

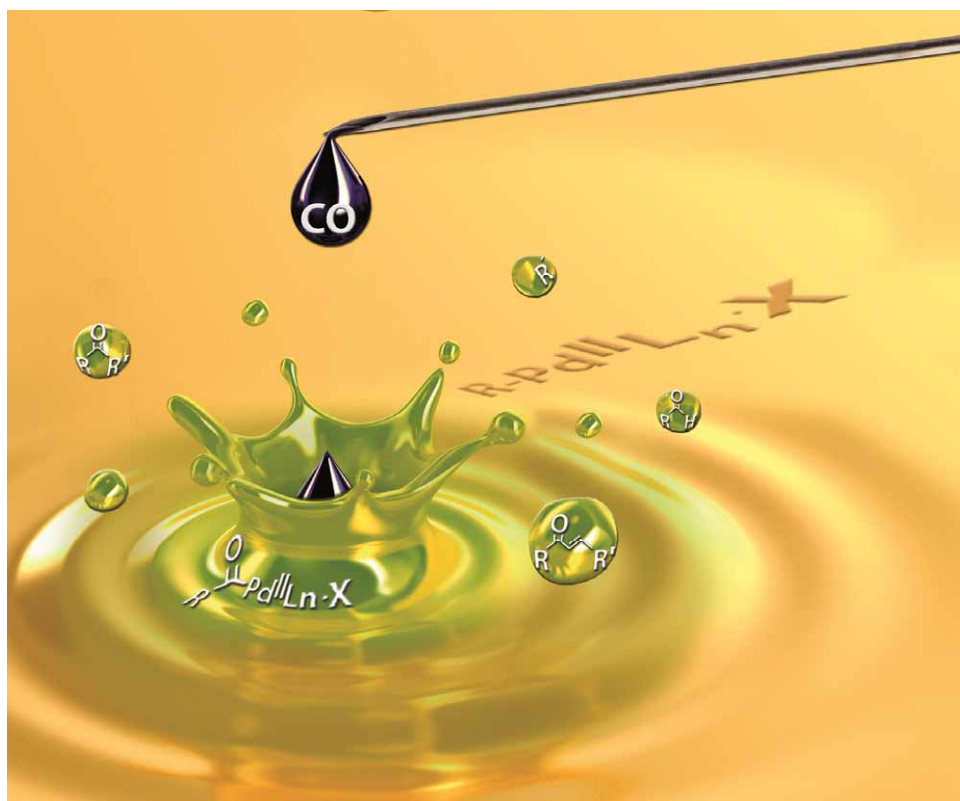
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TUTORIAL REVIEW

Silicon-based cross-coupling reaction: an environmentally benign version†

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Much attention has been paid to the cross-coupling reaction of organosilicon compounds due to their stability, non-toxicity, and natural abundance of silicon. In addition, the silicon-based cross-coupling has many advantages over other cross-coupling protocols. Successful examples of the silicon-based cross-coupling reaction are reviewed, focusing especially on the advances made in the last decade. Having had a number of highly effective palladium catalysts developed mainly for other cross-coupling reactions, the development of the silicon-based protocol owes heavily to the design of organosilicon reagents which effectively undergo transmetalation, a key elemental step of the silicon-based cross-coupling reaction. This *tutorial review* thus classifies various organosilicon reagents depending on substituents on silicon and surveys their cross-coupling reactions with various electrophiles.

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1. Introduction

There is a growing demand for organometallic reagents that exhibit favorable chemoselectivity and stereoselectivity in cross-coupling reactions. The stability of the organometallic reagents is also an important issue for securing purity of reagents. Furthermore, ready availability of reagents with the correct stoichiometry is essential for reproducibility and reliability. In terms of these criteria, the use of organosilicon compounds has received much attention in the cross-coupling



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Dr Yoshiaki Nakao (born in 1976) was educated in chemistry at Kyoto University (PhD mentored by Profs Tamejiro Hiyama and Eiji Shirakawa), Yale University (visiting student mentored by Prof. John F. Hartwig), and Max-Planck-Institut für Kohlenforschung (visiting scholar working for Prof. Manfred T. Reetz). Since 2002, he has been an assistant professor at Kyoto University. He received Mitsui Chemicals Catalysis Science Award of

Encouragement (2009), The Society of Silicon Chemistry Award of Encouragement (2009), Thieme Journal Award (2010), Mecer-Banyu Lectureship Award (2010), The Chemical Society of Japan Award for Young Chemists (2011), and The Commendation for Science and Technology by MEXT, The Young Scientists' Prize (2011). His research interest includes development of new synthetic reactions by metal catalysis for selective synthesis.



Tamejiro Hiyama

Tamejiro Hiyama was appointed to be an associate professor at Kyoto University in 1972, completed his PhD in engineering at KU in 1975 right before he performed postdoctoral research at Harvard University. In 1981 he started his own research at Sagami Chemical Research Centre. In 1992 he moved to Tokyo Institute of Technology as a full professor and further to Kyoto University in 1997. Since retirement from Kyoto University in 2010, he has been at Chuo University as an RDI

Professor. His research covers from novel synthetic methods (Hiyama reaction, Hiyama cross-coupling, Nozaki–Hiyama–Kishi reaction, etc.) to synthesis of biologically active substances and invention of novel functional materials.

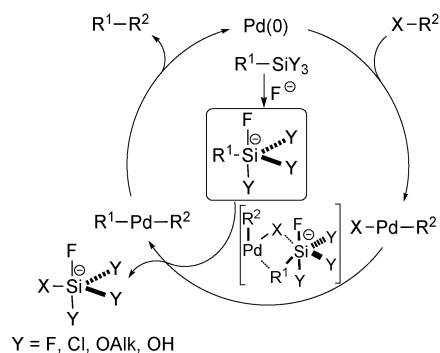
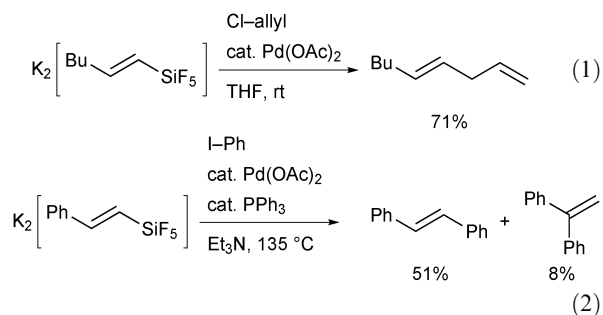
chemistry, because they offer many advantages over other organometallics and organometalloid reagents conventionally used in cross-coupling reactions.

Many types of organosilicon reagents are readily available by virtue of the rich history of organosilicon chemistry. Indeed, a wide range of organosilicon compounds are commercially available, and these are generally less expensive because of the rich natural abundance of silicon. Organosilicon reagents are, in general, highly stable owing to their less polarised C–Si bonds. This aspect makes the organosilicon reagents less reactive toward electrophiles than the other organometallic nucleophiles. Accordingly, one can expect high chemoselectivity associated with the cross-coupling reaction using silane-based reagents because of the forementioned inherent nature of the organosilicon reagents. These characteristics have made these reagents less familiar in the cross-coupling community until very recently.

In this tutorial review, the cross-coupling reaction using organosilicon reagents is surveyed. Generally, transmetalation, an elemental step that delivers a reacting organic group from silicon to a transition metal center such as palladium and nickel, is a key for successful catalysis of cross-coupling. The mechanism and efficiency of the transmetalation of organosilicon reagents heavily rely on types of organosilicon compounds, namely, tetra-, penta-, or hexacoordinate species. Thus, substituents on silicon significantly affect the transmetalation step. Availability and stability of organosilicon reagents also depend on the substituents on silicon. Therefore, this review classifies various silicon cross-coupling reactions based on types of substituents bound to a silicon center of organosilanes for cross-coupling and describes the features of the respective cross-coupling reaction briefly. Particular attention is paid to the cross-coupling of alkenyl-, aryl-, and alkylsilanes. Critical aspects of silicon-based cross-coupling reactions have often been reviewed before.¹

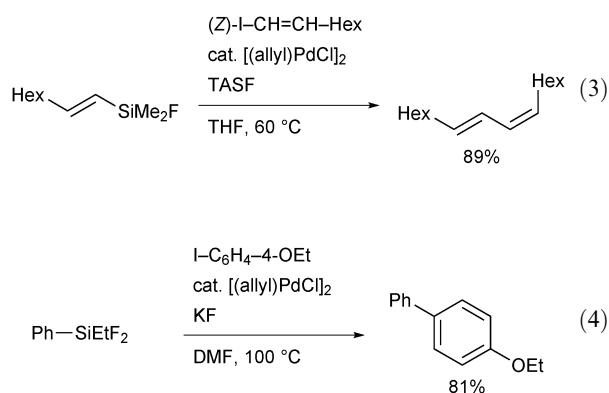
2. Use of organo(halo)silanes

In 1978, Kumada and his coworkers reported that organo(pentafluoro)silicates cross-couple with allylic electrophiles through transmetalation of pentafluoro silicates with palladium(II) (eqn (1)).² They also reported that the pentafluoro silicate reagents undergo the palladium-catalysed cross-coupling with aryl and alkenyl halides (eqn (2)).³ The need for preparation of the hexacoordinate silicate species, however, has rendered these protocols less practical for synthetic organic chemists. Nevertheless, these reports clearly suggested that hypervalent silicates are key organosilicon species to promote the transmetalation step, which is normally reluctant with less nucleophilic tetracoordinate organosilicon compounds.



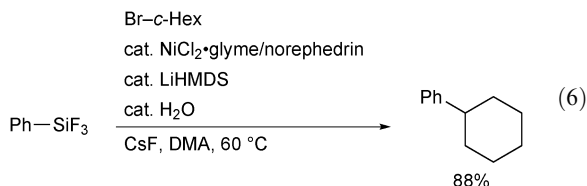
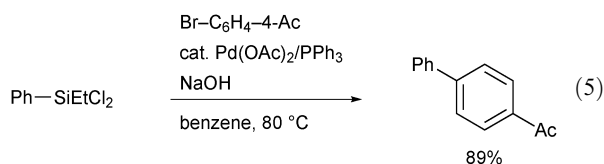
Scheme 1 A general catalytic cycle proposed for silicon cross-coupling reactions by fluoride activation.

The direct use of conventional tetracoordinate organosilanes was thus highly desired in view of practicality. Hiyama and Hatanaka made a significant step forward by developing a protocol to generate requisite hypervalent silicate species *in situ* from readily available tetracoordinate organosilanes. Thus, they reported that tetracoordinate alkenyl-⁴ and arylsilanes⁵ having fluorine substituents undergo the cross-coupling reaction with aryl and alkenyl halides in the presence of a palladium catalyst and a fluoride activator derived from tris(dimethylamino)sulfonium difluorotrimethylsilane (TASF) or tetrabutylammonium fluoride (TBAF) (eqn (3) and (4)). Pentacoordinate silicates generated *in situ* by the nucleophilic attack of a fluoride ion on silicon are supposed to be nucleophilic enough to participate in transmetalation through a four-membered cyclic transition state (hereby Si is temporarily hexacoordinated) with palladium(II) species, which is formed by the oxidative addition of the organic halides to palladium(0) (Scheme 1). The fluorine substituent apparently enhances the Lewis acidity of the silicon center so that the formation of pentacoordinate silicates is promoted and stabilised.⁴

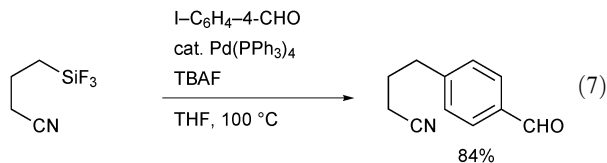


A similar effect of electron-withdrawing heteroatom substituents has subsequently been revealed also with a chloro group.⁶ Because the use of fluoride sources to promote the silicon-based cross-coupling has raised some disadvantages in terms of the cost of the reaction as well as chemoselectivity, a protocol to generate pentacoordinate silicates by nucleophilic hydroxide has been developed to establish fluoride-free conditions with the chlorosilane reagents (eqn (5)).⁷ Alkyl

halides cross-couple with aryl(trifluoro)silanes in the presence of a nickel catalyst to give alkylated arenes (eqn (6)).⁸

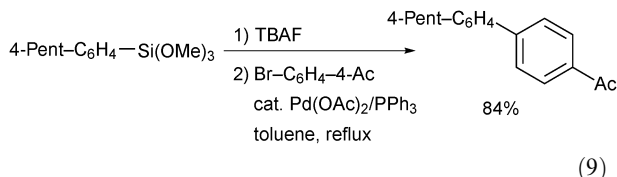
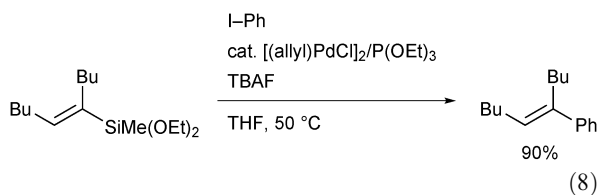


Alternatively, alkyl(trifluoro)silanes were found to be effective to transfer alkyl groups by the silicon cross-coupling reaction (eqn (7)).⁹ These original protocols, however, suffer from the instability of the halogenated silicon reagents toward acids, bases, and moisture. The use of highly nucleophilic fluoride or hydroxide as an activator makes the transformation less chemoselective, especially for substrates with a base-sensitive functionality and for common silyl ethers that are indispensable in the synthesis of complex natural products.



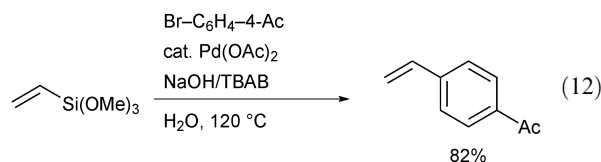
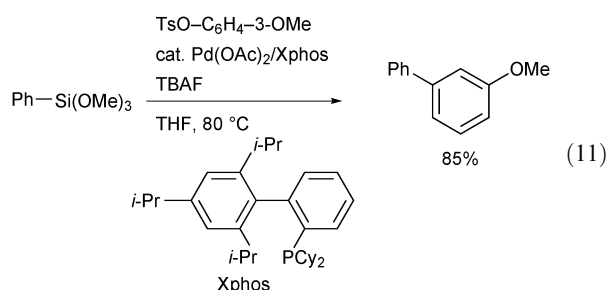
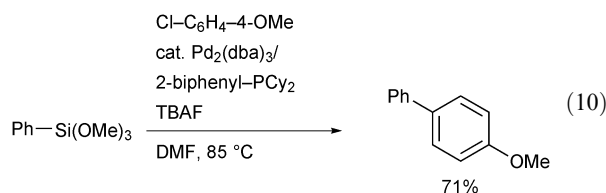
3. Use of organo(alkoxy)silanes

Alkoxy groups were found to serve as a surrogate of the fluoro or chloro substituents on silicon as first demonstrated by Tamao and Ito (eqn (8)).¹⁰ Especially, the reactions using aryl(trialkoxy)silanes have been extensively studied¹¹ since the initial report by Shibata and coworkers in 1997 (eqn (9)).¹²

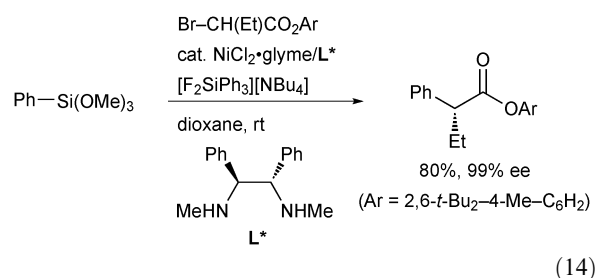
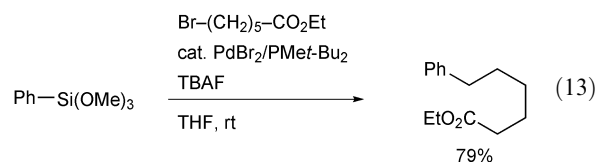


With this particular class of arylsilane reagents, recent developments in biaryl synthesis involve the use of inexpensive and readily available aryl chlorides (eqn (10)),¹³ tosylates (eqn (11)),¹⁴ and mesylates,¹⁵ which are synthesised from abundant phenol feedstock. Reaction conditions free from

the fluoride activation have also been developed for the arylsilanes as well as vinylsilanes (eqn (12), TBAB = tetrabutylammonium bromide).¹⁶

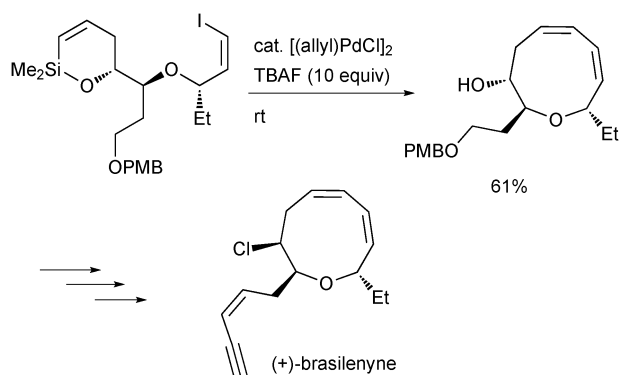


Palladium can also catalyse the coupling with alkyl halides (eqn (13)),¹⁷ whereas nickel catalysts are specifically effective for the arylation of secondary alkyl halides. The use of an optically active diamine ligand allows for dynamic kinetic resolution of α -bromocarboxylates to yield α -arylcarboxylates with high enantioselectivity (eqn (14)).¹⁸



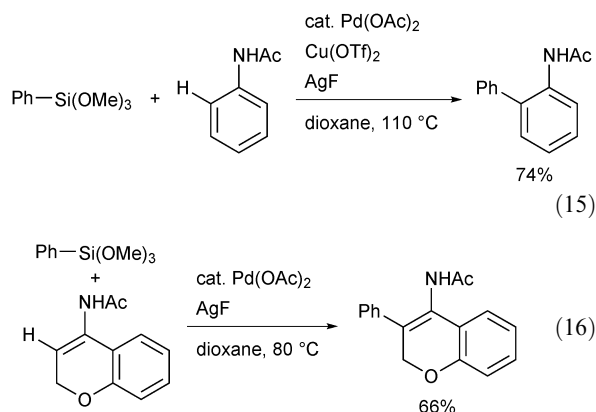
Intramolecular cross-coupling reactions of alkenyl(alkoxy)silanes have been demonstrated by Denmark and coworkers to allow for an extremely clever access to medium-sized ring compounds (Scheme 2).¹⁹ This protocol has been successfully applied to the total synthesis of (+)-brasilenyne.²⁰

Transition metal-catalysed functionalisation of unactivated C-H bonds has received increasing attention in the last decade.²¹ Related transformations using the arylsilane nucleophiles have appeared as a promising alternative to conventional cross-coupling



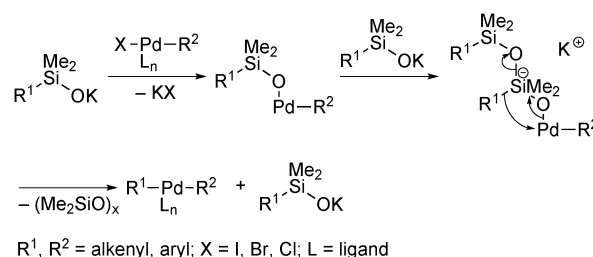
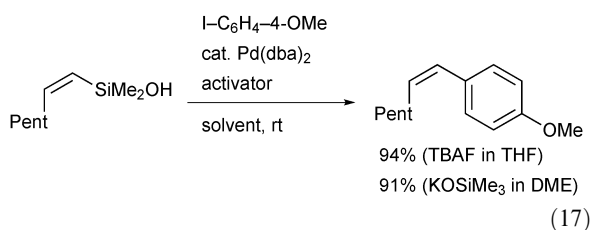
Scheme 2 Ring-opening and -closing intramolecular cross-coupling reaction of alkenyl(alkoxy)silanes: application to the total synthesis of (+)-brasilenyne.

reactions requiring prefunctionalised electrophilic coupling partners. For example, palladium-catalysed C–H arylation of acetanilides (eqn (15))²² and enamides (eqn (16))²³ proceeds with aryl(trimethoxy)silanes. A plausible catalytic cycle comprises the following steps in sequence: electrophilic palladation at the *ortho* or vicinal position of the electron-rich aromatic ring or double bond, transmetalation with the arylsilane reagents, reductive elimination, and finally oxidation of the resulting Pd(0) back to Pd(II) species.



4. Use of organosilanol

Organosilanol have received increasing attention in the last decade as highly reactive and relatively stable organosilicon reagents for cross-coupling chemistry.²⁴ Hiyama²⁵ and Denmark²⁶ independently reported that alkenylsilanol undergo the reaction under very mild reaction conditions (eqn (17)). The silicon reagents participate in the cross-coupling reaction using KOSiMe₃ in place of a fluoride activator (eqn (17)).²⁷

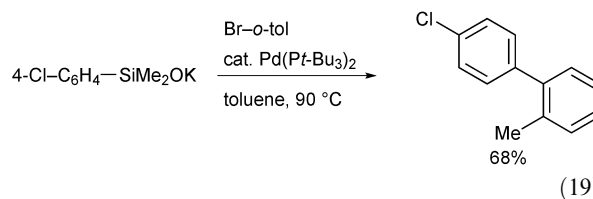
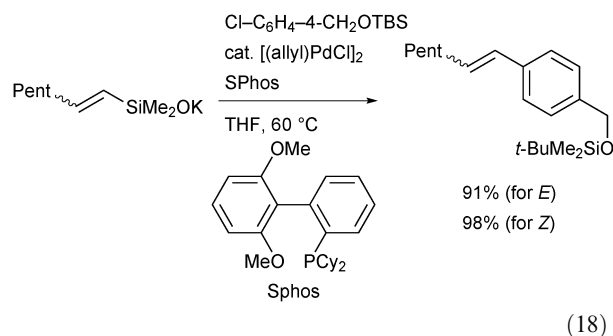


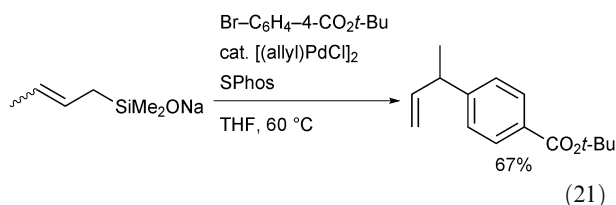
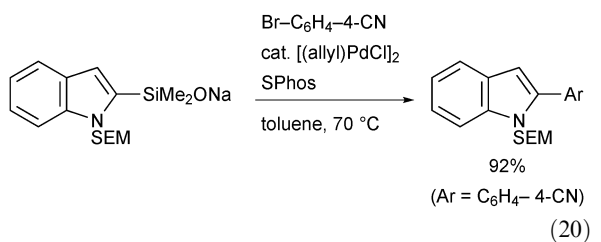
Scheme 3 A mechanism proposed for transmetalation of alkenylsilanolates to palladium(II).

Denmark and Sweis have extensively studied the mechanism of the transmetalation of the silanol reagents under the fluoride-free conditions. They considered that palladium silanolates were a key intermediate, which underwent intramolecular transfer of organic groups from silicon to palladium. The step has been recently disclosed to be promoted by a nucleophilic attack of another silanolate to make the silicon center pentacoordinate (Scheme 3). Thus, the transmetalation proceeds in a manner akin to that proposed for the pentacoordinate silicates shown in Scheme 1.²⁸

5. Use of organosilanolates

Denmark's group developed a protocol using preformed organosilanolates as a coupling partner through irreversible deprotonation of the corresponding organosilanol.²⁹ Most silanolate salts are in a bench-stable powdery form that can be isolated, stored, and handled easily. The use of silanolate salts eliminates the need for an added external base, thus suppressing both the undesirable dehydration of silanols to form siloxanes and the protodesilylation caused by conjugate acid derived from a base additive. A wide variety of alkenyl- (eqn (18))³⁰ and arylsilanolates (eqn (19))³¹ including hetero-arylsilanolates (eqn (20), SEM = CH₂OCH₂CH₂SiMe₃)³² undergo the palladium-catalysed cross-coupling reaction under mild conditions without any added bases. Crotylsilanolates react with aryl halides with γ -selectivity³³ to provide a wide variety of 3-arylbut-1-enes (eqn (21)).³⁴

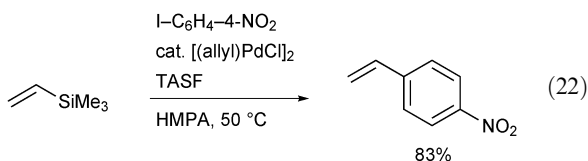




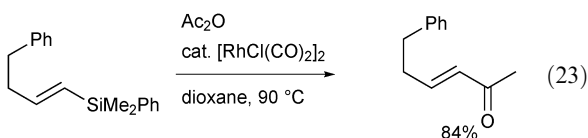
6. Use of tetraorganosilanes

6.1 Alkenyltrimethylsilane

As described above, the silicon-based cross-coupling reaction has met with significant progress with organosilicon reagents having an electron-withdrawing heteroatom on silicon. This is certainly a rational design of the organosilanes for cross-coupling, making the silicon center Lewis acidic enough to promote the formation of requisite pentacoordinate silicates, which can effect the key transmetalation step. Nevertheless, the use of tetraorganosilanes is highly desirable in terms of stability of organosilanes. However, tetraorganosilanes are generally reluctant to undergo transmetalation because of the less electrophilic silicon center unfavorable for the formation of reactive pentacoordinate silicates even with fluoride activation. Although Hiyama and Hatanaka reported that organo(trimethyl)silanes undergo the palladium-catalysed cross-coupling reaction with aryl and alkenyl halides in the presence of TASF in 1988 (eqn (22)),³⁵ the scope of transferable alkenyl and aryl groups was extremely limited.



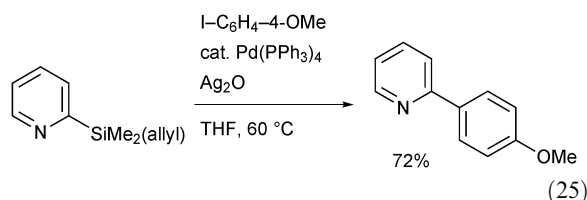
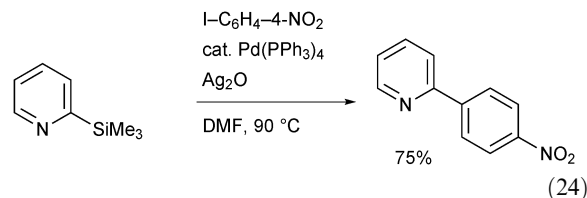
Acid anhydrides can be cross-coupled with alkenyldimethylphenylsilanes in the presence of a rhodium catalyst to give α,β -unsaturated ketones (eqn (23)).³⁶ It is worth noting that the highly stable tetraorganosilicon reagents, which are readily available through alkyne-hydrosilylation, undergo transmetalation to rhodium without any activators.



6.2 2-Pyridyltrimethylsilanes

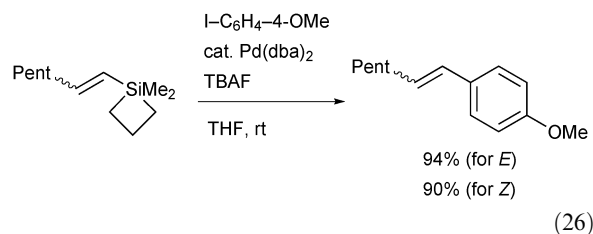
Given the importance and ubiquitous nature of C-2 substituted pyridines in pharmaceuticals and materials, cross-coupling

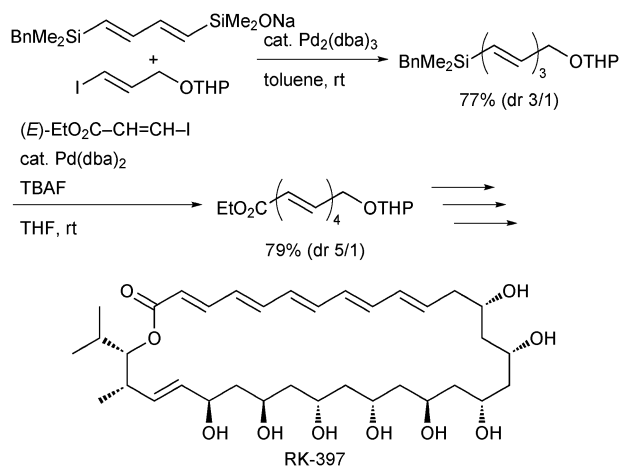
reactions to introduce 2-pyridyl groups have gained much attention. Whereas 2-pyridylboronic acids are too elusive to participate in the reaction,³⁷ stable 2-triorgano(2-pyridyl)silanes have been shown to undergo the palladium-catalysed cross-coupling reaction with aryl iodides in the presence of a stoichiometric amount of copper³⁸ or silver salts³⁹ (eqn (24) and (25)).



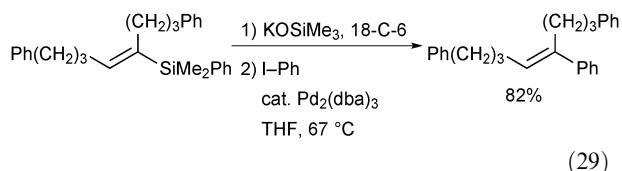
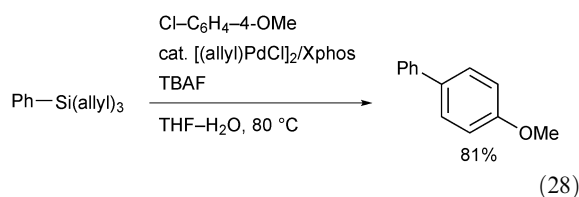
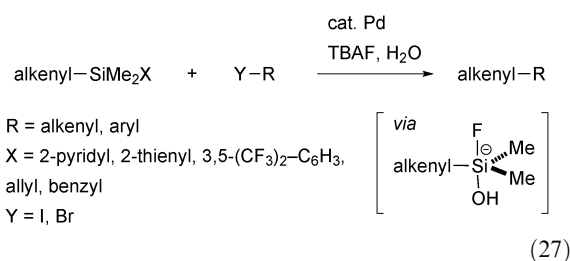
6.3 Masked silanols

Alkenylsilacyclobutanes were introduced by Denmark and coworkers to effect the cross-coupling reaction under mild reaction conditions (eqn (26)).⁴⁰ The reaction was, however, found to involve the formation of alkenylsilanols generated *in situ* by ring-opening reaction of the four-membered silacycle moiety upon nucleophilic attack of fluoride.⁴¹ This observation has led to the use of some tetraorganosilicon reagents as “masked fluorosilanes or silanols”. Aryl groups including 2-pyridyl,⁴² 2-thienyl,⁴³ and 3,5-bis(trifluoromethyl)phenyl,⁴⁴ as well as benzyl (eqn (27))⁴⁵ and allyl (eqn (28))⁴⁶ groups have been found to serve as a masking group to be substituted by a fluoro or a hydroxy group possibly through initial substitution of the organic group by a fluoride anion occasionally followed by hydrolysis of the resultant Si-F bond caused by a small amount of water contamination in TBAF. While masked silanols behave as very stable tetraorganosilanes and thus tolerate various synthetic manipulations, they undergo the cross-coupling reaction upon treatment with fluoride under mild conditions as described in Section 4. A phenyl group can also serve as a masking group, and the strong Si-Ph bond is supposed to be cleaved by a strong base to give silanols or siloxanes, which undergo the cross-coupling reaction (eqn (29)).⁴⁷





Scheme 4 Total synthesis of RK-397 through sequential cross-coupling of alkenylsilanolates and masked alkenylsilanolates.

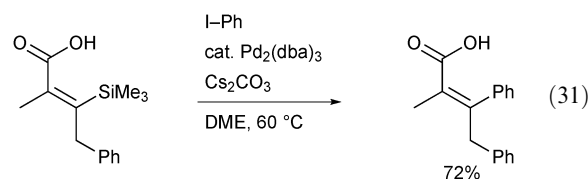
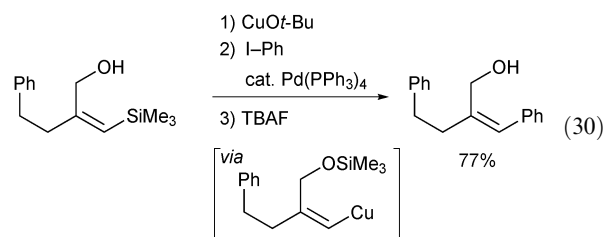


The masked silanol protocol coupled with *in situ* generation of alkenylsilanolates was nicely applied to the total synthesis of the polyene macrolide RK-397 (Scheme 4).⁴⁸ The benzyltrimethylsilyl group remains intact under the reaction conditions for the silanolate coupling. Thus, it subsequently undergoes a second coupling reaction with another alkenyl electrophile by the fluoride activation to assemble the stereochemically well-defined tetraene substructure requisite to access the target molecule. This example nicely demonstrates the power of silicon-based cross-coupling technology in modern organic synthesis.

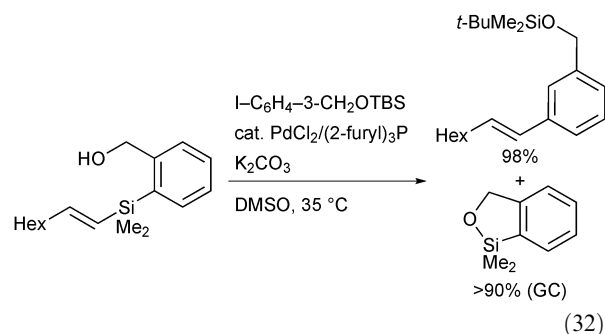
6.4 Organo[2-(hydroxymethyl)phenyl]dimethylsilanes

The cross-coupling reaction of tetraorganosilanes under mild and fluoride-free conditions with a broad scope of transferable organic groups has been a long-standing goal. Alkenyl-(trimethyl)silanes undergo the cross-coupling reaction without the fluoride activation only when a metal alkoxide is located at

an appropriate position in the same molecule, as is often seen in the Brook rearrangement.⁴⁹ Indeed, efficient transmetalation of alkenyl(trimethyl)silanes with copper(I) has been demonstrated by Takeda and coworkers: a palladium-catalysed cross-coupling reaction occurs with the aid of a proximal hydroxy group (eqn (30)).⁵⁰ A similar effect using a carboxylate group has also been reported by Shindo and coworkers (eqn (31)).⁵¹

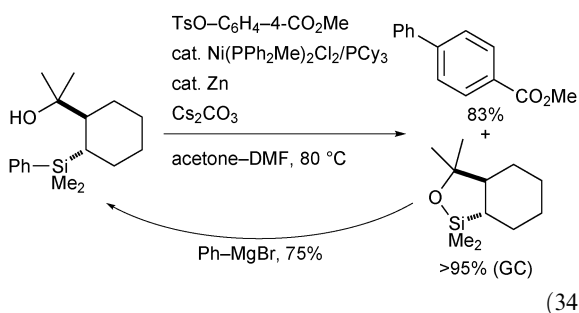
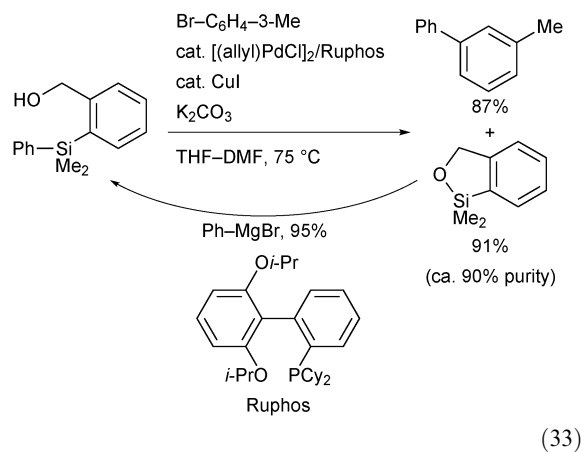


These two examples clearly demonstrate that intramolecular attack of a nucleophilic oxygen is highly effective to promote the transmetalation from silicon to transition metals. This effect is due presumably to the high oxophilicity of silicon, and it eliminates the need for strong nucleophiles such as fluoride and hydroxide to form hypervalent silicates. These observations combined with the related reagent design for carbonyl allylation and benzylation⁵² by Hudrlik and coworkers have led Hiyama and Nakao *et al.* to imagine the use of alkenyl- and aryl[2-(hydroxymethyl)phenyl]dimethylsilanes (HOMSi reagents) as a novel entry to tetraorganosilanes for the silicon-based cross-coupling.⁵³ These silicon reagents have many advantages over conventional ones: excellent chemostability based on the tetraorganosilicon structure, the hydroxy-containing activating group free from a transferring organic group, and recoverable and reusable cyclic silyl ether as a silyl residue. The alkenylsilanes indeed undergo palladium-catalysed cross-coupling in the presence of K_2CO_3 , a mild and inexpensive base activator. Excellent chemoselectivity tolerant toward a range of functional groups including common silyl protection has been achieved (eqn (32)).⁵⁴

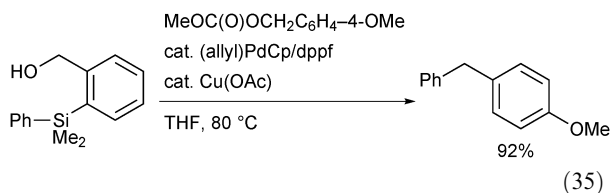


The coupling reaction of the corresponding arylsilanes also proceeds smoothly with the aid of an added copper(I)

cocatalyst, suggesting that sequential transmetalation from silicon to copper and then to palladium may be plausible (eqn (33)).⁵⁵ More recently, modified arylsilane reagents having a 2-(2-hydroxyprop-2-yl)cyclohexyl group on silicon are found to effect the biaryl synthesis using inexpensive nickel(0) catalysts (produced by reduction of Ni(II) with Zn), aryl chlorides, and aryl tosylates (eqn (34)).⁵⁶

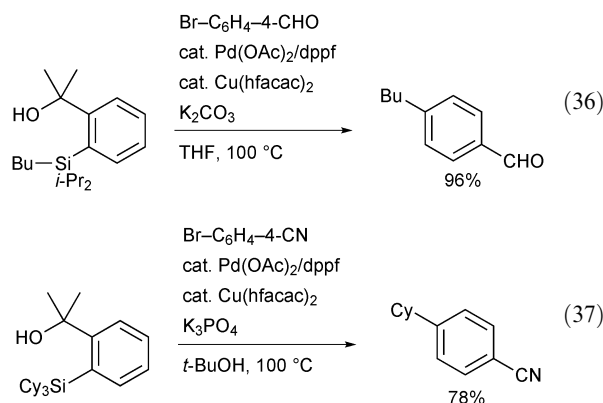


The cross-coupling reactions with allylic and benzylic carbonates proceed in the absence of an external base,⁵⁷ because the oxidative addition of the electrophiles is supposed to give palladium alkoxides⁵⁸ that should act as a base to promote transmetalation. The protocol allows for a silicon-based approach to diarylmethanes, which are found in many biologically active substances (eqn (35)).



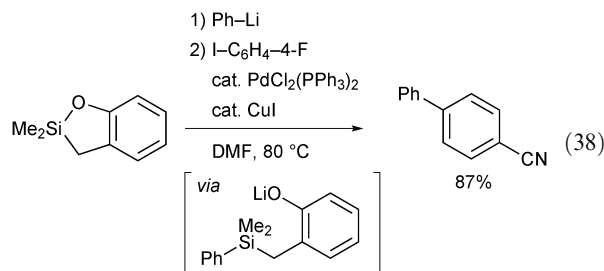
Even the very strong C(sp³)-Si bonds of tetraorganosilicon compounds can be activated by the same reagent design to achieve alkyl cross-coupling reactions with alkyltriorganosilicon reagents under fluoride-free conditions (eqn (36)).⁵⁹ In this particular case, benzylic *gem*-dimethyls are essential for a smooth reaction. Otherwise, oxidation occurs at the benzylic carbon, yielding a benzaldehyde derivative. This observation may suggest that the transmetalation of these organosilanes proceeds through a palladium alkoxide intermediate. Isopropyl groups on silicon allow for the discrimination of primary and secondary alkyls. The use of tricyclohexylsilyl variant allows for

transfer of the cyclohexyl group to cross-couple with aryl electrophiles (eqn (37)).

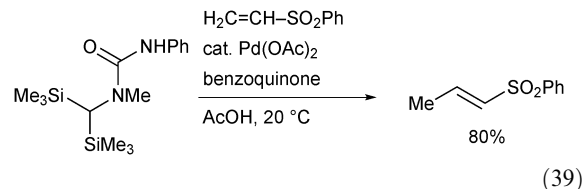


The free benzylic hydroxy group is essential for the successful C-Si bond activation of the silicon reagents; *O*-protection results in no cross-coupling reaction. Taking advantage of this simple switch in the reagent reactivity, electrophiles having the silyl group with *O*-protection undergo a cross-coupling reaction, with the *O*-protected silyl group remaining totally intact. The resulting biaryl can participate in the subsequent cross-coupling event upon *O*-deprotection. By simply repeating these operations using a variety of halogenated arylsilanes, oligoarenes can be assembled in a highly efficient and well-defined manner (Scheme 5).⁶⁰

A similar strategy to activate tetraorganosilanes has been demonstrated by employing *o*-hydroxybenzyl-substituted silicon reagents generated *in situ* (eqn (38)).⁶¹

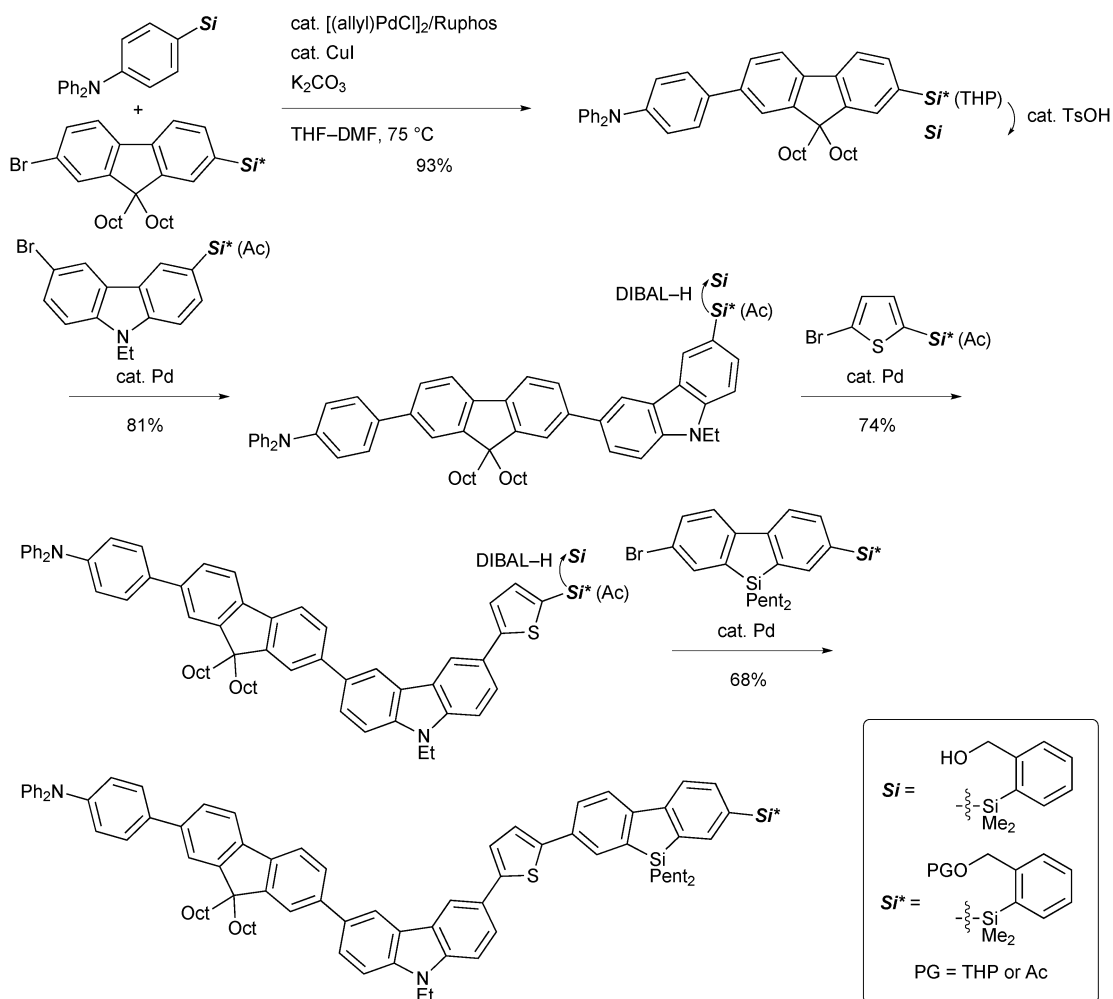


An amide carbonyl can also serve as an intramolecular activator to facilitate the cleavage of Me-Si bonds, allowing for the oxidative Heck-type methylation of electron-deficient olefins (eqn (39)).⁶²



7. Conclusions

The history of silicon-based cross-coupling chemistry is surveyed. Significant progress has been made especially in the last decade, making the silicon-based cross-coupling reaction highly practical and applicable to synthesis of even highly



Scheme 5 Linear synthesis of HOMSi-substituted oligoarenylidenes through iterative cross-coupling-deprotection sequences with halogenated aryl[2-(hydroxymethyl)phenyl]dimethylsilanes.

complex natural products. While the Suzuki–Miyaura cross-coupling reaction using organoboranes has been employed extensively in the synthetic community, the silicon-based one would be equally useful and practical, given the stability and availability associated with the state-of-the-art organosilicon cross-coupling reagents.

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