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Catalytic Generation of Silicon Nucleophiles

Koji Kubota and Hajime Ito

Institute for Chemical Reaction Design and Discovery (WPI-ICReDD), Hokkaido University, Sapporo, Hokkaido 060-8628, Japan
Faculty of Engineering, Division of Applied Chemistry and Frontier Chemistry Center, Hokkaido University, Kita 13 Nishi 8, Kita-ku, Sapporo, Hokkaido, 060-8628, Japan

1.1 Introduction

Silicon nucleophiles represent a class of important organometallic species for silicon–carbon, silicon–silicon, and silicon–boron bond formation reactions in synthetic chemistry [1]. Conventionally, the generation of silicon nucleophiles is accomplished by reactions of chlorosilanes with alkali metal (K, Na, Li), reactions of hydrosilanes with alkali metal hydride, cleavage of the silicon–silicon bond in disilanes or the silicon–boron bond in silylboron reagents by organometallic carbon nucleophiles, and transmetallation from other silicon-metal compounds [2]. However, these stoichiometric methods have significant limitations such as low functional-group compatibility due to the high reactivity of hard silyl anions with an alkali metal countercation. In this context, silicon-based organocuprates are widely used as soft silyl anion equivalents for silicon–carbon bond formation reactions, even though this method requires stoichiometric organometallic compounds and copper salt [3]. Recently, catalytic nucleophilic silylation reactions have attracted considerable attention because of their mild reaction conditions and unique selectivity and reactivity. This chapter mainly focuses on two types of activation modes for catalytic generation of silicon nucleophiles (Figure 1.1). First, transmetalation between silicon compounds containing a Si—X bond (X = Si, B, and Zn) and metal catalysts generates nucleophilic silyl metal intermediates (Figure 1.1a). Second, a catalytic amount of Lewis bases (Nu) activates the silicon–boron bond of silylboron reagents to form nucleophilic silyl species (Figure 1.1b). This chapter provides the recent advancements in the catalytic generation of silicon nucleophiles through these activation pathways and their applications in organic synthesis.

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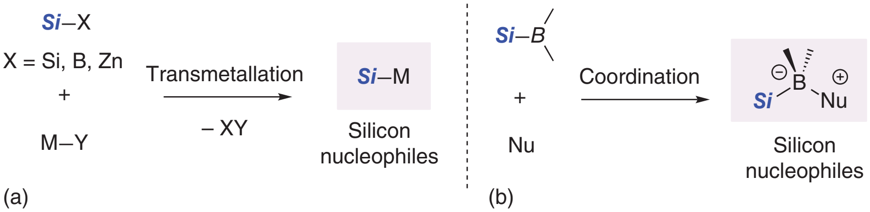


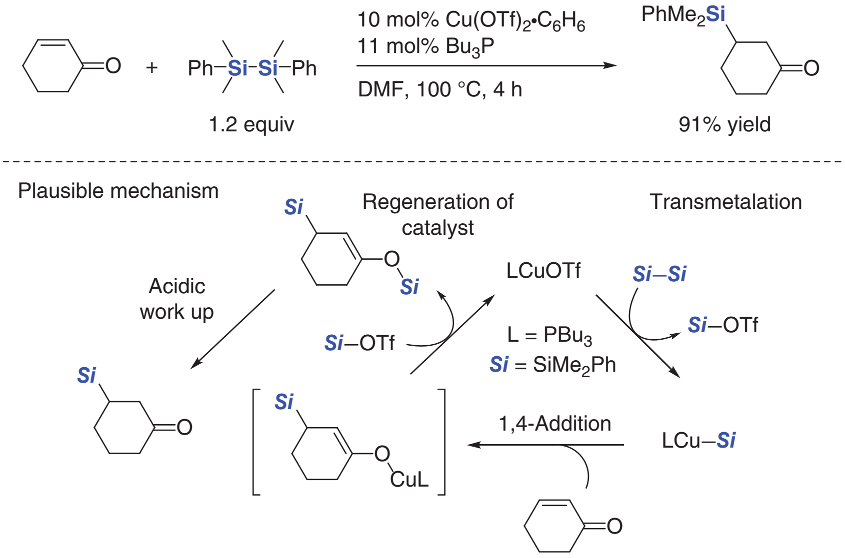
Figure 1.1 Representative pathways for catalytic generation of silicon nucleophiles. (a) Metal-catalyzed method. (b) Lewis base-catalyzed method.

1.2 Silicon Nucleophiles with Copper Catalysts

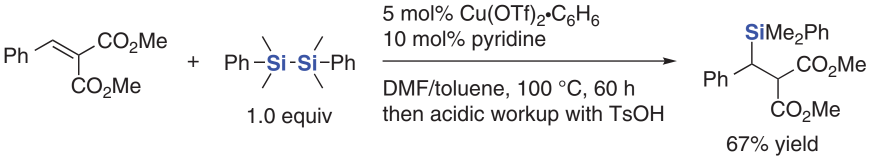
1.2.1 Copper-Catalyzed Nucleophilic Silylation with Disilanes

1.2.1.1 Silylation of α,β-Unsaturated Carbonyl Compounds

In 1998, the first example of copper-catalyzed nucleophilic 1,4-silylation of α,β-unsaturated carbonyl compounds with disilanes was reported by Ito et al. (Scheme 1.1) [4]. The reaction of cyclohexanone with a disilane in the presence of a copper salt and Bu_3P as a ligand proceeded to give the corresponding 1,4-silyl addition product in high yield. The silylation presumably goes through the σ-bond metathesis between a copper salt and a disilane to form the silylcopper intermediate, followed by its 1,4-addition to cyclohexanone. The copper catalyst is regenerated by the reaction between the resultant copper enolate and silyl triflate, which is formed at the first stage of this cycle. This mild protocol can be applied to a variety of substrates such as α,β-unsaturated cyclic and linear ketones and aldehydes to form the β-silyl carbonyl compounds in high yields.



Scheme 1.1 Copper-catalyzed silylation of α,β-unsaturated carbonyl compounds with a disilane.



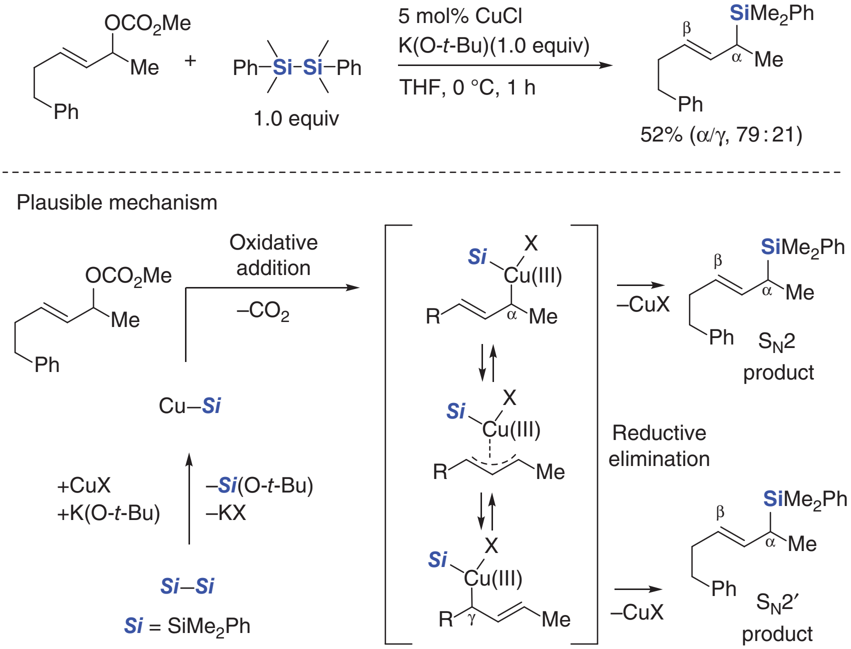
Scheme 1.2 Copper-catalyzed silylation of alkylidene malonates with a disilane.

1.2.1.2 Silylation of Alkylidene Malonates

Scheidt and coworkers reported the copper-catalyzed nucleophilic silylation of alkylidene malonates with disilanes in 2004 (Scheme 1.2) [5]. They found pyridine to be an effective ligand rather than phosphines for this reaction.

1.2.1.3 Silylation of Allylic Carbamates

In 2012, Ito et al. developed the copper-catalyzed allylic substitution with silicon nucleophiles (Scheme 1.3) [6]. This is the first example of a copper-catalyzed reaction between a disilane and allylic carbonates to produce allylsilanes, which are particularly useful reagents for stereoselective allylation of aldehydes in the presence of Lewis acids [7]. The regioselectivity of this reaction depends on the structure of substrates, suggesting that this reaction would proceed through the formation of a π-allyl copper(III) intermediate.



Scheme 1.3 Copper-catalyzed silylation of allylic carbamates with a disilane.

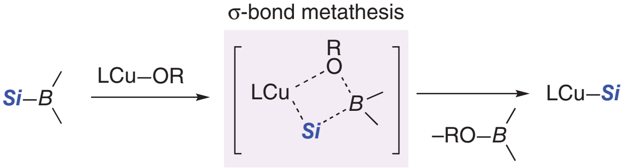


Figure 1.2 Activation of silicon–boron bond by σ-bond metathesis with a copper alkoxide.

1.2.2 Copper-Catalyzed Nucleophilic Silylation with Silylboronate

1.2.2.1 Silicon–Boron Bond Activation with Copper Alkoxide

Although disilanes are powerful sources for the generation of silicon nucleophiles as described, recent attention has focused on exploring the unique reactivity of silylboronates [8]. The difference in Lewis acidity between silicon and boron of silylboronates is exploited for facile boron–metal exchange at the silicon atom to generate silicon nucleophiles. The silicon–boron bond activation by σ-bond metathesis with copper alkoxide catalysts has become a general technique to access copper-stabilized silicon nucleophiles due to its mild reaction conditions (Figure 1.2) [8].

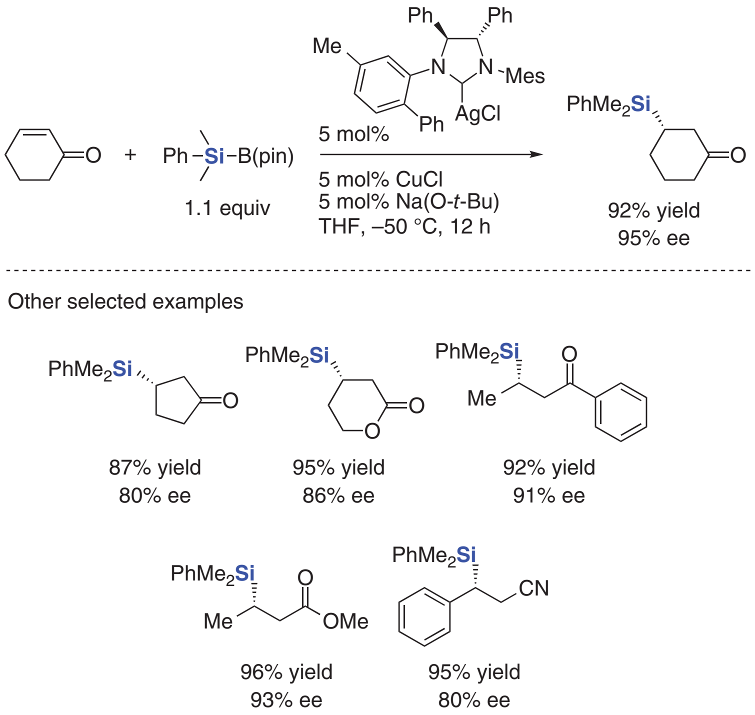
1.2.2.2 Silylation of α,β-Unsaturated Carbonyl Compounds

In 2010, the first example of copper-catalyzed nucleophilic silylation of α,β-unsaturated carbonyl compounds with silylboronates was reported by Hoveyda and a coworker (Scheme 1.4) [9]. They found that the copper-based chiral N-heterocyclic carbene (NHC) complex, generated in situ from the reaction of the corresponding silver-based carbene precursor with CuCl and Na(O-*t*-Bu), efficiently catalyzed conjugate silyl addition to cyclohexenone to form chiral β-silyl ketone in high yield with excellent enantioselectivity. Acyclic unsaturated ketones and cyclic dienones also undergo the enantioselective silyl conjugate addition with good to high enantioselectivity. Later, they also developed regio- and enantioselective conjugate silyl additions of acyclic and cyclic dienones and dienoates with a chiral NHC/copper complex catalyst [10].

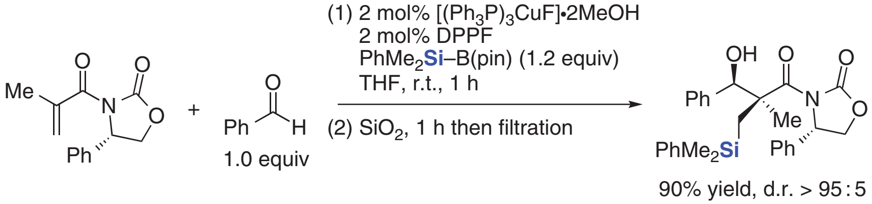
Soon after, Riant and coworkers reported the copper-catalyzed asymmetric silylative aldol reaction between α,β-unsaturated carbonyl compounds and aromatic aldehydes (Scheme 1.5) [11]. The in situ–generated silylcopper intermediate reacts with methacryloxazolidinones to form the β-silylcopper enolate, followed by a diastereoselective aldol reaction to give the products bearing a chiral quaternary carbon center with excellent stereoselectivity.

In 2011, Córdova and coworkers reported that a copper-catalyzed silylation method can be combined with a chiral amine cocatalyst for iminium activation, as exemplified by the catalytic enantioselective silyl addition to α,β-unsaturated aldehydes (Scheme 1.6) [12].

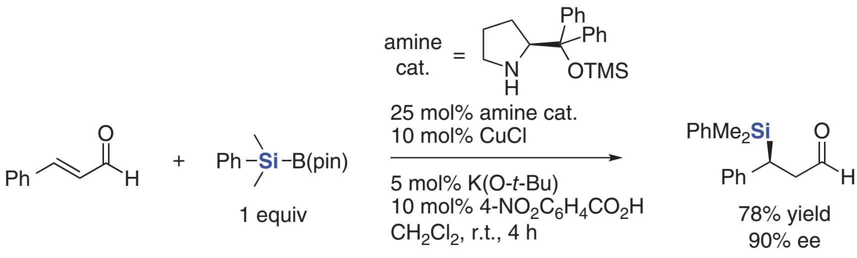
The known copper-catalyzed silylation methods are generally sensitive to moisture and need to be carried out under an inert atmosphere. However, in 2012, Santos and a coworker discovered that the conjugative silylation of carbonyl compounds in water under air was efficiently catalyzed by a copper salt and 4-picoline (Scheme 1.7) [13]. Both copper and pyridine are required in this



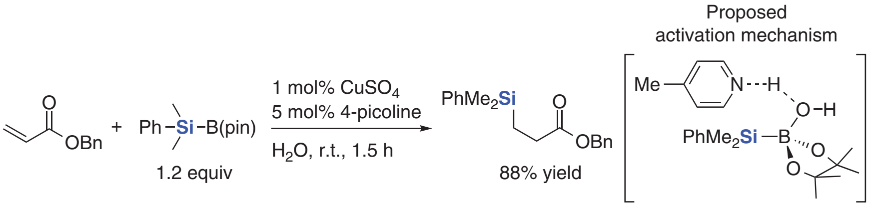
Scheme 1.4 Copper-catalyzed enantioselective conjugate silyl addition with a silylboronate.



Scheme 1.5 Copper-catalyzed silylative aldol reaction with a silylboronate.



Scheme 1.6 Enantioselective silylation of α,β-unsaturated aldehydes by a copper/chiral amine cooperative catalyst.

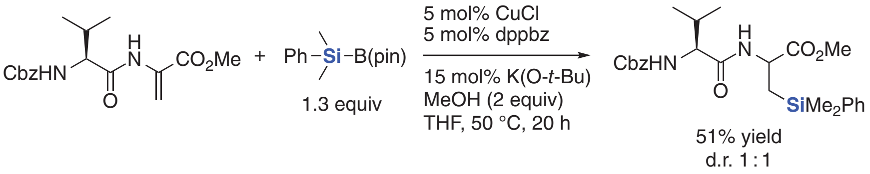


Scheme 1.7 Copper-catalyzed silylation of α,β-unsaturated carbonyl compounds in water at room temperature.

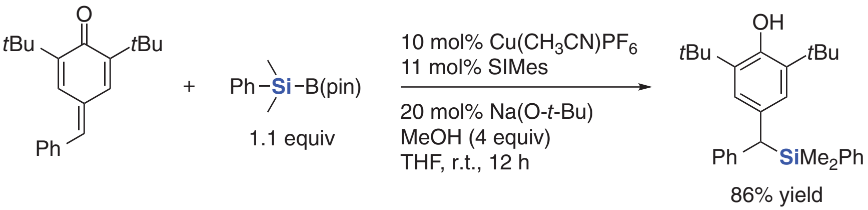
reaction. The role of the pyridine is proposed to deprotonate a nucleophilic water molecule to form an sp^3-hybridized silylboronate, followed by transmetalation with copper to generate a silylcopper active species.

The incorporation of silicon atoms into amino acids and peptides has attracted significant attention due to the large number of applications in chemical biology, and even as therapeutic agents [14]. The known methods for the preparation of silicon-containing amino acids have some limitations such as functional-group incompatibility due to the use of highly reactive carbon nucleophiles [15]. In 2015, Piersanti and coworkers developed the mild copper-based catalytic method for the regioselective silyl addition of dehydroalanine derivatives (Scheme 1.8) [16]. This transformation would serve as a useful platform for the preparation of silicon-containing peptide mimetics.

para-Quinone methides are useful intermediates for the synthesis of highly functionalized phenol derivatives. In 2015, Tortosa and coworkers found that the copper-catalyzed silylation–aromatization sequence of *para*-quinone methides afforded mono- and dibenzylic alkylsilanes in high yields (Scheme 1.9) [17]. The products, which react with electrophiles such as aldehydes, can be used as stable dibenzylic carbanion equivalents.



Scheme 1.8 Copper-catalyzed silylation of dehydroalanine derivatives for the synthesis of silicon-containing peptides.



Scheme 1.9 Copper-catalyzed silylation of *para*-quinone methides.

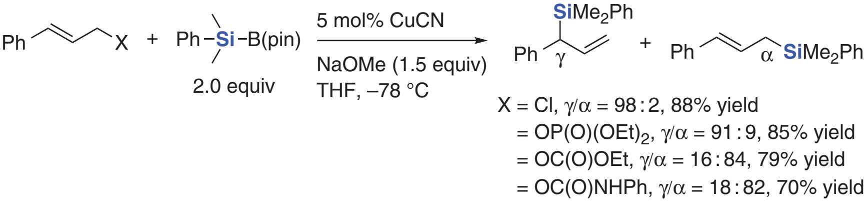
1.2.2.3 Catalytic Allylic Silylation

In 2010, the first example of copper-catalyzed allylic silylation with a silylboronate was reported by Oestreich and a coworker (Scheme 1.10) [18]. The reaction of allyl chlorides with a silylboronate in the presence of the copper catalyst and a stoichiometric amount of NaOMe in THF afforded the corresponding allylsilanes with excellent γ-selectivity. The regioselectivity of this transformation was significantly influenced by the nature of leaving groups; γ-selectivity for halides and phosphates and α-selectivity for oxygen leaving groups such as carbonates, carbamates, and carboxylates. Explanations for the effects of the leaving groups on the regioselectivity have remained unclear.

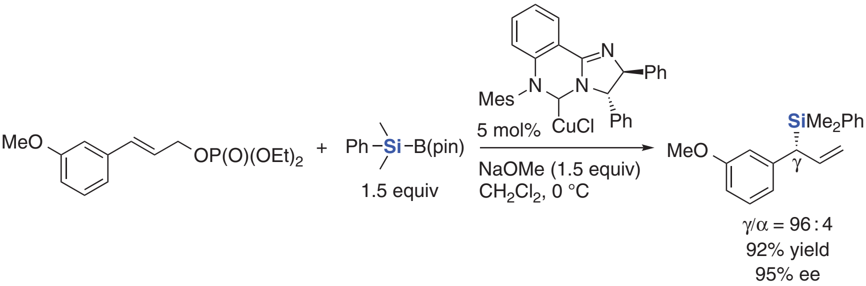
Afterwards, the same group reported the enantioselective allylic silylation using a chiral NHC/copper complex catalyst, providing synthetically useful chiral allylsilanes (Scheme 1.11) [19]. The six-membered NHC ligand, which was originally introduced by McQuade and a coworker [20], efficiently promoted the reaction with high enantioselectivity.

At almost the same time, Shintani and coworkers also reported the copper-catalyzed enantioselective allylic substitution of allyl phosphates with a silylboronate to provide chiral allylsilanes (Scheme 1.12) [21]. The use of a chiral NHC ligand bearing an alcohol functional group is a key to achieving high enantioselectivity of this reaction. Notably, this powerful catalytic system can be applied to the synthesis of chiral allylsilanes having a tetra-substituted carbon center with excellent regio- and enantioselectivity by employing γ,γ-disubstituted allyl phosphates as substrates.

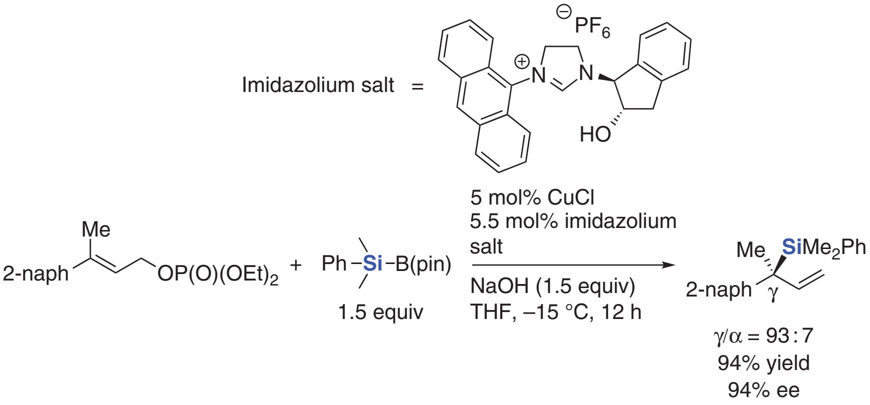
In 2015, Oestreich and coworkers found that McQuade's NHC/copper-catalyzed allylic silylation of racemic cyclic allyl phosphates underwent a



Scheme 1.10 Copper-catalyzed non-enantioselective allylic silylation.



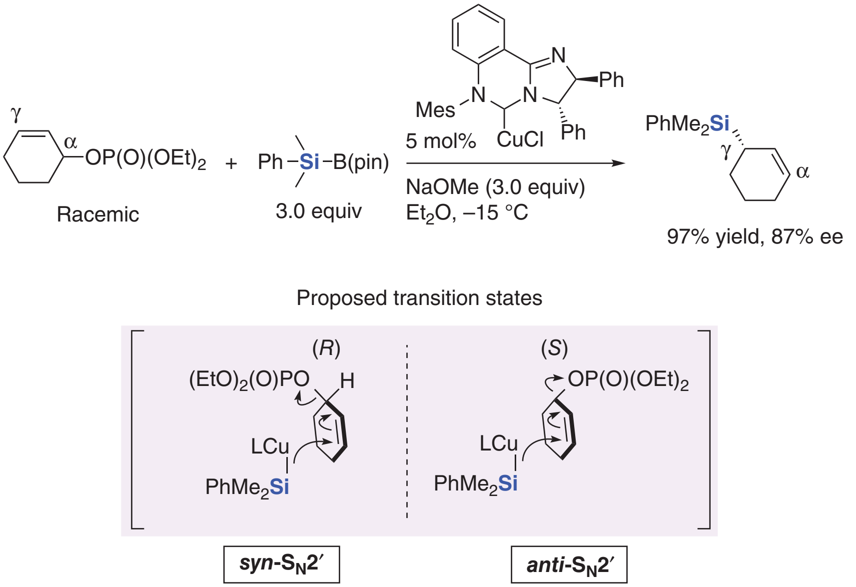
Scheme 1.11 Chiral NHC/copper-catalyzed enantioselective allylic silylation reported by Oestreich and coworkers.



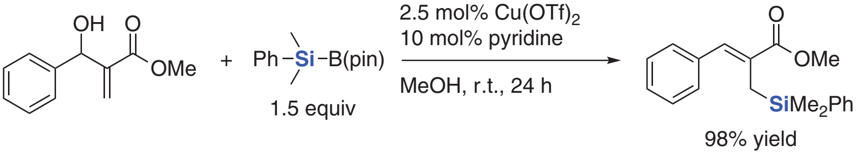
Scheme 1.12 Chiral NHC/copper-catalyzed enantioselective allylic silylation reported by Shintani and coworkers.

direct enantioconvergent transformation [22], where the enantiomeric allylic phosphates converged to the same enantiomer product by two distinctive S_N2' pathways with opposite diastereofacial selectivity (Scheme 1.13) [23].

For synthetic efficiency, it would be much more desirable to generate allylsilanes from allyl alcohols as allylic group precursors. In 2013, Li and coworkers reported that the allylic silylation of Morita–Baylis–Hillman alcohols with a silylboronate in the presence of the $Cu(OTf)_2$/pyridine catalyst in methanol proceeded smoothly to provide the corresponding allylsilanes in good yields with excellent



Scheme 1.13 Direct enantioconvergent transformation in the copper-catalyzed allylic silylation of cyclic allyl phosphates.



Scheme 1.14 Copper-catalyzed direct allylic silylation of allyl alcohols.

regioselectivity (Scheme 1.14) [24]. They proposed that the hydroxyl group of the substrate could be activated by the in situ–generated TfOH–pyridine complex through a hydrogen-bonding interaction. However, no experimental evidence for this activation mechanism were described.

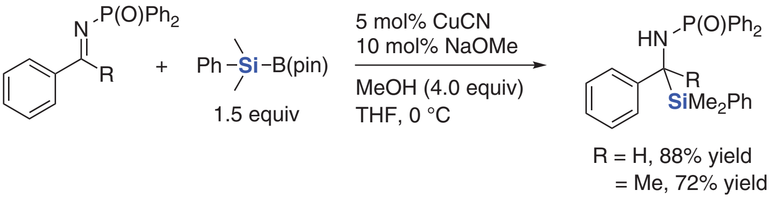
1.2.2.4 Catalytic Silylation of Imines

Due to the considerable interest in silicon-containing peptides and amino acids, a copper-catalyzed addition of silicon nucleophiles to imines is an important transformation to form α-aminosilanes bearing sensitive functional groups. In 2011, the first example of copper-catalyzed nucleophilic silylation of imines with a silylboronate was reported by Oestreich and coworkers (Scheme 1.15) [25]. A series of aldimines and ketimines were reacted with a silylboronate in the presence of CuCN as a catalyst precursor and a catalytic amount of NaOMe to afford the corresponding racemic α-aminosilanes in good to high yields.

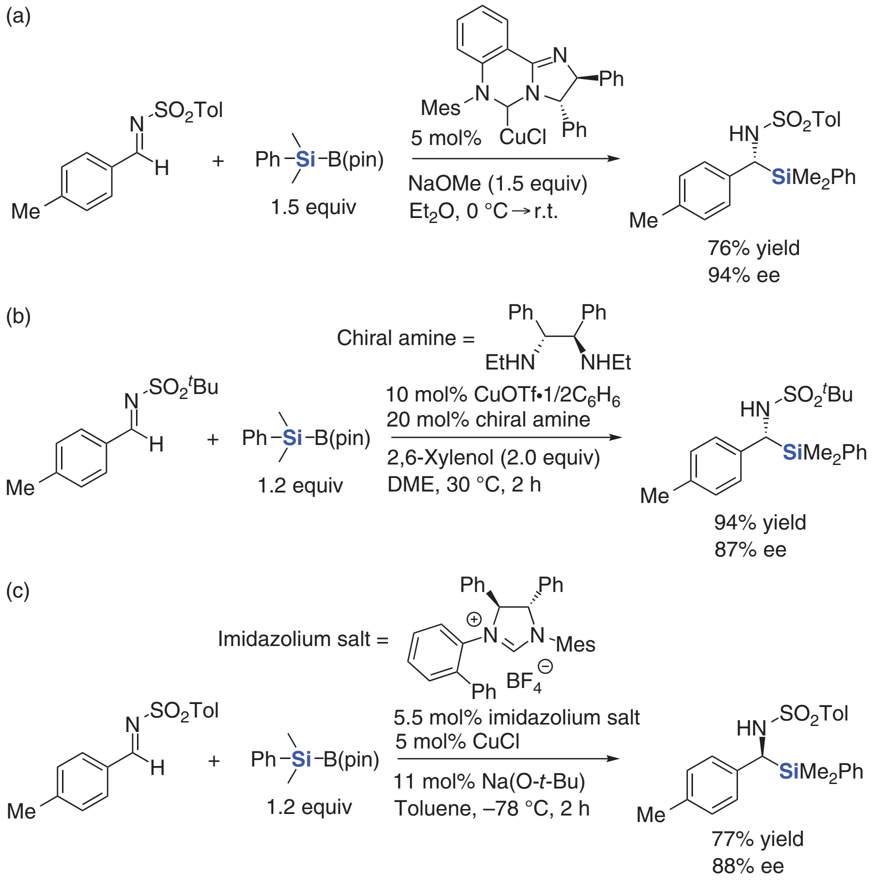
An enantioselective addition of silicon nucleophiles to aldimines was also developed by Oestreich and coworkers in 2014 (Scheme 1.16a) [26]. They found that the NHC/copper complex efficiently catalyzed the enantioselective silylation of aromatic and aliphatic aldimines with good to high enantioselectivity. At the almost same time, Mita et al. as well as He independently reported a similar copper-catalyzed method for the enantioselective addition of silicon nucleophiles to aldimines (Scheme 1.16b,c). The Mita and Sato group found that a copper/chiral diamine complex–catalyzed silylation of *N*-*tert*-butylsulfonylimines provided the optically active α-aminosilanes with high enantioselectivity (Scheme 1.16b) [27]. The He group used the C_1-symmetric chiral NHC ligand for this transformation, providing good yields and high enantioselectivity (Scheme 1.16c) [28].

1.2.2.5 Catalytic Silylation of Aldehydes

α-Hydroxylsilanes, useful intermediates in synthesis, have been used for several stereocontrolled rearrangements to access structurally complex molecules. Thus, the development of efficient synthetic methods for α-hydroxylsilanes has

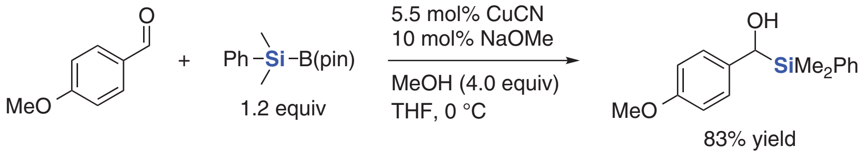


Scheme 1.15 Copper-catalyzed nucleophilic silylation of imines.

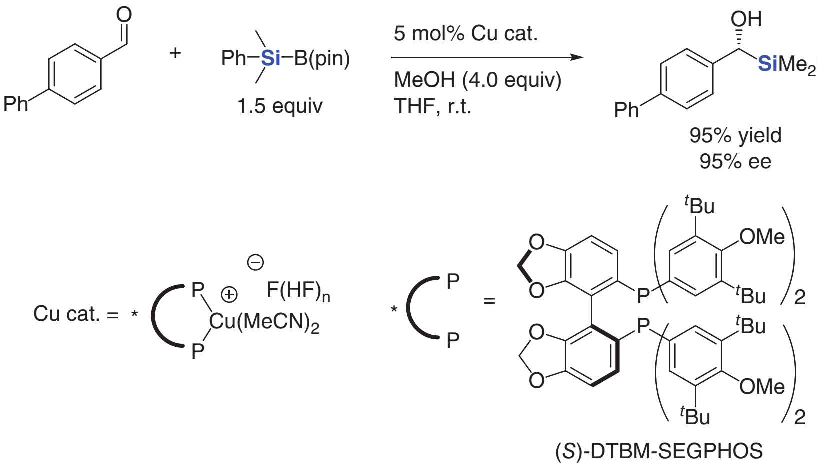


Scheme 1.16 Copper-catalyzed enantioselective nucleophilic silylation of aldimines. (a) Oestreich, (b) Mita and Sato, (c) He.

received increased attention in recent years. In 2011, the first example of copper-catalyzed nucleophilic silylation of aldehydes with a silylboronate was reported by Kleeberg et al. (Scheme 1.17) [29]. Both aromatic and aliphatic aldehydes reacted with a silylboronate to give the corresponding racemic α-hydroxylsilanes in high yields. The mechanism of this transformation was investigated in detail by stoichiometric and catalytic experiments as well as NMR spectroscopic measurements.



Scheme 1.17 Copper-catalyzed nucleophilic silylation of aldehydes.



Scheme 1.18 Copper-catalyzed enantioselective nucleophilic silylation of aldehydes.

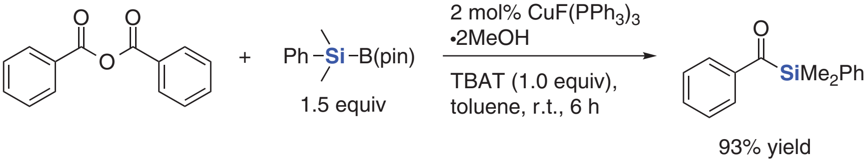
In 2013, Riant and coworkers reported the first enantioselective nucleophilic silylation of aldehydes by employing a newly developed copper/DTBM-SEGPHOS complex catalyst (Scheme 1.18) [30]. A series of aromatic and aliphatic aldehydes were converted into the corresponding chiral α-hydroxylsilanes in good yields with excellent enantioselectivity.

1.2.2.6 Catalytic Synthesis of Acylsilanes

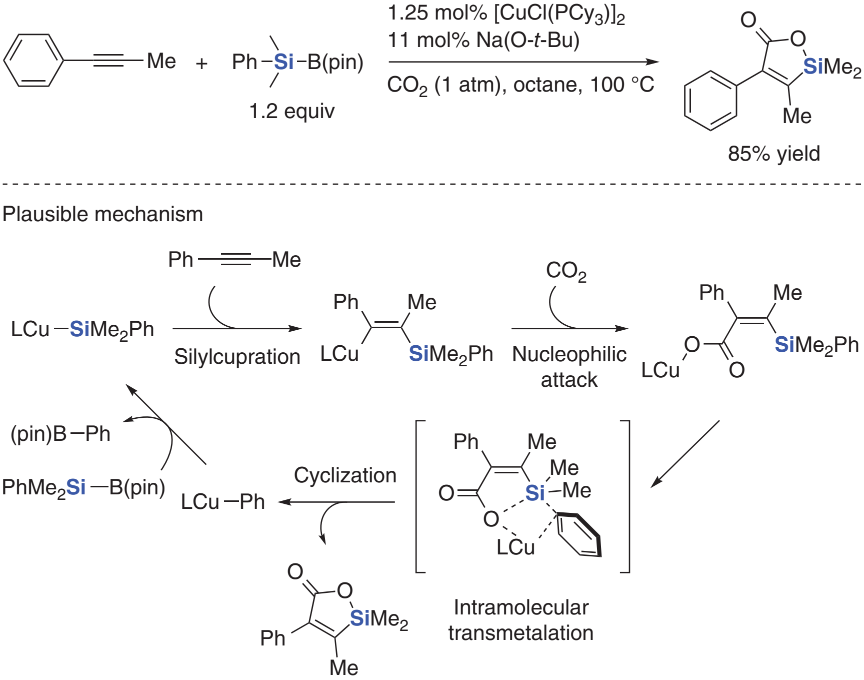
Acylsilanes are stable compounds in which a silyl fragment is directly attached to a carbonyl group. Recently, the use of acylsilanes in organic synthesis has attracted significant attention due to the discovery of valuable new transformations [31]. Therefore, the development of efficient, direct synthetic methods for acylsilanes is highly desirable. In 2013, Riant and coworkers reported the copper-catalyzed silylation of anhydrides with a silylboronate to form the corresponding acylsilanes in high yields (Scheme 1.19) [32]. Notably, this process can be carried out in a one-pot procedure starting from easily available carboxylic acids.

1.2.2.7 Silylative Carboxylation with CO_2

Carbon dioxide (CO_2) is a nontoxic, abundant, and renewable carbon source. Therefore, the utilization of CO_2 in carbon–carbon bond-forming reaction is one of the most important subjects in organic synthesis. In 2012, Fujihara et al. developed the copper-catalyzed silacarboxylation of internal alkynes with CO_2



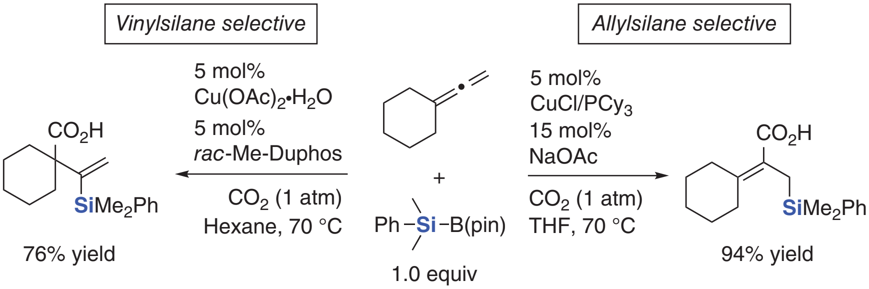
Scheme 1.19 Copper-catalyzed nucleophilic silylation of anhydrides to form acylsilanes.



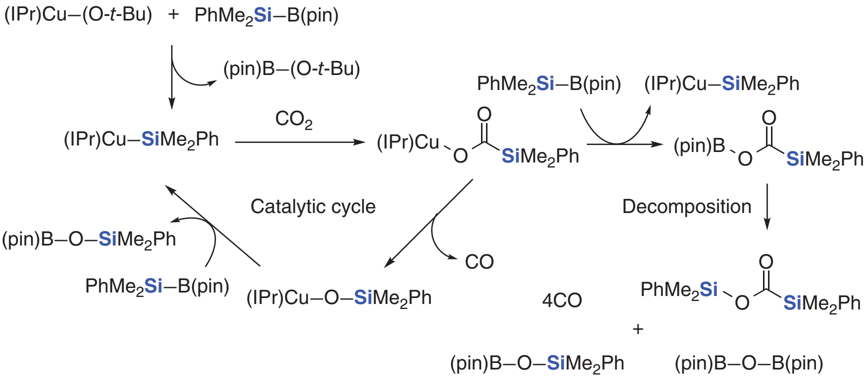
Scheme 1.20 Copper-catalyzed silacarboxylation of alkynes.

to give the silalactone derivatives (Scheme 1.20) [33]. The reaction presumably goes through the silylcupration of alkynes to form the silylated alkenylcopper intermediate, followed by the reaction with CO_2 to afford the copper carboxylate species. Then, intramolecular cyclization provides the phenylcopper complex by extrusion of the silalactone product. The catalyst is recovered by the σ-bond metathesis between the phenylcopper and a silylboronate.

The same group also reported the copper-catalyzed regiodivergent silacarboxylation of allenes with CO_2 (Scheme 1.21) [34]. The regioselectivity of the reaction is reversed by the proper choice of ligand; carboxylated vinylsilanes are obtained with *rac*-Me-Duphos as the ligand, whereas the use of PCy_3 provides carboxylated allylsilanes with high selectivity. The origin of the regioselectivity



Scheme 1.21 Copper-catalyzed regiodivergent silacarboxylation of allenes.



Scheme 1.22 CO_2 reduction with a silylboronate.

might be attributed to the difference in relative steric bulk of the copper/phosphine complex and a silyl group.

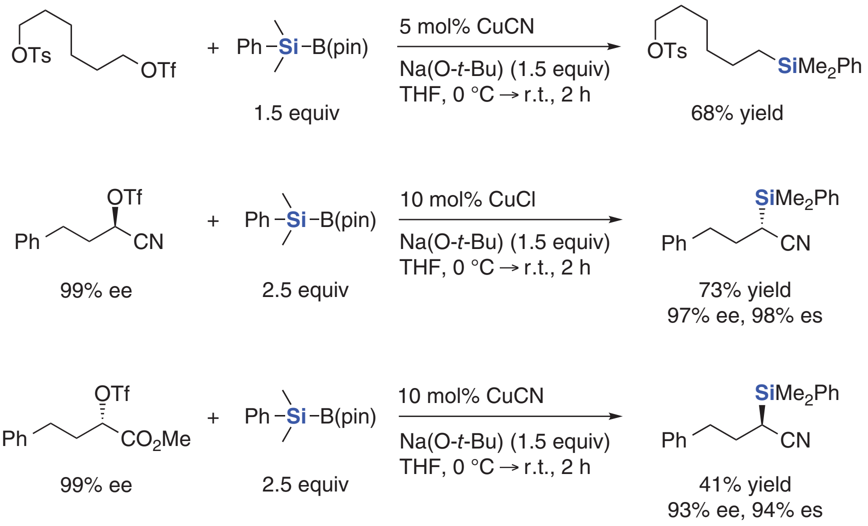
1.2.2.8 CO_2 Reduction via Silylation

In 2011, Kleeberg et al. studied the reaction of the [1,3-bis(diisopropylphenyl) imidazole-2-ylidene(IPr)]copper–silyl complex with CO_2 to form CO in detail experimentally (Scheme 1.22) [35]. The (IPr)copper-silyl complex reacted with CO_2 to provide the silanecarboxylic acid complex, followed by the formation of CO and a (IPr)Cu–O–$SiMe_2Ph$ linkage. This complex reacts with a silylboronate, regenerating the silyl complex and producing the (pin)B–O–$SiMe_2Ph$. It is also possible that the silanecarboxylic acid complex undergoes transmetalation with a silylboronate to form the silyl complex as well as decomposition byproducts, which were detected in the reaction mixture.

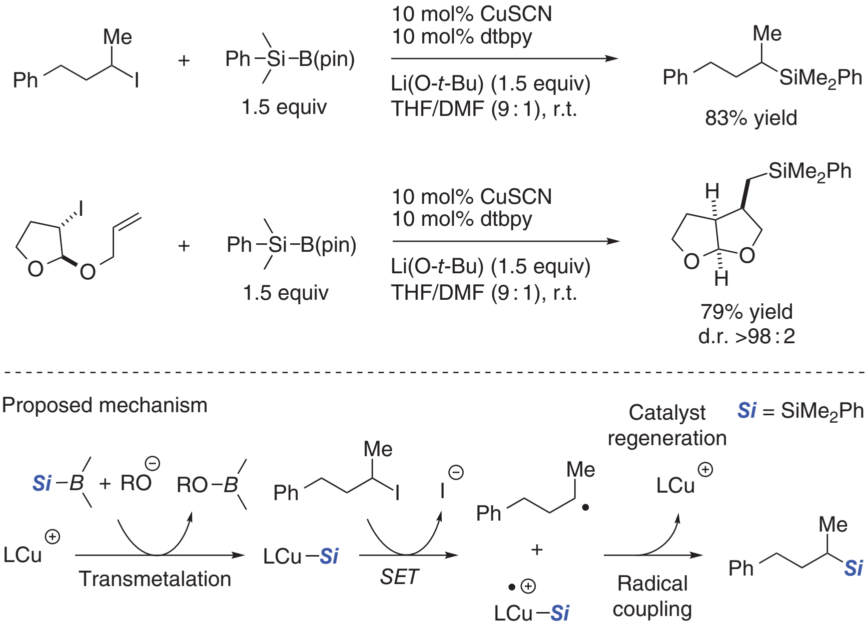
1.2.2.9 Silyl Substitution of Alkyl Electrophiles

Reactions for the carbon–silicon bond formation through a substitution of unactivated alkyl electrophiles with silicon nucleophiles have been practically unexplored until very recently. In 2016, the first example of copper-catalyzed nucleophilic silylation of alkyl triflates with a silylboronate was reported by Oestreich and a coworker (Scheme 1.23) [36]. Notably, this silylation is a stereospecific process, providing chiral silanes from the optically active substrates in a stereoinversion manner [37].

Afterwards, Oestreich's group extended their method to alkyl iodides (Scheme 1.24) [38]. Interestingly, in this case, the carbon–silicon bond-forming process proceeded through a radical mechanism. The catalytic cycle was investigated computationally in detail, leading to a full mechanistic picture that includes a single-electron-transfer (SET) process between the silylcopper intermediate and alkyl iodide to generate an alkyl radical intermediate, followed by a radical coupling to form the silylation product. They also demonstrated the silylative radical cyclization of alkenyl iodides to give the corresponding cyclic silylation compounds with high setereoselectivity.



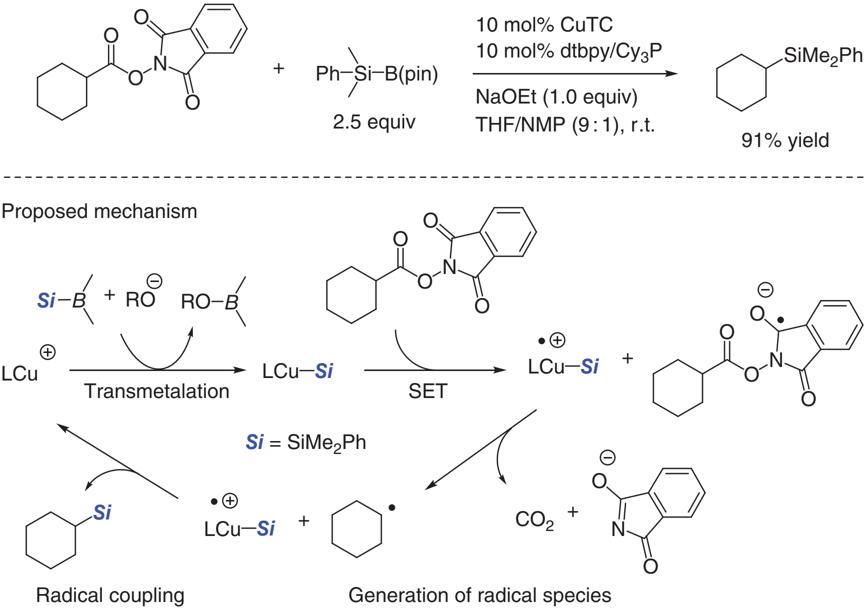
Scheme 1.23 Stereospecific copper-catalyzed silyl substitution of alkyl triflates.



Scheme 1.24 Copper-catalyzed silyl substitution of alkyl iodides via a radical mechanism.

1.2.2.10 Decarboxylative Silylation

In addition to the carbon–silicon bond-forming cross-coupling of alkyl triflates and halides, Oestreich and a coworker disclosed the copper-catalyzed decarboxylative radical silylation of aliphatic carboxylic acid derivatives (Scheme 1.25) [39]. The reaction of aliphatic *N*-hydroxyphthalimide (NHPI) esters with a silylboronate



Scheme 1.25 Copper-catalyzed decarboxylative silylation of NHPI esters.

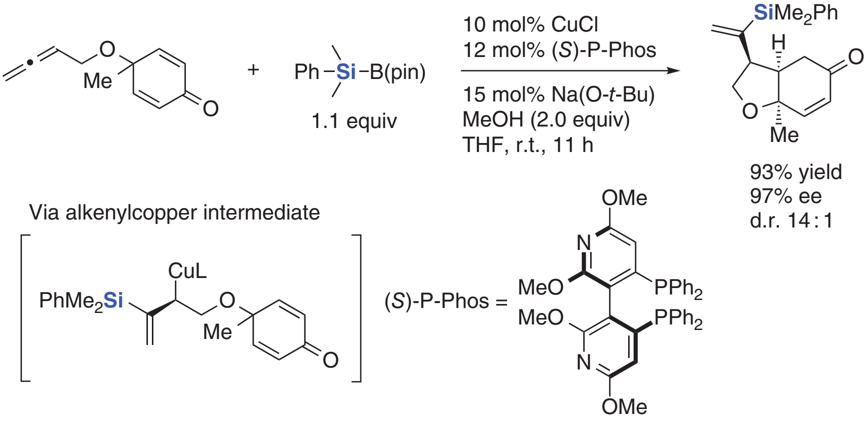
produced primary, secondary, and tertiary alkylsilanes in good to high yields. The radical-trapping and racemization experiments were consistent with a radical mechanism. They proposed the catalytic cycle involving an SET process from the silylcopper complex to the electron-accepting NHPI ester, followed by the radical coupling to give the silylation product, as shown in Scheme 1.25.

1.2.2.11 Silylative Cyclization

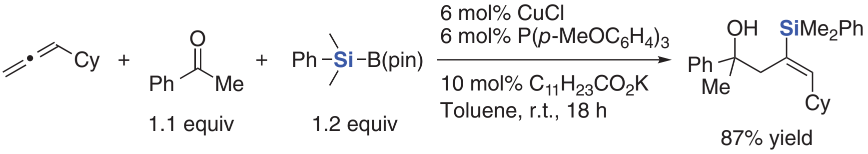
A silylation of carbon–carbon double bond with concomitant carbon–carbon bond formation would be highly beneficial for the efficient construction of structurally complex alkylsilanes. Tian and coworkers developed the copper-catalyzed enantioselective silylative cyclization with a silicon nucleophile to form three consecutive chiral carbon centers in one step (Scheme 1.26) [40]. This tandem reaction presumably goes through the regio- and enantioselective addition of a silylcopper intermediate to the allene and subsequent enantioselective 1,4-addition of a cyclohexadienone moiety to give the bicyclic silylation product with excellent stereoselectivity.

1.2.2.12 Silylative Allylation of Ketones

The addition of transition-metal species across allenes is a useful strategy for in situ generation of allylic nucleophiles. In 2015, Fujihara and Tsuji's group reported that the copper-catalyzed silylative allylation of ketones with allenes and silylboronates through in situ–generated β-silylated allylcopper intermediate (Scheme 1.27) [41]. Various ketones and allenes were converted into the corresponding homoallylic tertiary alcohols containing internal vinylsilane moieties in high yields.



Scheme 1.26 Copper-catalyzed silylative cyclization of allenes.

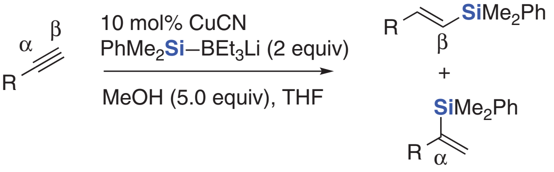


Scheme 1.27 Copper-catalyzed silylative allylation of ketones and allenes.

1.2.2.13 Silylation of Alkynes

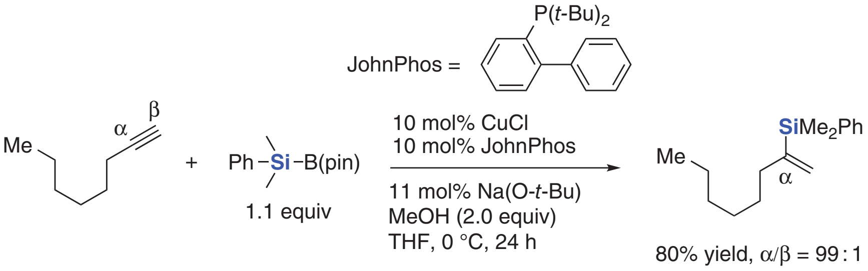
A regioselective addition of silicon nucleophiles across alkynes provides an efficient synthetic route to various vinylsilanes. In 1986, a pioneering study on the silylation of alkynes with silicon nucleophiles was reported by Nozaki et al. (Scheme 1.28) [42]. They discovered that the reaction of terminal alkynes with $PhMe_2SiBEt_3Li$ in the presence of a catalytic amount of CuCN and methanol as a proton source produced the corresponding β-vinylsilanes with moderate to high regioselectivity.

More than 20 years after the report of Nozaki et al., Loh and coworkers discovered that the monophosphine/copper complex–catalyzed regioselective protosilylation of terminal alkynes proceeded to form α-vinylsilanes (Scheme 1.29) [43]. The choice of the ligand significantly influenced the

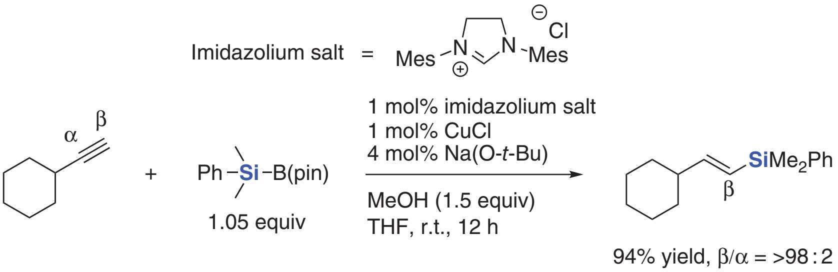


R = $-C_{10}H_{21}$, 89% yield,
α/β = 39 : 61
$-CH_2CH_2OBn$, 91% yield,
α/β = 32 : 68
$-CH_2OH$, 95% yield,
α/β = 0 : 100
$-SiMe_3$, 66% yield,
α/β = 0 : 100

Scheme 1.28 Pioneering study on copper-catalyzed protosilylation of alkynes.



Scheme 1.29 Monophosphine/copper complex–catalyzed regioselective protosilylation of alkynes.

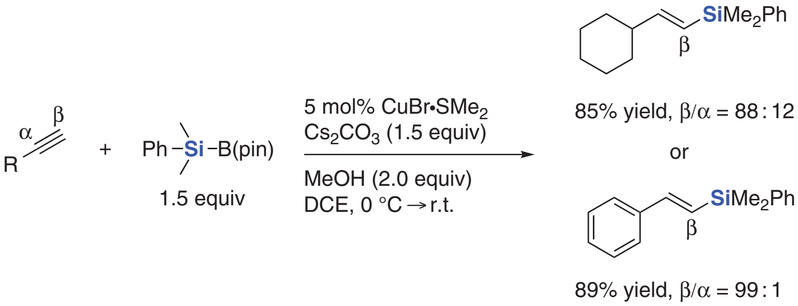


Scheme 1.30 NHC/copper complex–catalyzed regioselective protosilylation of alkynes.

regioselectivity in this reaction. It was found that the use of a bulky monophosphine ligand such as JohnPhos provided a high degree of Markovnikov selectivity.

In 2013, Hoveyda and coworkers reported that the NHC/copper complex–catalyzed protosilylation of terminal alkynes proceeded to form β-vinylsilanes with excellent regioselectivity (Scheme 1.30) [44]. Exclusive generation of the β-isomer, regardless of the electronic properties of the alkyne substituent, suggests that the regioselectivity can be controlled by steric factors, where the relatively larger dimethylphenylsilyl group is placed at the terminal carbon.

Later, Oestreich and coworkers reported a general method for the β-selective silylation without adding a ligand (Scheme 1.31) [45]. After fine-tuning the reaction parameters such as a copper precatalyst, base, and solvent, they found



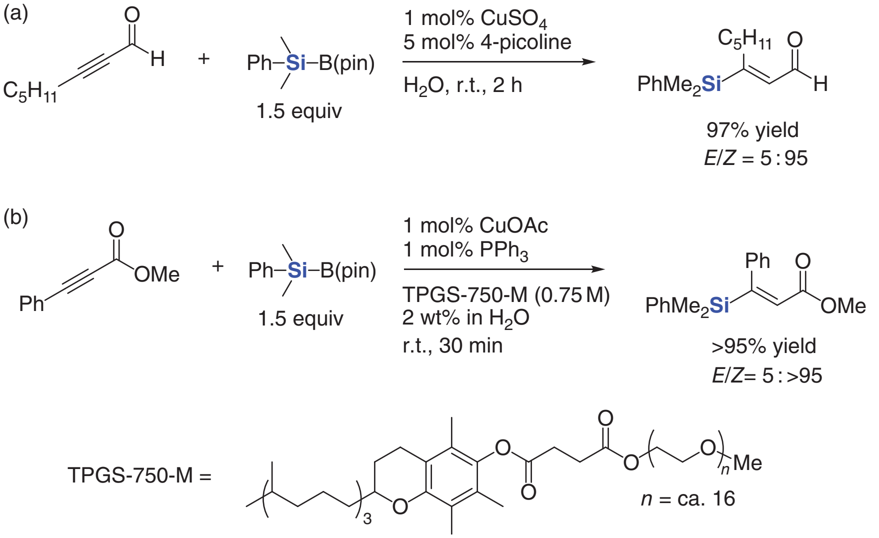
Scheme 1.31 Ligand-free copper-catalyzed protosilylation of alkynes.

that the use of $CuBr \cdot SMe_2$, Cs_2CO_3 and dichloroethane as a solvent afforded the desired β-selective silylation products in high yields with excellent regioselectivity. Both aromatic and aliphatic terminal alkynes were converted into the products with high β-selectivity.

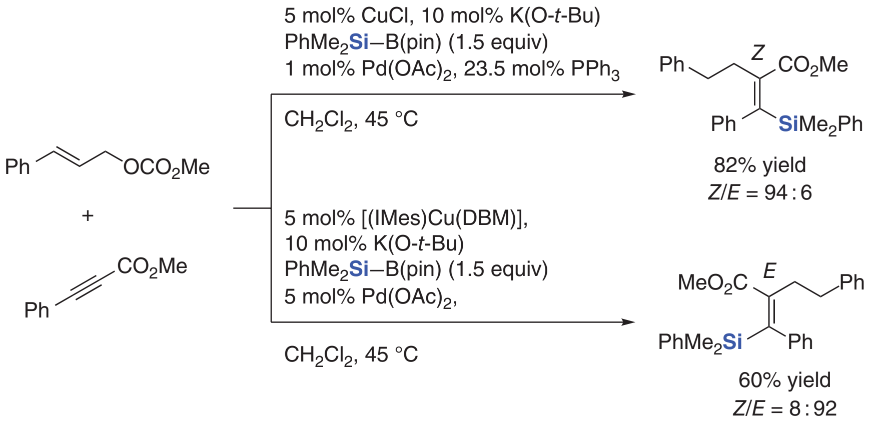
In 2014, new protocols for the silylation of alkynes in water were independently reported by Santos and Lipshutz' groups (Scheme 1.32) [46, 47]. Santos and a coworker found that the silylation of activated alkynes with a silylboronate in the presence of $CuSO_4$ and 4-picoline as a ligand in water proceeded smoothly to give the corresponding silyl conjugate addition products in high yields (Scheme 1.32a) [46]. Lipshutz's group discovered that the use of the commercially available surfactant TPG-750-M served as the reaction medium and efficiently promoted the copper-catalyzed conjugate silylation of alkynes in water (Scheme 1.32b) [47].

Cooperative catalysts can promote complex, challenging transformations that could not be realized by a single catalyst operation. Riant and coworkers developed a tunable and stereoselective dual copper/palladium catalytic system for the silylative allylation of activated alkynes in 2014 (Scheme 1.33) [48]. This reaction presumably proceeds through the silylcupration of alkynes, followed by transmetalation between the alkenylcopper species and the π-allylpalladium intermediate to form trisubstituted alkenylsilanes. Notably, fine-tuning the reaction conditions allows selective access to both *Z* and *E* isomers.

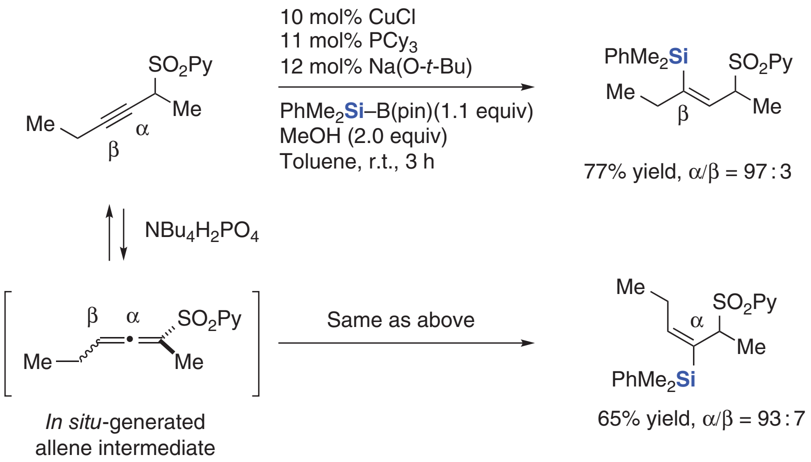
The precise control of the regioselectivity in copper-catalyzed silylation of alkynes still remains a challenging subject. In 2015, Carretero and coworkers developed the regiodivergent silylation of internal alkynes with a traceless



Scheme 1.32 Copper-catalyzed protosilylation of alkynes in water at room temperature. (a) Santos, (b) Lipshutz.



Scheme 1.33 Copper/palladium cooperative catalytic system for silylative allylation of alkynes.

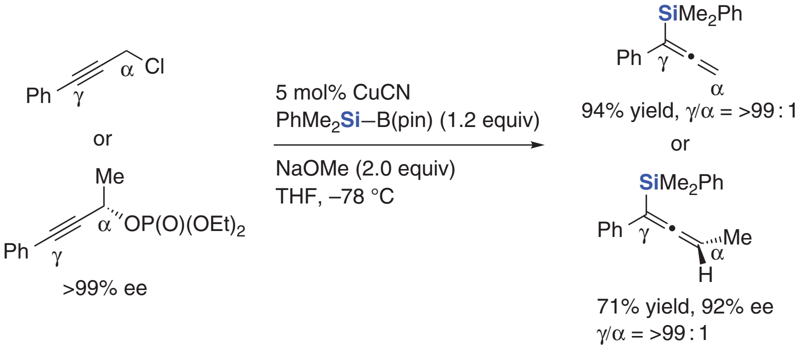


Scheme 1.34 Regiodivergent copper-catalyzed protosilylation of alkynes.

2-pyridylsulfonyl group as a directing group (Scheme 1.34) [49]. Either regioisomer could be obtained without modification of the starting substrates by virtue of an *in situ* base-promoted alkyne to allene equilibration which takes place prior to the addition of a silylcopper intermediate. In addition, this directing group could be removed after the silylation by the addition of carbon nucleophiles.

1.2.2.14 Propargylic Substitution

A γ-selective propargylic substitution is an efficient synthetic route to multi-substituted allenes. In 2011, the first copper-catalyzed propargylic substitution

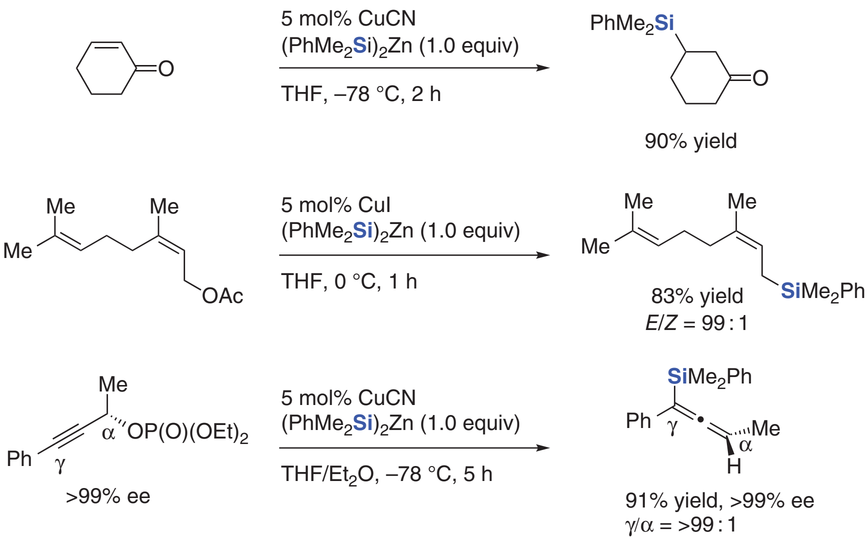


Scheme 1.35 Stereospecific γ-selective propargylic silyl substitution.

with silicon nucleophiles was reported by Oestreich and coworkers (Scheme 1.35) [50]. The reaction of a variety of propargylic chlorides in the presence of CuCN and NaOMe with a silylboronate afforded the corresponding allenylsilanes with excellent γ-selectivity. Notably, the central-to-axial chirality transfer was also observed in the silylation of the α-chiral propargylic phosphates to give the chiral allenylsilanes with high stereospecificity.

1.2.3 Copper-Catalyzed Nucleophilic Silylation with Silylzincs

In 2004, Oestreich and Weiner first introduced soft bis(triorganosilyl)zinc species, such as $(PhMe_2Si)_2Zn$, which can be used as a source for the generation of silicon nucleophiles in copper-catalyzed reactions [51]. In this context, Oestreich and coworkers developed a copper-catalyzed conjugate addition, silylation of allylic and propargylic electrophiles with $(PhMe_2Si)_2Zn$ reagent (Scheme 1.36) [52–54].



Scheme 1.36 Copper-catalyzed nucleophilic silylation with $(PhMe_2Si)_2Zn$ reagent.

1.3 Silicon Nucleophiles with Rhodium Catalysts

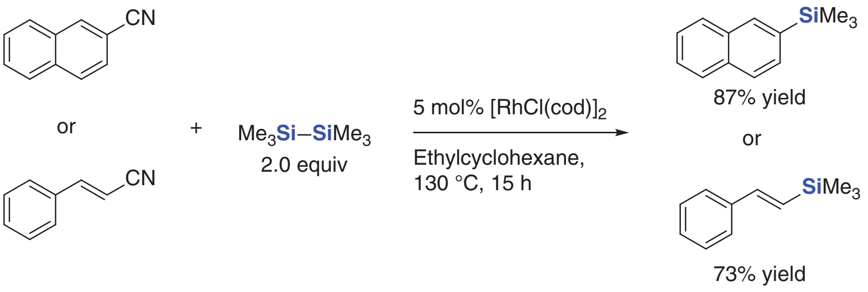
1.3.1 Rhodium-Catalyzed Nucleophilic Silylation with Disilanes

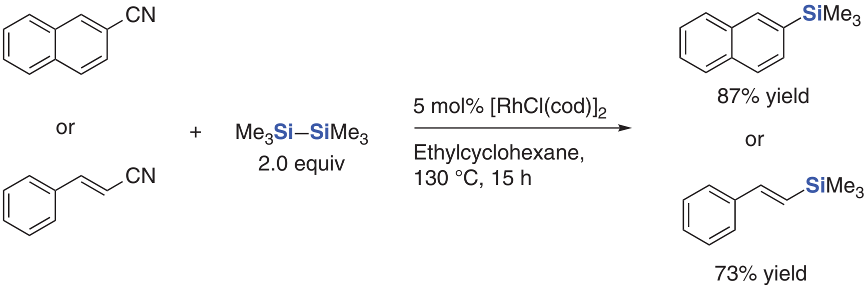
In 2006, the first example of catalytic generation of nucleophilic rhodium–silicon species with disilanes and its application to catalytic silylation of aryl and alkenyl cyanides was reported by Tobisu et al. (Scheme 1.37) [55]. The reaction mechanism was proposed to proceed via the silylmetalation of a cyano group by a silylrhodium species, which can be generated through reaction of rhodium chloride with a disilane, followed by the carbon–carbon bond-cleavage process.

1.3.2 Rhodium-Catalyzed Nucleophilic Silylation with Silylboronates

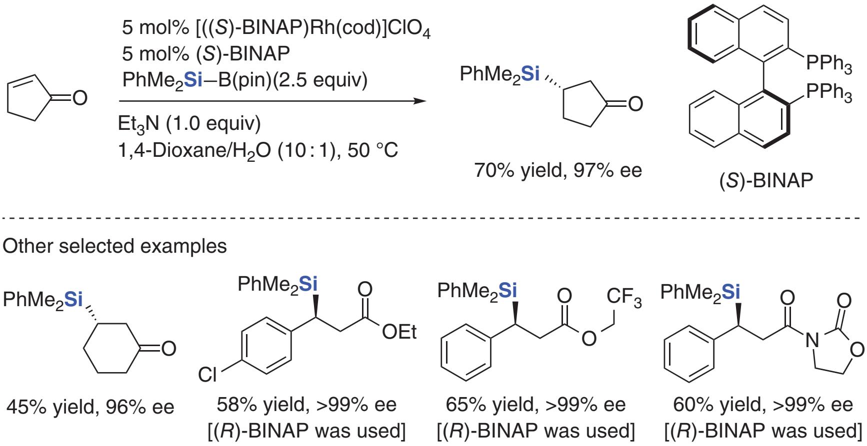
1.3.2.1 Conjugate Silylation

In 2006, the first example of rhodium-catalyzed conjugate silylation with a silylboronate was reported by Oestreich and coworkers (Scheme 1.38) [56]. The reaction of α,β-unsaturated carbonyl compounds with a silylboronate in the presence of a rhodium catalyst and Et_3N provided the 1,4-addition products in good to high yields. The same group also discovered that the use of (*S*)-BINAP as a chiral ligand in this reaction resulted in the formation of chiral silanes with excellent enantioselectivity [56–60]. This reaction presumably goes through the formation of a silylrhodium species and subsequent 1,4-silyl addition to α,β-unsaturated carbonyl compounds. The synthetic utility of this protocol was

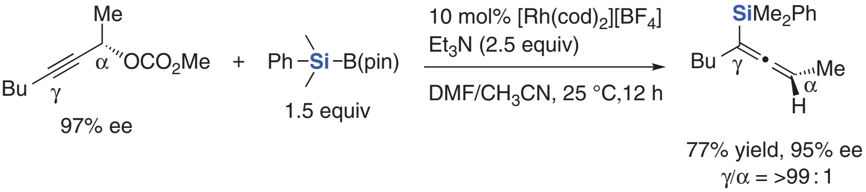



CN
or
CN
+
Me3Si–SiMe3
2.0 equiv
5 mol% [RhCl(cod)]2
Ethylcyclohexane,
130 °C, 15 h
SiMe3
87% yield
or
SiMe3
73% yield

Scheme 1.37 Rhodium-catalyzed silylation of aryl and alkenyl cyanides.



Scheme 1.38 Rhodium-catalyzed conjugate silylation with a silylboronate.



Scheme 1.39 Rhodium-catalyzed stereospecific silylation of propargylic carbonates.

successfully demonstrated by the synthesis of the C7–C16 fragment of (+)-Neopeltolide [59].

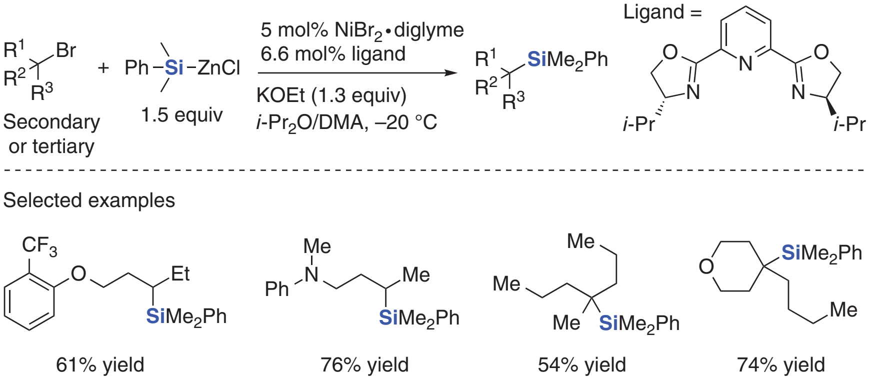
1.3.2.2 Coupling between Propargylic Carbonates to Form Allenylsilanes

In 2009, Sawamura and coworkers reported that the rhodium-catalyzed coupling reaction between propargylic carbonates and a silylboronate provided the corresponding allenylsilanes in high yields (Scheme 1.39) [61]. The reaction of an optically active substrate proceeded with excellent chirality transfer to form an axially chiral allenylsilane.

1.4 Silicon Nucleophiles with Nickel Catalysts

1.4.1 Nickel-Catalyzed Nucleophilic Silylation with Alkyl Electrophiles

The first metal-catalyzed cross-coupling reactions of unactivated secondary and tertiary alkyl electrophiles to form carbon–silicon bonds was reported by Fu and coworkers (Scheme 1.40) [62]. In the presence of a nickel/pybox catalyst, the cross-coupling reactions between secondary and tertiary alkyl bromides and a silylzinc reagent afforded a variety of alkyl silicon compounds. Stereochemical



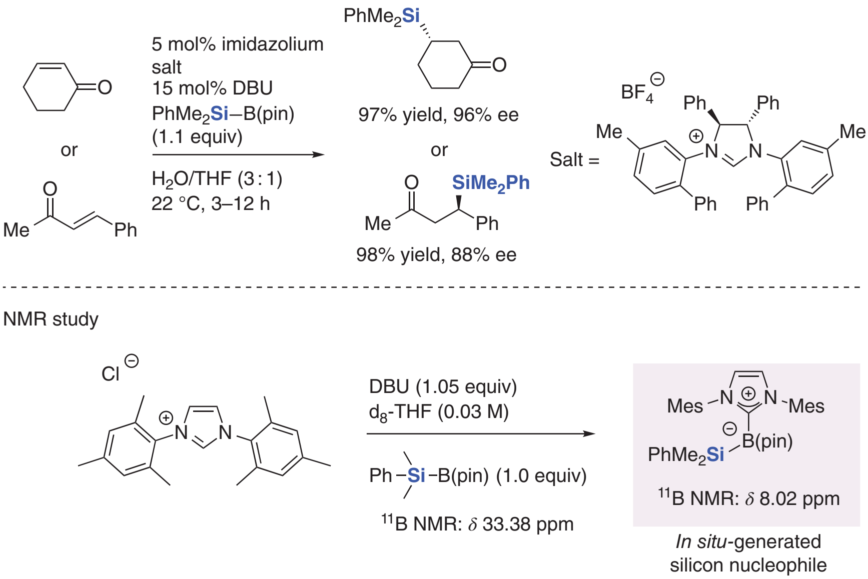
Scheme 1.40 Nickel-catalyzed silylation of unactivated alkyl electrophiles.

and radical-trap experiments are consistent with a radical mechanism involving a homolytic pathway for carbon–bromine bond cleavage.

1.5 Silicon Nucleophiles with Lewis Base Catalysts

1.5.1 N-Heterocyclic Carbene-Catalyzed Nucleophilic 1,4-Silylation

In 2011, Hoveyda and a coworker first discovered that NHCs, in the absence of a metal salt, activate the silicon–boron bond of a silylboronate to generate silicon nucleophiles (Scheme 1.41) [63]. The reaction of α,β-unsaturated carbonyl



Scheme 1.41 Chiral NHC-catalyzed enantioselective conjugate silylation.

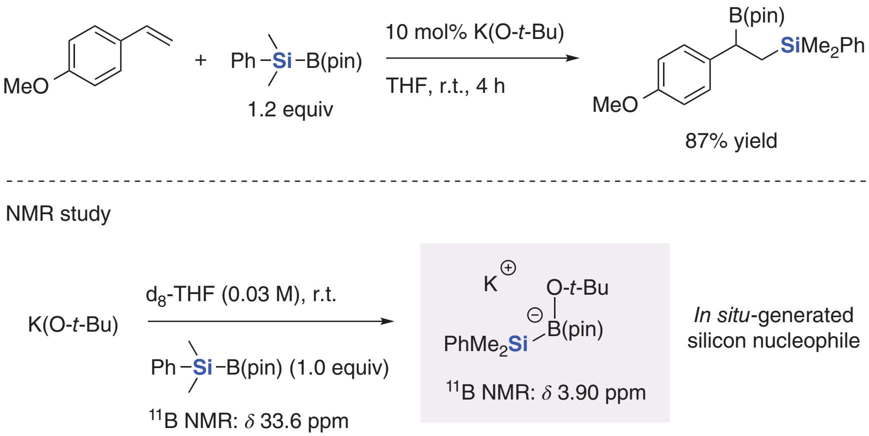
compounds with a silylboronate in the presence of catalytic amount of a imidazolium salt and 1,8-diazabicyclo(5.4.0)undec-7-ene (DBU) afforded the conjugate silyl addition products in high yields. Their *in situ* NMR studies suggested the formation of a NHC → B–Si ate complex in the reaction mixture. They also developed the enantioselective version of this process with a chiral NHC catalyst.

1.5.2 Alkoxide Base–Catalyzed 1,2-Silaboration

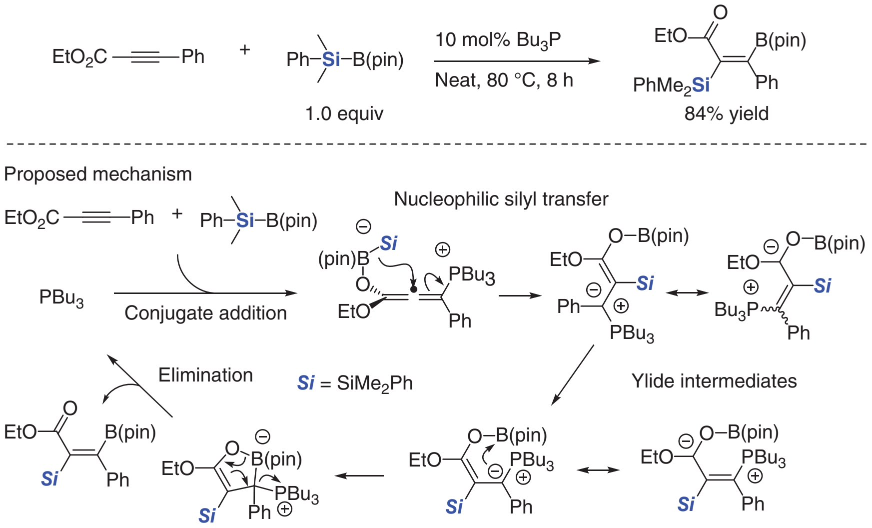
Alkoxide bases also activate the silicon–boron bond of a silylboronate to generate silicon nucleophiles. In 2012, the first alkoxide base–catalyzed reaction of a silylboronate was reported by Ito et al. (Scheme 1.42) [64]. In the presence of 10 mol% K(O-*t*-Bu), silylboration of aromatic alkenes with a silylboronate proceeded with excellent regioselectivity. Their *in situ* NMR studies revealed the formation of a *t*-BuO→B–Si ate complex in the reaction mixture. A related silylative cyclopropanation reaction of allyl phosphates with a stoichiometric amount of the alkoxide base was also reported by Shinatani et al. in 2014 [65].

1.5.3 Phosphine-Catalyzed 1,2-Silaboration

In 2015, Ohmiya and coworkers reported that trialkylphosphine-catalyzed *anti*-selective silaboration of alkynoates with a silylboronate produced β-boryl-α-silyl acrylates in high yields (Scheme 1.43) [66]. They proposed the reaction mechanism that includes the conjugate addition of Bu_3P to the alkynoate to form a zwitterionic allenolate intermediate, followed by nucleophilic silyl transfer from the activated silylboronate to give the ylide intermediates. Next, the nucleophilic attack of the ylide carbon to the boron atom bound to the enolate oxygen provides the cyclic borate and the subsequent elimination of Bu_3P associated with the boron–oxygen bond cleavage affords the *anti*-silaboration product.



Scheme 1.42 Alkoxide base–catalyzed silaboration of aromatic alkenes.



Scheme 1.43 Phosphine-catalyzed 1,2-silaboration of alkynyl esters.

1.6 Closing Remarks

A number of transition-metal-catalyzed reactions with *in situ*–generated silicon nucleophiles have been reported as alternative synthetic pathways for the preparation of a sensitive functional group containing sterically hindered silicon compounds. Different transition metals have specific reactivities in these silicon–carbon bond formation reactions. In particular, the combination of a copper catalyst and a silylboronate has been widely used for the catalytic generation of a soft silicon nucleophile, a silylcopper intermediate, which reacts with a broad range of electrophiles to form the corresponding silylation products with high selectivity. In addition to metal-catalyzed methods, less toxic metal-free protocols such as NHC- or alkoxide base–catalyzed nucleophilic silylations have also been developed in recent years. These significant achievements discussed in this chapter will find a wide range of applications in organic synthesis, pharmaceutical drug discovery, and materials science.

Abbreviations

THF	tetrahydrofuran
DMF	dimethylformamide
DME	1,2-dimethoxyethane
DMA	*N*,*N*-dimethylacetamide
DCE	dichloroethane
Ts	tosyl
Tf	trifluoromethanesulfonyl
2-naph	2-naphthyl

NMP	*N*-methyl-2-pyrrolidone
cod	1,5-cyclooctadiene
NHC	*N*-heterocyclic carbene
DBU	1,8-diazabicyclo(5.4.0)undec-7-ene
dppf	1,1′-bis(diphenylphosphino)ferrocene
TBAT	tetrabutylammonium difluorotriphenylsilicate
IMes	1,3-dimesitylimidazol-2-ylidene, 1,3-bis(2,4,6-trimethylphenyl)-imidazolium, 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene
SIMes	1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene
Cbz	benzyloxycarbonyl
Mes	mesityl
TMS	trimethylsilyl
dtbpy	4,4′-di-*tert*-butyl-2,2′-dipyridyl
Bn	benzyl
dppbz	1,2-bis(diphenylphosphino)benzene
Py	pyridine
Tol	*p*-tolyl
DBM	dibenzoylmethane
diglyme	1-methoxy-2-(2-methoxyethoxy)ethane
TC	thiophene-2-carboxylate

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