5342 *J. Org. Chem.* **2000,** *65,* 5342−5349

Palladium-Catalyzed Cross-Coupling of Silanols, Silanediols, and Silanetriols Promoted by Silver(I) Oxide

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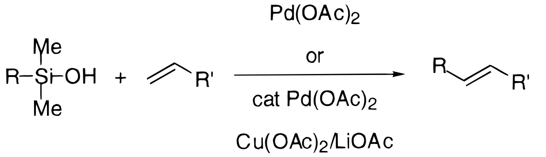
Received May 2, 2000

Palladium-catalyzed cross-coupling of aryl- or alkenylsilanols, silanediols, and silanetriols with a variety of iodoarenes by the catalysis of palladium(0) and in the presence of silver(I) oxide furnished the coupling products in good to excellent yields. The reactions of silanediols or silanetriols under similar conditions proceeded much faster than those of silanols to afford the corresponding coupling products in excellent yields within shorter reaction periods (5−12 h). The measurement of the X-ray diffraction (XRD) pattern of the silver residue after the reaction revealed that silver(I) oxide was converted to silver(I) iodide.

Introduction

Among versatile synthetic applications of organosilicon reagents utilization of silanol in organic syntheses have remained unexplored until recently.[1−6] Because participation of the hydroxy group to a metallic species enhances selectivity as well as reactivity in the reactions of such a metallic reagent to a neighboring functional group,[7] an olefinic substituent of a silanol effects the Simmons−Smith cyclopropanation,[2] Sharpless asymmetric epoxidation,[3] and regioselective dilithiation of allyl- or alkynylsilanols followed by reactions of the resulting dianions with electrophiles.[4] On the other hand, nucleophilic attack of a silanol oxygen atom effects allylic substitution[5] or halo-cyclization[6] and was utilized for the introduction of a oxygen−carbon bond into organic molecules.

In contrast with such synthetic utilization of silanols, effective transformation of a carbon−silicon bond of silanols to a carbon−carbon or carbon−heteroatom bond has not been achieved until recently. We have reported that aryl- and alkenylsilanols underwent Mizoroki−Heck-type reaction with an olefin as the first example of a carbon−carbon bond-forming reaction using silanol as shown in eq 1.[8]



(1)

Another entry for the carbon−carbon bond-forming reaction using silanol is the cross-coupling reaction with organic halides. Although various organosilicon reagents have been shown to undergo the cross-coupling reactions,[9] the reaction with silanol has not been studied so far.[10,11]

Herein, we report the palladium-catalyzed cross-coupling reactions of silanol, silanediol, and silanetriol with aryl iodide. These reactions were found to proceed particularly in the presence of silver(I) oxide as an activator. The role of the silver reagent in the cross-coupling is also discussed.

Results and Discussion

In light of the successful Mizoroki−Heck-type carbon−carbon bond-forming reaction using silanols,[8] we envisaged that the cross-coupling with an aryl halide would also be accessible. The reaction was first examined using tetrabutylammonium fluoride (TBAF) as an activator under conditions similar to those frequently employed for

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10.1021/jo000679p CCC: $19.00

Scheme 1

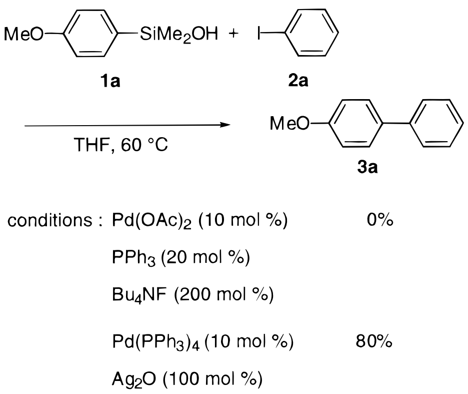


Table 1. Effect of an Additive in the Coupling Reaction of 1a with 2a[a]

entry	additive (mol %)	yield[b]/%
1	Ag_2O (100)	80[c]
2	(50)	61[d]
3	(10)	17[d]
4	(0)	0[d]
5	(200)	84[e]
6	CuO (100)	0
7	CaO	0
8	BaO	0
9	K_2CO_3	0
10	NaOH	0
11	AgOTf	21
12	$AgBF_4$	23
13	$AgNO_3$	16

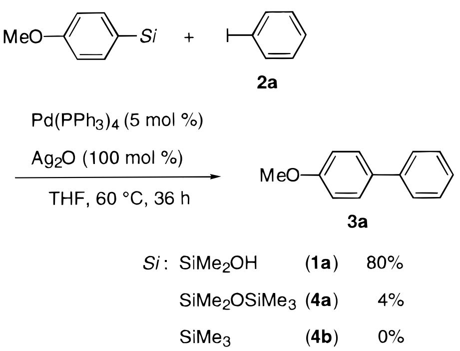
[a] The reaction was carried out using **1a** (0.24 mmol), **2a** (0.2 mmol), $Pd(PPh_3)_4$ (5 mol %), and additive in THF at 60 °C for 36 h. [b] The yields were estimated by ^1H NMR using 1,1,2-trichloroethylene as an internal standard. [c] Isolated yield. [d] The reaction time was 65 h. [e] The reaction time was 38 h.

Table 2. Solvent Effect of the Reaction of 1a with 2a[a]

entry	solvent	*T*/°C	yield[b]/%
1	THF	60	52
2	Bu_2O		27
3		100	63
4	dioxane		60
5	hexane	60	36
6	toluene		34 (40)
7		100	64
8	DMF		35 (60)
9	DMSO		7 (40)

[a] The reaction was carried out using **1a** (0.24 mmol), **2a** (0.2 mmol), $Pd(PPh_3)_4$ (5 mol %), and Ag_2O (0.2 mmol) in THF at 60 °C for 5 h. [b] In parentheses; % conversion of silanol **1a** to disiloxane $((ArylSiMe_2)_2O)$.

Scheme 2



the cross-coupling of difluoro(ethyl)phenylsilane.[11,12] However, treatment of (4-methoxyphenyl)dimethylsilanol (**1a**) with iodobenzene (**2a**) in the presence of TBAF, 10 mol % of $Pd(OAc)_2$, and 20 mol % of PPh_3 resulted in no reaction along with the formation of 1,3-di(4-methoxyphenyl)-1,1,3,3-tetramethyldisiloxane.

Thus, various additives instead of the fluoride ion were examined, and we found that the coupling reaction occurred when Ag_2O was employed as an activator.[13,14] For example, the reaction of **1a** with **2a** using Ag_2O (100 mol %) in THF at 60 °C for 36 h afforded 4-methoxybiphenyl (**3a**) in 80% yield (Scheme 1). Table 1 summarizes the results on the reaction of **1a** with **2a** in the presence of Ag_2O or other additives. The reaction using less than an equimolar amount of Ag_2O (50 mol % and 10 mol %) proceeded to give **3a** in 61 and 17% yield, respectively (entries 2 and 3) suggesting that the reaction by the catalytic use of Ag_2O gives the product in a yield corresponding to a slightly excess amount of Ag_2O. In addition, the reaction without silver resulted in no reaction (entry 4). On the other hand, excess amounts of Ag_2O exhibited little effect to improve the yield (entry 5). The attempted cross-coupling reactions using other additives were revealed to be totally inferior; the use of other metal oxides, CuO, CaO, or BaO, and inorganic bases, K_2CO_3 or NaOH, were found to give no reaction under similar conditions, and the reaction using an ionic silver salt, AgOTf, $AgBF_4$, or $AgNO_3$, proceeded to result in lower yields.

The cross-coupling reactions were then examined in several solvents as shown in Table 2. The reaction proceeded in THF at 60 °C in good yield (entry 1). Yields in other solvents such as Bu_2O, 1,4-dioxane, and toluene at 100 °C were comparable to the result in THF at 60 °C (entries 3, 4, and 7). In contrast, the use of hexane or an aprotic polar solvent such as DMF or DMSO appeared to be inferior (entries 8 and 9).

Scheme 2 shows the cross-coupling of other organosilicon reagents arylpentamethyldisiloxane **4a** and aryltrimethylsilane **4b** to furnish the corresponding coupling products in 4% and 0% yields, respectively, suggesting the significant role of the hydroxy group of silanol to undergo the reaction.

The reactions of aryl- and alkenylsilanols with a variety of organic halides are summarized in Table 3. In a sharp contrast to the reaction with iodobenzene, the use of bromobenzene and phenyl triflate resulted in much lower yields under similar conditions (entries 3 and 4). It is remarkable that the reactions of 1-bromo-4-iodobenzene (**2g**) and 4-iodophenyl triflate (**2h**) afforded **3g** and **3h**, respectively (entries 10 and 11), to react at the carbon−iodine bond with bromide or triflate remaining intact. The reactions with iodobenzenes bearing an electron-donating substituent also proceeded in good yields. In contrast, yields were relatively lower in the reactions of iodides with an electron-withdrawing substituent although the reactions proceeded, indeed.

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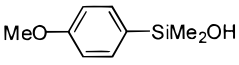
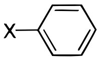
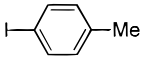
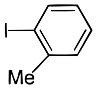
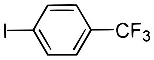
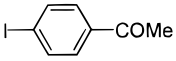
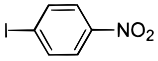
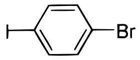
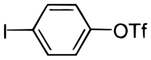
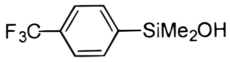
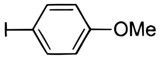
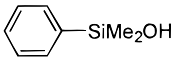
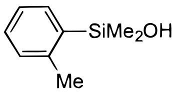
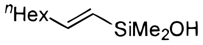
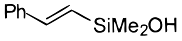
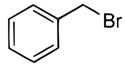
Table 3. Cross-Coupling Reaction of a Silanol with an Organohalide[a]

entry	silanol		halide		time/h	product	yield/%
1		(**1a**)		X = I (**2a**)	36	**3a**	80
2					5		52[b]
3				Br (**5a**)			2[b]
4				OTf (**5b**)			1[b]
5	**1a**			(**2b**)	36	**3b**	75
6	**1a**			(**2c**)		**3c**	69
7	**1a**			(**2d**)		**3d**	54
8	**1a**			(**2e**)		**3e**	50
9	**1a**			(**2f**)		**3f**	45
10	**1a**			(**2g**)		**3g**	60[c]
11	**1a**			(**2h**)		**3h**	55[d]
12		(**1b**)		(**2i**)		**3d**	84
13		(**1c**)	**2i**			**3a**	35
14		(**1d**)	**2i**			**3c**	30
15		(**1e**)	**2i**		4	**3i**	95
16		(**1f**)	**2i**		3	**3j**	67
17	**1a**			(**5c**)	36	**3k**	55

[a] Unless otherwise noted, the reactions were carried out under the following conditions: **1** (0.24 mmol), halide (0.2 mmol), $Pd(PPh_3)_4$ (5 mol %), Ag_2O (0.2 mmol), in THF (2 mL) at 60 °C. [b] Yields were estimated by ^1H NMR using 1,1,2-trichloroethylene as an internal standard. [c] The product was 4-$MeOC_6H_4C_6H_4$-4'-Br. [d] The product was 4-$MeOC_6H_4C_6H_4$-4'-OTf.

Other silanols similarly underwent the cross-coupling reactions in moderate to good yields. Arylsilanols with an electron-withdrawing substituent on their aromatic rings furnished the coupling products in good yields (entry 12). However, the reaction with dimethyl(phenyl)silanol (**1c**) showed poor reactivity (entry 13). The reaction with (2-methylphenyl)dimethylsilanol (**1d**) was also ineffective (entry 14). It should be pointed out that alkenylsilanols generally reacted much faster than arylsilanols (entry 15 and 16).[9b,15] Indeed, the reactions with octen-1-yl- and 2-phenylethenylsilanols proceeded within shorter reaction periods (3−4 h) to afford the corresponding products **3i** and **3j** in excellent yields. In addition, benzyl bromide also reacted with **1a** to give the diphenylmethane derivative **3k** in 55% yield.

Although the coupling of silanol proceeds, the reactions of arylsilanols, in general, require longer periods to afford the product in good yield. Hence, we are subsequently interested in the cross-coupling reaction of silanediols and silanetriol, which might show higher efficiency due to the presence of multiple hydroxy groups on silicon.

Syntheses of silanediols were carried out by a careful hydrolysis of the corresponding dichlorosilane **6**.[16] The reaction of dichloro(ethyl)(phenyl)silane (**6a**) was hydrolyzed with 2 mol amounts of $NaHCO_3$ in diethyl ether/H_2O (method A) or 2 mol amounts of aniline and H_2O

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(15) Such difference of the reactivity was also shown in the reactions of aryl- and alkenylsilacyclobutanes. See ref 9d,e.

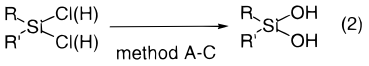
(16) (a) George, P. D.; Sommer, L. H.; Whitmore, F. C. *J. Am. Chem. Soc.* **1953**, *75*, 1585−1588. (b) Takiguchi, T. *J. Am. Chem. Soc.* **1959**, *81*, 2359−2361.

Table 4. Syntheses of Silanediols

entry	R	R'	X	method[a]	yield/%
1	Ph	Et	Cl (**6a**)	A	80
2	Ph	Me	Cl (**6b**)		
3	Ph	Me	H	C	90
4	4-MeC_6H_4	Et	Cl (**6c**)	B	65
5	4-$MeOC_6H_4$		Cl (**6d**)		79
6	PhCH=CH		Cl (**6e**)		74
7	PhCH=CPh		Cl (**6f**)		62

[a] Method A: **6** (1 mmol), $NaHCO_3$ (2 mmol), in Et_2O/H_2O at 0 °C. Method B: **6** (1 mmol), H_2O (2 mmol), $PhNH_2$ (2 mmol), in Et_2O at 0 °C. Method C: dihydrosilane (1 mmol), Pd/C (5 mol %), in dioxane/phosphate buffer (pH = 6.84) at rt.

(method B) in diethyl ether to yield silanediol **7a** in a good yield (eq 2). In contrast, similar hydrolysis of dichloro(methyl)(phenyl)silane (**6b**) gave silanediol **7b** in a very low yield probably along with complex mixture of silicone oligomers. However, synthesis of **7b** was alternatively achieved by the Pd/C catalyzed hydrolytic dehydrogenation of methyl(phenyl)silane (method C) in 90% yield.[17] Other silanediols were prepared by each of these methods A−C. The results on the preparation of silanediols are shown in Table 4. All of the synthesized silanediols given in Table 4 were solid at an ambient temperature. These produced crude solids were washed with hexane, to show sufficient purity for further cross-coupling reactions, and can be stored in a refrigerator for months under an argon atmosphere. However, the attempted recrystallization from hexanes−ether with slight heating resulted in decomposition of silanediols.



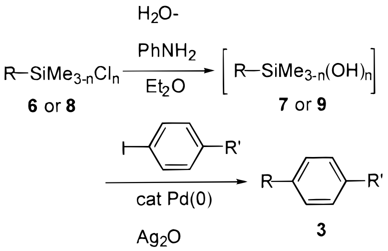
6 **7** (2)

The cross-coupling of silanediols with several substrates was performed in the presence of Ag_2O as shown in Table 5. The reaction of ethyl(phenyl)silanediol (**7a**) with 4-methoxyiodobenzene (**2i**) proceeded at 60 °C for 12 h in the presence of 5 mol % of $Pd(PPh_3)_4$ and 100 mol % of Ag_2O to give 4-methoxybiphenyl (**3a**) in 80% yield (entry 1). Since the reaction using silanol **1c** under similar conditions afforded the coupling product in only 35% yield (Table 3, entry 13), the reactivity of silanediol was found to be much superior to the corresponding silanol.

As observed in the cross-coupling of silanol, bromide and triflate also failed to give the product (entries 4 and 5). However, the reactions of silanediol **7b** with several iodides proceeded; excellent yields were achieved within a shorter reaction period (12 h) compared with those of silanols (36 h at 60 °C in THF). In addition, silanetriol **9a** also reacted with 4-methoxyiodobenzene in 83% at 60 °C for 12 h (entry 6).

The reactions of other arylsilanediols **7c** and **7d** proceeded with aryl iodides **2i** and **2a** in good yields, respectively (entries 11 and 12). Alkenylsilanediols **7e** and **7f** also effected the cross-coupling reactions (entries 13 and 14). Worthy of note, in addition, is the ease of purification in the coupling of silanediol and silanetriol by a simple silica gel column chromatography procedure. In contrast, the reaction with the corresponding silanol sometimes caused difficulty in the purification due to the contamination of a small amount of unidentified silicone impurities.

It should also be pointed out that several coupling reactions were found to proceed smoothly starting from the use of dichloro- or trichloroaryl and -alkenyl silicon reagents via hydrolysis and the cross-coupling sequence *without purifying the formed crude silanediols or a silanetriol*. In sharp contrast to the successful formation of methyl(phenyl)silanediol (**7b**) from the corresponding hydrosilane (method C), the attempted hydrolysis of dichloro(methyl)phenylsilane with aqueous $NaHCO_3$ (method A) resulted in the formation of a complex mixture of oligosiloxanes, whose ^1H NMR spectrum clearly indicated that most of the silanediol has been converted to the oligomers.[18] Nevertheless, the cross-coupling of such a complex mixture with **2j** under similar conditions, indeed, produced the corresponding coupling product in 77% yield. Attempts to isolate several silanediols and a silanetriol **9b** have also been unsuccessful by methods A−C. However, these crude mixtures were similarly converted to the coupling products in excellent yields as summarized in Table 6. Since further purification of crude silanediols that are obtained as a liquid is generally difficult, isolation of (1-hexenyl)methylsilanediol, methyl(2-phenylethenyl)silanediol, and (1-ethyl-1-butenyl)methylsilanediol in analytically pure form by the hydrolyses of dichlorosilanes **6g, 6h,** and **6i**, respectively, has not been achieved to give mixtures whose NMR measurements suggested contamination of inseparable silicone oligomers in considerable amounts along with the desired silanediol. The cross-coupling reactions using these crude mixture with **2i** or **2j** resulted to give the coupling products in excellent yields.[19] In addition, trichlorosilane **8b**, whose corresponding silanetriol were also unable to obtain, were similarly subjected to the hydrolysis-coupling sequence to afford the coupling products in 76% yield. Since an unstable silanediol probably exist in an equilibrium with the corresponding silicone oligomers, consumption of the silanediol by the coupling in the reaction mixture would facilitate further regeneration of the silanediol for the coupling to proceed. In contrast, the coupling reaction with a disiloxane **4a** (see Scheme 2) or an aged silanol that would reluctantly converted to the disiloxane did not proceed because regeneration of a silanol from the corresponding disiloxane hardly occurred (Scheme 3).



(3)

In view of the cross-coupling of silanols and silanediols, the role of Ag_2O as an activator is of considerable interest. Hence, analysis of the silver residue, after completion of

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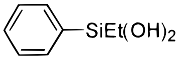
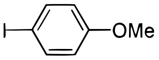
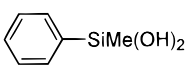
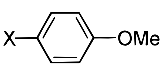
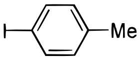
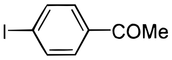
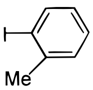
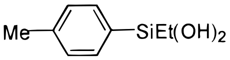
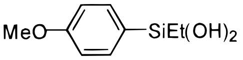
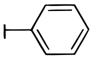
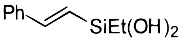
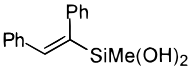
[17] Barnes, G. H., Jr.; Daughenbaugh, N. E. *J. Org. Chem.* **1966**, *31*, 885−887.

[18] See the Supporting Information.

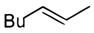
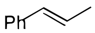
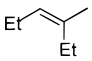
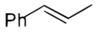
[19] A cross-coupling reaction with chlorosilanes in the presence of NaOH might also be formation of oligosiloxanes. See: Gouda, K.; Hagiwara, E.; Hatanaka, Y.; Hiyama, T. *J. Org. Chem.* **1996**, *61*, 7232−7233.

Table 5. Cross-Coupling Reaction of a Silanediol or Silanetriol 9a with an Aryl Halide[a]

entry	silanediol		halide		time/h	product	yield/%
1		(**7a**)		(**2i**)	12	**3a**	80
2		(**7b**)	 X = I	(**2i**)	5		$71^{b)}$
3					12		93
4			Br	(**5d**)	5		$7^{b)}$
5			OTf	(**5e**)	5		$0^{b)}$
6	Ph—Si(OH)$_3$	(**9a**)	**2i**		12	**3a**	83
7	**7b**			(**2b**)	12	**3b**	81
8	**7b**			(**2e**)	5	**3l**	$63^{b)}$
9					12		97
10	**7b**			(**2c**)	12	**3m**	84
11		(**7c**)	**2i**		12	**3b**	99
12		(**7d**)		(**2a**)	12	**3a**	95
13		(**7e**)	**2i**		12	**3j**	47
14					20		$68^{c)}$
15		(**7f**)	**2e**		24	**3n**	71

[a] The reactions were carried out using **7** or **9** (0.24 mmol), halide (0.2 mmol), Pd(PPh$_3$)$_4$ (5 mol %), Ag$_2$O (0.2 mmol) in THF at 60 °C. [b] Yields were estimated by ^{1}H NMR using 1,1,2-trichloroethylene as an internal standard. [c] The reaction was carried out using **7e** (6 mmol), **2i** (5 mmol), Pd(PPh$_3$)$_4$ (3 mol %), and Ag$_2$O (5 mmol), the coupling product **3j** was purified by recrystallization.

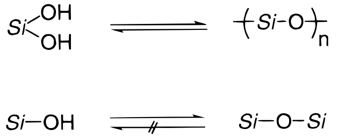
Table 6. Reactions of a Crude Silanediol or a Silanetriol with an Aryl Halide[a]

entry	R—	n		R'	time/h	yield/%
1	Ph—	2	(**6b**)	OMe	4	77
2		2	(**6g**)	CN	4	87
3				OMe	4	79
4		2	(**6h**)	OMe	12	95
5		2	(**6i**)	OMe	18	>99
6		3	(**8b**)	OMe	4	76

[a] The reactions were carried out using silanediol or silanetriol (0.6 mmol), aryl halide (0.5 mmol), Pd(PPh$_3$)$_4$ (5 mmol %), and Ag$_2$O (0.5 mmol) in THF at 60 °C.

the reaction of silanediol **7a** with **2i** in the presence of 100 mol % of Ag$_2$O, was carried out by the measurement of X-ray diffraction (XRD) pattern. The reaction to afford the corresponding coupling product in 93% yield gave a crude mixture of gray THF solution along with black precipitates, which were subjected to the XRD analysis. The results are summarized in Figure 1. As shown in **A** of Figure 1, the spectrum indicated that several new peaks appeared along with remaining Ag$_2$O (**C**). A part of new peaks were found identical with those of AgI (**D**). On the other hand, **B** of Figure 1 is the XRD pattern of the residue after the reaction using 50 mol % of Ag$_2$O.[20] The pattern shows that the relative intensity of the peaks of Ag$_2$O to those of AgI decreased in comparison with **A**.

Scheme 3



Thus, we consider that the stoichiometry of the Ag$_2$O-promoted cross-coupling reaction of silanol could be expressed as eq 4 being indicative that the reaction of a silicon reagent (1 mol amount) with 0.5 mol amount of Ag$_2$O give the coupling product along with an equimolar amount of AgI and 0.5 mol amount of disiloxane.[21] Accordingly, the result that the reaction of silanol **1a** with **2a** using 10 mol % of Ag$_2$O afforded the coupling product in 17% yield would also be likely (cf. Table 1, entry 3).

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(20) The reaction of **7a** with **2i** in the presence of 50 mol % of Ag$_2$O afforded **3a** in 43% yield.

(21) We also confirmed the formation of disiloxane in the coupling of 2-phenylethynyl(dimethyl)phenylsilane with an aryl iodide to give the corresponing coupling product along with 1,1,3,3-tetramethyl-1,3-diphenyldisiloxane in an excellent yield: Hirabayashi, K.; Kawashima, J.; Mori, A. Unpublished results.

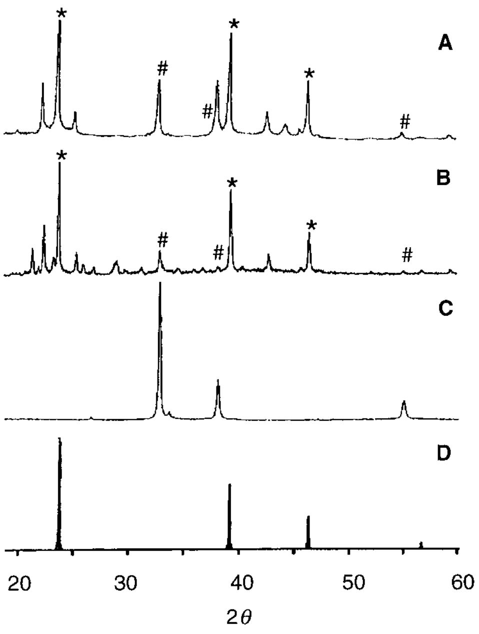

Figure 1. XRD patterns: (A) The silver residue by the reaction using 100 mol % of Ag_2O; (B) the silver residue by 50 mol % of Ag_2O; (C) Ag_2O; (D) AgI.

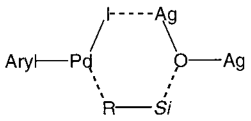

Figure 2. Plausible intermediate.

With these results in hand, the role of Ag_2O may be explained as follows: (i) Since the coupling of silanol is specifically effective for the reaction with aryl iodide, the silver would interact with intermediary organopalladium(II) iodide complex produced by the oxidative addition of aryl iodide to palladium(0) due to the strong affinity of iodine with silver.[22] The effect may induce abstraction of iodine to form a cationic palladium species[23] that would induce transmetalation of the organic group on silanol. (ii) Ag_2O or other basic species formed in situ may act as a nucleophilic activator of silanol to form pentacoordinate silicate species, which also facilitate the transfer of an organic group on silicon to palladium (transmetalation).

However, use of other silver salts such as AgOTf, $AgBF_4$, and $AgNO_3$, which may also be possible to form the cationic palladium, were less effective (Table 1). These findings are considerably unlikely to explain the role (i). On the other hand, the fact that almost no reaction has occurred in the use of aryl bromide and -triflate hardly account for the role (ii).[24] Thus, we consider that the role of Ag_2O may be cooperative with both (i) and (ii), interacting with iodine atom and silanols as shown in Figure 2.

Conclusion

In summary, the palladium-catalyzed cross-coupling of silanol, silanediol, and silanetriol was revealed to occur in the presence of Ag_2O. A variety of aryl iodides smoothly reacted with several aryl- and alkenylsilicon reagents. These reactions were found to be specifically effective when an aryl iodide was used as a substrate. Silanediols and silanetriols were found, in general, much reactive than silanols in the coupling reactions. XRD analyses revealed that Ag_2O was transformed to AgI through the cross-coupling reaction. These results suggest that organosilicon reagents bearing hydroxy group(s) on silicon can also be available as a cross-coupling reaction, which serves as the second example of the transformation of carbon−silicon bond of such compounds. Since syntheses of silanols, silanediols, and silanetriols can be carried out with simple procedures, synthetic application as a key reaction for the construction of a variety of natural and unnatural organic molecules would be available.

Experimental Section

General Methods. All reactions were carried out under an argon atmosphere. Bu_2O, dioxane, toluene, THF, and hexane were distilled from sodium/benzophenone and DMF and DMSO from calcium hydride. Hexamethylcyclotrisiloxane (D_3) was kindly donated by Shin-Etsu Chemical Co. Ltd. Ag_2O was purchased from Wako Pure Chemical Inc. and used without further purification. XRD patterns were measured with Rigaku X-RAY DIFFRACTIOMETER RINT Ultima+/PC.

Preparation of Arylsilanols. Synthesis of arylsilanols **1a**−**d** were carried out in a manner similar to that described in the literature.[8c]

General Procedure for the Coupling Reaction of a Silanol with an Aryl Halide. To a solution of $Pd(PPh_3)_4$ (11.6 mg, 0.01 mmol) and Ag_2O (46.3 mg, 0.2 mmol) in THF (2 mL) were added sequentially aryl halide (0.2 mmol) and silanol (0.24 mmol) at room temperature. The mixture was stirred at 60 °C for 36 h. The reaction mixture was diluted with diethyl ether and then was passed briefly through an alumina pad. The pad was washed with diethyl ether. The eluate was washed with 1 M HCl (aq), saturated $NaHCO_3$ (aq), and brine. The organic layers were dried over anhydrous $MgSO_4$, filtered, and then concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (ethyl acetate/hexanes or toluene/hexanes as eluents) to afford the corresponding product. The following coupling products were reported: 4-methoxy-4′-methyl-biphenyl (**3b**),[25] 4-methoxy-2′-methyl-biphenyl (**3c**),[26] 4-methoxy-4′-trifluoromethyl-biphenyl (**3d**),[3c,26] 4-acetyl-4′-methoxy-biphenyl (**3e**),[3b,25] 4-methoxy-4′-nitro-biphenyl (**3f**),[27] 4-bromo-4′-methoxy-biphenyl (**3g**),[28] 1-(4-methoxyphenyl)-1-octene (**3i**),[29] 4-methoxystilbene (**3j**),[30] and (4-methoxyphenyl)(phenyl)methane (**3k**).[31]

4′-Methoxybiphenyl-4-yl trifluoromethanesulfonate (3h): ^1H NMR ($CDCl_3$) δ 3.86 (s, 3H), 6.99 (d, 2H, $J = 9.0$ Hz), 7.31 (d, 2H, $J = 8.7$ Hz), 7.49 (d, 2H, $J = 8.7$ Hz), 7.60 (d, 2H, $J = 9.0$ Hz); ^{13}C NMR ($CDCl_3$) δ 55.4, 114.4, 118.8 (q, $J = 320.9$ Hz), 121.5, 128.2, 128.3, 131.7, 141.3, 148.5, 159.7; IR (KBr)

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[22] Ag_2O is known to serve as an activator in the Williamson ether synthesis, the reaction of alcohol with alkyl iodide. See: Walker, H. G., Jr.; Gee, M.; McCready, R. M. *J. Am. Chem. Soc.* **1962**, *27*, 2100−2102.

[23] Halide abstraction by silver salt from arylpalladium halide to give cationic palladium species. For example, see: Grove, D. M.; van Koten, G.; Louwen, J. N.; Noltes, J. G.; Spec, A. L. *J. Am. Chem. Soc.* **1982**, *104*, 6609−6616.

[24] Although aryl bromide or triflate is less reactive in the oxidative addition by Pd(0), such a drastic change in the yield (52% vs trace) seems unlikely.

[25] Farina, V.; Krishnan, B.; Marshall, D. R.; Roth, G. P. *J. Org. Chem.* **1993**, *58*, 5434−5444.

[26] Wallow, T. I.; Novak, B. M. *J. Org. Chem.* **1994**, *59*, 5034−5037.

[27] Brune, H. A.; Stapp, B.; Schmidtberg, G. *J. Organomet. Chem.* **1986**, *307*, 129−137.

[28] Kelkar, A. A.; Hanaoka, T.; Kubota, Y.; Sugi, Y. *Catal. Lett.* **1994**, *29*, 69−75.

[29] Li, G. M.; Kamogawa, T.; Segi, M.; Nakajima, T. *Chem. Express* **1993**, *8*, 53−56.

[30] Maccarone, E.; Mamo, A.; Perrini, G.; Torre, M. *J. Chem. Soc., Perkin Trans. 2* **1981**, 324−326.

[31] Fukuzawa, S.; Tsuchimoto, T.; Hiyama, T. *J. Org. Chem.* **1997**, *62*, 151−156.

1495, 1427, 1297, 1215 cm^{-1}. Anal. Calcd for $C_{14}H_{11}F_3O_4$: C, 50.60; H, 3.34. Found: C, 50.48; H, 3.28.

Ethyl(phenyl)silanediol (7a) (Method A). To a vigorously stirred solution of $NaHCO_3$ (0.84 g, 10.0 mmol) in diethyl ether/H_2O (10 mL/40 mL) was slowly added a solution of dichloro(ethyl)(phenyl)silane (1.03 g, 5.0 mmol) in 10 mL of diethyl ether over 20 min. After being stirred for 5 min, the phases were separated and the aqueous was extracted with diethyl ether. The combined organic layers were washed with brine, dried over sodium carbonate, and concentrated in vacuo. The residue was washed with hexane to give 0.67 g of **7a** (80% yield): mp 69−70 °C dec; ^{1}H NMR ($CDCl_3$) δ 0.86 (q, 2H, J = 7.5 Hz), 1.04 (t, 3H, J = 7.5 Hz), 2.65 (br s, 2H), 7.36−7.45 (m, 3H), 7.64−7.69 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 6.3, 6.5, 127.9, 130.2, 133.8, 135.0; IR (KBr) 3250 (br), 959, 878, 830 cm^{-1}; HRMS (EI, *m*/*e*) calcd for $C_8H_{12}O_2Si$ (M^+) 168.0606, found 168.0599.

Methyl(phenyl)silanediol (7b)[32] **(Method C).** To a solution of methyl(phenyl)silane (0.69 mL, 5.0 mmol) in phosphate buffer (pH = 6.84)/dioxane (0.9 mL/10 mL) was added 0.10 g of Pd/C (5%). After being stirred at room temperature for 3 h, the mixture was poured into diethyl ether/H_2O and the phases were separated. The aqueous layer was extracted with diethyl ether. The combined organic layers were washed with brine, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The residue was recrystallized from hexane to afford 0.69 g of **7b** (90% yield): mp 85−86 °C dec; ^{1}H NMR ($CDCl_3$) δ 0.44 (s, 3H), 2.66 (s, 2H), 7.36−7.47 (m, 3H), 7.65−7.68 (m, 2H); ^{13}C NMR ($CDCl_3$) δ −1.8, 127,9, 130.2, 133.5, 136.0; IR (KBr) 3350 (br), 1028, 885, 787 cm^{-1}.

Ethyl(4-methylphenyl)silanediol (7c) (Method B). To a solution of aniline (1.82 mL, 20 mmol) and H_2O (0.36 mL, 20 mmol) in 10 mL of diethyl ether was slowly added a solution of dichloro(ethyl)(4-methylphenyl)silane (2.20 g, 10 mmol) dissolved in 5 mL of diethyl ether over 20 min to form a white precipitate, which was filtered off. The filtrate was concentrated under reduced pressure to leave a solid. Hexane was added to the solid, and the suspension was vigorously stirred. Then the mixture was filtered and dried under reduced pressure to furnish 1.19 g of **7c** (65% yield). The product could be used for the coupling reaction without further purification, although the attempted recrystallization was unsuccessful due to the decomposition: mp 70−71 °C dec; ^{1}H NMR ($CDCl_3$) δ 0.85 (q, 2H, J = 7.5 Hz), 1.03 (t, 3H, J = 7.5 Hz), 2.37 (s, 3H), 3.15 (brs, 2H), 7.22 (d, 2H, J = 8.1 Hz), 7.56 (d, 2H, J = 8.1 Hz); ^{13}C NMR ($CDCl_3$) δ 6.4, 6.6, 21.6, 128.7, 131.5, 133.8, 140.2; IR (KBr) 3250 (br), 1119, 799 cm^{-1}; HRMS (EI, *m*/*e*) calcd for $C_9H_{14}O_2Si$ (M^+) 182.0762, found 182.0766.

Ethyl(4-methoxyphenyl)silanediol (7d). Synthesis of **7d** was carried out in a manner similar to that of **7c** (method B), 79% yield (white solid). The product was used for the coupling reactions without further purification: mp 69−70 °C dec; ^{1}H NMR ($CDCl_3$) δ 0.84 (q, 2H, J = 8.0 Hz), 1.03 (t, 3H, J = 8.0 Hz), 3.77 (brs, 2H), 3.82 (s, 3H), 6.84 (d, 2H, J = 8.7 Hz), 7.53 (d, 2H, J = 8.7 Hz); ^{13}C NMR ($CDCl_3$) δ 6.4, 6.7, 55.0, 113.6, 126.2, 135.4, 161.2; IR (KBr) 3221 (br), 1283, 1030, 862 cm^{-1}; HRMS (EI, *m*/*e*) calcd for $C_9H_{14}O_3Si$ (M^+) 198.0711, found 198.0716.

Ethyl[(*E*)-2-phenylethenyl]silanediol (7e). Synthesis of **7e** was carried out in a manner similar to that of **7c** (method B), 74% yield (white solid). The product was used for the coupling reactions without further purification: mp 106−107 °C dec; ^{1}H NMR ($CDCl_3$) δ 0.78 (q, 2H, J = 7.7 Hz), 1.06 (t, 3H, J = 7.7 Hz), 2.63 (br s, 2H), 6.33 (d, 1H, J = 19.5 Hz), 7.17 (d, 1H, J = 19.5 Hz), 7.26−7.39 (m, 3H), 7.43−7.51 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 6.3, 6.8, 122.4, 126.7, 128.5, 128.6, 137.5, 147.5; IR (KBr) 3220, 994, 882, 737 cm^{-1}; HRMS (EI, *m*/*e*) calcd for $C_{10}H_{14}O_2Si$ (M^+) 194.0762, found 194.0761.

Methyl[(*Z*)-1,2-diphenylethenyl]silanediol (7f). Synthesis of **7f** was carried out in a manner similar to that of **7c** (method B), 62% yield (white solid). The product was used for the coupling reactions without further purification: mp (dec) 85−86 °C; ^{1}H NMR ($CDCl_3$) δ 0.35 (s, 3H), 2.45 (br, 2H), 6.99−7.02 (m, 2H), 7.09−7.14 (m, 6H), 7.24−7.35 (m, 3H); ^{13}C NMR ($CDCl_3$) δ −2.6, 126.2, 127.5, 127.8, 127.9, 128.8, 129.8, 136.5, 140.2, 140.8, 141.9; IR (KBr) 3250 (br), 968, 926, 908 cm^{-1}; HRMS (EI, *m*/*e*) calcd for $C_{15}H_{16}O_2Si$ (M^+) 256.0919, found 256.0904.

Phenylsilanetriol (9a).[16b] Synthesis of **9a** was carried out in a manner similar to that of **7a** (method A), 71% yield (white solid). The produced **9a** was subjected to the coupling reaction without further purification: mp (dec) 125−126 °C; IR (KBr) 3220 (br), 999, 908, 858 cm^{-1}.

General Procedure for the Cross-Coupling Reaction of a Silanediol or a Silanetriol with an Aryl Iodide (Representative as the Reaction of 7e and 2i). To a mixture of silver(I) oxide (1.16 g, 5.0 mmol), **7e** (1.16 g, 6.0 mmol), and $Pd(PPh_3)_4$ (0.16 g, 0.14 mmol) were successively added 20 mL of THF and **2i** (1.17 g, 5.0 mmol). The resulting mixture was then heated at 60 °C, and stirring was continued for 20 h. The mixture was cooled to room temperature, passed through an alumina pad, and washed with diethyl ether. The filtrate was washed with 1 M HCl (aq), saturated $NaHCO_3$ (aq), and brine. The organic layer was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was recrystallized from hexanes to give 0.71 g of **3j** (68% yield). Other reactions were carried out in a similar manner. For the reactions in smaller scales, the purification could also be carried out by column chromatography on silica gel using hexanes/EtOAc or hexanes/toluene as an eluent. The spectroscopic data of 1,2-diphenyl-1-(4-methoxyphenyl)ethene (**3n**),[33] was identical with those in the literature.

General Procedure for the Cross-Coupling through the Hydrolysis-Coupling Sequence without Isolation of the Crude Silanediols or Silanetriols. Dichloro[(*E*)-1-hexenyl]methylsilane (0.12 g, 0.6 mmol) were subjected to the hydrolysis by the method B to leave a liquid, which is a complex mixture of oligomers (for ^{1}H and ^{13}C NMR; see Supporting Information). The liquid was used directly to the cross-coupling reaction in a manner similar to that of a silanediol. All products obtained were identical with authentic samples. Specroscopic data of 1-(4-cyanophenyl)-1-hexene (**3o**),[19] 1-(4-methoxyphenyl)-1-hexene (**3p**),[34] and 1-(4-methoxyphenyl)-1-ethyl-1-butene (**3q**)[35] were identical with those of respective literature references.

Preparation of a Sample for XRD Analysis. The procedure described for the cross-coupling reaction was followed using **1a** (0.19 g, 1.2 mmol), 4-methoxyiodobenzene (0.23 g, 1.0 mmol), $Pd(PPh_3)_4$ (58 mg, 0.05 mmol), and Ag_2O (0.23 g, 1.0 mmol, or 0.12 g, 0.5 mmol). The mixture involving a black precipitate was filtered off and washed with ethanol and then diethyl ether. The resulting solid was dried under reduced pressure to give a black powder, which was subjected to a glass plate for the XRD analysis and set in the diffractiometer. The results were shown below.

Residue with 100 mol % of Ag_2O: 2θ (rel intensity) 18.582 (87), 20.558 (135), 26.698 (325), 32.841 (14663), 33.700 (795), 38.100 (4211), 47.180 (69), 51.456 (61), 54.981 (1946), 65.521 (1062), 68.879 (381).

Residue with 50 mol % of Ag_2O: 2θ (rel intensity) 22.359 (1256), 23.701 (3613), 25.321 (507), 32.840 (1431), 38.101 (1444), 39.202 (2553), 42.640 (594), 44.320 (279), 46.321 (1445), 55.001 (183), 59.301 (128), 64.500 (219).

Ag_2O: 2θ (rel intensity) 7.718 (927), 8.478 (502), 9.640 (221), 12.841 (263), 21.321 (433), 22.360 (757), 23.259 (234), 23.702 (1777), 25.320 (329), 25.905 (136), 28.941 (209), 32.857 (357), 39.200 (1308), 42.640 (284), 46.320 (630),

AgI:[36] 2θ (rel intensity) 23.070 (100), 39.133 (60), 46.308 (30), 56.667 (6), 62.258 (8), 71.028 (8), 76.082 (6), 84.285 (4), 89.100 (4), 97.186 (4), 125.101 (4).

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Acknowledgment. This work was supported by Yamada Science Foundation and Asahi Glass Foundation. Organosilicon reagents were kindly donated by Shin-Etsu Chemical Co. Ltd.

Supporting Information Available: ^{1}H and ^{13}C NMR spectra of new silanediols (**7a**,**c**−**f**) and of the crude silanediol by the hydrolysis of dichloro[(*E*)-1-hexenyl]silane (**6g**) and comparison of ^{1}H NMR spectra of **7b** with the hydrolysis product, giving the mixture of the corresponding oligosiloxanes from **6b**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO000679P