield as a sole product; by contrast, the corresponding alkenylsilanol could effect the MH type reaction (Table 6, Entries 16 and 17).

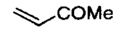
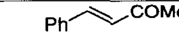
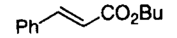
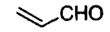
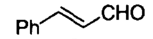
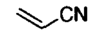
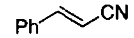
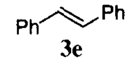
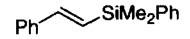
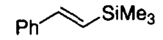
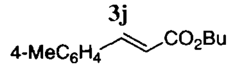
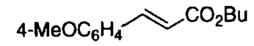
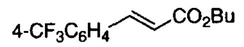
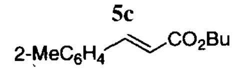
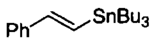
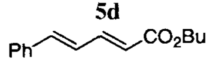


8a **2b** **3b**

conditions:

$Pd(OAc)_2$; 100 mol%, in DMF	60%
$Pd(OAc)_2$; 10 mol%, $Cu(OAc)_2$; 3 mmol, LiOAc; 2 mmol, in DMF	80%
$Pd(OAc)_2$; 10 mol%, NaOAc; 4 mmol, in AcOH	0%

Table 7. Reactions of Organotin Compounds with Olefins in the Presence of Pd(OAc)$_2$[a]

Entry	Organotin	Olefin	Product	Yield/%
1	Ph–SnBu$_3$ **8a**	 **2a**	 **3a**	64[b]
2		 **2b**	 **3b**	77[b]
3		 **2c**	 **3c**	58
4		 **2d**	 **3d**	59[c]
5		 **2e**	 **3e**	73[b]
6		 **2j**	 **3i**	50
7		 **2k**	 **3j**	17[d]
8	4-MeC$_6$H$_4$–SnBu$_3$ **8b**	 **2b**	 **5a**	86
9	4-MeOC$_6$H$_4$–SnBu$_3$ **8c**		 **5b**	60
10	4-CF$_3$C$_6$H$_4$–SnBu$_3$ **8d**		 **5c**	50[e]
11	2-MeC$_6$H$_4$–SnBu$_3$ **8e**		 **5d**	71
12	 **9**			0[f]

a) Unless otherwise noted, all the reaction was carried out in DMF (2 mL), using organotin reagent (0.3 mmol), an olefin (0.3 mmol), Pd(OAc)$_2$ (0.03 mmol), Cu(OAc)$_2$ (0.9 mmol), and LiOAc (0.6 mmol) at 100 °C for 24 h. b) The amont of organotin reagent used were 0.36 mmol. c) $E/Z = 76/24$ by ^{1}H NMR. d) Other Product: Ph–Ph (90%). e) A by-product (4-CF$_3$C$_6$H$_4$)$_2$ 41%. f) The reaction gave homo-coupling product (PhCH=CH)$_2$ (**10**) in 51% yield based on **9**.

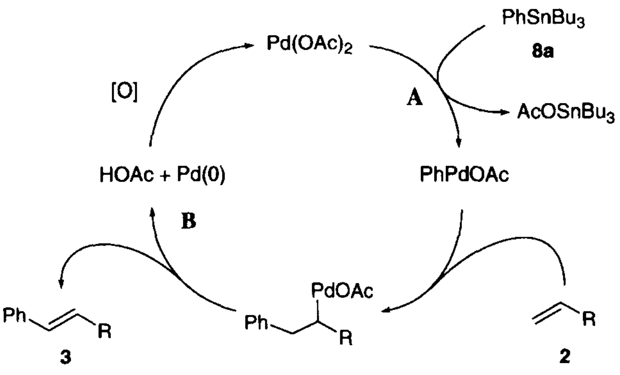
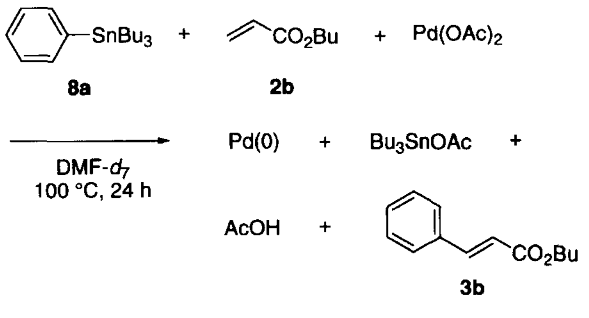


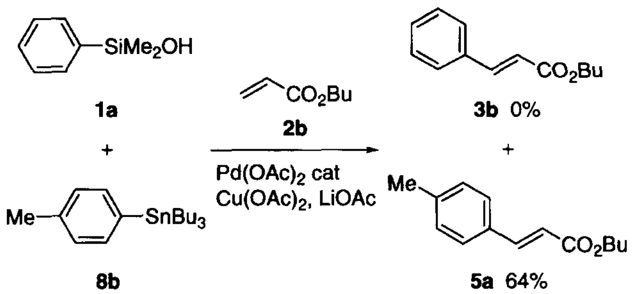
Fig. 2. The MH type reaction mechanism of an organotin compound.

According to the MH type reaction mechanism presented in Figs. 1 and 2, hydroxy(dimethyl)silyl acetate or tributylstannyl acetate should be initially generated by the reaction of dimethyl(phenyl)silanol (**1a**) or tributyl(phenyl)tin (**8a**) with palladium(II) acetate. Thus, we examined a stoichiometric reaction of **1a** and **2b** with palladium(II) acetate in DMF-d_7. However, the hydroxy(dimethyl)silyl acetate could not be detected by ^{1}H NMR, probably because the hydroxy(dimethyl)silyl acetate was too labile and was readily converted into (oligo)siloxanes. We next examined the similar reaction of **8a** and **2b** in DMF-d_7 at 100 °C for 24 h and monitored by NMR to observe signals at 1.93 ppm (^{1}H) and 7.7 ppm (^{119}Sn). These NMR spectra were identical with a mixture of tributylstannyl acetate and acetic acid in DMF-d_7 (Eq. 5).[24] Thus, the generation of tributylstannyl acetate in the reaction mixture is confirmed and the results clearly suggest the migration of the phenyl group in **8a** to palladium center (transmetalation) to furnish a phenyl palladium species. Relative reactivity of dimethyl(phenyl)silanol (**1a**) (1 mmol) and tributyl(4-methylphenyl)tin (**8b**) (1 mmol) was tested by the reaction with **2b** (1 mmol) (Eq. 6); **8b** afforded **5a** in 64% yield, while **3b** was not obtained at all. A similar reaction of dimethyl(4-methylphenyl)silanol (**4a**) and tributyl(phenyl)tin (**8a**) afforded **3b** in 73% along with 7% of **5a** (Eq. 7). These results definitely show that organotin compounds are superior in the reactivity of MH type reaction.

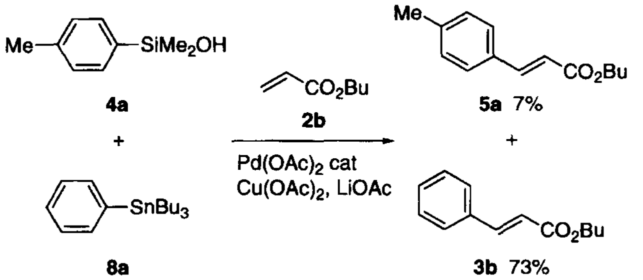


(5)

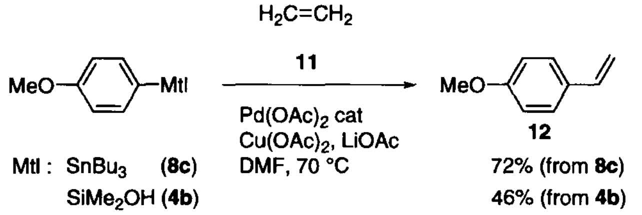
Tributyl(4-methoxyphenyl)tin (**8c**) reacted with ethene (**11**, 1 atm) under the catalytic condition at 70 °C for 24 h to afford 4-vinylanisole (**12**) in 72% yield. Silanol **4b** also gave **12**, but in a slightly lower yield (46%) (Eq. 8). The MH reaction of phenyl halides with **11** is reported to give a mixture of styrene and stilbene at an ambient pressure of ethene. Thus, higher pressure (ca. 10 atm) is necessary to produce styrene selectively.[10a,10b,10d] In contrast, the MH type reaction of silanol **4b** and organotin **8c** with ethene proceeds selectively under an atmospheric pressure to give styrene derivative **12**. Repeated MH type reaction of **12** with **4a** or **4c** afforded stilbene derivatives **13a** or **13b** in moderate yields (Eq. 9). Thus, the overall transformation allows us to synthesize unsymmetrical stilbene derivatives.



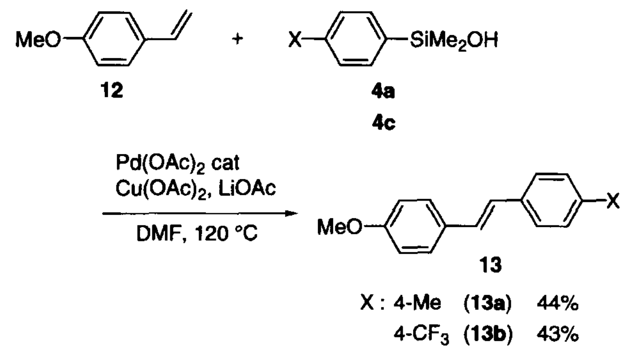
(6)



(7)



(8)



(9)

Conclusion

We have found that silanols and organotin compounds react with various olefins in the presence of palladium(II) acetate to give the MH type products. The reaction proceeds in a catalytic system of palladium(II) acetate/copper(II) acetate/lithium acetate. Aryltin compounds, in general, show reactivity superior to silanols, although undesired homo-coupling sometimes accompanies these reactions. Arylsilanols or aryltin compounds react with ethene to give styrene derivatives without any formation of stilbenes.

Experimental

All reactions were carried out under an argon atmosphere. ^{1}H NMR spectra ($CHCl_3$ as an internal standard) and ^{13}C NMR spectra ($CDCl_3$ as an internal standard) were measured on a Varian Mercury 300 NMR spectrometer, the chemical shifts were given in ppm. IR spectra were recorded with a Shimadzu FTIR-8000A spectrometer in neat liquid. GC analyses were performed on a Shimadzu GC-14A equipped with a flame ionization detector using Shimadzu CAPILLARY COLUMN (CBP1-M25-025) and Shimadzu C-R7A-Chromatopac integrator. Mass spectra were recorded with a Shimadzu QP-5000 GC-MS system. Elemental analyses were carried out by Elemental Analysis Center, Tokyo Institute of Technology, using Yanako MT2 CHN CORDER. High-resolution mass spectra were obtained on a JEOL MStation. For thin layer chromatography (TLC) analyses throughout this work, Merck precoated TLC plates (silica gel 60 GF_{254}, 0.25 mm) were used. Flash column chromatography was performed using Merck Kieselgel 60 (70—230 mesh) or Nacalai Silica gel 60, spherical (150—325 mesh). Hexane, DME, and toluene were distilled from sodium/benzophenone and stored over MS-4A under an argon atmosphere. DMF, acetonitrile, and DMSO were distilled from calcium hydride and stored over MS-4A under an argon atmosphere. Acetic acid was distilled from acetic acid tetraanhydride with boric acid. Anhydrous THF was purchased from Kanto Chem. Co., Inc. and used without further purification. Hexamethylcyclotrisiloxane (D_3) was kindly donated by Shin-Etsu Chemical Co., Ltd. and used as such. $Cu(OAc)_2$ was purchased as a monohydrate, which was dehydrated by heating at 100 °C under vacuum for 12—24 h. Organofluorosilanes were prepared according to the reported procedures.[25]

Dimethyl(phenyl)silanol (1a).[4] To a solution of hexamethylcyclotrisiloxane (0.74 g, 3.3 mmol) in diethyl ether (20 mL) was slowly added PhLi (9.3 mL, 10.0 mmol, 1.08 M (1 M = 1 mol dm^{-3}) in hexane) at 0 °C. The resulting solution was allowed to warm to room temperature and then stirred for an additional period of 14 h. The reaction mixture was poured into diethyl ether/H_2O (10 mL/10 mL); the organic layer was separated. The aqueous layer was extracted with diethyl ether (20 mL×3). The combined organic layer was washed with brine (10 mL), dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by bulb-to-bulb distillation under reduced pressure to give **1a** (1.29 g, 86% yield) as a colorless oil, bp 110 °C (0.6 mmHg, bath temp). IR (neat) 3300, 2925, 1428, 1254, 868, 830 cm^{-1}; ^{1}H NMR ($CDCl_3$) $\delta = 0.41$ (s, 6H), 1.87 (br, 1H), 7.36—7.43 (m, 3H), 7.57—7.63 (m, 2H); ^{13}C NMR ($CDCl_3$) $\delta = 0.0$, 127.9, 129.6, 133.1, 139.2; MS *m*/*z* (%) 152 (M^{+}; 17), 137 (100), 77 (13), 75 (17). HRMS Found: *m*/*z* 152.0650. Calcd for $C_9H_{14}OSi$: M, 152.0657.

Preparation of 1b and 1c. A solution of chloro(diethyl)phenylsilane or chloro(methyl)diphenylsilane (10.0 mmol) in diethyl ether (10 mL) was slowly added to a solution of sodium hydroxide

(0.48 g, 12.0 mmol) in diethyl ether/H_2O (14 mL/7 mL) at 0 °C over 1 h. The mixture was stirred at 0 °C for 10 min and then extracted with diethyl ether (10 mL×3). The combined organic layer was washed with brine (5 mL), dried over Na_2SO_4 and concentrated in vacuo. The residue was bulb-to-bulb distilled to give **1b** or **1c**. The spectra of **1c** were identical with those of the authentic sample.[4b]

Diethyl(phenyl)silanol (1b). Obtained in 53% yield as a colorless oil, bp 120 °C/0.5 mmHg (bath temp, 1 mmHg = 133.32 Pa). IR (neat) 3300, 2957, 2878, 1458, 1428, 1237, 1115, 959, 843 cm^{-1}; ^{1}H NMR ($CDCl_3$) $\delta = 0.84$ (m, 2H), 0.98 (m, 6H), 1.75 (br, 1H), 7.35—7.42 (m, 3H), 7.54—7.60 (m, 2H); ^{13}C NMR ($CDCl_3$) $\delta = 6.3$, 6.5, 127.8, 129.5, 133.5, 137.2. Found: C, 66.62; H, 8.68%. Calcd for $C_{10}H_{16}OSi$: C, 66.61; H, 8.94%.

Pentamethyl(phenyl)disiloxane (1f).[26] Chloro(trimethyl)silane (1.69 mL, 13.3 mmol) was added to a solution of dimethyl(phenyl)silanol (2.0 g, 13.3 mmol) and triethylamine (2.0 mL, 14.0 mmol) in diethyl ether (15 mL) at 0 °C. The resulting mixture was stirred vigorously at room temperature for 1 h to give white precipitates. Dilution of the mixture with dry hexane (20 mL), followed by filtration through a Celite pad and concentration in vacuo, gave a crude oil, which was bulb-to-bulb distillated at 80 °C/0.5 mmHg to give **1f** (2.4 g, 82% yield) as a colorless oil. IR (neat) 3071, 2959, 1429, 1254, 1121, 1059, 841 cm^{-1}; ^{1}H NMR ($CDCl_3$) $\delta = 0.09$ (s, 9H), 0.32 (s, 6H), 7.35—7.37 (m, 3H), 7.53—7.56 (m, 2H); ^{13}C NMR ($CDCl_3$) $\delta = 0.9$, 2.0, 127.7, 129.2, 133.0, 140.1.

Preparation of 4a, 4b, 4c, 4d, and 6a. To a solution of an aryl bromide (12.0 mmol) in diethyl ether (15 mL) was slowly added BuLi (7.6 mL, 12.0 mmol, 1.59 M in hexane) at −78 °C. The mixture was stirred at −78 °C for 1 h before hexamethylcyclotrisiloxane (0.55 g, 2.47 mmol) was added. The resulting mixture was stirred at room temperature for 13 h, and then poured into diethyl ether/H_2O (10 mL/10 mL). The organic layer was separated; the aqueous layer was extracted three times with diethyl ether (15 mL). The combined extracts were washed with brine (10 mL), dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by bulb-to-bulb distillation under reduced pressure to give the corresponding aryl(dimethyl)silanols. Spectra of **6a** were identical with reported ones.[6a,6b]

Dimethyl(4-methylphenyl)silanol (4a). Obtained in 73% yield as a colorless oil, bp 135 °C/1.2 mmHg (bath temp). IR (neat) 3287, 2923, 2867, 1912, 1503, 1445, 1314, 1192, 1113, 868 cm^{-1}; ^{1}H NMR ($CDCl_3$) $\delta = 0.01$ (s, 6H), 1.80 (br, 1H), 2.36 (s, 3H), 7.21 (d, $J = 7.9$ Hz, 2H), 7.50 (d, $J = 7.9$ Hz, 2H); ^{13}C NMR ($CDCl_3$) $\delta = 0.0$, 21.5, 128.7, 133.1, 135.6, 139.5. Found: C, 64.81; H, 8.42%. Calcd for $C_9H_{14}OSi$: C, 65.00; H, 8.49%.

4-Methoxyphenyl(dimethyl)silanol (4b). Obtained in 63% yield as a colorless oil, bp 130 °C/0.5 mmHg (bath temp). IR (neat) 3300, 2957, 2838, 1595, 1505, 1464, 1399, 1281, 1183, 1032, 866 cm^{-1}; ^{1}H NMR ($CDCl_3$) $\delta = 0.39$ (a, 6H), 1.84 (br, 1H), 3.82 (s, 3H), 6.93 (dt, $J = 2.1$, 8.7 Hz, 2H), 7.53 (dt, $J = 2.1$, 8.7 Hz, 2H); ^{13}C NMR ($CDCl_3$) $\delta = 0.0$, 55.0, 113.5, 130.2, 134.6, 160.6. Found: C, 59.16; H, 7.69%. Calcd for $C_9H_{14}OSi$: C, 59.30; H, 7.74%.

Dimethyl(4-trifluoromethylphenyl)silanol (4c). Obtained in 83% yield as a colorless oil, bp 115 °C/0.7 mmHg (bath temp). IR (neat) 3300, 2963, 1393, 1327, 1258, 1167, 1130, 1061, 1020, 959, 870 cm^{-1}; ^{1}H NMR ($CDCl_3$) $\delta = 0.43$ (s, 6H), 1.94 (br, 1H), 7.62 (d, $J = 8.3$ Hz, 2H), 7.71 (d, $J = 8.3$ Hz, 2H); ^{13}C NMR ($CDCl_3$) $\delta = -0.1$, 124.1 (q, $J = 272$ Hz), 124.4 (q, $J = 4$ Hz), 131.5 (q, $J = 32$ Hz), 133.3, 143.8. Found: C, 49.13; H, 5.26%. Calcd for $C_9H_{11}F_5OSi$: C, 49.08; H, 5.03%.

Dimethyl)(2-methylphenyl)silanol (4d). Obtained in 81% yield as a colorless oil, bp 105 °C/0.4 mmHg (bath temp). IR (neat) 3300, 3006, 1592, 1408, 1379, 1285, 1202, 1059, 864 cm^{-1}; ^{1}H NMR ($CDCl_3$) $\delta = 0.46$ (s, 6H), 2.52 (s, 3H), 7.17—7.31 (m, 4H), 7.55 (d, $J = 7.5$ Hz, 1H); ^{13}C NMR ($CDCl_3$) $\delta = 0.9$, 22.7, 124.8, 129.7, 129.7, 134.1, 137.3, 143.1; MS m/z (%) 166 (M$^+$; 20), 151 (100), 133 (16), 123 (14), 91 (21), 75 (11). HRMS Found: m/z 166.0813. Calcd for $C_9H_{14}OSi$: M, 166.0813.

Dimethyl(1-octenyl)silanol (6b). A mixture of 1-octyne (3.0 mL, 0.020 mol), $(Bu_4N)_2PtCl_6$[27] (1.7 mg, 0.002 mmol), and chloro(dimethyl)silane (2.2 mL, 0.020 mol) was placed in a sealed screw-capped glass tube and heated in an oil bath under agitation at 70 °C. An exothermic reaction occurred in a few minutes. The sealed tube was immediately placed in an ice-cooled bath, and the mixture was stirred at 0 °C for 5 h. The reaction was monitored by ^{1}H NMR with an aliquot of the mixture. After completion of the reaction, this material was subjected to bulb-to-bulb distillation (100 °C/0.8 mmHg) to give chlorodimethyl(1-octenyl)silane (3.0 g, 74% yield). All of the product was used directly for the next step. A solution of 1-chloro(dimethyl)silyl-1-octene (3.0 g, 14.7 mmol) in diethyl ether (10 mL) was slowly added to a solution of sodium hydroxide (0.68 g, 17.0 mmol) in diethyl ether/H_2O (20 mL/10 mL) at 0 °C over 1 h. The mixture was stirred at 0 °C for 10 min and then extracted with diethyl ether (15 mL×3). The combined extracts were washed with brine, dried over Na_2SO_4 and concentrated in vacuo. The residue was subjected to bulb-to-bulb distillation (170 °C/1.0 mmHg) to give **6b** (2.1 g, 78% yield) as a colorless oil. IR (neat) 3278, 2959, 2928, 1619, 1379, 1252, 1067, 990, 866 cm^{-1}; ^{1}H NMR ($CDCl_3$) $\delta = 0.20$ (s, 6H), 0.89 (t, $J = 6.6$ Hz, 3H), 1.27—1.43 (m, 8H), 1.55 (br, 1H), 2.08—2.17 (m, 2H), 5.64 (dt, $J = 1.8$, 18.6 Hz, 1H), 6.19 (dt, $J = 6.3$, 18.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) $\delta = 0.1$, 14.2, 22.7, 28.6, 29.0, 31.8, 36.7, 128.3, 149.5; MS m/z (%) 186 (M$^+$; 2), 171 (23), 149 (12), 116 (12), 75 (100). HRMS Found: m/z 186.1440. Calcd for $C_{10}H_{22}OSi$: M, 186.1440.

General Procedure for Stoichiometric MH Type Reaction of Silanols with Olefins. To a solution of $Pd(OAc)_2$ (67 mg, 0.30 mmol) in DMF (2 mL) placed in a screw-capped sealed glass tube were added sequentially silanol **1** (0.30 mmol) and olefin **2** (0.30 mmol) at room temperature. The mixture was stirred at 100 °C for 13 h. The reaction mixture was passed briefly through a Celite pad. Concentration of the eluate under reduced pressure left a crude oil, which was further purified by flash column chromatography on silica gel (hexanes/AcOEt as an eluent) to afford the corresponding product.

General Procedure for Catalytic MH Type Reaction of Silanols with Olefins. To a solution of $Pd(OAc)_2$ (6.8 mg, 0.03 mmol), $Cu(OAc)_2$ (163 mg, 0.90 mmol), and LiOAc (40 mg, 0.60 mmol) in DMF (2 mL) placed in a screw-capped sealed glass tube were added successively silanol **1** (0.30 mmol) and olefin **2** (0.30 mmol) at room temperature; then the mixture was heated at 100 °C. After the reaction was completed, the mixture was cooled to room temperature and diluted with diethyl ether (10 mL). The mixture was passed briefly through a Celite pad. The tube and the pad were washed with diethyl ether (10 mL×2). The combined eluates were washed with sequentially 1 M aq HCl (5 mL), sat. aq $NaHCO_3$ (5 mL), and brine (5 mL). The combined organic layer was dried over $MgSO_4$, filtered and then concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (hexane/AcOEt) to afford the product.

General Procedure for Catalytic MH Type Reaction of Organotin Compounds with Olefins. To a solution of $Pd(OAc)_2$ (6.8 mg, 0.03 mmol), $Cu(OAc)_2$ (163 mg, 0.90 mmol), and

LiOAc (40 mg, 0.60 mmol) in DMF (2 mL) placed in a screw-capped sealed glass tube were added successively organotin compound **8** or **9** (0.30—0.36 mmol) and olefin **2** (0.30 mmol) at room temperature; then the mixture was stirred at 100 °C before dilution with diethyl ether (10 mL). Insoluble materials were filtered off briefly through a Celite pad. The reaction vessel and the pad were washed with diethyl ether (10 mL×2). The combined organic layers were washed with 0.5 M aq NH_3 (20 mL×5), with sat. aq NH_4Cl (10 mL), and with brine (5 mL). The combined organic fractions were dried over $MgSO_4$, filtered and then concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (hexane/AcOEt as eluents) to afford the product. Butyl 3-phenylpropenoate (**3b**),[28] diethyl 2-phenylmaleate (**3h**),[29] butyl 3-(4-methylphenyl)propenoate (**5a**),[28] and butyl 3-(4-methoxypheny)propenoate (**5b**)[28] were compared with the spectra of respective authentic samples.

Butyl 3-(4-Trifluoromethylphenyl)propenoate (5c). IR (neat) 2963, 1719, 1644, 1416, 1325, 1208, 1069, 833 cm^{-1}; ^1H NMR ($CDCl_3$) $\delta = 0.97$ (t, $J = 7.5$ Hz, 3H), 1.45 (m, 2H), 1.70 (m, 2H), 4.23 (t, $J = 6.6$ Hz, 2H), 6.51 (d, $J = 16.2$ Hz, 1H), 7.64 (s, 4H), 7.69 (d, $J = 16.2$ Hz, 1H); ^{13}C NMR ($CDCl_3$) $\delta = 13.7$, 19.2, 30.7, 64.7, 120.9, 123.8 (q, $J = 273$ Hz), 125.8 (q, $J = 4$ Hz), 128.1, 131.7 (q, $J = 33$ Hz), 137.8 (d, $J = 9$ Hz), 142.6, 166.4. Found: C, 61.96; H, 5.70%. Calcd for $C_{14}H_{15}F_3O_2$: C, 61.76; H, 5.55%.

Butyl 3-(2-Methylphenyl)propenoate (5d). IR (neat) 2961, 1715, 1636, 1603, 1462, 1314, 1275, 1219, 1175, 1065 cm^{-1}; ^1H NMR ($CDCl_3$) $\delta = 0.97$ (t, $J = 7.5$ Hz, 3H), 1.45 (m, 2H), 1.70 (m, 2H), 2.44 (s, 3H), 4.22 (t, $J = 6.6$ Hz, 2H), 6.36 (d, $J = 15.9$ Hz, 1H), 7.18—7.30 (m, 3H), 7.55 (d, $J = 7.2$ Hz, 1H), 7.97 (d, $J = 15.9$ Hz, 1H); ^{13}C NMR ($CDCl_3$) $\delta = 13.8$, 19.2, 19.8, 30.8, 64.4, 119.3, 126.3, 130.0, 130.7, 133.4, 137.6, 142.2, 167.1; MS *m/z* (%) 218 (M^+; 7), 161 (2), 146 (6), 74 (100). HRMS Found: *m/z* 218.1308. Calcd for $C_{14}H_{18}O_2$: M, 218.1306.

Competitive Reaction of 1a (or 4a) with 8b (or 8a). To a solution of $Pd(OAc)_2$ (4.5 mg, 0.02 mmol), $Cu(OAc)_2$ (109 mg, 0.60 mmol), and LiOAc (26 mg, 0.40 mmol) in DMF (2 mL) placed in a screw-capped sealed glass tube were added successively silanol **1a** or **4a** (0.20 mmol), organotin compound **8b** or **8a** (0.20 mmol) and butyl acrylate (29 μL, 0.20 mmol) at room temperature. The mixture was stirred at 100 °C for 24 h before dilution with diethyl ether (10 mL) and brief filtration with a Celite pad. The filtrate was washed with 1 M aq HCl (10 mL), with sat. aq $NaHCO_3$ (10 mL), and with brine (10 mL), and dried over Na_2SO_4. Filtration and concentration left an oil, which was purified by flash column chromatography on silica gel (hexane/AcOEt) to give the desired product. The ratio of the products was determined by ^1H NMR ($PhCH{=}C\underline{H}CO_2Et$: 7.69 ppm vs. $4\text{-}MeC_6H_4CH{=}C\underline{H}CO_2Et$: 7.66 ppm).

Reaction of 4b or 8c with Ethene. A solution of $Pd(OAc)_2$ (4.5 mg, 0.02 mmol), $Cu(OAc)_2$ (109 mg, 0.60 mmol), and LiOAc (26 mg, 0.40 mmol) in DMF (4.0 mL) was placed in a Schlenk tube. The atmosphere in the tube was replaced by ethene. To the mixture was added 4-methoxyphenyl(dimethyl)silanol (**4b**) (33 μL, 0.20 mmol) or tributyl(4-methoxyphenyl)stannane (**8c**) (76 μL, 0.20 mmol) at room temperature. The reaction mixture was stirred at 70 °C for 24 h. Work-up and flash column chromatography on silica gel (eluent: hexanes/AcOEt = 20/1) gave 4-vinylanisol (**12**) (12.2 mg, 46% yield based on **4b**; 14.7 mg, 55% yield based on **8c**). The reaction of the obtained sample of 4-vinylanisol (**12**) (27 μL, 0.20 mmol) with silanol **4a** or **4c** (0.20 mmol) was carried out according to the procedure described above at 120 °C for 38 h to afford (*E*)-4-methoxy-4′-methylstilbene (**13a**)[30] (45 mg, 44% yield) or (*E*)-4-methoxy-4′-trifluoromethylstilbene (**13b**)[31] (56 mg, 43% yield), respectively.

The MH Reaction of 4-Iodoanisole with Ethene. A solution of $Pd(OAc)_2$ (1.1 mg, 0.005 mmol), tris(2-methylphenyl)phosphine (3.0 mg, 0.01 mmol), and 4-iodoanisole (117 mg, 0.50 mmol) in acetonitrile (1 mL) and triethylamine (1 mL) was placed in a Schlenk tube. The atmosphere was replaced by ethene. The reaction mixture was stirred at 70 °C for 24 h, diluted with diethyl ether (10 mL), and then passed through a Celite pad. The reaction tube and the pad were washed with diethyl ether (10 mL×2). The combined organic layer was washed with 1 M aq HCl (15 mL), with sat. aq $NaHCO_3$ (15 mL), and finally with brine (10 mL), dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (hexanes/AcOEt) to give a mixture of 4-vinylanisol (**12**) and 4,4′-dimethoxystilbene. The ratio of the products was determined by ^1H NMR with trichloroethylene as an internal standard. Yields of mono- and di-substituted products were 46%, 20% based on consumed 4-iodoanisole.

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