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Cross-Coupling

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Copper(I)-Catalyzed Alkylation of Aryl- and Alkenylsilanes Activated by Intramolecular Coordination of an Alkoxide**

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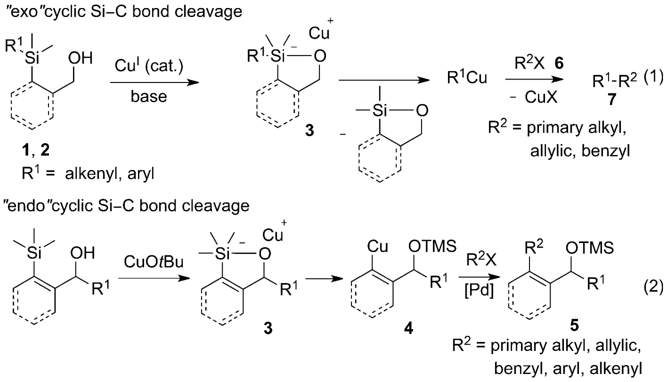
Dedicated to Professor Teruaki Mukaiyama

Organosilicon-based cross-coupling has attracted much attention as a useful tool for carbon–carbon bond formation because of the low toxicity, high availability, and high chemical stability of organosilicon compounds.[1] Activation of the unreactive Si–C bond, however, has been imperative and hence heteroatom-functionalized organosilanes such as halo- and alkoxysilanes have practically been employed in conjunction with a fluoride-ion activator for palladium-catalyzed cross-couplings.[2] In recent advances, organosilanols and silanolates,[3] as well as silacyclobutanes[4] have been introduced as silane coupling partners in the Hiyama coupling. The intramolecular coordination of heteroatoms to the silicon atom also activates the Si–C bond in the silicon-based coupling reactions.[5] In this regard, the transition-metal-catalyzed cross-couplings of aryl- and alkenyldimethyl[(2-hydroxymethyl)phenyl]silanes were extensively studied.[6] In the Hiyama coupling, C(sp^2)–X electrophiles such as aryl and alkenyl (pseudo)halides have been successfully employed, but little is known about the coupling with unreactive C(sp^3)–X electrophiles.[7,8] In this context, we aimed at the development of a catalytic cross-coupling of alkenyl- (**1**) and arylsilanes (**2**) with C(sp^3)–X electrophiles [Scheme 1, Eq. (1)].

We have developed new methods for the generation of the alkenyl and arylcopper species by the copper(I) *tert*-butoxide-promoted Brook-like silyl migration from an sp^2-carbon atom to an oxygen atom.[9,10] The 1,4-silyl migration proceeds by formation of the five-membered cyclic silicates **3**, which undergo the transmetallation to copper(I) to form the organocopper species **4** by the "endo"cyclic Si–C bond cleavage in association with the silyl migration [Scheme 1, Eq. (2)].[9a–d] The organocopper species **4** reacts with alkyl, allylic, and benzylic halides [C(sp^3)–X electrophiles] to give the alkylation products **5** in good yields. The organocopper species **4** are also reactive toward alkenyl and aryl halides in the presence of a catalytic amount of [Pd(PPh$_3$)$_4$].



Scheme 1. Formation of organocopper species via cyclic silicates. TMS = trimethylsilyl.

The five-membered silicate intermediates similar to those in our copper(I)-promoted silyl migration have been assumed to be key intermediates in the palladium-catalyzed Hiyama cross-coupling of organo[2-(hydroxymethyl)phenyl]silanes. The palladium-catalyzed cross-coupling of organolithiums and aryl and alkenyl halides in the presence of 1-oxa-2-silacyclopentene as a silicon-based transfer agent was also categorized into the same type of reaction[11] because of the similarity of their cyclic silicate intermediates.[12] Stoichiometric allylation, benzylation, and silylation of electrophiles such as aldehydes, ketones, and enones via similar cyclic silicates generated from lithium alkoxides of [2-(hydroxymethyl)phenyl]silanes[13] and (3-hydroxypropyl)silanes[14] were also classified in this category.

Based on our results on the formation of organocopper species by the "endo"cyclic Si–C bond cleavage of the cyclic silicates, we conceived that the silanes **1** and **2** bearing a hydroxy group should undergo copper(I)-catalyzed cross-coupling with organic halides [**6**; C(sp^3)–X electrophiles] to give the C(sp^2)–C(sp^3) coupling products **7** through the "exo"cyclic Si–C bond cleavage of the cyclic silicates **3** [Eq. (1)]. Herein we describe fluoride-free copper(I)-catalyzed C(sp^2)–C(sp^3) cross-couplings of alkenyl- and arylsilanes with organic halides effected by intramolecular activation through the formation of cyclic silicate intermediates.

In initial experiments, we examined the cross-coupling of the alkenylsilanes **1a**,**b**, bearing a hydroxypropyl group as an intramolecular activator, using 2 equivalents of copper(I) *tert*-butoxide (Table 1). Thus, the reaction of the (*Z*)-stylylsilane

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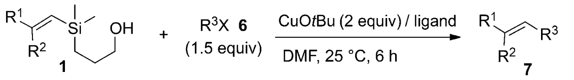
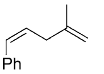
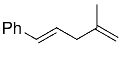
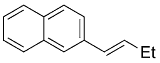
Table 1: CuO*t*Bu-promoted reaction of the alkenylsilanes **1a**,**b**[a] with **6a**,**b**.

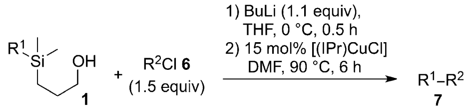


R^1 = H; R^2 = Ph [(*Z*)-**1a**], R^1 = Ph; R^2 = H [(*E*)-**1a**], R^1 = 2-Naph; R^2 = H [(*E*)-**1b**]
R^3X = H_2C=CMeCH_2Cl (**6a**), EtI (**6b**)

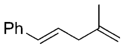
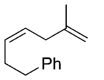
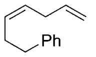
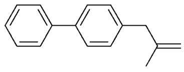
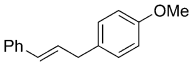
Entry	1	6	Ligand	Product	7	Yield [%][b]
1	(*Z*)-**1a**	**6a**	none		(*Z*)-**7a**	76
2	(*E*)-**1a**	**6a**	none		(*E*)-**7a**	44
3			P(OEt)$_3$			80
4	(*E*)-**1b**	**6b**	P(OEt)$_3$		(*E*)-**7b**	55

[a] The alkenylsilanes **1** were prepared by the hydroboration/oxidation of the corresponding allylalkenyldimethylsilanes (for details, see the Supporting Information). [b] Yield of isolated product. DMF = *N*,*N*-dimethylformamide.

Table 2: Copper(I)-catalyzed cross-coupling of silanes (**1**) with allylic and benzylic halides (**6**).



R^1 = (*E*)-PhCH=CH [(*E*)-**1a**], (*Z*)-Ph$(CH_2)_2$CH=CH [(*Z*)-**1c**], 4-PhC_6H_4 (**1d**)
R^2 = H_2C=CMeCH_2 (**6a**), H_2C=CHCH_2 (**6c**), 4-MeOBn (**6d**)

Entry	1	6	Product	7	Yield [%][a]
1	(*E*)-**1a**	**6a**		(*E*)-**7a**	72[b] (trace)[c]
2	(*Z*)-**1c**	**6a**		(*Z*)-**7c**	70
3	(*Z*)-**1c**	**6c**		(*Z*)-**7d**	72
4	**1d**	**6a**		**7e**	66
5	(*E*)-**1a**	**6d**		(*E*)-**7f**	56

[a] Yield of isolated product. [b] (*E*)-**7a** was partially isomerized to the conjugate diene, (*E*)-1-phenyl-4-methylpenta-1,3-diene [(*E*)-**8a**; (*E*)-**7a**/(*E*)-**8a** = 34:66]. [c] Carried out with 15 mol% CuO*t*Bu/P(OEt)$_3$ and LiO*t*Bu (1.1 equiv) in DMF at 90°C for 6 h. THF = tetrahydrofuran.

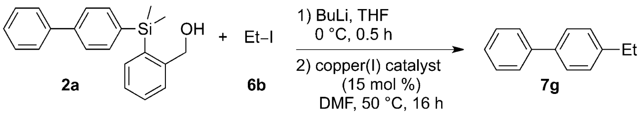
(*Z*)-**1a** with methallyl chloride (**6a**) in the presence of copper(I) *tert*-butoxide in DMF for 6 hours produced the coupling product (*Z*)-**7a** in good yield (entry 1). In contrast to (*Z*)-**1a**, use of triethyl phosphite as a ligand was requisite for successful cross-coupling of the *E* counterpart, (*E*)-**1a** with **6a** (entries 2 and 3). Alkylation of (*E*)-**1b** with iodoethane (**6b**) also underwent to give (*E*)-**7b** (entry 4). These coupling reactions proceeded with complete retention of configuration of the double bond in **1**.

Encouraged by the above stoichiometric cross-coupling, we looked into the copper(I)-catalyzed reaction (Table 2). When the triethyl phosphite/copper(I) *tert*-butoxide complex was used as a catalyst in the reaction of (*E*)-**1a** with **6a**, only a trace amount of the cross-coupling product (*E*)-**7a** was produced. After exploration of catalytic conditions, we found that the cross-coupling of the lithium alkoxide of (*E*)-**1a** was effectively catalyzed with 15 mol% of the [(IPr)CuCl] complex [IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene] in DMF at 90°C although the cross-coupling product (*E*)-**7a** was partially isomerized to the conjugate diene (*E*)-**8a** (entry 1). With the optimized reaction conditions in hand, the cross-couplings of alkenyl and arylsilanes **1a**,**c**,**d** with allylic and benzylic chlorides **6a**,**c**,**d** were performed. In all cases, the cross-coupling products **7** were obtained as single isomers in good yields without the isomerization to the conjugate dienes **8**. The double-bond geometry of **1** remained unchanged during the reaction. Unfortunately the catalytic reaction of **1** with primary alkyl iodides failed to produce the alkylated products.

Next, our attention was focused on the copper(I)-catalyzed cross-coupling of aryl- and alkenylsilanes with unreactive primary alkyl halides. We chose the aryl[2-(hydroxymethyl)phenyl]dimethylsilanes **2** as substrates for the copper(I)-catalyzed reaction on the assumption that they would easily form pentacoordinate silicates because of their rigid molecular structure. Under the catalytic conditions similar to those described above, the alkylation of **2a** with **6b** proceeded in the presence of 15 mol% [(IPr)CuCl] to produce 4-ethylbiphenyl (**7g**), though the yield was unsatisfactory (Table 3, entry 1). Tetramethylethylenediamine (TMEDA) was also found to be a less effective ligand (entry 2). After extensive exploration of ligands, we found that the phosphorous ligands such as phosphites and phosphines were promising ligands (entries 3–6). In all the cases examined, none of the coupling product caused by the endocyclic Si–C bond cleavage was formed. Among them, we adopted 15 mol% CuI/P(OEt)$_3$ as the best catalyst because P(OEt)$_3$ is inexpensive and readily available (entry 5). It was confirmed that none of the cross-coupling product **7g** was formed in the absence of the copper(I) catalyst (entry 7).

We then explored the scope of the reaction with respect to the silanes **2** and organic halides **6** under the catalytic

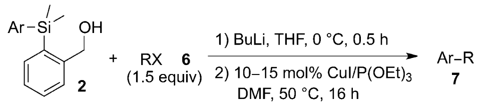
Table 3: Effect of copper(I) catalyst on the cross-coupling of **2a** with iodoethane (**6b**).



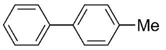
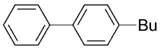
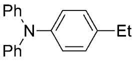
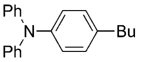
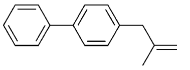
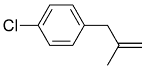
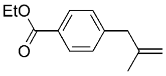
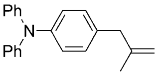
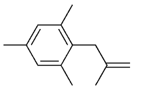
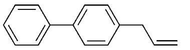
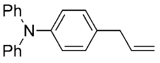
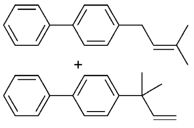
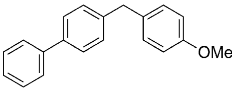
Entry	Copper(I) catalyst	Yield [%][a]
1	[(IPr)CuCl]	27
2	CuI/TMEDA	35
3	CuI/P(OPh)$_3$	56
4	CuI/P(O*i*Pr)$_3$	72
5	CuI/P(OEt)$_3$	78
6	CuI/PPh$_3$	74
7	none	trace

[a] Yield of isolated product.

Table 4: Copper(I)-catalyzed cross-coupling of **2** with organic halides (**6**).[a]



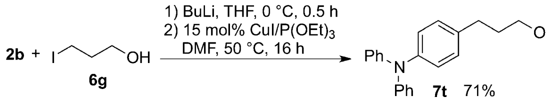
Ar = 4-PhC_6H_4 (**2a**), 4-$Ph_2NC_6H_4$ (**2b**), 4-ClC_6H_4 (**2c**), 4-$EtO_2CC_6H_4$ (**2d**), 2,4,6-$Me_3C_6H_2$ (**2e**)
RX = $H_2C{=}CMeCH_2Cl$ (**6a**), $H_2C{=}CHCH_2Cl$ (**6c**), $Me_2C{=}CHCH_2Cl$ (**6g**), 4-MeOBnCl (**6d**), EtI (**6b**), MeI (**6e**), BuI (**6f**)

Entry	2	6	Product	7	Yield [%][b]
1[c]	**2a**	**6e**		**7h**	89
2	**2a**	**6f**		**7i**	63, 79[d]
3	**2b**	**6b**		**7j**	83
4	**2b**	**6f**		**7k**	91
5[e]	**2a**	**6a**		**7e**	88, 70[f]
6	**2c**	**6a**		**7l**	52
7	**2d**	**6a**		**7m**	62
8[c]	**2b**	**6a**		**7n**	91, 75[g]
9[c]	**2e**	**6a**		**7o**	63
10[c]	**2a**	**6c**		**7p**	86, 86[g]
11[c]	**2b**	**6c**		**7q**	81
12	**2a**	**6g**		**7r**	85 (α/γ=70:30)
13	**2a**	**6d**		**7s**	51[g]

[a] Used 0.3 mmol of **2** and 15 mol% of CuI/P(OEt)$_3$ unless otherwise noted. [b] Yield of isolated product. [c] Used 10 mol% CuI/P(OEt)$_3$. [d] Used 1 mmol of **2a**. [e] Used 7 mol% CuI/P(OEt)$_3$. [f] Carried out with K_2CO_3 (1.1 equiv) and 15 mol% CuI/P(OEt)$_3$. [g] Carried out with Li*Ot*Bu (1.1 equiv) and 15 mol% CuI/P(OEt)$_3$.

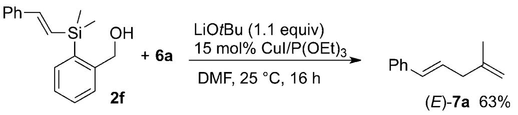
conditions (Table 4). The primary alkyl iodides were applicable to the C(sp^2)–C(sp^3) coupling of **2** and the alkylated arenes **7h–k** were obtained in good yields by the reaction with iodomethane, iodoethane, and iodobutane (**6b,e,f**; entries 1–4). The butylation of **2a** on large scale proceeded similarly in better yield (entry 2). The reactive organic halides such as allylic and benzylic halides (**6a,c,d,g**) also coupled with the silanes **2a–e** under identical reaction conditions to give **7e** and **7l–s** (entries 5–13). The reaction of **2a** with prenyl chloride (**6g**) produced a mixture of the formal S_N2 and S_N2' products **7r**, in which the former predominated (entry 12). The cross-coupling between **2a** with such reactive halides was successful even when weaker bases such as K_2CO_3 (entry 5) or Li*Ot*Bu (entries 8, 10, and 13) were used instead of BuLi. In all the allylations examined, no isomerization to conjugate dienes was observed. Ester, amine, and halogen functional groups were compatible with the coupling conditions. In general, the arylsilanes **2** bearing electron-rich arenes gave the coupling products **7** in higher yield compared with those bearing electron-deficient arenes.

A synthetic advantage of this cross-coupling was demonstrated by the fact that an unprotected hydroxy group in the electrophilic coupling partner **6** did not interfere with the reaction (Scheme 2). Thus, the reaction of the arylsilane **2b** with 3-iodopropan-1-ol (**6g**) readily proceeded under the reaction conditions described above to furnish the primary alcohol **7t** in good yield.



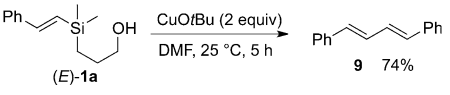
Scheme 2. Cross-coupling of **2b** with 3-iodopropan-1-ol (**6g**).

This catalytic process is not restricted to aryl–alkyl coupling. The same procedure is applicable to the coupling of alkenylsilanes. The reaction of the alkenylsilane **2f** with **6a** was effectively catalyzed by 15 mol% CuI/P(OEt)$_3$ in the presence of Li*Ot*Bu (1.1 equiv) to give the skipped diene (*E*)-**7a** in good yield (Scheme 3).



Scheme 3. Cross-coupling of **2f** with methallyl chloride (**6a**).

We assumed that these reactions proceed by the formation of either aryl- or alkenylcopper intermediates through transmetallation of the Cu^I complex with pentacoordinate cyclic silicates.[6d,9,10] Indeed, the formation of the alkenylcopper species was implied by the observation that the treatment of (*E*)-**1a** with CuO*t*Bu in the absence of an organic halide produced the homocoupling product, (1*E*,3*E*)-1,4-dipehnylbuta-1,3-diene (**9**; Scheme 4). The 1,3-diene **9** is formed by the dimerization of the alkenylcopper species with complete retention of configuration at the double bond.[15]



Scheme 4. Copper(I)-promoted homocoupling of the alkenylsilane (*E*)-**1a**.

In conclusion, we have developed the fluoride-free copper(I)-catalyzed cross-coupling between aryl- and alkenylsilanes [C(sp^2) nucleophiles] and organic halides [C(sp^3)

electrophiles] including primary alkyl iodides. The Si–C bond was activated by the formation of the cyclic silicates to promote the transmetallation from silicon to copper. A variety of functional groups was tolerated and even a free OH group in the electrophiles does not affect the reaction. Extension of the silicon-based copper(I)-catalyzed cross-coupling to various silanes is now under investigation.

Experimental Section

Typical procedure for the catalytic allylation of the alkenylsilanes **1**: BuLi (1.58M in hexane, 0.21 mL, 0.33 mmol) was added dropwise to a solution of the alkenylsilane (*Z*)-**1c** (75 mg, 0.30 mmol) in THF (0.75 mL) at 0°C under Ar. After stirring for 30 min, [(IPr)CuCl] (22 mg, 0.045 mmol) and a solution of methallyl chloride (**6a**; 41 mg, 0.45 mmol) in DMF (1.5 mL) were successively added at 0°C. The mixture was heated at 90°C for 6 h. The reaction was quenched by addition of 3.5% aqueous NH_3 and the product was extracted with diethyl ether. The extract was washed with H_2O and dried over Na_2SO_4. The solvent was evaporated under reduced pressure and the residue was purified by PTLC (*n*-hexanes) to give (*Z*)-**7c** (39 mg, 70%).

Typical procedure for the catalytic alkylation of the arylsilanes **2**: BuLi (1.58M in hexane, 0.21 mL, 0.33 mmol) was added dropwise to a solution of the alkenylsilane **2b** (123 mg, 0.30 mmol) in THF (0.75 mL) at 0°C under Ar. After 30 min, CuI (8.6 mg, 0.045 mmol) and a mixture of $P(OEt)_3$ (7.5 mg, 0.045 mmol) and 1-iodobutane (**6f**; 83 mg, 0.45 mmol) in DMF (1.5 mL) were successively added. The reaction mixture was heated at 50°C for 16 h. After usual work-up, described above, **7k** (82 mg, 91%) was obtained.

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