

## III.2.4 Overview of Other Palladium-Catalyzed Cross-Coupling Protocols

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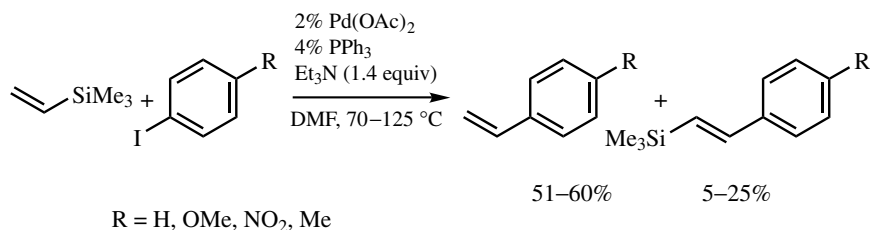
### A. INTRODUCTION

In this section is reviewed the cross-coupling reaction of organometallic compounds containing a main group metal such as Si, Ge, Cd, In, Hg, Pb, or Bi, not covered in **Sects. III.2.1–III.2.3**. The carbon–metal bond of these compounds, although less polarized than those of the organometallics covered in preceding sections, has sufficient but not immoderate nucleophilicity to react with palladium(II) complexes. This character leads to chemoselective cross-coupling reactions. Organosilicon compounds have a weakly polarized C—Si bond and thus often need activation by a Lewis base to couple with electrophiles. Organolead compounds having electron-withdrawing ligands sometimes act as an electrophile to react with nucleophilic organometallic compounds, giving cross-coupled products.

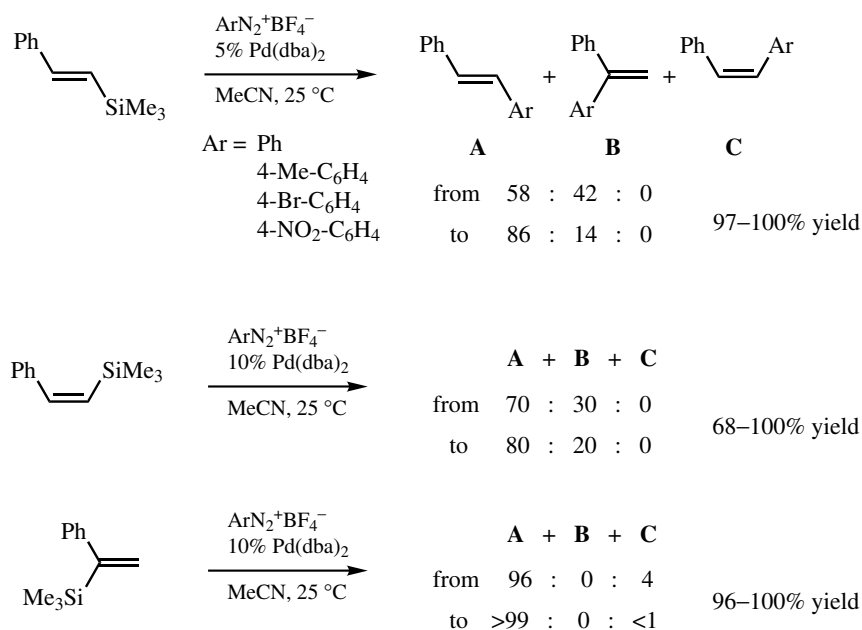
### B. ORGANOSILICON COMPOUNDS<sup>[1]–[4]</sup>

#### B.i. Alkenylsilane

Neutral organosilanes (R—SiMe<sub>3</sub>) are weak nucleophiles among the organometallics described in this section and generally do not undergo a desilylative coupling reaction with aryl halides in the presence of a palladium catalyst except for the following examples. Hallberg and Westerlund<sup>[5]</sup> reported that although trimethyl(vinyl)silane could transmetalate with an arylpalladium(II) complex to afford coupled products, aryl-substituted alkenylsilanes formed through the Heck type reaction also accompanied (**Scheme 1**). On the other hand, Kikukawa and co-workers<sup>[6]–[8]</sup> found that the reaction of trimethyl(α- or β-styryl)silanes with arenediazonium tetrafluoroborates gave a regioisomeric mixture of coupling products. The catalytic cycle of the reaction is considered to involve carbopalladation toward the C—C double bond of an alkenylsilane by an arylpalladium intermediate followed by tetrafluoroborate-assisted elimination of the silyl group and palladium(0) (**Scheme 2**).



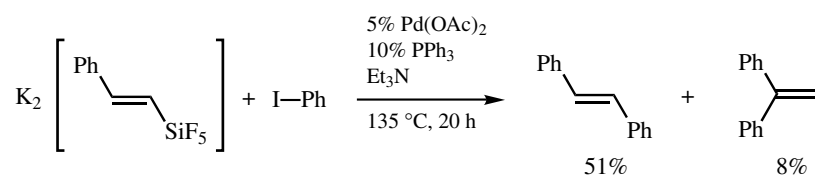
Scheme 1



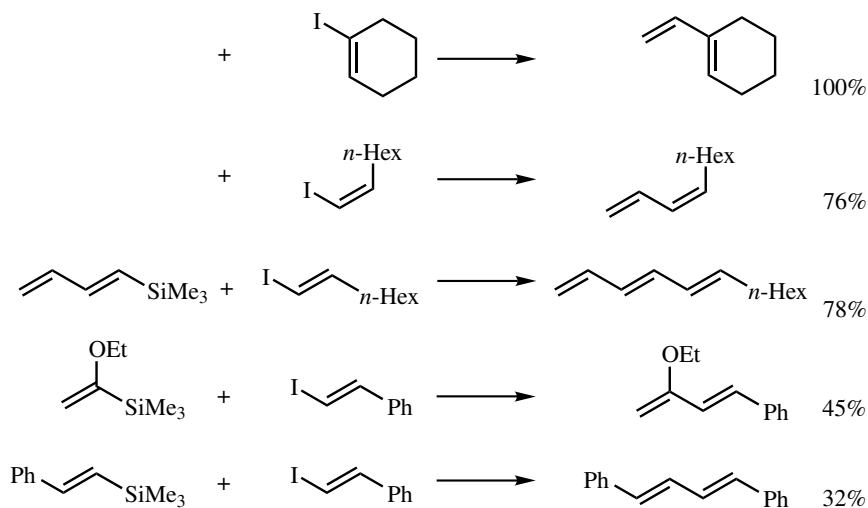
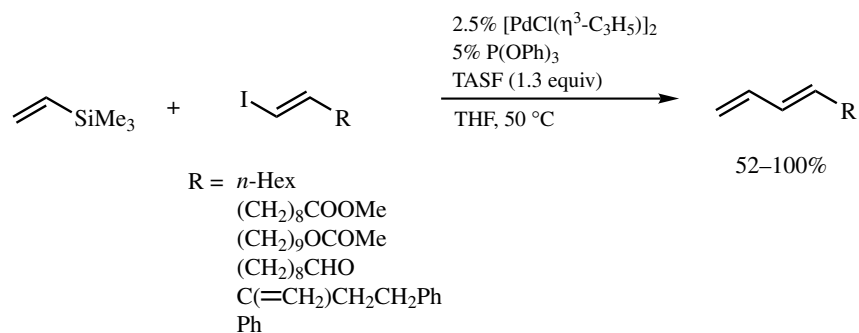
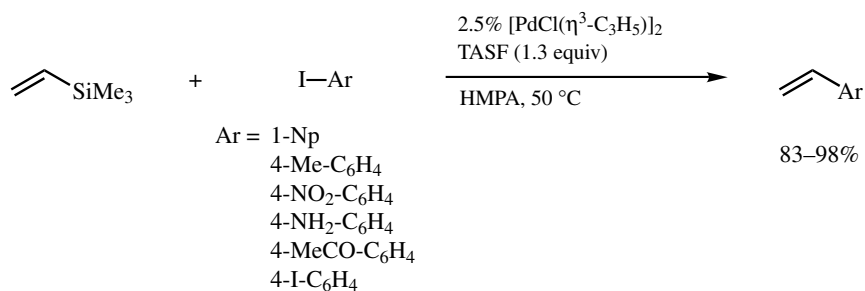
Scheme 2

In 1982 Yoshida et al.<sup>[9]</sup> disclosed that an organofluorosilicate underwent desilylative coupling with iodobenzene in the presence of a palladium catalyst under rather drastic reaction conditions (**Scheme 3**). Although the nucleophilicity at the carbon atom having a silicate group is apparently enhanced, a mixture of regioisomers resulted.

From the standpoint of organic synthesis, the coupling through carbopalladation of a C—C double bond of alkenylsilanes is not useful because the reactions afford a mixture of isomers and the substrate is limited to alkenylsilanes. Hatanaka and Hiyama<sup>[10]</sup> overcame these drawbacks by using fluoride salts to *in situ* activate organosilicon compounds. Thus, an alkenyl(trimethyl)silane coupled with an aryl or alkenyl halide in the presence of a palladium catalyst and (Et<sub>2</sub>N)<sub>3</sub>S<sup>+</sup>(Me<sub>3</sub>SiF<sub>2</sub>)<sup>−</sup>, abbreviated as TASF, with retention of the double bond geometry of both substrates (**Scheme 4**).<sup>[10]</sup> Upon activation by a fluoride ion, the nucleophilicity of alkenylsilanes becomes adequate to complete transmetallation. This cross-coupling reaction is tolerant of a wide variety of functional groups such as ester, ketone, aldehyde, and alcohol. Furthermore, mild reaction conditions



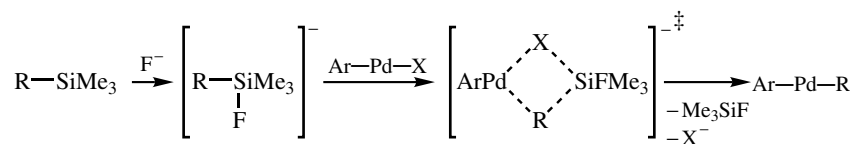
Scheme 3



Scheme 4

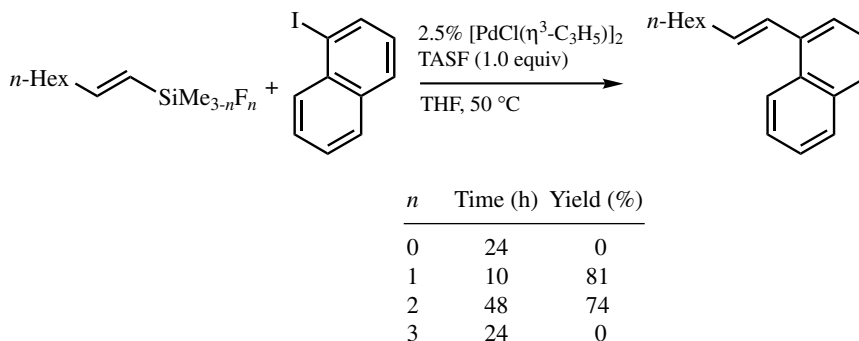
prevent degeneration and/or isomerization of products: thermally labile trienes do not isomerize before the completion of the reaction.  $n\text{-Bu}_4\text{N}^+\text{F}^-$  (TBAF) is equally effective but in some cases inferior to TASF; CsF and KF are futile for diene synthesis.<sup>[11]</sup> Under similar conditions, alkynyl- and allyl(trimethyl)silane also reacted with alkenyl or allyl bromides (*vide infra*).

The following mechanism is suggested for the cross-coupling of alkenylsilanes. Nucleophilic attack of a fluoride ion to the silicon atom of alkenylsilanes should afford a penta-coordinated silicate, whose nucleophilicity of the silicon-substituted carbon and Lewis acidity of silicon are both enhanced to undergo transmetalation effectively through a four-centered transition state (**Scheme 5**). The importance of Lewis acidity on the silicon is evidenced by the fact that the pentafluorosilicates, which should have sufficient nucleophilicity but lack a coordination site on silicon, were not effective substrates for the cross-coupling reaction (**Scheme 3**, *vide supra*).

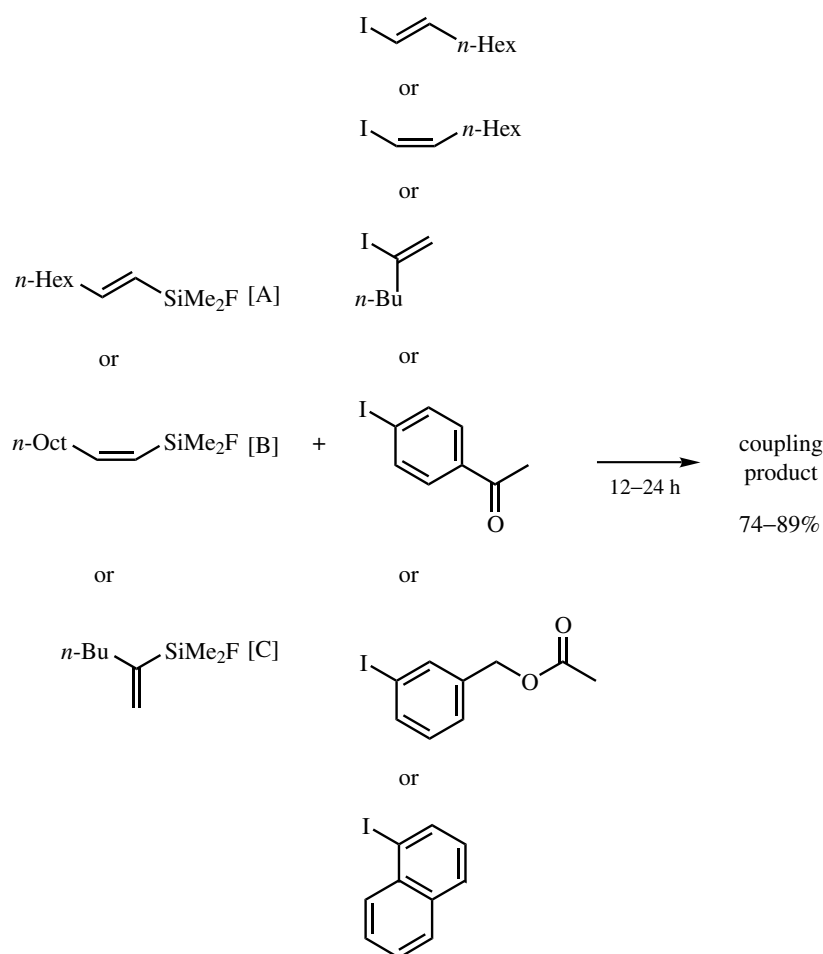


Scheme 5

Trimethyl(vinyl)silanes having an aliphatic substituent on vinyl, however, failed to couple with an aryl iodide under similar conditions, probably because they could not afford pentacoordinated silicates efficiently owing to the electron-donating nature of the substituent. To assist the formation of the pentacoordinated intermediates, the methyl group on the silicon atom was replaced by fluorine.<sup>[12]</sup> The coupling reaction of (*E*)-1-fluoro(methyl)silyl-1-octene with 1-iodonaphthalene clearly suggested that introduction of one or two fluorine atom(s) on silicon was effective (**Scheme 6**). Inertness of (*E*)-1-trifluorosilyl-1-octene is attributed to the formation of an unreactive hexacoordinated silicate. These findings led to the successful coupling reaction of various alkenylsilanes with aryl and alkenyl iodides with complete retention of configuration of both the coupling partners (**Scheme 7**).



Scheme 6



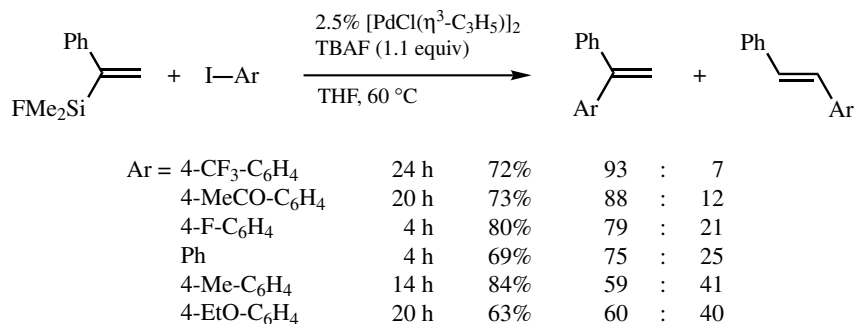
[A] 2.5%  $[\text{PdCl}(\eta^3\text{-C}_3\text{H}_5)]_2$ , TASF (1.5 equiv), THF, 60 °C

[B] 5%  $\text{Pd}(\text{PPh}_3)_4$ , TASF (1.5 equiv), THF, 60 °C

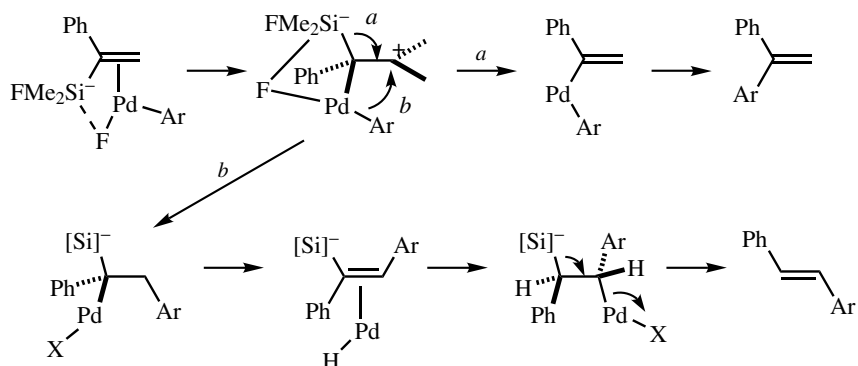
[C] 2.5%  $[\text{PdCl}(\eta^3\text{-C}_3\text{H}_5)]_2$ , TBAF (1.5 equiv), THF, 60 °C

**Scheme 7**

The cross-coupling reaction of alkenyl(fluoro)silanes with aryl halides sometimes produces small amounts of *cine*-coupled products in addition to the desired *ipso*-coupled products.<sup>[13]</sup> The *cine*-coupling is often striking in the reaction with organotin compounds. The isomer ratio of products produced by the reaction of 1-fluoro(dimethyl)silyl-1-phenylethene with aryl iodides is found to depend on the electronic nature of the substituent on aryl iodides (**Scheme 8**). An electron-withdrawing group like trifluoromethyl and acetyl favors the formation of the *ipso*-coupled product. To explain the substituent effect, a mechanism is proposed for the transmetalation of alkenylsilanes with palladium(II) complexes and is depicted in **Scheme 9**. It is considered that an electron-donating substituent on Ar enhances the nucleophilicity of the aryl group to promote an intramolecular nucleophilic attack of Ar to the cationic  $\beta$ -carbon (path *b*), leading to the *cine*-coupled product.



Scheme 8



Scheme 9

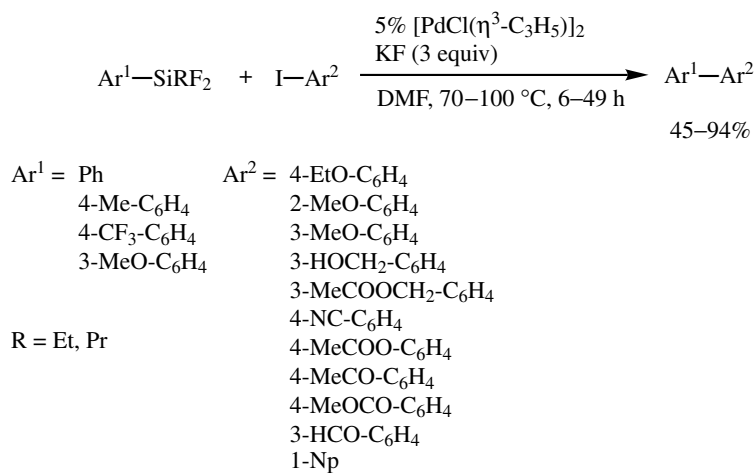
### B.ii. Arylsilane

The coupling reaction of arylsilanes with aryl iodides is also mediated by a palladium catalyst and a fluoride ion.<sup>[14],[15]</sup> Optimized reaction conditions are as follows: (i) two fluorine atoms on silicon are required; (ii) an ethyl or propyl group as a dummy alkyl ligand is preferred, because a methyl group competitively participates in the cross-coupling reaction; and (iii) TBAF, a highly effective fluoride ion source, can be replaced by inexpensive KF. Various unsymmetrical biaryls are synthesized under the conditions (Scheme 10).

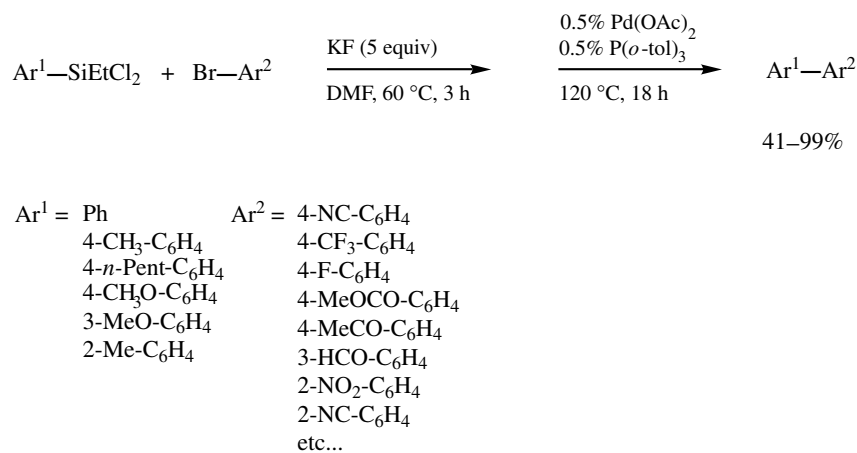
Aryl(chloro)silanes, upon pretreatment with KF, smoothly undergo the Pd-catalyzed coupling with aryl bromides and iodides to give various biaryls. For this procedure, Pd(OAc)<sub>2</sub> (0.5 mol %)/P(*o*-tol)<sub>3</sub> (0.5 mol %) is convenient (Scheme 11).

Under an atmospheric pressure of carbon monoxide, aryl- and alkenylsilanes undergo a carbonylative coupling reaction with aryl and alkenyl halides.<sup>[16],[17]</sup> The optimized conditions for arylsilanes were use of *N,N*-dimethyl-2-imidazolidinone (DMI) as a solvent and KF as a fluoride ion source (Scheme 12), whereas alkenylsilanes preferred THF and TBAF (Scheme 13).

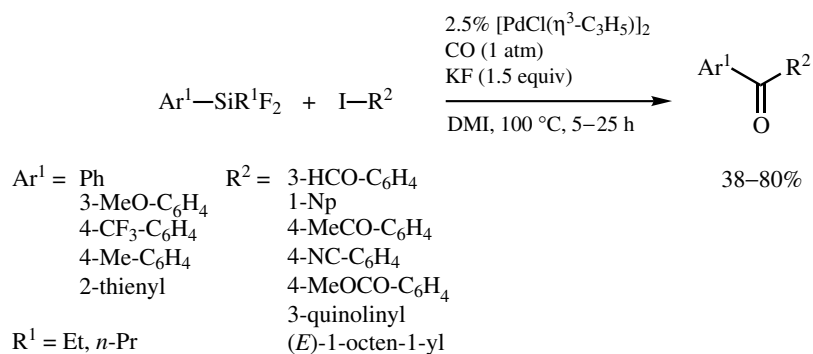
Recently, Shibata and co-workers<sup>[18]</sup> found that aryl(trimethoxy)silanes were also applicable to the Pd-catalyzed cross-coupling reaction with aryl bromides (Scheme 14). A similar procedure using phenyl-, vinyl- and allyl(trialkoxy)silanes was also reported by Mowery and DeShong.<sup>[19]</sup>



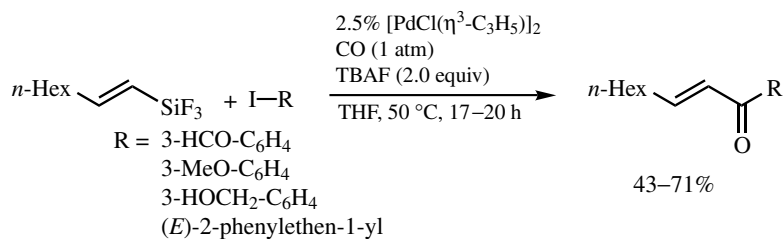
Scheme 10



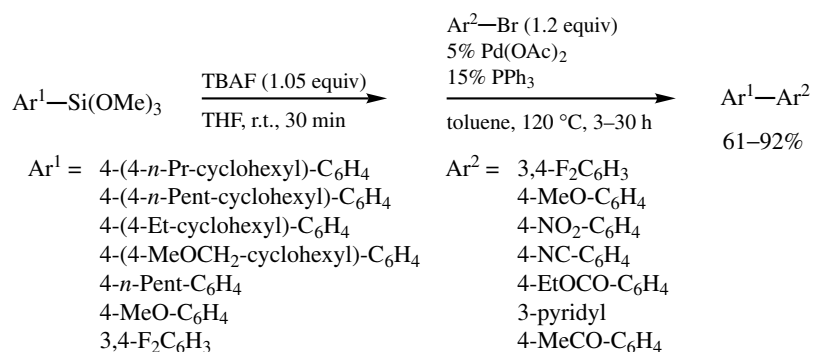
Scheme 11



Scheme 12

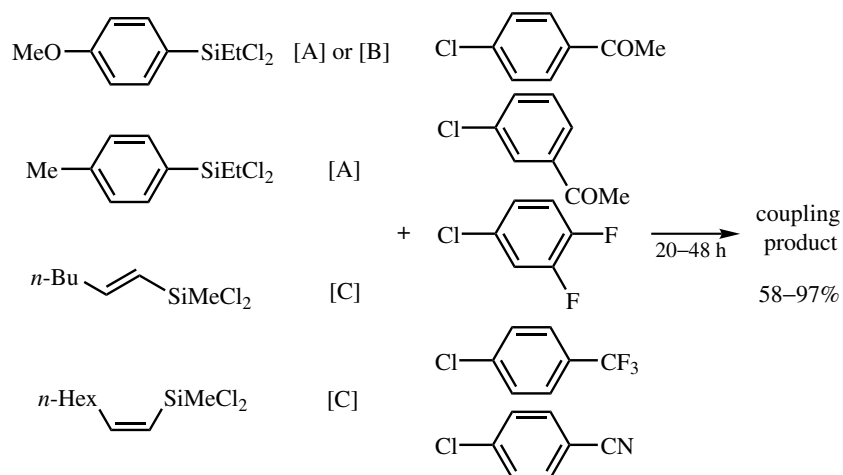


Scheme 13



Scheme 14

Aryl chlorides that are usually unreactive in Pd-catalyzed cross-coupling reactions are applicable to the reaction with aryl- and alkenylchlorosilanes using a fluoride ion reagent and a catalytic amount of  $(i\text{-Pr}_3\text{P})_2\text{PdCl}_2$ ,  $(\text{Cy}_2\text{PCH}_2\text{CH}_2\text{PCy}_2)\text{PdCl}_2$ , or  $[\text{PdCl}(\eta^3\text{-C}_3\text{H}_5)]_2$  (Scheme 15).<sup>[20]</sup>



[A] 0.5%  $\text{PdCl}_2(i\text{-Pr}_3\text{P})_2$ , KF (6 equiv), DMF, 120 °C

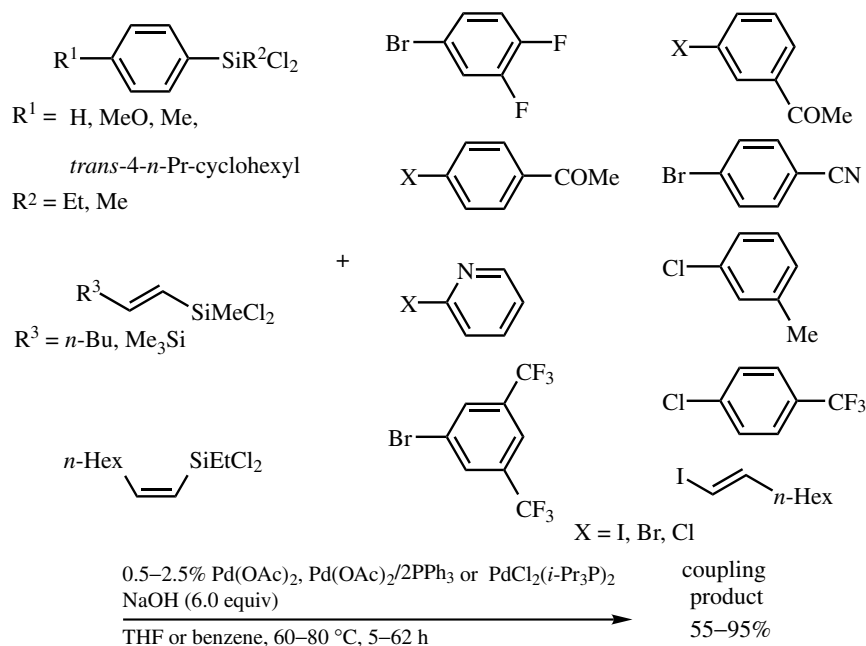
[B] 2.0%  $\text{PdCl}_2(\text{Cy}_2\text{PCH}_2\text{CH}_2\text{PCy}_2)$ , KF (10 equiv), DMF, 120 °C

[C] 0.5%  $[\text{PdCl}(\eta^3\text{-C}_3\text{H}_5)]_2$ , TBAF (3.6 equiv), THF, 90 °C in a sealed tube

Scheme 15

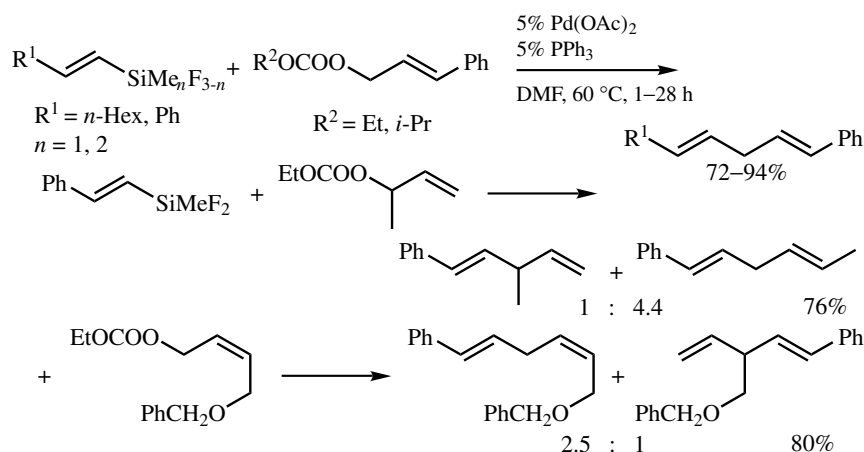


The role of a fluoride ion as an activator and as a ligand on silicon can be played by a hydroxide ion and a chloride ligand, respectively.<sup>[21]</sup> Thus, the Pd-catalyzed coupling of aryl- and alkenylchlorosilanes with aryl and alkenyl halides was accomplished in the presence of NaOH under mild conditions (**Scheme 16**).



Scheme 16

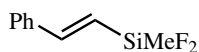
Allyl carbonates (**Schemes 17 and 18**) and diene monoxides (**Scheme 19**) were also employed in the Pd-catalyzed coupling reaction of aryl- and alkenylsilanes.<sup>[22],[23]</sup> The reaction does not require activation by a fluoride ion or an additional base like a hydroxide ion.



Scheme 17



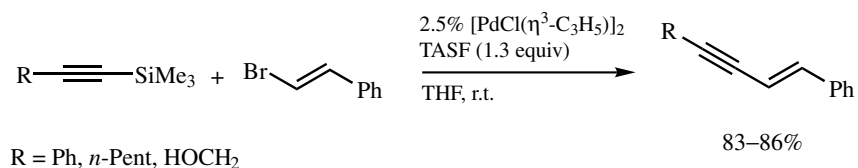
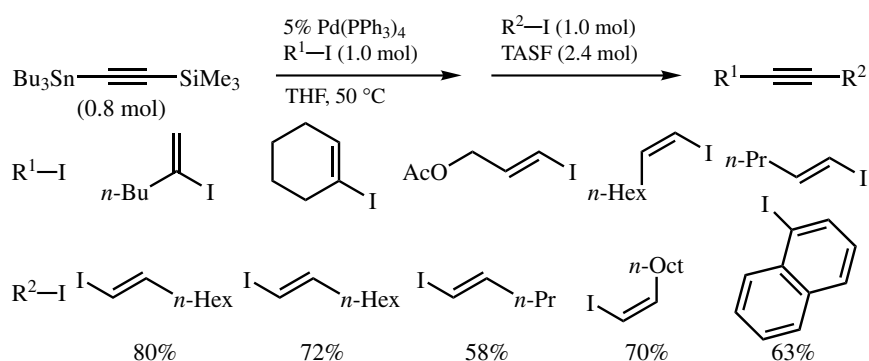
### Scheme 18



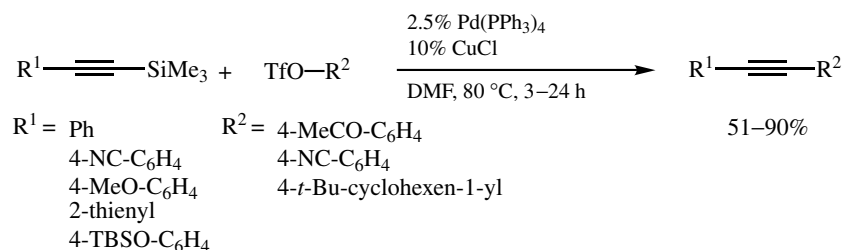
### Scheme 19

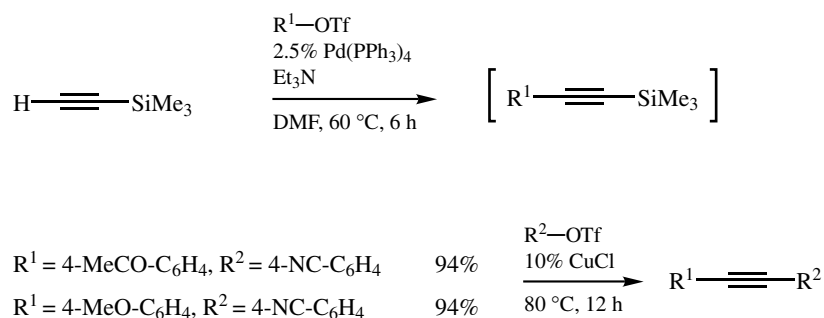
**B.iii. Alkynylsilane**

Alkynyl(trimethyl)silanes smoothly couple with alkenyl halides at room temperature in the presence of a palladium catalyst and TASF (**Scheme 20**).<sup>[13]</sup> The difference in reactivity between alkynylstannanes and -silanes was utilized in a Pd-catalyzed three-component cross-coupling reaction. Thus, the Pd-catalyzed sequential reaction of tributylstannyl(trimethylsilyl)ethyne first with an alkenyl halide and second with another alkenyl or aryl iodide in the presence of newly added TASF afforded conjugated dienes or arylenyne (**Scheme 21**).<sup>[24]</sup>

**Scheme 20****Scheme 21**

A catalytic amount of CuCl was found to also activate alkynyltrimethylsilanes in the Pd-catalyzed coupling reaction with aryl and alkenyl triflates (**Scheme 22**).<sup>[25]</sup> The catalytic cycle is considered to involve the transfer of an alkynyl group from an alkynylsilane to Cu(I), then to Pd(II). A sequential Pd-catalyzed reaction of trimethylsilylacetylene gives unsymmetrical diarylacetylenes (**Scheme 23**).

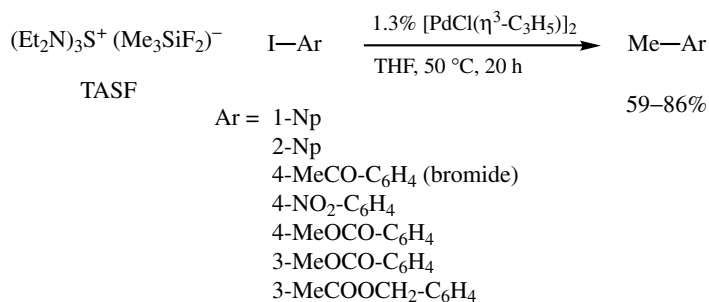
**Scheme 22**



Scheme 23

**B.iv. Alkylsilane**

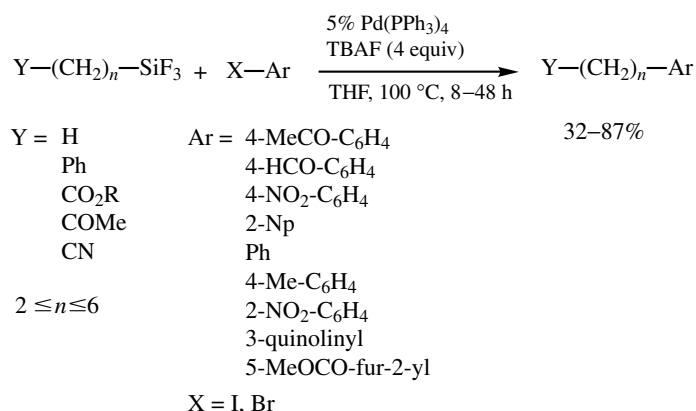
Pentacoordinated silicate TASF, one of the best activators of organosilicon compounds in the Pd-catalyzed cross-coupling reaction as we have seen, is found to be involved in the coupling reaction with aryl halides in the absence of other organosilanes to give methylated arenes (**Scheme 24**).<sup>[26]</sup> Recently, DeShong and co-workers also reported that tetrabutylammonium triphenyldifluorosilicate, another pentacoordinated silicate, is applicable for the phenylation of allyl benzoates<sup>[27]</sup> and aryl halides<sup>[28]</sup> in the presence of a palladium catalyst.



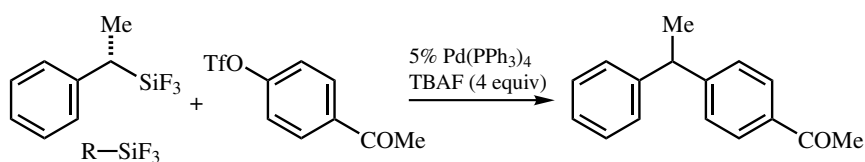
Scheme 24

Alkylsilanes activated *in situ* by TBAF are also applicable to the cross-coupling reaction with aryl halides (**Scheme 25**).<sup>[29],[30]</sup> The fact that the reaction requires excess amount of a fluoride ion for giving products in acceptable yields is ascribed to the trapping of the fluoride ion by coproduced  $\text{SiF}_4$ , which is converted into  $(\text{SiF}_5)^-$  or  $(\text{SiF}_6)^{2-}$ .

The cross-coupling reaction of an optically active alkylsilane gives us valuable information on the stereochemistry in transmetalation.<sup>[31]</sup> The reaction of (*S*)-1-phenyl-1-(trifluorosilyl)ethane (34% ee) with 4-acetylphenyl triflate in the presence of 5 mol % of  $\text{Pd(PPh}_3)_4$  and TBAF (2 equiv) at 50 °C gave (*S*)-1-phenyl-1-(4-acetylphenyl)ethane of 33% ee with nearly complete retention of configuration. At higher temperatures, ee of the product decreased linearly, and above 75 °C inversion of configuration predominated (**Scheme 26**). Similar temperature dependency was observed also in the reaction of 3-formylphenyl triflate.



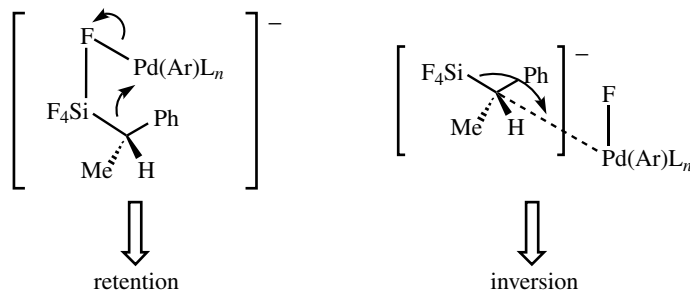
Scheme 25



from ( <i>S</i> )-R—SiF <sub>3</sub> of 34% ee							
Temperature (°C)	50	60	70	80	90	100	in THF
% ee (Configuration)	33 ( <i>S</i> )	23 ( <i>S</i> )	10 ( <i>S</i> )	7 ( <i>R</i> )	18 ( <i>R</i> )	20 ( <i>R</i> )	
from ( <i>S</i> )-R—SiF <sub>3</sub> of 38% ee							
Solvent	THF	DMF–THF (1:10)	DMSO–THF (1:10)	HPMA–THF (1:10)			at 60 °C
% ee (Configuration)	23 ( <i>S</i> )	16 ( <i>S</i> )	16 ( <i>S</i> )	8 ( <i>R</i> )			

Scheme 26

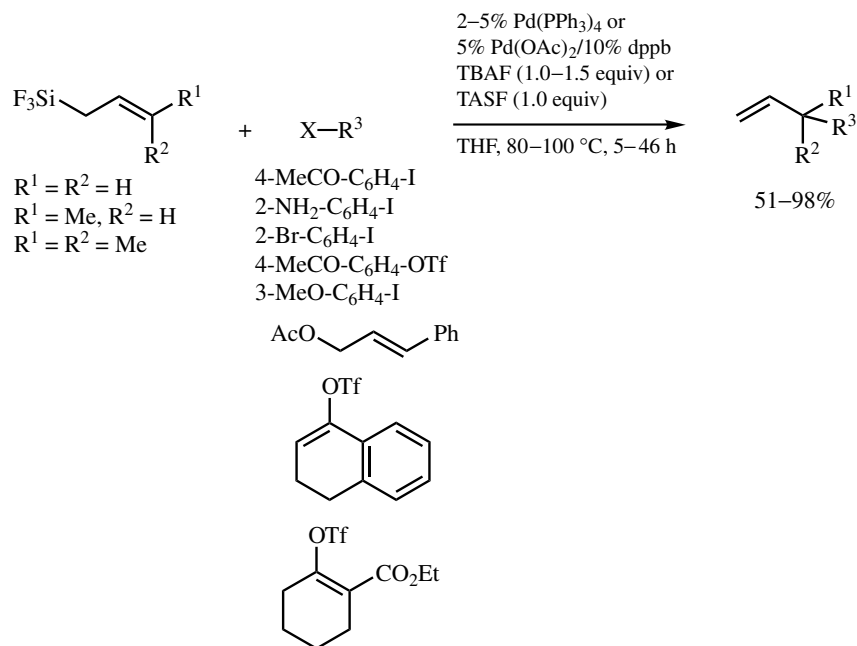
The stereochemistry is also affected by the solvent polarity (**Scheme 26**). The reaction using (*S*)-1-phenyl-1-(trifluorosilyl)ethane of 38% ee at 60 °C resulted in retention (23% ee, *S*) in THF, but inversion (8% ee, *R*) in HMPA–THF (1:10). Higher temperature and polar solvents are considered to change the reaction mechanism of transmetalation from a four-centered transition state [ $S_E2$  (cyclic)] to a backside attack of the palladium(II) complex [ $S_E2$  (open)] (**Scheme 27**).



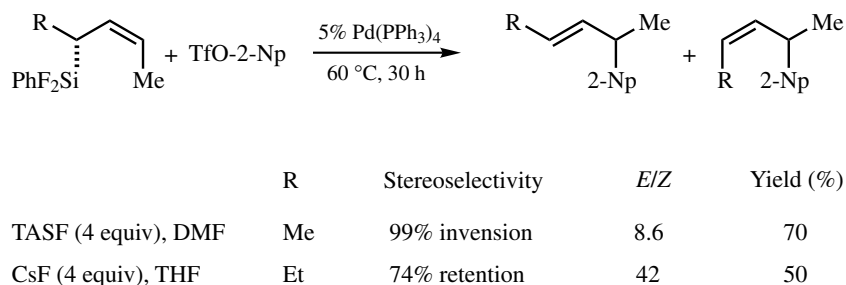
Scheme 27

**B.v. Allylsilane**

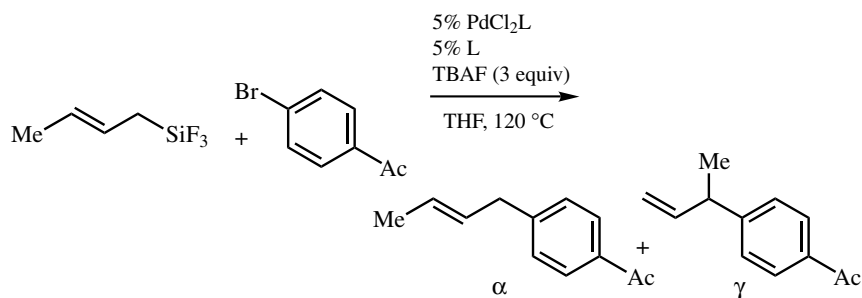
Allyltrifluorosilanes undergo the cross-coupling reaction with aryl halides, an allyl acetate, or alkenyl triflates exclusively at the  $\gamma$ -carbon to give allylated products (**Scheme 28**).<sup>[32]</sup> The  $\gamma$ -selectivity is noteworthy, because the cross-coupling reaction using other allylmetals usually takes place via  $\alpha$ -attack.

**Scheme 28**

The reaction of optically active allyl(difluoro)phenylsilanes with aryl triflates affords optically active allylarenes with high stereoselectivities, wherein the absolute configuration of the newly generated chiral carbon can be controlled by the choice of a fluoride salt and the solvent polarity (**Scheme 29**).<sup>[33]</sup> Aryl and alkenyl triflates are effective coupling partners not only for allylsilanes but also for alkenyl-, aryl-, alkyl-, and alkynylsilanes<sup>[34]</sup> as we have been seen in some examples of the preceding sections.

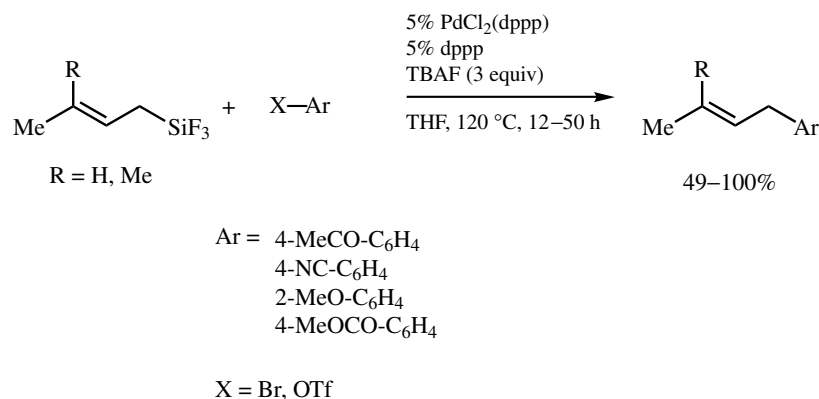
**Scheme 29**

Bisphosphine ligands having a certain bite angle, however, change the regioselectivity of allylsilane coupling from  $\gamma$ - to  $\alpha$ -carbon (**Scheme 30**).<sup>[35]</sup> Retardation of a reductive elimination step by use of a dppe or dppp ligand is assumed, and this is considered to induce isomerization of the secondary  $\gamma(\sigma)$ -allyl in an allyl(aryl)Pd(II) complex to a primary  $\alpha$ -allyl complex. The  $\alpha$ -selective reaction was applied to various aryl bromides or triflates (**Scheme 31**).



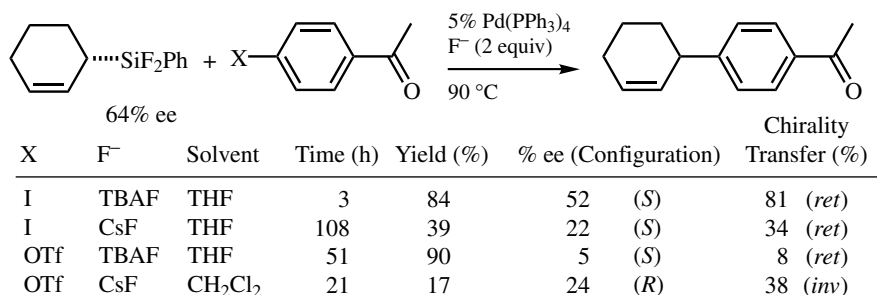
L	Time (h)	Yield (%)	$\alpha : \gamma$	E/Z in $\alpha$
$\text{Ph}_2\text{PCH}_2\text{PPh}_2$	23	85	55:45	4.6:1
$\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2$	18	86	97:1	8.1:1
$\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2$	15	92	99:1	7.2:1
$\text{Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2$	6	57	16:84	4.3:1
$\text{Ph}_2\text{P}(\text{CH}_2)_5\text{PPh}_2$	41	77	6:94	4.8:1
$\text{Ph}_3\text{P}$	12	97	0:100	—

Scheme 30



Scheme 31

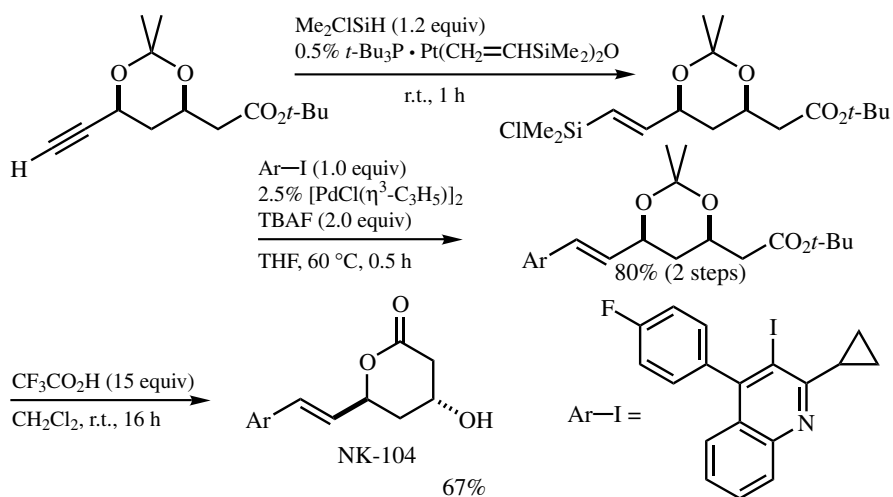
The kind of fluoride ion activator and the leaving group in electrophiles affect the stereochemistry in the cross-coupling reaction of allylsilanes as exemplified with 2-cyclohexenyl(difluoro)phenylsilane (**Scheme 32**).<sup>[36]</sup>



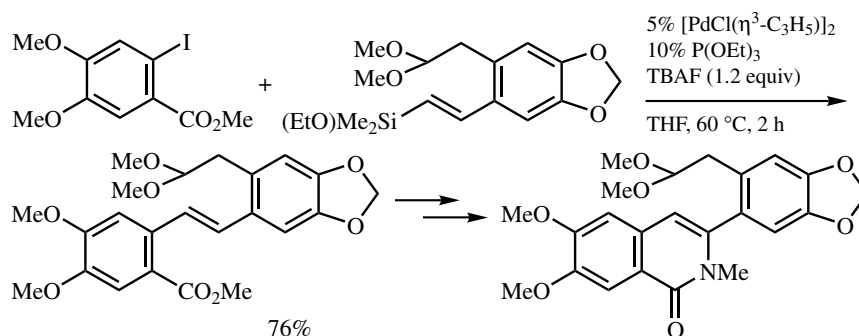
Scheme 32

### B.vi. Synthetic Applications

The Pd-catalyzed cross-coupling reaction of organosilicon compounds is applied to the synthesis of biologically active compounds. Some examples are described in the following schemes: artificial HMG-CoA reductase inhibitor, NK-104 (**Scheme 33**)<sup>[37]–[39]</sup>; a precursor of a DNA topoisomerase inhibitor (**Scheme 34**);<sup>[40]</sup> and nucleosides (**Scheme 35**).<sup>[41]</sup>

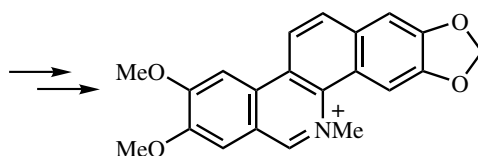


Scheme 33

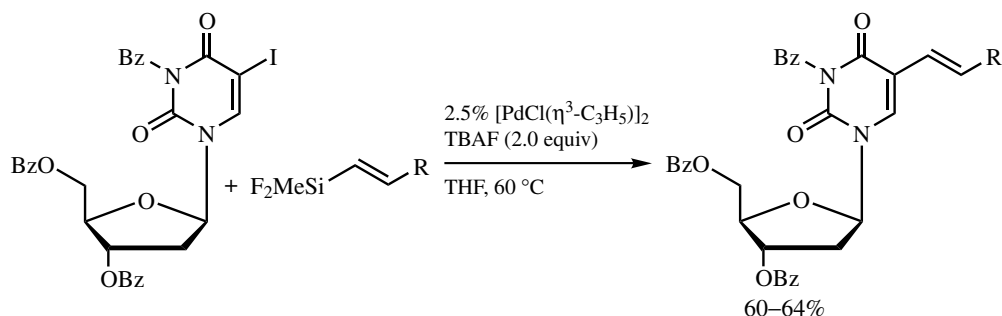


Scheme 34





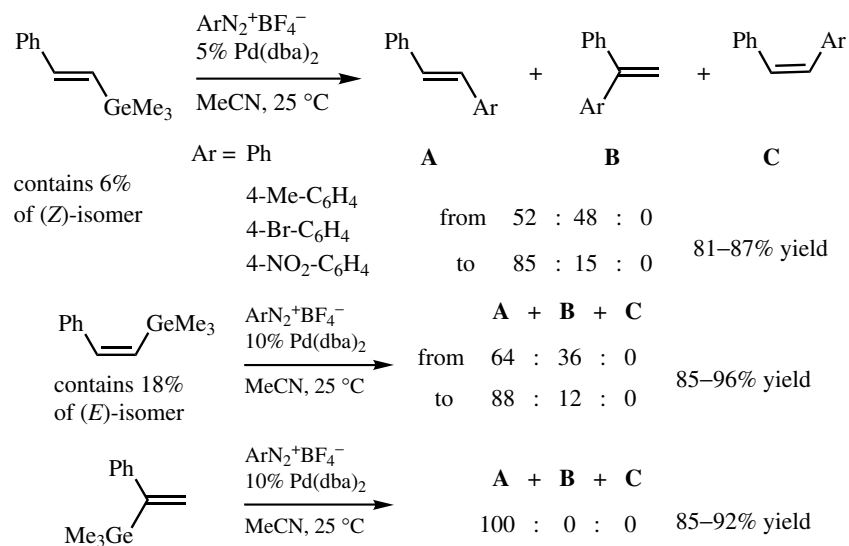
Scheme 34 (Continued)



Scheme 35

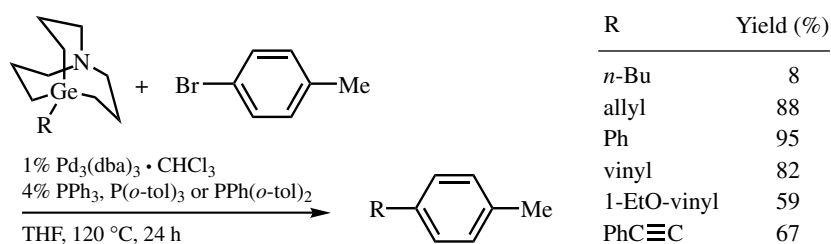
### C. ORGANOGERMANIUM COMPOUNDS

Ikenaga et al.<sup>[42]</sup> reported that trimethyl(styryl)germanes coupled with arenediazonium tetrafluoroborates in the presence of a palladium catalyst (**Scheme 36**). Although the reaction proceeds smoothly under mild conditions, stereochemistry of the alkenylgermanes is not retained as was observed with alkenylsilanes shown in **Scheme 2**. The mechanism is ascribed to a carbopalladation route as discussed with alkenylsilanes.



Scheme 36

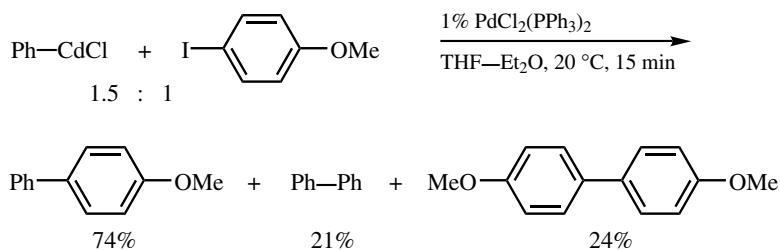
An alkyl, allyl, aryl, or alkynyl group on germanium in addition to an alkenyl group was applicable to the cross-coupling reaction with an aryl bromide (**Scheme 37**).<sup>[43]</sup> Kosugi and co-workers used organogermanes having a nucleophilic nitrogen activating center, which assists the transmetalation by nucleophilic coordination to germanium.



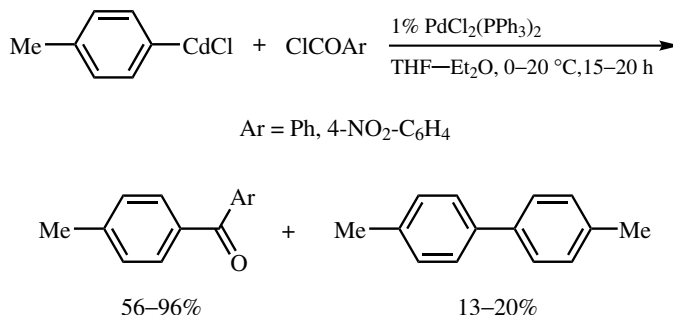
Scheme 37

#### D. ORGANOCADMIUM COMPOUNDS

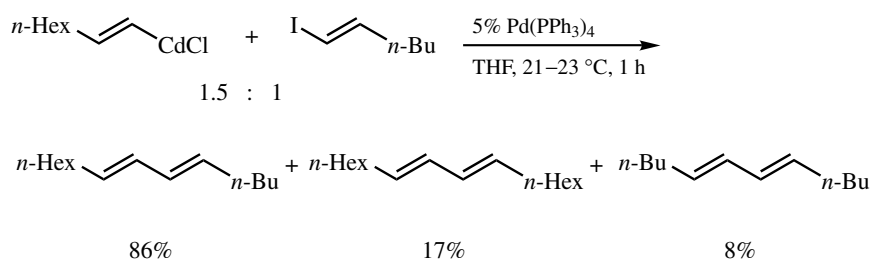
Organocadmium compounds also couple with organic halides in the presence of a palladium catalyst. The reaction of arylcadmium chlorides with aryl or alkenyl halides was disclosed by Bumagin et al.<sup>[44]</sup> (**Schemes 38** and **39**). Similarly, an alkenylcadmium chloride couples with an alkenyl iodide as reported by Negishi et al.<sup>[45]</sup> (**Scheme 40**). Although the cross-coupling products are produced in good yields, homocoupling products derived from both substrates accompany in all cases.



Scheme 38



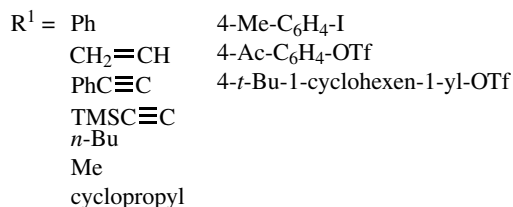
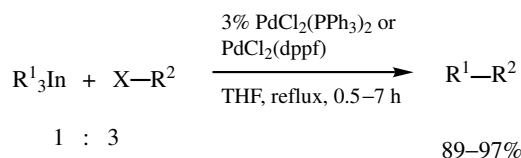
Scheme 39



Scheme 40

### E. ORGANOINDIUM COMPOUNDS

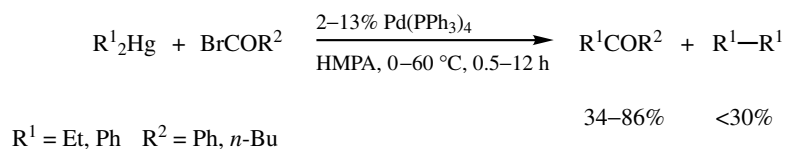
The Pd-catalyzed cross-coupling reaction of organoindium compounds was first reported in 1999.<sup>[46]</sup> The reaction was applied to triaryl-, trialkenyl- and trialkynylindiums, which coupled with aryl iodides, aryl triflates, or alkenyl triflates in high yields (**Scheme 41**). It is noteworthy that all of the organic groups on indium can participate in the coupling reaction.



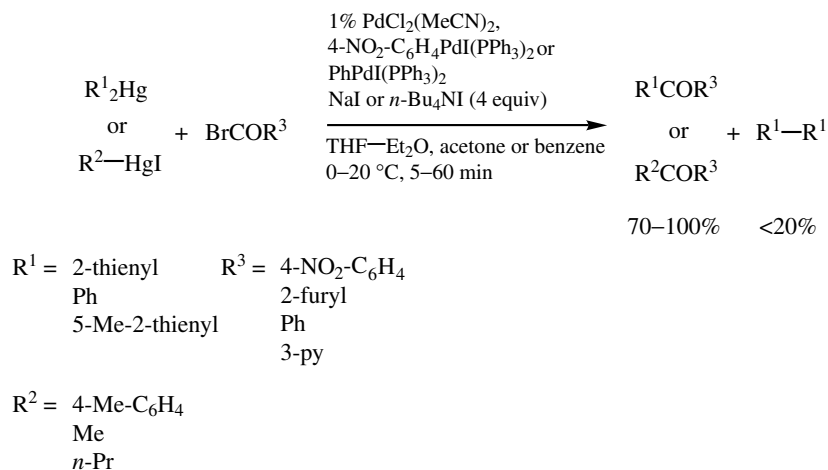
Scheme 41

### F. ORGANOMERCURY COMPOUNDS

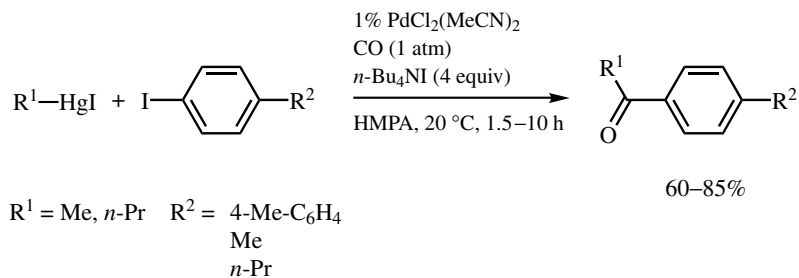
There have been many reports on the cross-coupling reaction of organomercury compounds, although their toxicity results in limited synthetic applications. Takagi and co-workers<sup>[47]</sup> reported the Pd-catalyzed reaction of dialkyl- and diphenylmercury with acyl halides (**Scheme 42**). Additional examples of this particular combination of substrates in addition to a carbonylative cross-coupling were reported later by Bumagin et al.<sup>[44],[48]</sup> (**Schemes 43 and 44**). The coupling reaction of organomercury compounds as applied also for the synthesis of biaryls (**Scheme 45**)<sup>[49],[50]</sup> and conjugated dienes (**Scheme 46**).<sup>[45]</sup>



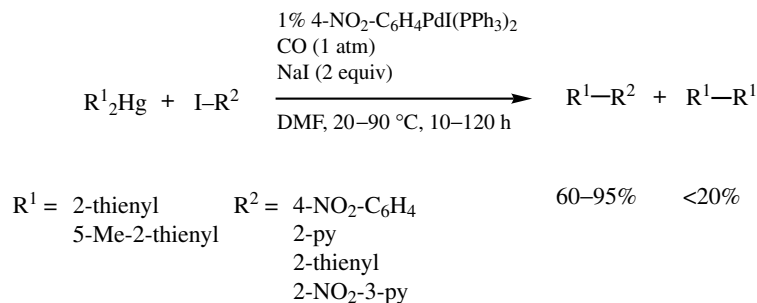
Scheme 42



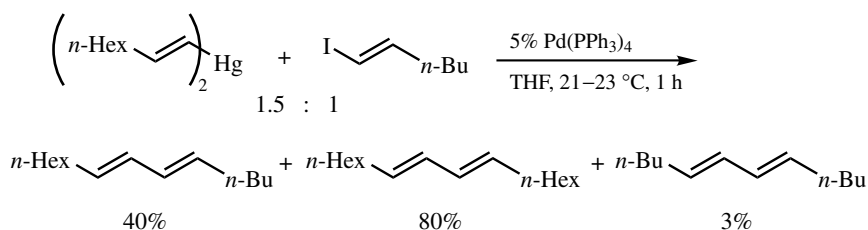
Scheme 43



Scheme 44

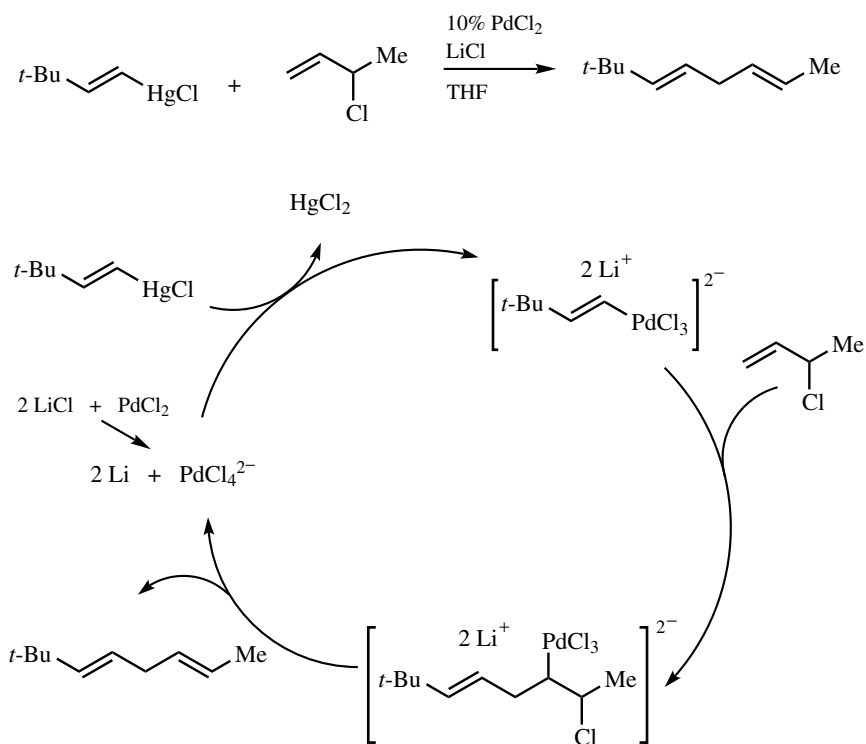


Scheme 45



Scheme 46

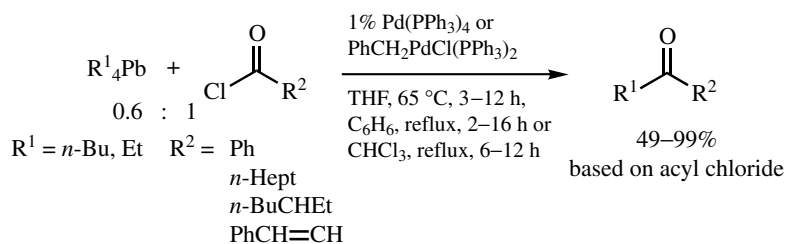
Larock and others<sup>[51]–[58]</sup> reported many examples of the Pd-catalyzed reaction of organomercury compounds with allylic electrophiles, although the catalytic cycle was not considered to include a reductive elimination step (**Scheme 47**).<sup>[51]</sup>



Scheme 47

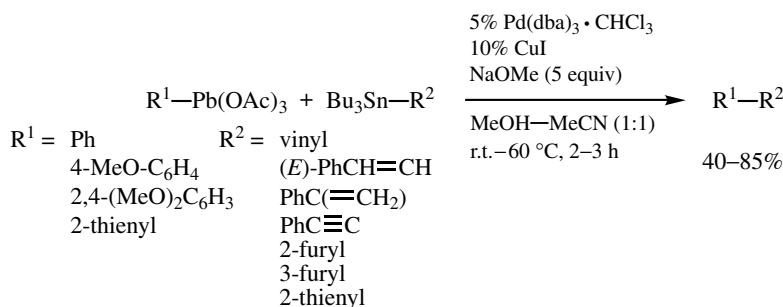
## G. ORGANOLEAD COMPOUNDS

Organolead compounds as a substrate for the Pd-catalyzed cross-coupling was reported in 1987 by Yamada and Yamamoto<sup>[59]</sup>, who observed tetraalkylleads coupled with various acyl chlorides (**Scheme 48**). Two alkyl groups on lead are considered to be utilized for the reaction, because the use of 0.3 equiv of tetraalkyllead lowered the yield.

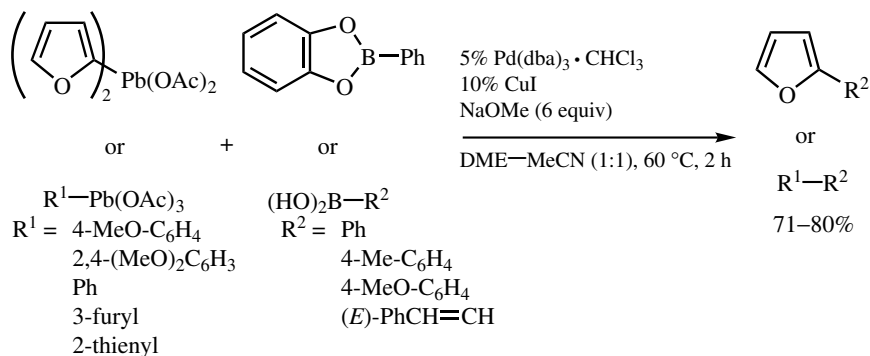


Scheme 48

Organolead compounds sometimes act as electrophiles. Thus, arylleads having acetoxy ligands coupled with organostannane nucleophiles with a palladium catalyst (**Scheme 49**).<sup>[60]</sup> The same strategy was applied also to the coupling with arene- and alkeneboronic acid esters (**Scheme 50**).<sup>[61]</sup>



Scheme 49

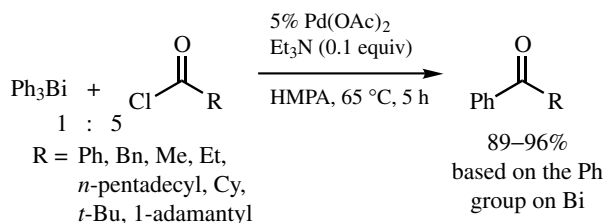


Scheme 50

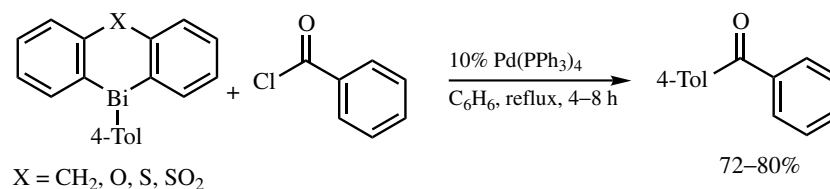
## H. ORGANOBISMUTH COMPOUNDS

The Pd-catalyzed cross-coupling reaction of an organobismuth compound was first recorded by Barton and co-workers in 1988.<sup>[62]</sup> Thus, the reaction of triphenylbismuth with acyl halides took place in the presence of catalytic amounts of Pd(OAc)<sub>2</sub> and

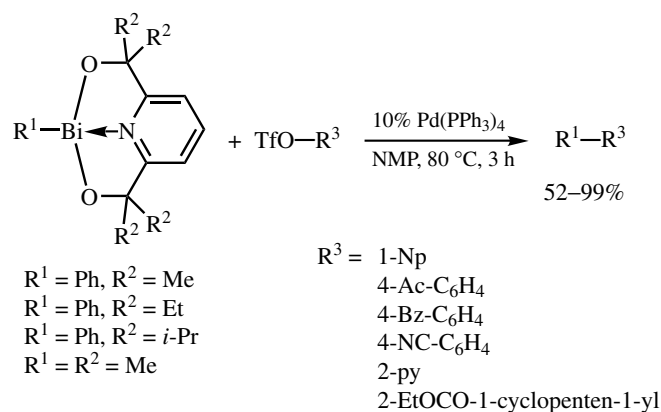
triethylamine; all three phenyl groups on Bi were used for the reaction (**Scheme 51**). Organobismuth compounds having a coordinative moiety were later employed for coupling with acyl halides (**Scheme 52**),<sup>[63]</sup> aryl triflates, and alkenyl triflates (**Scheme 53**).<sup>[64]</sup>



Scheme 51



Scheme 52



Scheme 53

## I. SUMMARY

The cross-coupling reactions described feature high chemoselectivity, that is, high functional group tolerance. On the other hand, the toxicity that is inherent in some heavy metals seems to have limited their synthetic applications. Organosilicon compounds, having little or no toxicity, have an advantage in this respect and should be the most desirable organometallic reagents for the cross-coupling reaction. Their utility will be definitely enhanced by appropriate activation of otherwise inert reagents. Some examples have already been seen in the literature.

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