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Cross-coupling reaction of pentacoordinate alkenylsilicates with organic halides and triflates catalyzed by a palladium complex [1][†]

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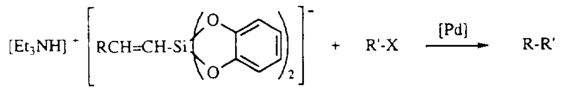
Summary – Isolated pentacoordinate alkoxy-substituted alkenylsilicates, are readily prepared by mixing alkenyltrialkoxysilane, catechol and triethylamine at room temperature. Cross-coupling reactions of these alkenylsilicates with organic halides or triflates are catalyzed by a palladium complex and proceed very smoothly and cleanly to give the corresponding alkenes. The cross-coupling reactions could be also attained by a one pot operation without isolation of pentacoordinate organosilicates. The mechanism of this cross-coupling reaction is also described here.

alkoxy-substituted alkenylsilicate / pentacoordinate silicate / cross-coupling / palladium catalyst / aryl halide / aryl triflate / styrene derivative / 1,3-diene

The chemo-, stereo-, and regioselective carbon-carbon bond formation continues to be of utmost importance in organic synthesis. One of the previous methods for this process was based on the transition-metal-catalyzed cross-coupling reactions of organometallics with organic halides [2]. A number of reactions have been reported, some of which proceed in highly stereo- and chemoselective manners. Müller, and Tamao and Kumada have reported carbon-carbon bond formation reactions using hexacoordinate alkenyl- and arylpentafluorosilicates promoted by palladium, silver, or copper salts [2c, 3, 4]. Moreover, Hatanaka and Hiyama recently reported cross-couplings of organosilanes with organic halides mediated by a palladium catalyst and tris(diethylamino)sulfonium difluorotrimethylsilicate (TASF). Under the influence of the palladium catalyst, TASF catalyzes the transfer of alkenyl and aryl groups from the corresponding fluorosilanes to aryl halides with high chemoselectivity to afford coupling compounds in moderate to high yields [2e, 5, 6]. These reactions are summarized in scheme 1.

We have recently demonstrated that pentacoordinate allylsilicates reveal remarkably enhanced reactivities towards carbonyl compounds, relative to tetracoordinate allylsilanes, and are convenient and useful reagents for the stereo- and regioselective allylation without catalyst [7]. Similarly, since triethylammonium bis(catecholato)alkenylsilicate **2** is easily prepared from alkenyltrimethoxysilane **1**, catechol, and triethylamine (eq 2), it is possible that the isolated alkenylsilicates **2** become attractive reagents. In the course of our studies on the use of high-coordinate alkoxy-substituted organosilicon compounds in organic synthesis [8] we now report cross-coupling reactions of pentacoordinate alkenylsilicates **2** with organic halides and triflates using a palladium catalyst [9] (eq 1). This is the first example of a transition-metal-catalyzed cross-coupling reaction using alkoxy-substituted organosilicates.



2

(eq 1)

Results and discussion

We found that pentacoordinate triethylammonium bis(catecholato)alkenylsilicates **2** were readily prepared from alkenyltrialkoxysilane **1**, two equivalents of catechol, and triethylamine, in a similar manner to the preparation of triethylammonium bis(catecholato)allylsilicates [7] (eq 2). At the outset of this work, the cross-coupling reaction of vinylsilicate **2a** with 1-iodo-4-nitrobenzene **3a** was explored in detail, in the presence of a catalytic amount of a palladium

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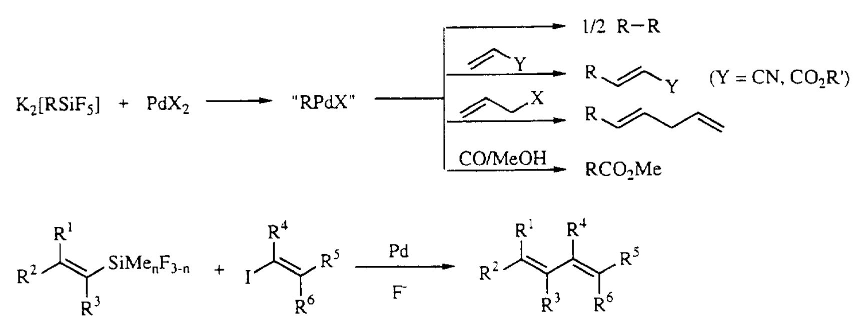
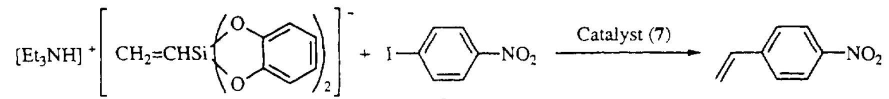
[†] This paper is dedicated to Professor Dr Raymond Calas in recognition of his prominent work on silicon chemistry.

[*] Correspondence and reprints (University of Tsukuba).



Scheme 1. Palladium promoted coupling reactions of organofluorosilicates.

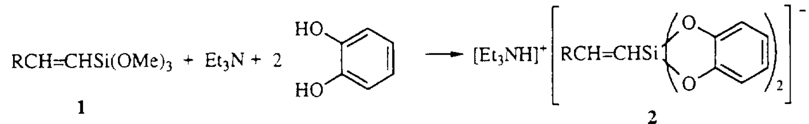
Table I. Cross-coupling reactions of triethylammonium bis(catecholato)vinylsilicate **2a** with 4-iodonitrobenzene **3a**[a].



2a **3a** **4a**

Entry	Catalyst 7	Conditions	%Yield[b]
1	$Pd(PPh_3)_4$ (**7a**)	HMPA, 90 °C, 40 h	29
2	7a	dioxane, reflux, 40 h	17
3	$PdCl_2(PhCN)_2$ (**7b**)	HMPA, 90 °C, 40 h	20
4	**7b**	dioxane, reflux, 40 h	40
5	**7b**[c]	dioxane, reflux, 40 h	55
6[d]	**7b**[c]	dioxane, reflux, 10 h	95 (90)[e]
7	$[PdCl(C_3H_5)]_2$ (**7c**)	HMPA, 90 °C, 40 h	34
8	7c	dioxane, reflux, 40 h	67
9	7c[c]	HMPA, 90 °C, 40 h	34
10	7c[c]	dioxane, reflux, 40 h	59
11	7c[c]	dioxane, reflux, 60 h	76 (54)[e]

[a] Unless noted, the reactions were carried out with **2a** (0.5 mmol) and **3a** (0.5 mmol) in the presence of 5 mol% of a catalyst. [b] Determined by ^1H NMR. [c] $P(OEt)_3$ (10 mol%) was added. [d] **2a** (1.0 mmol) was used. [e] Isolated yield by TLC.

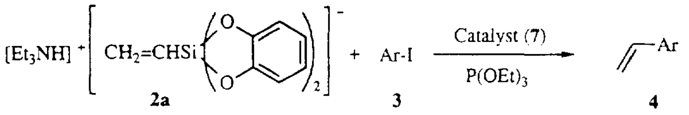


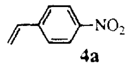
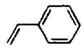
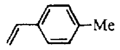
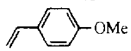
1 **2** (eq 2)

complex and under various conditions. The results are summarized in table I.

Although palladium complexes, such as $Pd(PPh_3)_4$ **7a**, $PdCl_2(PhCN)_2$ **7b**, and $[PdCl(C_3H_5)]_2$ **7c**, work as catalysts to give the corresponding cross-coupling product, 4-nitrostyrene **4a** in high yields, nickel complexes are not effective for the conversion. The addition of triethyl phosphite gives bet-

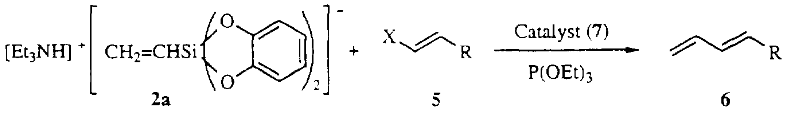
Table II. Reactions of vinylsilicate **2a** with aryl iodides **3**[a].

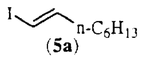
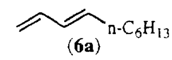
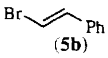
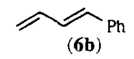


Entry	Ar	**2a** (mmol)	**3** (mmol)	**7**	Product **4**	Condition Time (h)	%Yield[b]
1	*p*-$O_2NC_6H_4$ (**3a**)	0.5	1.0	**7b**	 **4a**	10	95
2	**3a**	0.5	0.5	**7c**	**4a**	60	76
3	C_6H_5 (**3b**)	0.6	1.0	**7b**	 **4b**	10	77[c]
4	**3b**	0.6	0.5	**7c**	**4b**	60	30[c]
5	*p*-$CH_3C_6H_4$ (**3c**)	0.5	0.75	**7c**	 **4c**	60	38
6	*p*-$CH_3OC_6H_4$ (**3d**)	0.6	0.5	**7b**	 **4d**	60	35
7	**3d**	0.5	1.5	**7b**	**4d**	10	67
8	**3d**	0.5	0.75	**7c**	**4d**	60	29
9[d]	**3d**	0.6	0.5	**7c**	**4d**	110	33

[a] All reactions were carried out in the presence of 5 mol% of a catalyst (**7b** : $PdCl_2(PhCN)_2$, **7c** : $[PdCl(C_3H_5)]_2$) and 10 mol% of $P(OEt)_3$ in dioxane at reflux. [b] Determined by ^1H NMR. [c] Determined by GLC.

Table III. Palladium-catalyzed reactions of vinylsilicate **2a** with (*E*)-1-alkenyl halides **5**[a].

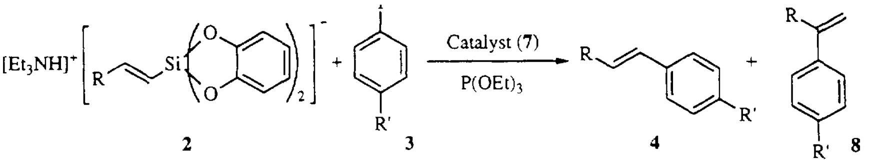


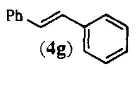
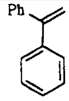
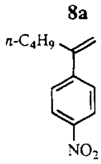
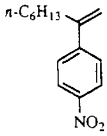
Entry	**5**	Catalyst (**7**)	Reaction Time (h)	Product **6**	%Yield[b]
1	 (**5a**)	$PdCl_2(PhCN)_2$ (**7b**)	20	 (**6a**)	65
2	**5a**	$[PdCl(C_3H_5)]_2$ (**7c**)	20	**6a**	51
3	 (**5b**)	**7b**	30	 (**6b**)	49
4	**5b**	**7c**	20	**6b**	46

[a] All reactions were carried out with **1** (0.5 mmol) and **2** (1.0 mmol) in the presence of 5 mol% of the catalyst and 10 mol% of $P(OEt)_3$ in dioxane at reflux. [b] Determined by GLC.

ter results than the various phosphines and phosphites such as PPh_3, $P(OPh)_3$, $Ph_2P(CH_2)_3PPh_2$ (dppp), and $Ph_2P(CH_2)_2PPh_2$ (dppe) examined. Satisfactory results were obtained using $[PdCl(C_3H_5)]_2$ and $PdCl_2(PhCN)_2$ in dioxane at reflux, but THF and DMF were inadequate as solvents. Although bases, which efficiently copromote the cross-coupling reaction of organoboranes were examined, no improvement of the yields was observed. The use of an excess of aryl halides improves the yield of the cross-coupling reaction since it

Table IV. Palladium-catalyzed reactions of (E)-1-alkenylsilicates **2** with iodobenzenes **3** in the presence of $P(OEt)_3$[a].



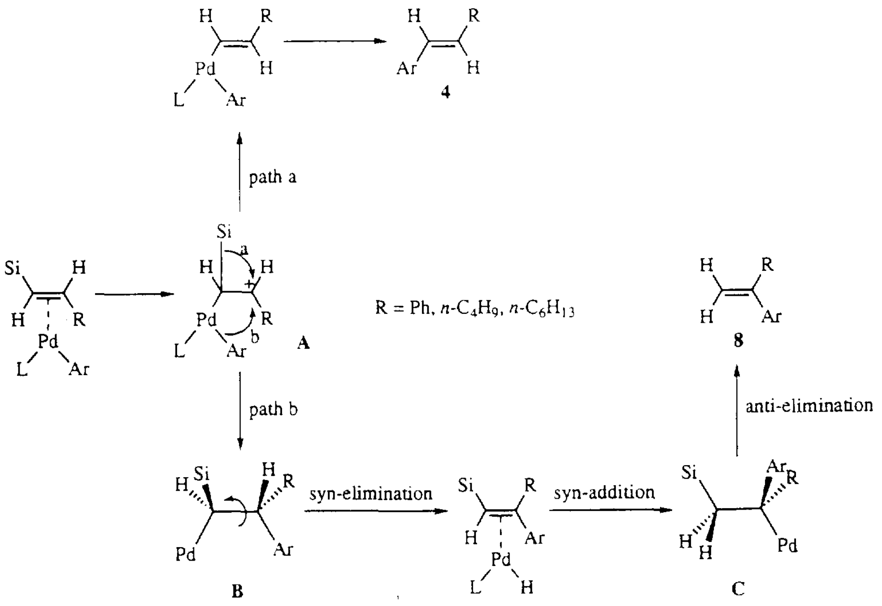
Entry	2 R	3 R'	Catalyst (7)	Reaction Time (h)	Product (%Yield) 4	 8
1	Ph (**2b**)	H (**3b**)	$PdCl_2(PhCN)_2$ (**7b**)	60	 (**4g**) (32)	 (13) (**8a**)
2	**2b**	**3b**	$[PdCl(C_3H_5)]_2$ (**7c**)	110	**4g** (48)	**8a** (25)
3	n-C_4H_9 (**2c**)	NO_2 (**3a**)	**7b**	110		 (64) (**8b**)
4	n-C_6H_{13}(**2d**)	**3a**	**7b**	110		 (51) (**8c**)

[a] All reactions were carried out with **2** (0.5 mmol) and **3** (1.5 mmol) in the presence of 5 mol% of the catalyst and 10 mol% of $P(OEt)_3$ in dioxane at reflux.

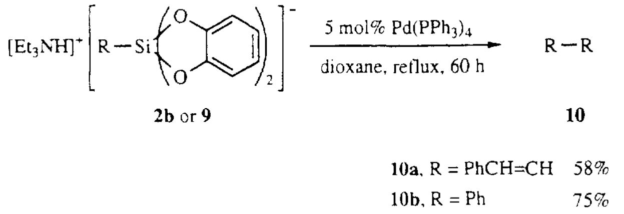
prevents the formation of the homo-coupling products. Prolonged reaction time at reflux does not give good results, probably due to polymerization of the product. In summary, the higher yield of **4a** was obtained with a combination of $PdCl_2(PhCN)_2$ and $P(OEt)_3$ in dioxane. Various substituted iodobenzenes (**3a**, **3c** and **3d**) reacted with vinylsilicate **2a** to afford the corresponding substituted styrene derivatives (**4a**, **4c** and **4d**, respectively) in fairly good yields, depending on the reaction conditions (table II). Aromatic iodides bearing an electron-withdrawing group such as the nitro group gave better yields than those bearing an electron-donating substituent such as methoxy and methyl groups (entries 1, 3, 5 and 7). Instead of aryl iodides, treatment of **2a** with terminal bromoalkenes and iodoalkenes gave the cross-coupled products in a stereospecific manner (table III). For example, (E)-1-iodo-1-octene **5a** (entries 1 and 2) and β-bromostyrene **5b** can be used in this reaction (entries 3 and 4). Thus, this provides the first example of the cross-coupling reaction of an alkoxy-substituted vinylsilicate with aryl halides and alkenyl halides, catalyzed by a transition metal complex.

These cross-coupling reactions are synthetically quite useful because the starting 1-alkenylsilanes are easily prepared by stereospecific hydrosilyation of 1-alkynes. Moreover, 1-alkenylsilicates should cross-couple with retention of the stereochemistry around the geometry of the olefinic bond. Therefore, from the viewpoint of the stereochemistry with respect to the olefin geometry of alkenylsilicates, the reaction of 1-alkenylsilicates **2b-d** with iodobenzenes was then examined. The results are shown in table IV. Unfortunately, it was found that the reaction of **2** with iodobenzene **3b** proceeded with loss of the site-specificity in which the newly formed carbon-carbon bond does not always occur at the sp^2-carbon of the alkenyl group bearing the silyl group of the silicate. Thus, in the case of styrylsilicate **2b**, the expected cross-coupled product, *trans*-stilbene **4g**, was obtained stereoselectively in 48% yield, together with 1,1-diphenylethene **8a** in 25% yield (entry 2). Furthermore, the reaction of (E)-1-hexenylsilicate **2c** with 1-iodo-4-nitrobenzene **3a** afforded only 1-butyl-1-(4-nitrophenyl)ethene **8b** in 64% yield. The carbon-carbon bond formation thus took place at the β-carbon of the alkenylsilicate and no normal coupling product was obtained (entry 3). (E)-1-Octenylsilicate **2d** also revealed a similar result to give only 1,1-disubstituted product **8c** in 51% yield (entry 4). Tamao and Kumada have also reported that the reaction of hexacoordinate styrylpentafluorosilicate with iodobenzene gave 1,1-diphenylethene as a minor product [3c].

The cross-coupling reaction plausibly proceeds as described in the following scheme [10] (scheme 2). At first palladium metal coordinates the olefinic part of the alkenylsilicate. The palladium then shifts to the carbon bearing the silicon atom of the silicate to form an intermediate **A**. In the β carbenium intermediate **A** in path a, β-elimination of the silyl group occurs to give the corresponding 1,2-substituted ethene **4**, the normal coupling product in which the carbon-carbon bond formation takes place at the root carbon bearing the silyl group. On the other hand intermediate **A** in Path b sug-



Scheme 2. Reaction mechanism of palladium-catalyzed cross-couplings.



Scheme 3. Homo-coupling reactions of pentacoordinate organisilicates catalyzed by Pd(PPh$_3$)$_4$.

gests that 1,1-disubstituted alkenes are probably generated *via* a carbo-palladation process. Thus, the aryl ligand transfers to the β-carbon to form intermediate **B**, and then the Pd group in **B** eliminates *via* a *syn*-elimination to generate a π complex. Readdition of a Pd-H moiety generates intermediate **C**, followed by an *anti*-elimination of Pd(0) and Si moieties from **C** [11] gives 1,1-disubstituted ethene **8**.

When alkenylsilicate **2b** and phenylsilicate **9** were conducted to react without aryl halide **3** in the presence of a palladium (0) complex catalyst, the corresponding homo-coupling products (**10a** and **10b**, respectively) were obtained in considerably high yields (58 and 75%) (scheme 3).

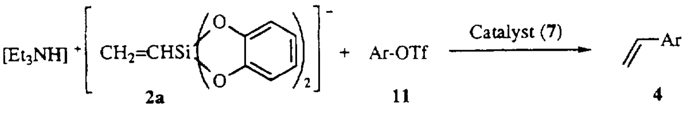
It should be noted that organic trifluoromethanesulfonates (triflates) **11a-d** also react with **2** to give similar results as aryl halides **3**. The results are shown in table V. The yields were comparable to those obtained with alkenyl halides. In this case Pd(PPh$_3$)$_4$ was a rather effective catalyst for the conversion. Lithium chloride was also an important co-promoter for this reaction. Thus it was found that aryl trifluoromethanesulfonates which are easily prepared from phenol derivatives [12], were good reagents for the present palladium-catalyzed cross-coupling reactions using alkoxy-substituted alkenylsilicates.

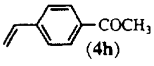
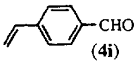
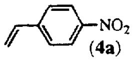
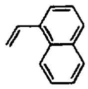
1,1-Disubstituted alkenes are similarly obtained in the reaction of alkenylsilicates with organic triflates. Thus (*E*)-1-octenylsilicate **2d** with 4-nitrophenyl trifluoromethanesulfonate **11c** afforded 1-hexyl-1-(4-nitrophenyl)ethene **8c** in 56% yield (scheme 4).

From the synthetic viewpoint, it is important and convenient to use a technique without isolation of the starting pentacoordinate alkenylsilicates **2**. We have previously found that the reduction of carbonyl compounds using trialkoxy-substituted silanes takes place by *in situ* generated high-coordinate hydridosilicates [8]. It has been shown that the regiospecific allylation can also be attained by the one-pot operation without isolation of pentacoordinate allylsilicates [7b]. Therefore it may be considered that the present cross-coupling reaction can be achieved in a one-pot operation from alkenyltrialkoxysilanes and organic halides and triflates.

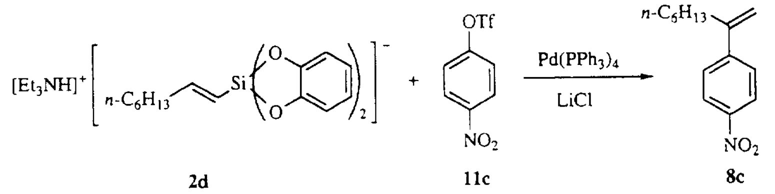
After treatment of vinyltrimethoxysilane **1a** with two equivalents of neat catechol and neat triethylamine at room temperature, 1-iodo-4-nitrobenzene **3a**, a catalytic amount of [PdCl(C$_3$H$_5$)]$_2$ **7c**, and dioxane as the solvent were added to this flask, and the reaction mixture was stirred at reflux to afford p-nitrostyrene **4a** in 87% yield. Similarly, vinyltrimethoxysilane **1a** reacted with other organic halides and triflates in the presence of a palladium catalyst. The results are listed in table VI. Aryl iodides **3** (entries 3 and 4), alkenyl

Table V. Palladium-catalyzed reactions of vinylsilicate **2a** with aryl trifluoromethanesulfonates **11**[a].



Entry	11 Ar	7	Additive (equiv.)	Reaction Time (h)	Product 4	%Yield[b]
1	p-$CH_3COC_6H_4$ (**11a**)	**7a**	—	60	 (**4h**)	27 (30)[c]
2	**11a**	**7a**	LiCl (3)	30	**4h**	73 (68)[c]
3	p-$OHCC_6H_4$ (**11b**)	**7a**	—	12	 (**4i**)	27
4	**11b**	**7a**	LiCl (3)	30	**4i**	61
5	p-$O_2NC_6H_4$ (**11c**)	**7a**	—	12	 (**4a**)	57
7	**11c**	**7a**	LiCl (3)	30	**4a**	85
9	**11c**	**7b**	—	12	**4a**	0
11	**11c**	**7b**	$P(OEt)_3$ (0.1)	12	**4a**	15
10	**11c**	**7c**	—	12	**4a**	0
12	**11c**	**7c**	$P(OEt)_3$ (0.1)	12	**4a**	21
6	1-Naphthyl (**11d**)	**7a**	—	12	 (**4j**)	31
8	**11d**	**7a**	LiCl (3)	30	**4j**	62 (59)[c]

[a] All reactions were carried out with **2a** (0.5 mmol) and **11** (1.0 mmol) in the presence of 5 mol% of the catalyst (**7a** : $Pd(PPh_3)_4$, **7b** : $PdCl_2(PhCN)_2$, **7c** : $[PdCl(C_3H_5)]_2$) in dioxane at reflux. [b] Determined by ^{1}H NMR. [c] Isolated yields by TLC.



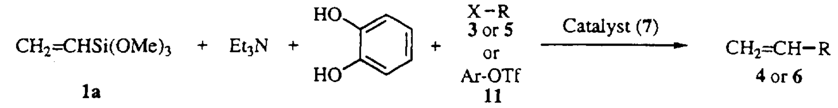
Reaction Time (h)	%Yield
12	35
60	56

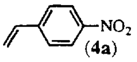
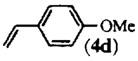
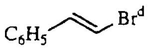
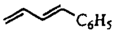
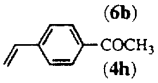
Scheme 4. Reactions of (E)-1-Octenylsilicate **2d** with 4-nitrophenyl trifluoromethanesulfonate **11c** catalyzed by a palladium catalyst in the presence of LiCl.

bromide **5** (entry 5), and aryl triflates **11** (entries 6 and 8) react with vinyltrimethoxysilane **1a** in the presence of catechol and triethylamine by the one-pot procedure to afford the corresponding cross-coupled products in high yields. Similar results to the reactions of isolated alkenylsilicates **2** were obtained in terms of the yields and also the stereo- and regiochemistries.

This work has shown that pentacoordinate alkoxy-substituted 1-alkenylsilicates seem to be less active than dimethylfluorosilane/F$^-$ system [2e] presumably due

Table VI. Palladium-catalyzed reactions of trimethoxyvinylsilane **1a** with organic halides (**3** or **5**) or triflates **11** in the presence of triethylamine and catechol[a].



Entry	X–R or Ar-OTf	3 or 5 / 11	7	Additive (equiv.)	Reaction Time (h)	Product 4 or 6	%Yield[b]
1	p-$O_2NC_6H_4I$	(**3a**)	**7b**	$P(OEt)_3$ (0.1)	30	 (**4a**)	71 (64)[c]
2	**3a**		**7c**	—	30	**4a**	76
3	**3a**		**7c**	$P(OEt)_3$ (0.1)	30	**4a**	87 (86)[c]
4	p-$CH_3OC_6H_4I$	(**3d**)	**7c**	$P(OEt)_3$ (0.1)	30	 (**4d**)	53
5		(**5b**)	**7b**	$P(OEt)_3$ (0.1)	110	 (**6b**)	48[e]
6	p-$CH_3COC_6H_4OTf$	(**11a**)	**7a**	LiCl (3)	30	 (**4h**)	45
7	p-$O_2NC_6H_4OTf$	(**11c**)	**7a**	—	12	**4a**	67
8	**11c**		**7a**	LiCl (3)	30	**4a**	73

[a] Unless otherwise noted, the reactions were carried out with **1a** (0.5 mmol) and **3** or **5** or **11** (1.0 mmol) in the presence of 5 mol% of the catalyst (**7a** : $Pd(PPh_3)_4$, **7b** : $PdCl_2(PhCN)_2$, **7c** : $[PdCl(C_3H_5)]_2$) in dioxane at reflux. [b] Determined by ^1H NMR. [c] Isolated yield by TLC. [d] **1a**:**5b** = 1:3. [e] Determined by GLC.

to the lone pair electrons of the oxygen atom, since transmetalation of alkenylsilicates with the palladium complex might be prevented.

The synthetic utility of the present cross-coupling reactions was mostly displayed by the readily available starting materials, convenient and simple manipulation of the conversion, mild conditions of the cross-coupling reactions. Much more remains to be discovered in the area of high-coordinate organosilicon compounds which are quite new and provide important strategies in organic synthesis using organosilicon compounds. The results obtained here will attract organic chemists from the viewpoint of both synthetic and theoretical chemistry.

Experimental section

General

Diethyl ether and tetrahydrofuran (THF) were freshly distilled over benzophenone ketyl under nitrogen atmosphere or distilled and stored over molecular sieves (3 Å). Acetonitrile, dichloromethane, chloroform, hexamethylphosphoric triamide (HMPA), and dimethyl sulfoxide were distilled over calcium chloride after standing overnight and stored over molecular sieves (3 Å). Dioxane was distilled over sodium under nitrogen and stored over molecular sieves (3 Å). Absolute methanol and ethanol were distilled over magnesium alkoxide after standing overnight and stored over molecular sieves (3 Å). Amines and vinyltrimethoxysilane were commercially available. Catechol was used after recrystallization from hexane/benzene.

All melting points were determined on a Gallenkamp apparatus and are uncorrected. Bulb-to-bulb distillation was conducted with a Sibata glass tube oven GTO-250RS apparatus. Infrared (IR) spectra were recorded on sodium chloride plates on a Shimadzu IR-460 spectrometer. Proton nuclear magnetic resonance (^1H NMR) spectra were determined on Jeol PMX-60 (60 MHz), FX-90Q (90 MHz), and INM-GX400 (400 MHz) spectrometers with tetramethylsilane as an internal standard in carbon tetrachloride or deuteriochloroform. ^{13}C NMR spectra were recorded on Jeol FX-90Q (22.7 MHz) or a Jeol INM-GX400 (100.5 MHz) spectrometer in deuteriochloroform as a solvent and an internal standard. ^{29}Si NMR were determined on a Jeol INM-GX400 (79.4 MHz) spectrometer in deuteriochloroform as a solvent with TMS as an internal standard. Mass spectra (MS) were recorded on a Jeol JMS-DX303 spectrometer and a Jeol JMA-DA-5000 data processor by electron impact (EI) or fast atom bombardment (FAB) ionization methods. Preparative thin-layer chromatography (TLC) was performed on Merck Silica gel GF 254 (type 60) (SiO_2). For the gas-liquid chromatographic (GLC) analysis and the preparative purification, Shimadzu GC-8A and GC-6A gas chromatographs, equipped with a 2 m column packed with 30% SE-30 or DC-550 on Celite, were used. GC peak integrals were recorded by using a Shimadzu Chromatopac C-R3A or C-R1B integrator.

Tetrakis(triphenylphosphine)palladium (0) ($Pd(PPh_3)_4$) [13], dichlorobis(benzonitrile)palladium (II) ($PdCl_2(PhCN)_2$) [14], and chloropropenylpalladium (II) dimer ($[(\eta$-$C_3H_5)PdCl]_2$) [15] were prepared according to the reported procedures.

Pentacoordinate alkenylsilicates. A general procedure

A mixture of alkenyltrimethoxysilane (1 mmol), catechol (2 mmol), and triethylamine (4 mmol) was stirred at room temperature for 4 h. The resulting precipitates were dried *in vacuo* and were used without further purification.

- *Triethylammonium bis(catecholato)vinylsilicate* **2a**

^{1}H NMR ($CDCl_3$) δ 1.24 (t, J = 7 Hz, 9H), 3.17 (q, J = 7 Hz, 6H), 5.59-6.24 (m, 3H), 6.67 (m, 8H), 7.48 (bs, 1H).

^{13}C NMR ($CDCl_3$) δ 8.75 (q), 28.88 (t), 110.8 (d), 118.8 (d), 133.0 (t), 137.8 (d), 149.4 (s).

^{29}Si NMR ($CDCl_3$) δ −87.45.

IR (KBr) ν 3 020, 1 485, 1 245, 830 cm^{-1}.

MS (negative FAB MS) : m/z 271 for the anion.

Anal calc for $C_{20}H_{27}NO_4Si$: C, 64.31; H, 7.29; N, 3.75. Found : C, 64.22; H, 7.26; N, 3.74.

- *Triethylammonium bis(catecholato)-(E)-(2-phenylethenyl)silicate* **2b**

^{1}H NMR ($CDCl_3$) δ 1.21 (t, J = 7 Hz, 9H), 3.15 (q, J = 7 Hz, 6H), 6.30 (d, J = 19 Hz, 2H), 6.68 (m, 8H), 6.72-7.35 (m, 6H), 7.75 (bs, 1H).

IR (KBr) ν 3 010, 1 490, 1 245, 830, 740 cm^{-1}.

Anal calc for $C_{26}H_{31}NO_4Si$: C, 69.45; H, 6.92; N, 3.12. Found : C, 69.33; H, 6.95; N, 3.09.

- *Triethylammonium bis(catecholato)-(E)-1-hexenylsilicate* **2c**

^{1}H NMR ($CDCl_3$) δ 0.72-2.30 (m, 9H), 1.23 (t, J = 7 Hz, 9H), 3.14 (q, J = 7 Hz, 6H), 5.47 (d, J = 7 Hz, 1H), 6.00-7.27 (m, 9H).

- *Triethylammonium bis(catecholato)-(E)-1-octenylsilicate* **2d**

^{1}H NMR ($CDCl_3$) δ 0.65-1.50 (m, 20H), 1.78-2.22 (m, 2H), 3.04 (q, J = 7 Hz, 6H), 5.46 (d, J = 18 Hz, 1H), 6.25 (dd, J = 18 Hz and 6 Hz, 1H), 6.66 (m, 8H), 7.76 (bs, 1H).

Preparation of (E)-1-iodo-1-octene **5a** *[16]*

The reaction was carried out under nitrogen atmosphere. A solution of 1-octyne (5.50 g, 0.05 mol) in *n*-heptane (2 mL) was cooled below −50°C in a dry ice/methanol bath. To the solution was added dropwise diisobutylaluminum hydride (DIBAL-H) (1.5 M, 33.3 mL, 0.05 mol) while the temperature maintained below −40°C. The reaction mixture was heated for 4 h at 50°C, after the addition was complete. This mixture was cooled to −50°C, and a solution of iodine (12.7 g, 0.1 mol) in THF (20 mL) was added dropwise at such a rate that the color disappeared between drops. This reaction mixture was slowly warmed to room temperature while stirring for 12 h. The solution was then cooled to 0°C, and 20% sulfuric acid (20 mL) was added dropwise with stirring. The vinyl iodide was extracted into *n*-heptane and the combined extracts were washed with water, sodium thiosulfate, and sodium bicarbonate and then dried over potassium carbonate. After removal of the solvent, the residue was distilled *in vacuo* to give 7.10 g (0.03 mol, 60% yield) of a pale yellow liquid, bp 53-54°C (0.5 mmHg).

^{1}H NMR (CCl_4) δ 0.50-2.50 (m, 13H), 5.96 (d, J = 15 Hz, 1H), 6.50 (m, 1H).

Preparation of (E)-styryltrimethoxysilane **1b** *[17]*

Hydrosilylation [18] of phenylacetylene (8.17 g, 80 mmol) with trichlorosilane (8.0 mL, 90 mmol) catalyzed by $H_2PtCl_6 \cdot 6H_2O$ (2×10^{-3} mol%) was carried out in a sealed glass tube at rt for 60 h. Distillation of the reaction mixture under reduced pressure gave 11.73 g (49 mmol, 62% yield) of a colorless liquid, bp 120-123°C (20 mmHg). A solution of this styryltrichlorosilane and triethylamine (9.0 g, 89 mmol) dissolved in dry ether (30 mL) was cooled in an ice-water bath. A solution of absolute methanol (5.7 g, 178 mmol) and triethylamine (9.7 g, 96 mmol) in dry ether (20 mL) was added slowly dropwise with vigorous stirring. After the addition was complete, the mixture was stirred at room temperature for 3 h. The resulting mixture was filtered and the filtrate was distilled to give 4.66 g (21 mmol, 42% yield) of a colorless liquid, bp 94-99°C (0.4 mmHg).

^{1}H NMR (CCl_4) δ 3.48 (s, 9H), 5.90 (d, J = 19 Hz, 1H), 6.86-7.47 (m, 6H).

Preparation of (E)-1-hexenyltrimethoxysilane **1c**

This compound was prepared by hydrosilylation of 1-hexyne with trichlorosilane followed by alkoxylation in 51% yield; bp 97-99°C (17 mmHg).

^{1}H NMR (CCl_4) δ 0.63-2.38 (m, 9H), 5.22 (m, 1H), 6.30 (m, 1H).

Anal calc for $C_9H_{20}O_3Si$: C, 52.90; H, 9.87. Found : C, 52.36; H, 9.53.

Preparation of (E)-1-octenyltrimethoxysilane **1d**

This compound was prepared by hydrosilylation of 1-octyne with trichlorosilane followed by alkoxylation in 54% yield; bp 125°C (13 mmHg).

^{1}H NMR (CCl_4) δ 0.50-2.40 (m, 13H), 3.48 (s, 9H), 5.23 (d, J = 20 Hz, 1H), 6.26 (dt, J = 20 Hz and 6.5 Hz, 1H).

Anal calc for $C_{11}H_{24}O_3Si$: C, 56.85; H, 10.41. Found : C, 56.39; H, 10.14.

Preparation of trifluoromethanesulfonic anhydride [19]

A mixture of trifluoromethanesulfonic acid (19.95 g, 133 mmol) and phosphorus pentoxide (18.87 g, 133 mmol) was heated at 110-130°C. The reaction mixture started to reflux after heating for 2 h. After additional heating for 2 h, the reaction mixture was distilled to give 11.80 g (84 mmol, 64% yield) of a colorless oil, bp 79-81°C.

Preparation of aryl trifluoromethanesulfonate **11** *: a typical procedure [12]*

To a cold mixture of a phenol derivative (14 mmol) and pyridine (5 mL) was added trifluoromethanesulfonic acid anhydride (2.75 mL, 16.3 mmol). The resulting mixture was stirred at room temperature for 40 h, after the addition was complete. The mixture was poured into cold water and extracted into ether (3 x 15 mL). The combined extracts were washed with water (10 mL), hydrochloric acid (1 M, 3 x 10 mL), water (2 x 10 mL), and brine (10 mL). After drying over anhydrous $MgSO_4$, the solvent was removed under reduced pressure. The crude triflate was separated by column chromatography on silica gel using hexane/ethyl acetate (20:1) as an eluent and bulb-to-bulb distillation gave a pure product.

- *4-Acetylphenyl trifluoromethanesulfonate* **11a** *[12] (79%)*

A colorless oil; bp (bulb-to-bulb) 90-95°C (0.5 mmHg).

IR (neat) ν 1 694, 1 597, 1 499, 1 429, 1 220, 1 140, 893 cm^{-1}.

^1H NMR (CCl_4) δ 2.53 (s, 3H), 7.27 (d, J = 9 Hz, 2H), 7.96 (d, J = 9 Hz, 2H).

- *4-Formylphenyl trifluoromethanesulfonate* **11b** *[12] (25%)*

A colorless oil; bp (bulb-to-bulb) 70-75°C (0.5 mmHg).

IR (neat) ν 2 840, 1 715, 1 695, 1 500, 1 430, 1 250 cm^{-1}.

^1H NMR (CCl_4) δ 7.47 (d, J = 9 Hz, 2H), 8.01 (d, J = 9 Hz, 2H), 10.05 (s, 1H).

- *4-Nitrophenyl trifluoromethanesulfonate* **11c** *[12] (85%)*

White leaves; mp 52-53°C.

IR ν 1 625, 1 592, 1 534, 1 488, 1 424, 1 351, 1 214, 1 134, 899 cm^{-1}.

^1H NMR ($CDCl_3$) δ 7.50 (d, J = 9 Hz, 2H), 8.40 (d, J = 9 Hz, 2H).

- *1-Naphthyl trifluoromethanesulfonate* **11d** *[12] (85%)*

A colorless oil; bp (bulb-to-bulb) 100-110°C (0.5 mmHg).

IR (neat) ν 1 782, 1 602, 1 423, 1 390, 1 249, 1 220, 1 139, 1 007, 897, 816 cm^{-1}.

^1H NMR (CCl_4) δ 7.10-8.10 (m).

Cross-coupling of pentacoordinate alkenylsilicates with organic halides catalyzed by a palladium complex : a typical procedure

Under argon atmosphere a mixture of an alkenylsilicate **2** (0.5 mmol), an organic halide, **3** or **5** (1.0 mmol), a palladium complex **7** (0.025 mmol), and triethyl phosphite (0.05 mmol) in dioxane (2 mL) was stirred at reflux temperature. After cooling, ether and saturated aqueous sodium bicarbonate were added to the reaction mixture and the resulting mixture was stirred for 30 min and extracted with ether (3 × 20 mL). The combined organic layers were washed with 10% sodium hydroxide (20 mL), water (3 × 20 mL), and brine (20 mL). After drying over anhydrous Na_2SO_4, the solvent was removed *in vacuo*. The residue was purified by preparative thin-layer chromatography on silica gel or preparative gas-liquid chromatography.

Cross-coupling of alkenylsilicates and triflates catalyzed by a palladium complex : a typical procedure

Lithium chloride (64 mg, 1.5 mmol) was dried at 200°C *in vacuo* for 2 h. Under an argon atmosphere, to the lithium chloride was added a solution of a triflate **11** (1.0 mmol) in 1,4-dioxane (1 mL), a solution of an alkenylsilicate **2** (0.5 mmol) in 1,4-dioxane (1 mL), and $Pd(PPh_3)_4$ (0.025 mmol) in 1,4-dioxane (1 mL), generated from $Pd(OAc)_2$ (0.025 mmol), PPh_3 (1.5 mmol), and butyllithium (0.5 mmol). The mixture was stirred at reflux temperature. After cooling, pyridine (1 mL) was added and the resulting mixture was stirred for 30 min and extracted into ether (3 × 15 mL). The combined extracts were washed with 5% sodium hydroxide (20 mL), water (3 × 15 mL), hydrochloric acid (2 × 15 mL), water (2 × 15 mL), and then brine (20 mL). After drying over anhydrous Na_2SO_4, the solvent was removed under reduced pressure and the residue was purified by preparative thin-layer chromatography on silica gel.

- *4-Nitrostyrene* **4a** *[22]*

IR (neat) ν 1 600, 1 514, 1 342 cm^{-1}.

^1H NMR (CCl_4) δ 5.35 (d, J = 10 Hz, 1H), 5.77 (d, J = 18 Hz, 1H), 6.68 (dd, J = 17 and 19 Hz, 1H), 7.36 (d, J = 8 Hz), 8.04 (d, J = 8 Hz).

- *4-Methylstyrene* **4c** *[21]*

^1H NMR (CCl_4) δ 2.17 (s, 3H), 5.00 (d, J = 10 Hz, 1H), 6.50 (dd, J = 17 Hz and 10 Hz, 1H), 6.70-7.33 (m, 4H).

- *4-Methoxystyrene* **4d** *[22]*

^1H NMR (CCl_4) δ 3.66 (s, 3H), 5.00 (d, J = 10 Hz, 1H), 5.48 (d, J = 17 Hz, 1H), 6.27-6.84 (m, 3H), 7.35 (d, J = 8 Hz, 2H).

- *(*E,E*)-1,3-Decadiene* **6a** *[23]*

^1H NMR ($CDCl_3$) δ 0.88-2.11 (m, 13H), 4.89-5.17 (m, 2H), 5.53-6.52 (m, 3H).

- *(*E.E*)-4-Phenyl-1,3-butadiene* **6b** *[24]*

IR (neat) ν 3 085, 1 807, 1 603, 1 495, 1 450, 1 003 cm^{-1}.

^1H NMR ($CDCl_3$) δ 5.09-5.42 (m, 2H), 6.29-6.95 (m, 3H), 7.21-7.43 (m, 5H).

GC-MS m/z 131 (M^+ + 1, 9.6), 130 (M^+, 88), 129 (M^+ − 1, 100).

- trans-*Stilbene* **4g** *[24]*

^1H NMR ($CDCl_3$) δ 7.10 (s, 2H), 7.22-7.58 (m, 10H).

GC-MS m/z 131 (M^+ + 1, 8.4), 130 (M^+, 78), 117 (100).

- *1,1-Diphenylethene* **8a** *[25]*

^1H NMR (CCl_4) δ 5.27 (s, 2H), 6.90-7.56 (m, 10H).

- *2-(4-Nitrophenyl)-1-hexene* **8b**

IR (neat) ν 3 090, 2 960, 2 935, 1 597, 1 518, 1 346, 858, 713 cm^{-1}.

^1H NMR (CCl_4) δ 0.80-2.51 (m, 9H), 5.23 (s, 1H), 5.39 (s, 1H), 7.52 (d, J = 9 Hz, 2H), 8.17 (d, J = 9 Hz, 2H).

Anal calc for $C_{12}H_{15}NO_2$ C : 70.22; H, 7.37; N, 6.82. Found : C, 70.00; H, 7.44; N, 6.76.

- *2-(4-Nitrophenyl)-1-octene* **8c**

bp (bulb-to-bulb) 150°C (0.9 mmHg).

IR (neat) ν 2 690, 2 935, 2 860, 1 597, 1 519, 1 511, 1 343, 858 cm^{-1}.

^1H NMR (CCl_4) δ 0.60-2.70 (m, 13H), 5.20 (s, 1H), 5.37 (s, 1H), 7.43 (d, J = 8 Hz, 2H), 8.13 (d, J = 8 Hz, 2H).

Anal calc for $C_{14}H_{15}NO_2$: C, 72.07; H, 8.21; N, 6.00. Found : C, 72.10; H, 8.24; N, 6.06.

- *1-(4-Vinylphenyl)ethanone* **4h** *[12]*

IR (neat) ν 3 095, 1 681, 1 607, 1 404, 1 359, 1 260, 1 182, 846 cm^{-1}.

^1H NMR (CCl_4) δ 2.50 (s, 3H), 5.27 (d, J = 10 Hz, 1H), 5.70 (d, J = 18 Hz, 1H), 6.70 (m, 1H), 7.33 (d, J = 8 Hz, 2H), 7.77 (d, J = 8 Hz, 2H).

- *4-Vinylbenzaldehyde* **4i** *[12]*

IR (neat) ν 2 830, 1 704, 1 606, 1 214, 1 167, 841 cm^{-1}.

^1H NMR (CCl_4) δ 5.33 (d, J = 10 Hz, 1H), 5.77 (d, J = 18 Hz, 1H), 6.70 (m, 1H), 7.35 (d, J = 8 Hz, 2H), 7.68 (d, J = 8 Hz, 2H).

- *1-Vinylnaphthalene* **4j** *[26]*

IR (neat) ν 3 090, 1 509, 1 433, 1 342 cm^{-1}.

^{1}H NMR (CCl_4) δ 5.45 (d, J = 11 Hz, 1H), 5.76 (d, J = 18 Hz, 1H), 7.21-8.16 (m, 8H).

In situ *palladium catalyzed cross-coupling reactions of trialkoxy-substituted alkenylsilane, catechol, and triethylamine with organic halides and triflates. A typical procedure*

A solution of an alkenylsilane (0.5 mmol), an organic halide or triflate (0.5 mmol), catechol (1.0 mmol), and triethylamine (0.5 mmol) in 1,4-dioxane was added to the catalyst system (0.025 mmol). The resulting mixture was stirred at reflux. After cooling, ether and saturated sodium bicarbonate (10 mL) were added and the resulting mixture was extracted with ether (3 × 15 mL). The combined extract was washed as usual. The solvent was removed under reduced pressure and the residue was purified by the preparative thin-layer chromatography.

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