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Abstract: Silicone, polyorganosiloxane, serves as an organosilicon reagent for palladium-catalyzed cross-coupling reactions. Treatment of polymethylphenylsiloxane, poly(alkenyl)methylsiloxane, or cyclic oligosiloxanes with various aryl iodides in the presence of silver(I) oxide or tetrabutylammonium fluoride and a catalytic amount of Pd(0) affords the corresponding coupling product in a good to excellent yield.

Silicone, which is a polysiloxane bearing organic substituents on the silicon atom, has been widely utilized to prepare a variety of materials with unique characteristics due to the strength and flexibility of the Si-O bonds. The thermal and chemical stability of siloxane compounds has led to the wide applicability of silicone rubber, grease, and oil. In addition, silicone and its copolymers bearing a functional group on the organic substituent of the silicon atom also serve as various specialty polymers.[1]

Because of the breadth of the silicone industry, a number of silicone compounds with various organic substituents are now readily available. However, treatment of a large quantity of silicone waste as well as over-produced silicone materials has become a significant problem that remains to be solved.

Organosilicon compounds have been demonstrated to be valuable carbon-carbon bond

forming reagents in organic synthesis.[2] Several variants of organosilanes such as fluoro, chloro, alkoxy, hydroxy, and alkylsilanes are reactive in palladium-catalyzed cross-coupling reactions.[3,4]

Accordingly, the usage of silicone materials as a source of a pseudo organometallic reagent in coupling chemistry could be a practical solution to the above problem even though silicone has been considered to be inert and not useful in organic synthesis. Herein, we describe our initial efforts to utilize silicone compounds with an aryl or alkenyl substituent as organosilicon reagents for palladium-catalyzed coupling reactions.

As shown in Scheme 1, we first examined the reaction of a polysiloxane bearing a phenyl group, which is a component of highly thermo-resistant silicone oil. The palladium-catalyzed cross-coupling reaction with an aryl iodide was examined using silver(I) oxide (previously shown to be an effective activator for our recent cross coupling of silanols)[4a-c] or commonplace activator, tetrabutylammonium fluoride (TBAF).[3b,4e-h]

Scheme 1.
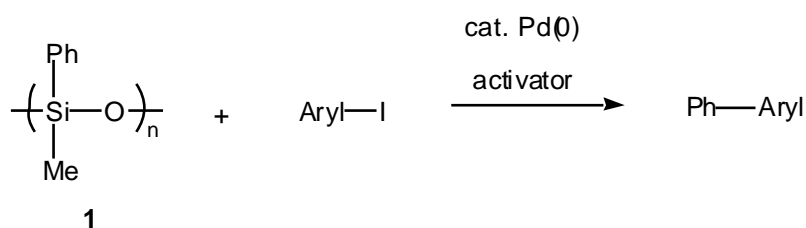
The reaction of poly(phenylmethylsiloxane) (**1**)[5] with 4-iodoacetophenone in the presence of 5 mol % of $Pd(PPh_3)_4$ and Ag_2O at 60 °C in THF for 20 h afforded the corresponding coupling product in 67% yield. TBAF was also found to be an efficient activator for the coupling reaction, which proceeded with 2.5 mol % of $Pd_2(dba)_3 \cdot CHCl_3$. Under these conditions aryl iodides bearing an electron-donating or

-withdrawing substituent on the aromatic ring underwent the coupling reaction in good yields although the reactivity was slightly inferior to that of silonols and silanediols. In addition, a cyclic siloxane bearing phenyl groups, 1,3,5-trimethyl-1,3,5-triphenylcyclotrisiloxane; D_3^{Ph} (**2**), which had been used as a precursor of silicone polymers by ring opening polymerization,[1] was also found to be reactive in the coupling reaction.   These results are shown in Table 1.

Table 1. Cross coupling of a polysiloxane or a cyclic siloxane bearing phenyl group.[a]

siloxane	I-Aryl	conditions	time	%yield[c]
1	4-I-C$_6$H$_4$-COMe	A	20	67
		B		53
	4-I-C$_6$H$_4$-OMe	A		52
		B		79
	4-I-C$_6$H$_4$-NO$_2$	A	24	96
	3-I-C$_6$H$_4$-OMe	A		59
	4-I-C$_6$H$_4$-CN	A		97
2	4-I-C$_6$H$_4$-COMe	A		55
		B	40	36
	4-I-C$_6$H$_4$-OMe	A	120	39

[a] The reaction was carried out at 60 °C in THF (3 mL) using **1** (1.0 mmol; per unit) or **2** (0.2 mmol) and aryl iodide (0.2 mmol).
[b] Condition A: Pd(PPh$_3$)$_4$ (5 mol %), Ag$_2$O (0.2 mmol), condition B: Pd$_2$(dba)$_3$·CHCl$_3$ (2.5 mol%), TBAF (0.24 mmol).
[c] Isolated yield bsed on Aryl-I.

We then focused on the coupling of alkenyl siloxanes. Although polysiloxanes bearing an alkenyl group are not available, such compounds can be easily synthesized using a commercially available polysiloxane bearing silicon-hydrogen bonds, poly(methylhydrosiloxane) (PMHS).[6,7]

The hydrosilylation of a terminal alkyne with PMHS using (Bu$_4$N)$_2$PtCl$_6$ as a catalyst proceeded smoothly and quantitatively generating alkenyl siloxanes **3a** and **3b** in a highly regio- and stereoselective manner as shown in Scheme 2.[8,9] These compounds could be stored in aerobic conditions at room temperature for months and were used for the coupling reactions without further purification.
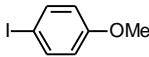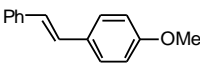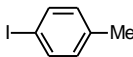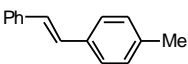
Scheme 2.
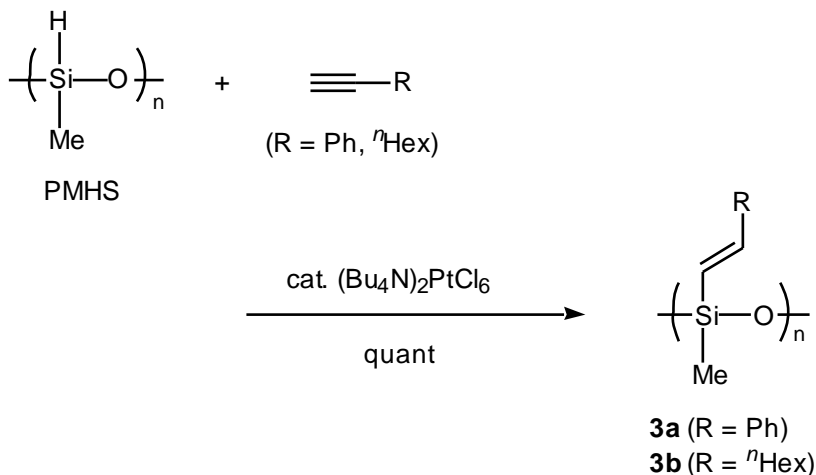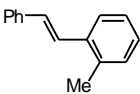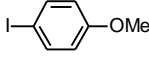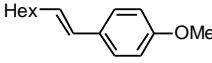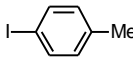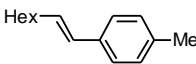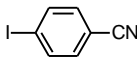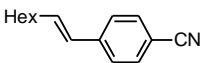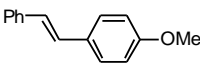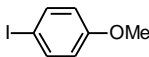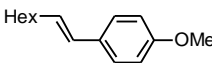
The obtained poly(alkenylsiloxane)s were subjected to the palladium-catalyzed coupling reactions as described in Table 2. TBAF was found to be a suitable activator in the coupling of alkenylsiloxanes, which took place faster than that of phenylsiloxanes. Indeed, the reaction of **3** proceeded within 1-2 hours giving the desired products in excellent yields. Although 3-5 equivalents of phenylsiloxanes **1** and **2** was employed for the reaction, use of a slightly excess amounts (1.2 equiv) of **3** also underwent the coupling reaction smoothly. In sharp contrast to the coupling reaction with Ag_2O as an activator, a palladium catalyst with $(Pd(PPh_3)_4)$ and without $(Pd_2(dba)_3 \cdot CHCl_3)$ phosphine ligand was found to be equally effective for the coupling of polyalkenylsiloxanes. Indeed, the reactions were applicable to a wide range of aromatic iodides.

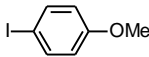In addition to the poly(alkenylsiloxane)s, cyclic siloxanes **4a** (R=Ph) and **4b** (R=Hex) that were prepared by the similar hydrosilylation with the corresponding cyclic hydridosiloxane, 1,3,5,7-tetramethylcyclotetrasiloxane (D_4^H) also took part in the cross-coupling reactions.

When polyalkenylsiloxane **3a** (M_n = 8300) was treated with TBAF and stirred at room temperature for 1 h, SEC (size exclusion chromatograpphy) analysis of the resulting mixture showed the number average molecular weight (M_n) of 2400.[10] The result indicates that **3** would be cleaved into smaller segments but not converted completely to monomeric species. Accordingly, we consider that a certain oligomer would be involved in the cross-coupling reaction by the activation of TBAF.

Table 2. Cross-coupling reaction of polysiloxanes bearing alkenyl group with aryl iodides.[a]

siloxane	I-Aryl	time/h	product	%yield[b]
3a	I—⟨⟩—OMe	1 1	Ph—⟨⟩—OMe	80 (>99) 94[c]
	I—⟨⟩—Me	1	Ph—⟨⟩—Me	>99
	I—⟨⟩—Me (ortho)	1	Ph—⟨⟩—Me (ortho)	97
3b	I—⟨⟩—OMe	1 1	Hex—⟨⟩—OMe	90 (>99) 98[c]
	I—⟨⟩—Me	1	Hex—⟨⟩—Me	51 (>99)
	I—⟨⟩—CN	2	Hex—⟨⟩—CN	90
4a	I—⟨⟩—OMe	1 1	Ph—⟨⟩—OMe	99 85[c]
4b	I—⟨⟩—OMe	1 1 3	Hex—⟨⟩—OMe	88 79[c] 96[d]

[a] Unless otherwise noted, the reaction was carried out using 1.0 mmol (5 equiv per unit) of **3** or 0.2 mmol of **4**, 0.2 mmol of aryl iodide, 0.24 mmol of TBAF, and 0.005 mmol of $Pd_2(dba)_3 \cdot CHCl_3$ at 60 °C in 3 mL of THF. [b] Isolated yield by silica gel chromatography. The yield estimated by ^{1}H NMR is given in parentheses. [c] The amount of employed polysiloxane **3** or **4** was 0.24 mmol (1.2 equiv per unit). [d] $Pd(PPh_3)_4$ (5 mol %) was used as a palladium catalyst.

Typical experimental procedure for the cross-coupling reaction in the presence of silver(I) oxide or TBAF follows: **4-Nitrobiphenyl:** To a mixture of $[Ph(Me)SiO]_n$ (**1**, 1.36 g), Ag_2O (0.46 g, 2.0 mmol) and $Pd(PPh_3)_4$ (116 mg, 0.1 mmol) in 3 mL of THF was added 4-iodo-nitrobenzene (0.50 g, 2.0 mmol). After stirring at 60 °C for 24 h, 20 mL of diethyl ether was added to the resulting mixture and stirring was continued for 10 min. The mixture was passed through a Celite pad to remove the silver residue. The pad was washed with 20 mL of diethyl ether. Concentration of the combined filtrate left a crude oil, which was chromatographed on silica gel (hexane:toluene=10:1) to afford 0.38 g of 4-nitrobiphenyl (96%).

4-Methoxystilbene: To a solution of **3a** (0.97 g, 6.0 mmol) in 20 mL of THF was added TBAF (6 mL of 1M THF solution, 6.0 mmol) at room temperature under argon. To the mixture were successively added 4-methoxy-iodobenzene (1.17 g, 5.0 mmol) and $Pd_2(dba)_3 \cdot CHCl_3$ (125 mg, 0.13 mmol). The solution was heated at 60 ˚C and the reaction was continued for 3 h. After being cooled to an ambient temperature the resulting mixture was passed through a Celite pad. The filtrate was concentrated in vacuo to leave a dark brown liquid, which was purified by chromatography on silica gel to yield 0.94 g of 4-methoxystilbene (89%).

In conclusion, although silicone has traditionally been considered to be an inert compound, we have shown it to be a valuable substrate for a variety of palladium-catalyzed cross-coupling reactions. Once activated by the addition of Ag_2O or TBAF, the stable silicone compound becomes reactive towards palladium. Further studies of other metal-catalyzed synthetic reaction for carbon-carbon and carbon-heteroatom bond forming reactions are in progress.

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(6) Available from Aldrich Chemical Co.   The average degree of polymerization of PMHS is estimated to be ca. 45-50 by ^{1}H NMR analysis.

(7) Recent papers using PMHS as a reducing agent: (a) Kobayashi, Y.; Takahisa, E.; Nakano, M.; Watatani, K. *Tetrahedron* **1997**, *53*, 1627;   (b) Appella, D. H.; Moritani, R.; Shintani, R.; Ferreira, R. E.; Buchwald, S. L. *J. Am. Chem. Soc.* **1999**, *121*, 9473;   (c) Maleczka Jr., R. E.; Gallagher, W. P.; Terstiege, I. *J. Am. Chem. Soc.* **2000**, *122*, 384 and references cited therein.

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(9) Although platinum catalyzed hydrosilylation under the conditions generally gives the regio- and stereoisomers, those of **3a** and **3b** were not observed by [1]H

NMR measurement.

Poly[methyl(2-phenylethenyl)siloxane] (3a): To a screw-capped tube equipped with a magnetic stirring bar were added $(Bu_4N)_2PtCl_6$ (9 mg, 0.01 mmol), phenyl acetylene (2.0 g, 20 mmol), and PMHS (1.2 g; 20 mmol per unit). The resulting mixture was heated at 60 ˚C for 24 h to form crude **3a**, which was confirmed by ^{1}H NMR. SEC analysis showed M_n of 8300 (M_w/M_n=3.22). ^{1}H NMR (300 MHz, CDCl$_3$) δ -0.2-0.4 (br, 3H), 5.7 (br, 1 H), 6.16 (br, 1H), 6.8-7.4 (br, 5 H).

Poly[methyl(1-octen-1-yl)siloxane] (3b): ^{1}H NMR (300 MHz, CDCl$_3$) δ 0-0.3 (brs, 3H), 0.88 (brs, 3 H), 1.3 (br, 8 H), 2.05 (br, 2 H), 5.47 (brd, J = 20 Hz, 1 H), 6.1 (br, 1H).

These compounds were used for the cross-coupling reactions without purification.

(10) Size exclusion chromatography (SEC) was carried out with JASCO 800 HPLC system equipped with a UV detector using THF as an eluent: flow rate, 1.0 mL·min^{-1} with a Shodex KF806L column. Molecular weights and molecular weight distributions were estimated on the basis of the calibration curve obtained by standard polystyrenes.