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Catalytic Reactions Involving the Oxidative Addition of Si—Halogen and Si—Pseudohalogen Bonds as a Key Step

Naoto Chatani*[a, b]

The oxidative addition of C-halogen bonds of aryl halides or alkyl halides is a critical step in a wide variety of transition-metal-catalyzed C—C and C–heteroatom bond formation reactions. In contrast, the oxidative addition of Si-halogen bonds of halosilanes has not been used in the development of transition metal-catalyzed reactions, although halosilanes are known to be highly reactive in many organic reactions with oxygen-containing compounds. However, recent progress in transition metal-catalyzed reactions using halosilanes has resulted in several synthetically useful and revolutionary methodologies concerning organosilicon synthesis through the oxidative addition of Si–halogen bonds, even less reactive Si—Cl bonds. This review will focus on transition metal-catalyzed reactions of C—C multiple bonds, such as alkenes, alkynes, and 1,3-dienes with R_3Si-X (I, Br, Cl, and OTf), in which the oxidative addition of a Si—X bond appears to be a key step. In addition, the transition metal-catalyzed cross-coupling, cross-electrophile coupling, and three-component cross-electrophile coupling reactions with R_3Si-X (I, Br, Cl, F, and OTf) are also discussed.

1. Introduction

Organosilicon compounds have many synthetic applications for preparing various types of useful and high value-added compounds, but also have their own applications as adhesives, sealants for LED and OLED devices, automotive lubricants, coatings, silicone rubber, computer chips, functional organic materials, and small molecule drugs.[1–5] Regarding synthetic organic chemistry, it is known that the reactivity of organosilicon reagents (R_3Si-X) is highly dependent on the high oxophilicity of the silyl group, which makes the X group more nucleophilic. Because of this, many organosilicon reagents are known to react with a variety of oxygen- or nitrogen-containing substrates, such as aldehydes, ketones, acetals, epoxides, imines, and other groups in the presence of Lewis acids as a catalyst.[6] In fact, various types of organosilicon reagents, such as enol silyl ethers, ketene silyl acetal, arylsilanes, allylsilanes, vinylsilanes, and silyl cyanide are known to be powerful synthetic reagents in Lewis acid-mediated reactions.

Halosilanes are one of the most widely used silylation reagents for the preparation of other organosilicon compounds. These reactions proceed via coupling reactions with nucleophiles, such as Grignard reagents, organolithium reagents, and enol species. Given the synthetic utility of C-halogen bonds of aryl halides in transition metal-catalyzed reactions, halosilanes would also be expected to have potential for use in preparing a variety of high value-added organosilicon compounds. However, compared with C-halogen bonds in aryl halides, the oxidative addition of a Si-halogen bond to transition metal complexes is very rare. This is probably attributed either to $p\pi-d\pi$ back bonding or an increased ionic contribution to bonding.[7]

In 1988, Tanaka reported that Me_3SiBr oxidatively adds to $Pt(PEt_3)_3$ at 90 °C to give the trans-$Me_3SiPtBr(PEt_3)_2$ **1** in 90% yield (Scheme 1).[8] The structure of this complex was confirmed by X-ray crystallographic analysis. While Me_3SiI reacted easier to give trans-$Me_3SiPtI(PEt_3)_2$, Me_3SiCl was unreactive, even at 120 °C. This complex **1** is the first example of an oxidative addition complex of a Si-halogen bond whose structure was determined by X-ray analysis. Since then, other examples of stoichiometric reactions involving the activation of Si-halogen bonds have appeared in the literature and their structures were confirmed by X-ray crystallographic analysis, but there are still only a few examples.[9–15]

This review will focus on transition metal-catalyzed reactions of C—C multiple bonds, such as alkenes, alkynes, and 1,3-dienes with R_3Si-X (I, Br, Cl, and OTf), in which the oxidative addition of a Si—X bond appears to be a key step.[16–20] In addition, the transition metal-catalyzed cross-coupling, cross-electrophile coupling, and three-component cross-electrophile coupling reactions using R_3Si-X (I, Br, Cl, F, and OTf) are also discussed. Reaction examples in each chapter will be presented in the order in which the papers were published.

2. Reaction with Alkenes

As shown above, Tanaka and coworkers reported the first example of the oxidative addition complex of a Me_3Si—X (X = Br and I) bond to a Pt(0) complex whose structure was determined by X-ray crystallographic analysis in 1988 (Scheme 1).[8] Three years later, in 1991, Tanaka and coworkers reported that the

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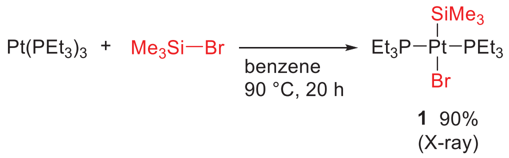
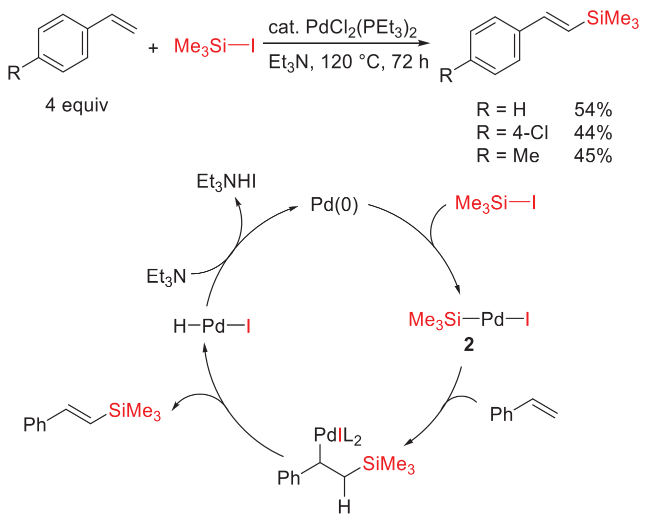


Scheme 1. Oxidative addition of Me$_3$SiBr to Pt(PEt$_3$)$_3$.



Scheme 2. Pd-catalyzed reaction of styrenes with Me$_3$SiI.

reaction of an excess amount styrene derivatives with Me$_3$SiI in Et$_3$N both as a solvent and a base in the presence of PdCl$_2$(PEt$_3$)$_2$ as the catalyst at 120 °C results in a silyl-Mizoroki–Heck type reaction to give 2-arylvinylsilanes with a high degree of E-selectivity (Scheme 2).[21]

The reaction is proposed to proceed through essentially the same as that for the Mizoroki–Heck reaction. Thus, the oxidative addition of Me$_3$SiI to the Pd(0) complex gives a Me$_3$SiPdI species **2** which then undergoes silylpalladation with an alkyne followed by β-hydride elimination to afford 2-phenylvinylsilane along with HPdI species which reacts with Et$_3$N to regenerate the Pd(0) species. While this reaction is a pioneering example of catalytic reaction involving the activation of a Si-halogen bond, only three examples of styrenes were included in the paper, and product yields were moderate (44%–54% yields based on Me$_3$SiI as a limiting reagent).

In 1997, Tanaka and coworkers reported the synthesis of a series of R$_3$Si-Pt—X phosphine complexes by the oxidative addition of various halosilanes with Pt(0) phosphine complexes, the structures of which were identified by ^{1}H, ^{13}C, ^{29}Si, ^{31}P, and ^{195}Pt NMR and IR and/or elemental analysis.[12] The order of reactivity of the halosilane derivatives was found to be Si-Cl $<<$ Si-Br $<$ Si—I bonds, which reflects the dissociation energies of Si-X bonds. It was also found that electron-donating phosphine ligands accelerate the oxidative addition. The reaction of **1** with 2 equiv. of styrene in benzene-d_6 at 120 °C for 5 h in an NMR tube gave the silyl-Mizoroki–Heck type product in 5% yield with the 95% conversion of **1**.

Watson and coworkers re-examined the reaction conditions of the silyl-Mizoroki–Heck type reaction. As a result, they successfully developed more efficient reaction conditions under which the reaction proceeds even at 50 °C using styrene as the limiting reagent (Scheme 3).[22] A key to the success of the reaction was the use of (cod)Pd(CH$_2$TMS)$_2$ as a catalyst precursor and an electron-rich and bulky phosphine ligand, P^{t}BuPh$_2$ (Tolman angle $\theta = 157°$).[23] Gratifyingly, the scope of the reactions for alkenes could be expanded not only to styrene derivatives including 2-vinylpyridines and *N*-vinylcarbazole but also aliphatic terminal alkenes, the latter being proceeded even at room temperature to give allylsilanes with a high E-selectivity. However, product yields in the reaction of aliphatic terminal alkenes were relatively low due to a significant amount of isomerization of the starting alkene. Compared with Me$_3$SiI, Me$_3$SiCl is more readily available in large quantities at low cost. It was found that the addition of LiI (5 equiv.) allows the use of Me$_3$SiCl in place of Me$_3$SiI in the reaction of 4-tert-butylstyrene to give the corresponding product in 94% yield, indicating that in situ generation of Me$_3$SiI is needed due to the low reactivity of Me$_3$SiCl toward the oxidative addition to Pd(0) complex. It was found that various functional groups are tolerated in the reaction.

In 2013, Watson and coworkers reported that a Si—OTf bond also participates in the silyl-Mizoroki–Heck type reaction of styrene derivatives in the presence of a catalytic amount of an iodide additive. The Pd-catalyzed reaction of styrenes with Me$_2$Si(OTf)$_2$, which can be easily prepared by the reaction of

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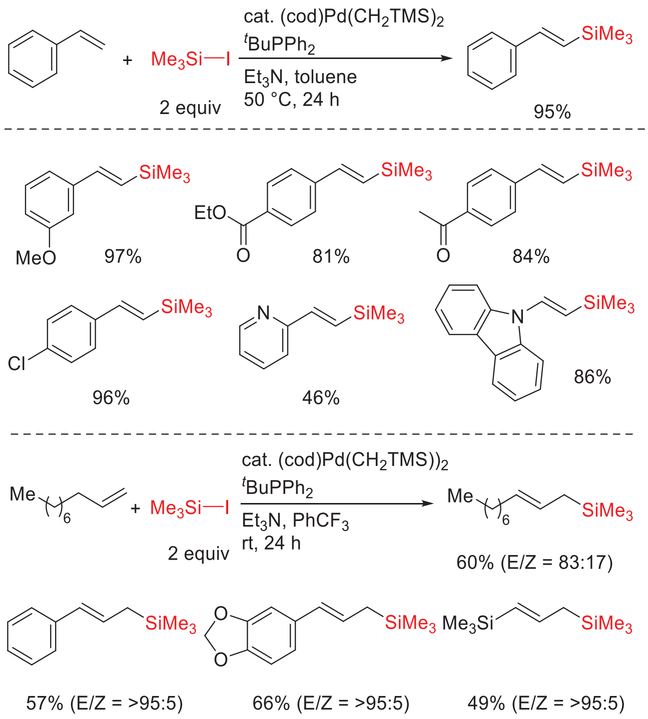


Scheme 3. Pd-catalyzed reaction of alkenes with Me_3SiI.

Ph_2SiMe_2 and TfOH, in the presence of 5 mol% of NaI, gave 2-arylvinylsilanes (Scheme 4a).[24] The use of alcohols as quenching reagents gave vinylsilane **3**, which is well known as suitable compounds for use in Hiyama–Denmark cross-coupling reactions. When H_2O was used as a quenching reagent, divinylsiloxane **4** was formed. In all cases, neither Z-isomers nor regioisomers were detected. The reaction displayed good functional group tolerance, and the substrate scope was also wide.

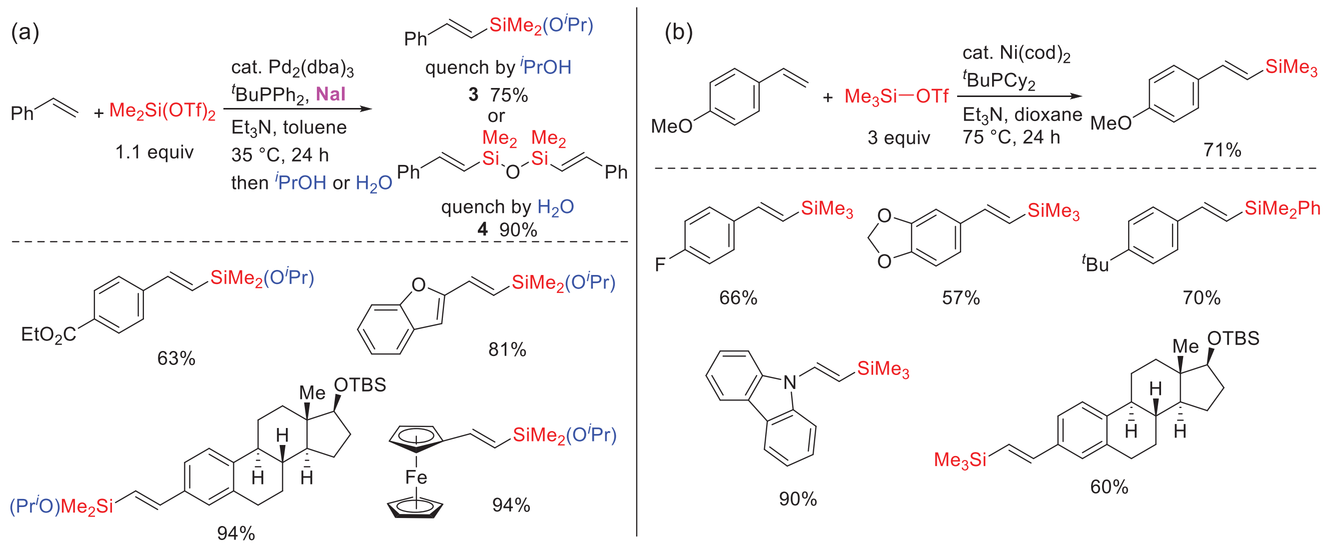
Watson and coworkers subsequently reported the first example of the Ni-catalyzed silyl-Mizoroki–Heck type reaction of styrenes with Me_3SiOTf (Scheme 4b).[25] In this system, the use of NaI additive was not necessary for the reaction to proceed, suggesting that the reaction involves the direct oxidative addition of a Si—OTf bond to a Ni(0) center or to an $Me_3SiPR_3^+$ OTf^- species, which is generated by the reaction of Me_3SiOTf with phosphine and could function as a silyl electrophile. This discovery was the trigger that led to the further development of this field. Less bulky phosphine ligands were found to be ineffective, but curiously, bulkier PBu^t_3 and PBu^tCy_2 were also less reactive than P^tBuPh_2, suggesting that moderate bulkiness of phosphine ligands appears to be an important factor. While a nonprecious metal, such as Ni can be used as the catalyst, some functional groups, such as dimethylamino, ethyl ester, and chloro groups were not tolerated the reaction.

As shown in Scheme 3, the isomerization of the starting terminal alkenes into internal alkenes led to a decrease in the yields of the desired products.[22] Watson and coworkers reported a new catalytic system for the silyl-Mizoroki–Heck type reaction of terminal aliphatic alkenes (Scheme 5).[26] It was found that the use of a newly designed, bench-stable JessePhos, which is an electron-rich phosphine with a large cone angle, suppresses the isomerization of the starting terminal alkenes, which results in improved product yields of the desired allylsilanes. The oxidative addition complex **5** using an analogous phosphine ligand was successfully isolated as a light green crystal, and the T-shaped structure was determined by X-ray crystallography.

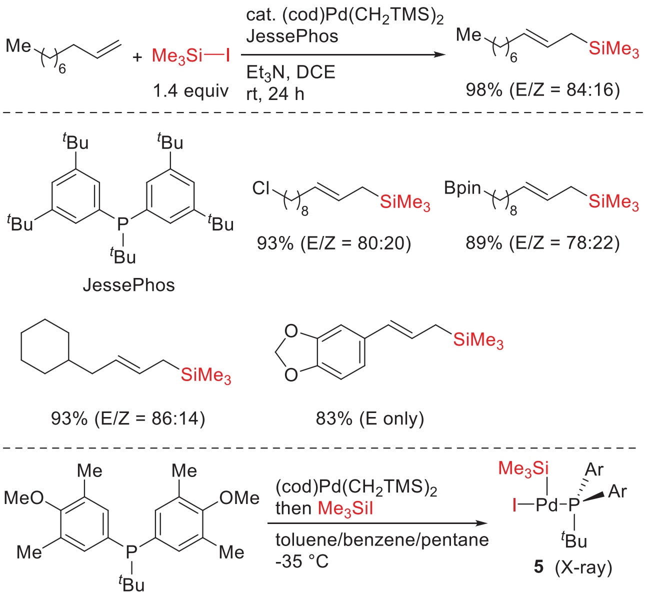
Watson and coworkers conducted a rational design of Pd catalyst and found that the combination of JessePhos and the widely available bench stable $Pd_2(dba)_3$ in place of the thermally sensitive $(cod)Pd(CH_2TMS)_2$ leads to an increase in catalytic activity for the Pd-catalyzed silyl-Mizoroki–Heck type reaction of styrenes.[27] In addition, Watson and coworkers reported that temperature, moisture, and air stable $[(JessePhos)PdI_2]_2$, which can be easily prepared by the reaction of PdI_2 with JessePhos, provides a higher reactivity toward the silyl-Mizoroki–Heck type reaction of styrenes and terminal aliphatic alkenes compared to previously reported systems.[28] In these newly designed catalytic systems, even bulkier iodosilane derivatives, such as $PhMe_2SiI$, Ph_2MeSiI, and $BnMe_2SiI$ groups were found to be applicable to the reaction, unlike the first-generation catalyst, $(cod)Pd(CH_2TMS)_2$/JessePhos.

In 2018, Shimada, Nakajima, and coworkers reported the Ni-catalyzed silyl-Mizoroki–Heck type reaction using Me_2SiCl_2 in the presence of a Lewis acid (Scheme 6).[29] Me_2SiCl_2 is one of the more readily available feedstock materials in the silicone industry. It was found that the addition of a sub-stoichiometric amount (50 mol%) of Lewis acid was crucial for the activation of a strong Si-Cl bond, the bond dissociation energy of which is much higher than that for Si-Br or Si-I bonds ($Me_3Si—Cl$ 113 kcal/mol > $Me_3Si—Br$ 96 kcal/mol > $Me_3Si—I$ 77 kcal/mol).[7] Among the various Lewis acids examined, Me_3Al gave the best result. The reaction of $MeSiCl_3$ proceeded at a lower reaction temperature (60 °C) to give **6** as the major product. It was found that less reactive monochlorosilanes, such as Me_3SiCl, $PhMe_2SiCl$, and $Ph_2MeSiCl$ also participate in the reaction, but higher reaction temperatures (120 °C) and the use of $^iPr_2NEt$ as a base and 2.2 equiv. of monochlorosilanes are required. The proposed mechanism is essentially the same as that proposed in the Pd-catalyzed reaction. The role of Me_3Al is proposed to activate a Si—Cl bond by coordination to afford the Si—Ni(II) cationic species **7**. The migratory insertion of styrene into a Si-Ni bond in **7** followed by β-hydride elimination gives the desired product along with an H—Ni(II) cationic species which reacts with the amine to regenerate the Ni(0) species.

In 2019, Watson and coworkers reported the first example of an intramolecular silyl-Mizoroki–Heck type reaction, leading to the preparation of five- or six-membered unsaturated silacycles (Scheme 7).[30] The course of the reaction was highly dependent in the tether length. The reaction of (4-pentenyl)chlorosilane **8** exclusively resulted in 6-endo cyclization to give a 1:1 mixture of the six-membered silacycles **9** and **10**, and the 5-exo-cyclization product **11** was not formed. The oxidative addition of a Si—Cl bond in **8** or an in-situ generated Si—I to the Pd(0) complex gives **12**, which undergoes 6-endo cyclization to give **13**. Subsequent non-regioselective β-hydride elimination gives **9** and **10**. The reaction of (3-butenyl)chlorosilane **14** also resulted in endo-cyclization to give a 1:1 mixture of **15** and **16** in a total yield of 80% and the 4-exo cyclization product **17** was not formed. On the other hand, 6-exo cyclization selectively took place to give only



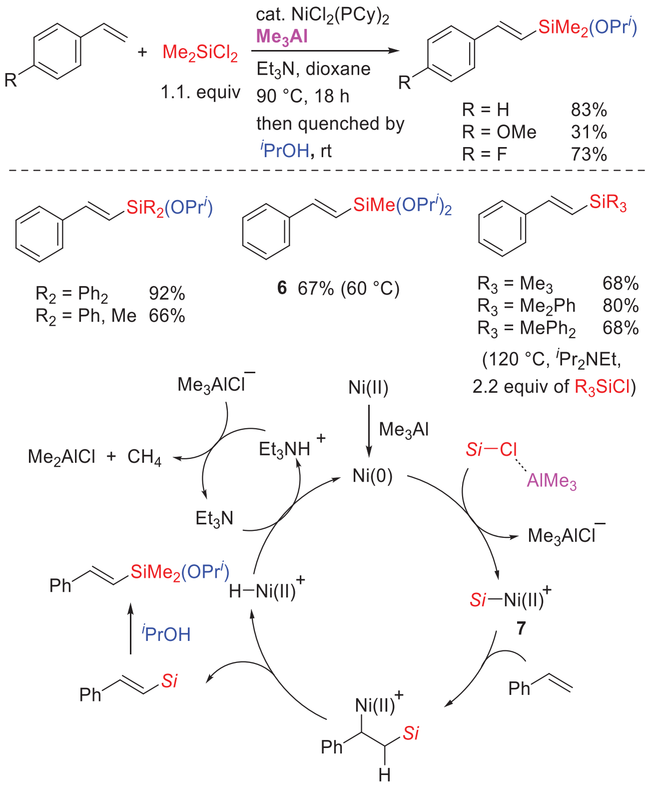
Scheme 4. a) Pd-catalyzed reaction of styrenes with $Me_2Si(OTf)_2$ in the presence of a catalytic amount of NaI. b) Ni-catalyzed reaction of styrenes with $Me_3Si(OTf)$ in the absence of iodide source (right).



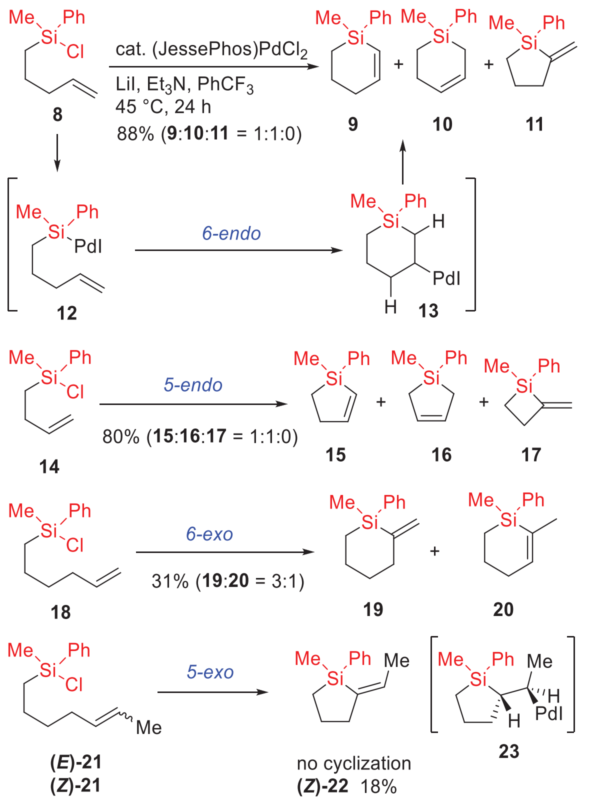
Scheme 5. Pd-catalyzed reaction of terminal aliphatic alkenes with Me_3SiI.

6-membered silacycles **19** and **20** when (5-hexenyl)chlorosilane **18** was used as a substrate. It was found that a substitution of olefinic carbon also affects the course of the reaction. Although no cyclization was observed in the reaction of ((E)-5-methyl-4-pentenyl)chlorosilane ***(E)*-21** even at 100 °C, 5-exo cyclization selectively took place to give **(Z)-22** when ((Z)-5-methyl-4-pentenyl)chlorosilane ***(Z)*-21** was used as the substrate. The reaction is proposed to proceed through oxidative addition, 5-exo-cyclization, C—C bond rotation, and subsequent syn-periplanar β-hydride elimination via intermediate **23**.

In 2022, Zhang and coworkers reported the Ni-catalyzed reaction of styrenes with chlorodimethylvinylsilane (**24**) in the presence of 3 equiv. of propyl bromide and 2 equiv. of Mn (Scheme 8).[31] The use of 6,6′-dimethyl-2,2′-bipyridine as a ligand gave silylation products in good yields. Neither the bipyridine nor 4,4′-dimethyl-2,2′-bipyridine as ligands gave the desired product, suggesting that steric hindrance of a ligand is vital for stabilizing the transient reactive species. The reaction was applicable to styrene derivatives but also to vinylheterocycles, such as thiophene, indole, and carbazole. Although the reason was not discussed, the presence of a vinylsilane moiety is necessary for the reaction to proceed. The addition of TEMPO (2,2,6,6-tetramethylpiperidine 1-oxyl) completely quenched the



Scheme 6. Ni-catalyzed reaction of styrenes with chlorosilanes in the presence of Me_3Al.



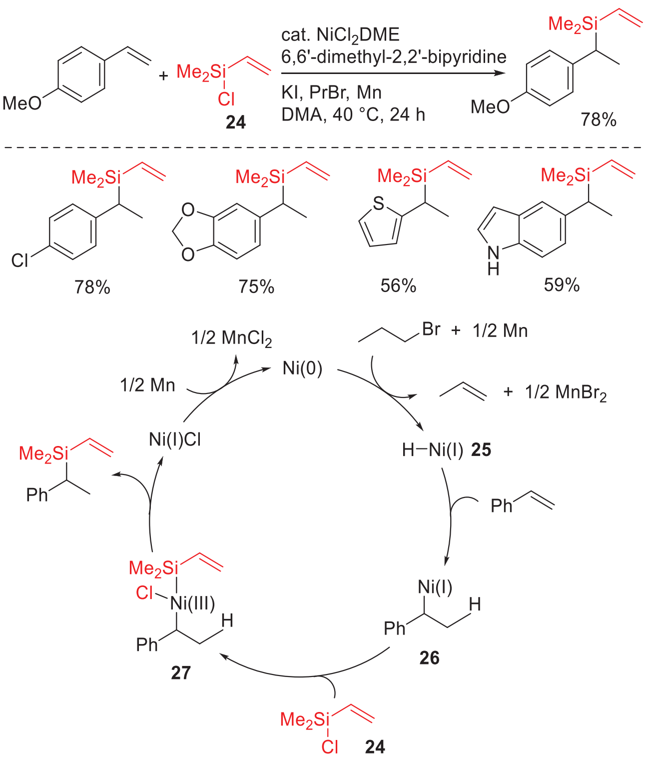
Scheme 7. Pd-catalyzed intramolecular reaction of alkenylsilyl chlorides.

reaction, but BHT (dibutylhydroxytoluene) had only a minor effect on the efficiency of the reaction.

Unlike the reactions described above, Ni(0) is not proposed to be a key catalytic species, but H-Ni(I) species **25** is proposed to act as a key catalytic species. The oxidative addition of a propyl bromide to Ni(0) in the presence of Mn(0) followed by β-hydride elimination gives the H—Ni(I) species **25**, which reacts with styrene to give an alkyl-Ni(I) intermediate **26**. The complex **26** is sufficiently nucleophilic to allow for the oxidative addition of a Si—Cl bond in **24** (or in-situ generated Si—I bond) to occur, thus generating the Ni(III) intermediate **27**. Reductive elimination then affords the final product and a Ni(I)Cl species. A Ni(I)Cl species is converted into Ni(0) species via the reduction by Mn to complete the catalytic cycle.

3. Reaction with Alkynes

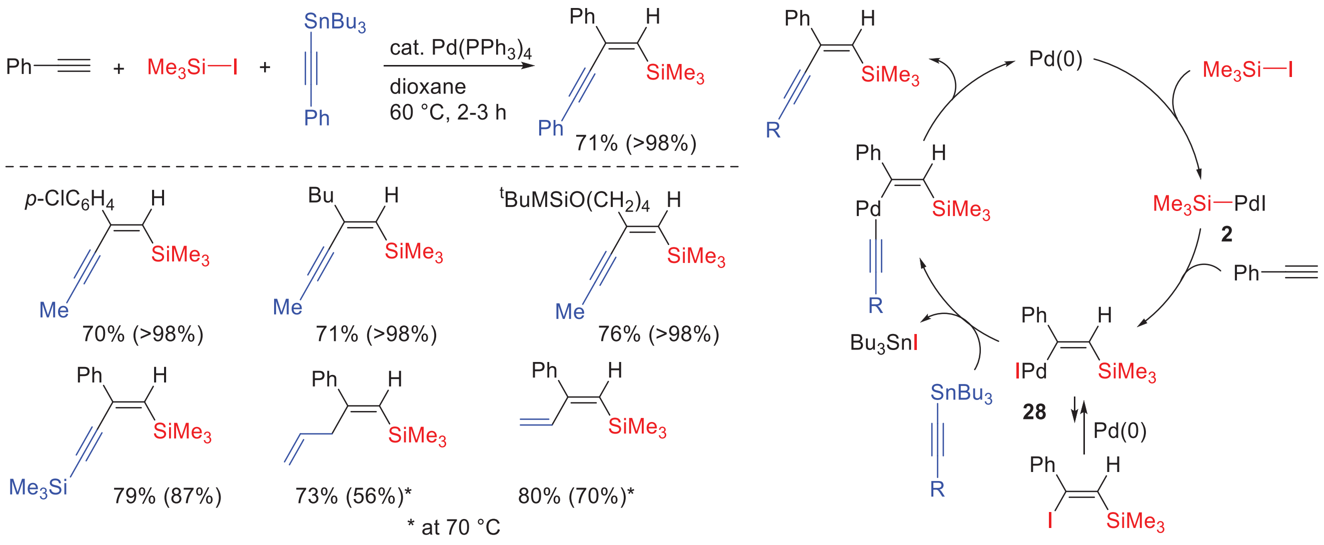
In 1984, we reported the Pd-catalyzed regio- and stereoselective silylcyanation of terminal alkynes with Me_3SiCN.[32,33] The reaction is proposed to proceed via the oxidative addition of Me_3SiCN to a Pd(0) complex, silylpalladation to an alkyne in a syn-manner, followed by reductive elimination. Inspired by this reaction, if the oxidative addition of Me_3SiI to a Pd(0) center were to occur, a similar type of transformation would be expected to take place. However, because the resulting C(sp^2)—I bond in **28** would be highly reactive under the Pd-catalyzed reaction conditions at high temperature, we designed a three-component coupling reaction between alkynes, Me_3SiI, and alkynylstannanes to trap the resulting reactive vinyl Pd complex **28** by alkynylstannanes (Scheme 9).[34] In the year 1991 when Tanaka and coworkers reported the silyl-Mizoroki-Heck reaction of styrenes (Scheme 2),[21] we also reported the Pd-catalyzed reaction of terminal alkynes with Me_3SiI and alkynylstannanes, leading to the production of silyl-substituted 1,3-enynes. The reaction exhibited high regio- and stereoselectivities. Thus, a trimethylsilyl group was added to the terminal carbon of an alkyne and a trimethylsilyl group and an alkynyl group were added to the alkyne in a syn-manner. The use of Me_3SiMe_2SiI in place of Me_3SiI also gave the expected product without the cleavage of a Si-Si bond.



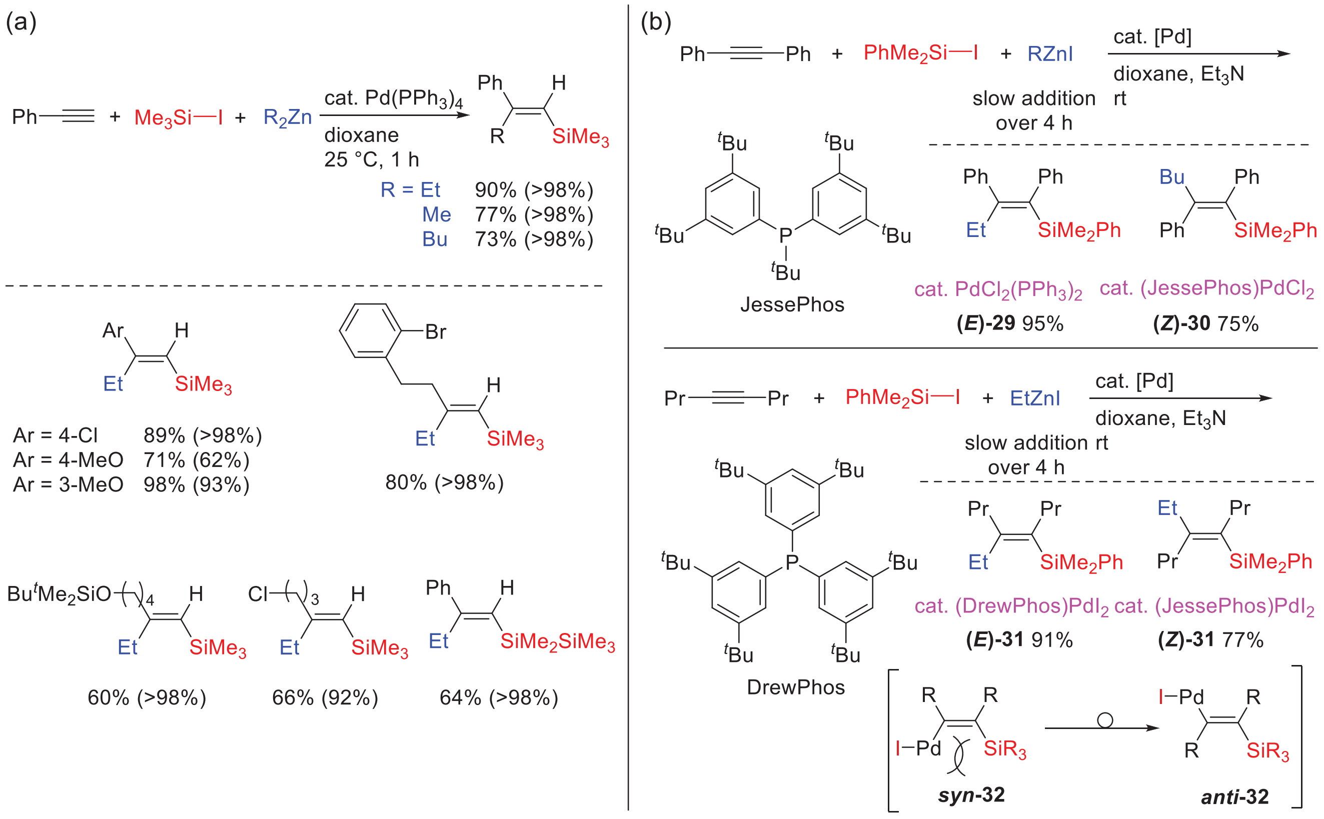
Scheme 8. Ni-catalyzed reaction of styrenes with chlorovinylsilanes.

The proposed mechanism involves the oxidative addition of Me_3SiI to Pd(0), forming the key intermediate, a silylpalladium iodide **2**, which undergoes migratory insertion of an alkyne followed by transmetalation with alkylnylstannanes and subsequent reductive elimination to give the final conjugated enynes. Silylpalladation of an alkyne with **2** would be the regio- and stere-determining step. While the reaction was also found to be applicable to allyl and vinylstannanes, the stereoselectivity was rather low. This may reflect the relative rate of transmetalation between vinyl Pd moiety in **28** and an oraganostannane.

The reaction could be extended to the three-component coupling reaction using organozinc reagents in place of alkynylstannanes as a nucleophile (Scheme 10a).[35] Both aromatic and aliphatic terminal alkynes participated in the three-component coupling reaction. While it is known that a methoxy group reacts with Me_3SiI to undergo demethylation, a methoxy group was intact under the reaction conditions. Various organozinc reagents including Me_2Zn, Et_2Zn, Bu_2Zn, $(Me_3SiCH_2)_2Zn$, BuZnI, and Bu_3ZnLi gave the corresponding coupling products. Like



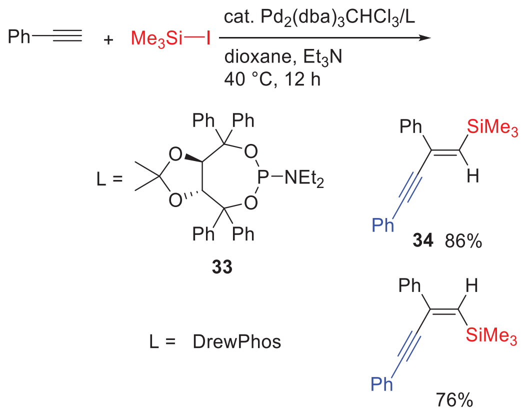
Scheme 9. Pd-catalyzed three-component coupling reaction of terminal alkynes, iodosilanes, and organostannanes.



Scheme 10. a) Pd-catalyzed three-component coupling reaction of terminal alkynes, iodosilanes, and organozinc reagents. b) Pd-catalyzed three-component coupling reaction of internal alkynes, iodosilanes, and alkylzinc iodides.

the above alkynylation, the trimethylsilyl group was added to the terminal carbon of the alkynes, and the trimethylsilyl group and the alkyl group were added to the alkyne in a syn-manner. Although other silyl electrophiles, such as Me_3SiBr, Me_3SiCl, Me_3SiOTf, Me_3SiSPh, and $Me_3SiSePh$ did not react, the reaction using Me_3SiMe_2SiI and $Me_3SiMe_2SiMe_2SiI$ gave the corresponding products.

In both cases shown in Scheme 9[34] and Scheme 10a,[35] only terminal alkynes were applicable for the reaction. In 2020, Watson and coworkers reported that internal alkynes also participate in the Pd-catalyzed three-component coupling reaction of alkynes, R_3SiI, and alkylzinc reagents to give tetra-substituted vinylsilanes (Scheme 10b).[36] It was found that the slow addition of Et_2Zn (over 4 h), and the use of $PhMe_2SiI$ and Et_3N (3 equiv.)



Scheme 11. Pd-catalyzed reaction of terminal alkynes with Me_3SiI.

were key factors for an efficient reaction to proceed with a high syn-selectivity in the presence of $PdCl_2(PPh_3)_2$ catalyst. It was also found that the use of EtZnI results in an equally efficient reaction to give **(*E*)-29** in 95% yield. However, these conditions were not suitable for the reaction of internal aliphatic alkynes and poor syn/anti ratios were obtained. After reoptimizing the reaction conditions, the use of (DrewPhos)PdI_2 in place of $(PPh_3)_2PdCl_2$ as a catalyst gave the desired coupling product **(*E*)-31** with excellent syn-selectivity (>95:5). Curiously, the use of (JessePhos)PdI_2 as the catalyst led to excellent anti-selectivity, as in **(*Z*)-31**. Thus, E/Z selectivity was significantly affected by the nature of ligands being used in the reaction. This interesting information was applicable to the reaction of diphenylacetylene with BuZnI, in which an anti-selective reaction was achieved to give **(*Z*)-30**. The authors proposed that a bulky ligand, JessePhos sterically destabilized the syn-β-silylvinyl-Pd intermediate **syn-32** to undergo double bond isomerization to give **anti-32**, which is trapped by the alkylzinc reagent to give the anti-product. The products were found to applicable for use in Hiyama–Denmark cross-coupling reactions.

In 2022, Cao, Xu, and coworkers reported the Pd-catalyzed reaction of terminal alkynes with Me_3SiI to give silyl-substituted 1,3-enynes without the use of alkynylstannanes (Scheme 11).[37] Thus, two molecules of an alkyne were incorporated into the product. The stereoselectivity was highly dependent on the choice of ligands. Thus, the use of the TADDOL-derived phosphoramidite **33** as a ligand gave anti-addition products **34** with a high stereoselectivity and the use of DrewPhos gave syn-addition products.

4. Reaction with Dienes

Kambe and coworkers reported the Ni-catalyzed reaction of 1,3-dienes with chlorosilanes and Grignard reagents, which results in the dimerization of 1,3-butadiene and regioselective carbosilylation.[38] While the reaction mechanism is not clear, the proposed mechanism involves the reaction of π-allyl Ni anionic intermediate with chlorosilanes as a key step. It therefore appears that the oxidative addition of chlorosilane or the related reaction is not involved.

Shu and coworkers reported the Ni-catalyzed reductive [4+1] cycloaddition of 1,3-dienes with dichlorosilanes, leading to the production of silacyclo-3-pentenes (Scheme 12).[39] While no reaction was observed when hexane was used as a solvent, the addition of DMI (1,3-dimethyl-2-imidazolidinone) in hexane (1:10) significantly improved the product yield. The use of Zn in place of Mn as a reducing reagent gave only a trace amount of the desired product with most of the diene being recovered. Although simple phosphine ligands or dipyridine ligands were ineffective in this reaction, the use of a phosphine–oxazoline ligand, such as **35** gave the desired products in good yields. The reaction of 1,4-disubstuited 1,3-diene and simple 1,3-butadiene did not give desired products. The reaction was also applied to the synthesis of spirosilole derivatives, which have potential applications in material sciences, when dichlorodibenzosilole **36** were used in place of dichlorodiphenylsilane. The reaction exhibited good functional group compatibility. While the enantioselective reaction was also achieved, further optimization will be required (up to 86%ee).

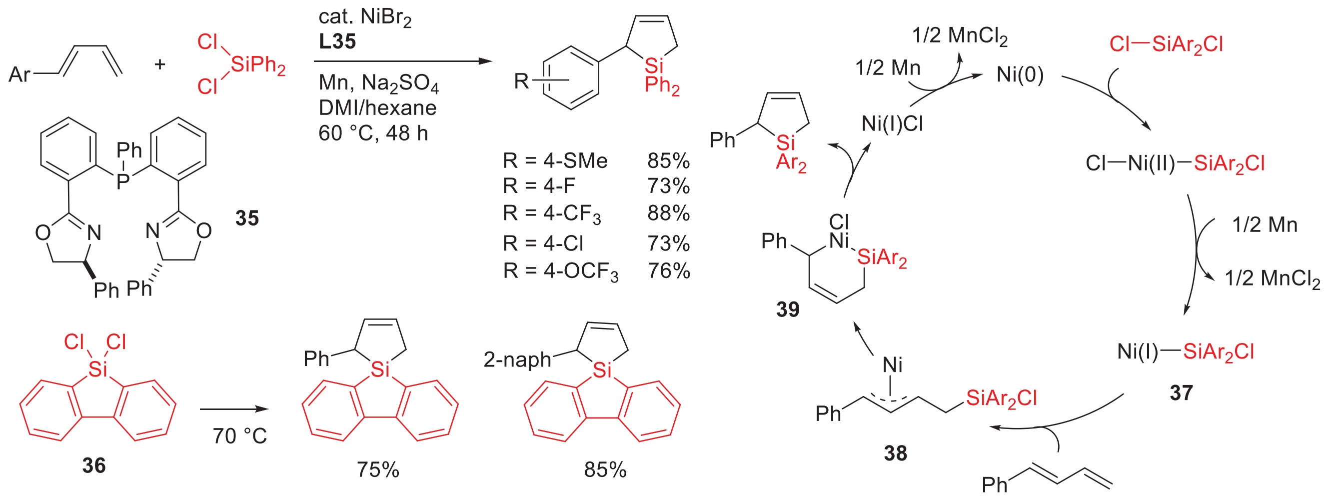
The results of some controlled experiments suggest that Ni(0) reacts with dichlorosilane first. Based on these results, the following mechanism is proposed. The oxidative addition of a Si—Cl bond in Ar_2SiCl_2 to Ni(0) followed by one-electron reduction by Mn gives the Si—Ni(I)Cl species **37**. The migratory insertion of the 1,3-diene into the Si—Ni bond in **37** gives the π-allylnickel intermediate **38**. Intramolecular oxidative addition of a Si—Cl to give a six-membered sila-nickelacycle **39** which is followed by reductive elimination to give silacyclopentene with the generating of the Ni(I) species, which is reduced by Mn to regenerate Ni(0) species. Although the authors did not discuss in the manuscript, the intermediacy of silylene Ni species cannot be completely excluded.

The reactions shown in Scheme 12 were limited to the [4+1] cycloaddition of 1,3-dienes with dichlorosilanes.[39] In 2025, Tang, Zhou, and coworkers successfully extended this transformation to the [4+1] cycloaddition of 1,3-dienes with di, tri, and tetrachlorosilanes by using a Ni complex ligated by pyridine-diimine (PDI) **40** as the catalyst (Scheme 13).[40] The reaction proceeded even at rt with a wide range of 1,3-dienes. The reaction of 2 equiv. of 1,3-dienes with readily available and inexpensive $SiCl_4$ resulted in the direct double [4+1] cycloaddition to give the spirosilole derivative **41**. However, the reaction with $SiCl_4$ was limited to only 2,3-disubstituted 1,3-dienes.

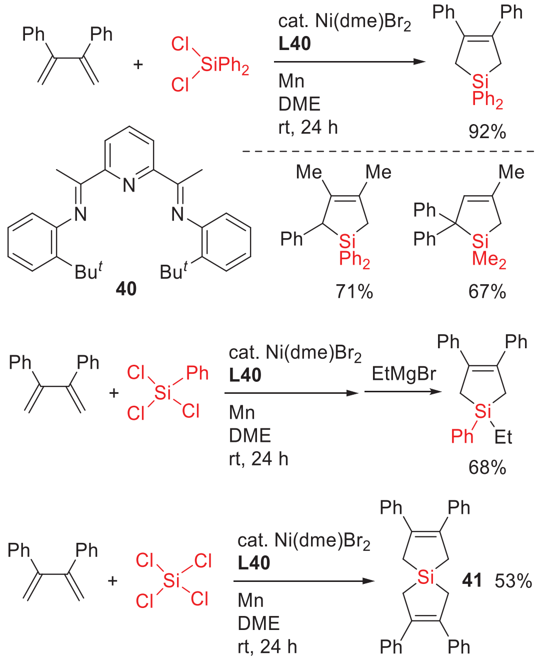
The reaction is proposed to proceed through essentially the same mechanism shown in Scheme 12. A (PDI)Ni complex with analogous structures to the catalytically active species was detected by ACPI-HRMS.

5. Cross-Coupling Reaction

The transition metal-catalyzed cross-coupling reaction of aryl or alkyl halides with organometallic nucleophiles represents one of the most reliable approaches for preparing carbon-carbon and carbon-heteroatom bonds because it allows the construction of complex molecules from simple precursors. In fact, there are many cross-coupling reactions, which are named after their



Scheme 12. Ni-catalyzed [4+1] cycloaddition of 1,3-dienes with dichlorosilanes.



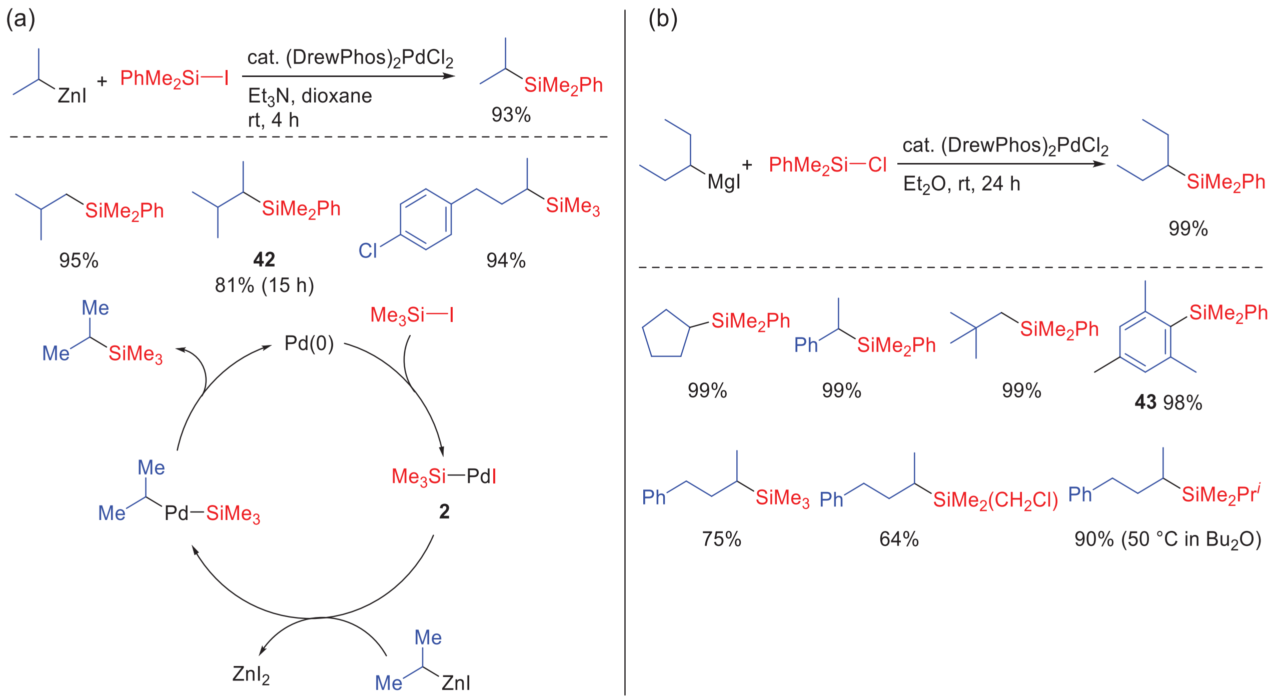
Scheme 13. Ni-catalyzed [4 + 1] cycloaddition of 1,3-dienes with di, tri, and tetrachlorosilanes.

discoverers, such as Tamao–Kumada–Corriu, Negishi, Suzuki–Miyaura, Kosugi–Migita–Stille, Murahashi, and Hiyama–Denmark cross-coupling reactions.[41]

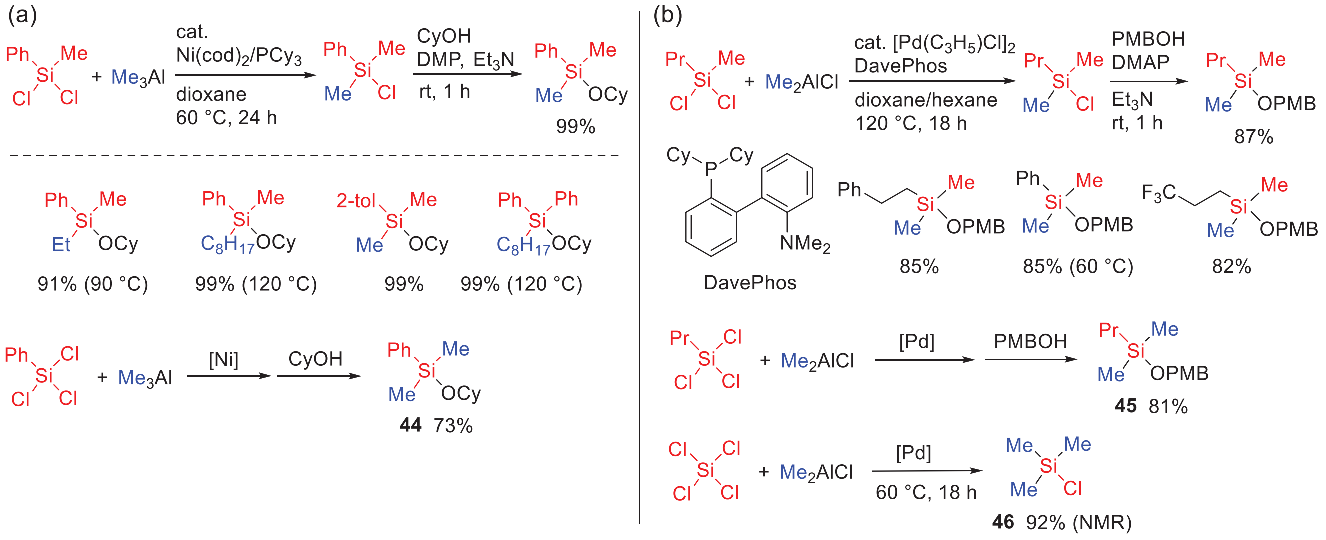
Although the metal-free nucleophilic substitution reaction of halosilanes with primary organometallic nucleophiles is a classical and widely used method for the preparation of primary-alkylsilanes, the reaction with sterically demanding primary-alkyl or secondary-alkyl organometallic nucleophiles are generally thought to be ineffective because of their low reactivity and/or the competitive rearrangement to primary-alkyl nucleophiles under the reaction conditions. Watson and coworkers reported the Pd-catalyzed silyl-Negishi type reaction of secondary-alkylzinc halides with iodosilanes, leading to the selective production of secondary-alkylsilanes (Scheme 14a).[42] No reaction took place in the absence of a Pd catalyst. The addition of Et_3N (1 equiv.) improved product yield and suppressed the production of rearranged primary-alkylsilanes. It was also found that the use of an electron-rich and sterically bulky phosphine, such as DrewPhos suppresses the production of primary-alkylsilanes. Other silyl electrophiles, such as Me_3SiBr, Me_3SiCl, and Me_3SiOTf failed to give desired products, even in the presence of 3 equiv. of NaI. The reaction of a sterically bulky zinc reagent, such as 1,2-dimethylpropylzinc iodide gave the expected product **42** in 81% yield without the formation of isomerized 3-methylbutylsilane.

The reaction is proposed to proceed through an oxidative addition/transmetalation/reductive elimination sequence to release the coupling product and turnover, which is similar to that of well-known C—C bond forming cross-coupling reactions.

As described above, Watson and coworkers found that only iodosilanes can serve as silyl electrophiles in the silyl-Negishi type cross-coupling reaction and that other silyl electrophiles are unreactive. In a subsequent study, Watson and coworkers reported that less reactive monochlorosilanes, which are more abundant than iodosilanes, can be used in this Pd-catalyzed cross-coupling reaction with sterically bulky primary- and secondary-alkyl Grignard reagents (Scheme 14b).[43] No background reaction took place in the case of the reaction of $PhMe_2SiCl$ with isopropyl Grignard bromide. Thus, a Pd catalyst was required for the reaction to proceed. A significant solvent effect was observed in the case of the reaction in THF which resulted in a 3:7 mixture of the desired isopropylsilane and isomerized propylsilane. The reaction in Et_2O exclusively, however, gave only the desired isopropylsilane. The halides of the Grignard reagents also affected the reactivity ($RMgI \geq RMgBr >> RMgCl$). To examine whether the halogen exchange between a chlorosilane and the halide of the Grignard reagent takes place with the generation of the more reactive bromosilane or iodosilane, the reaction was carried out under all chlorides conditions using $(DrewPhos)PdCl_2$, $PhMe_2SiCl$, and isopropyl MgCl. While an increased reaction temperature (rt to 50 °C) was needed, the desired product was obtained in 70%



Scheme 14. a) Pd-catalyzed reaction of iodosilanes with alkylzinc halides. b) Pd-catalyzed reaction of monochlorosilanes with alkyl Grignard reagents.



Scheme 15. a) Ni-catalyzed reaction of dichloro- and trichlorosilanes with trialkylaluminium reagents. b) Pd-catalyzed reaction of di-, tri-, and tetrachlorosilanes with Me_2AlCl.

yield, suggesting that bromide or iodide are not required for the reaction to proceed. A sterically demanding aryl Grignard reagent also reacted to give the corresponding product **43** in 98% yield. A variety of chlorosilanes participated in the reaction. The reaction was successfully carried out on a 100 mmol scale.

Although Watson's strategy shown above is attractive for the preparation of tetra-substituted organosilicon compounds, the reaction was not applicable to the synthesis of monochlorosilanes from dichlorosilanes. In 2019, Naganawa, Nakajima, and coworkers reported the Ni-catalyzed mono-alkylation of aryldichlorosilanes with trialkylaluminium reagents, leading to the production of mono-chlorosilanes (Scheme 15a).[44] The reaction of $PhMeSiCl_2$ with Me_3Al in the presence of $Ni(cod)_2/PCy_3$ at 60 °C followed by treatment with cyclohexanol (CyOH) gave $PhMe_2SiOCy$ in 99% yield and the di-methylation product $PhSiMe_3$ was not detected. Thus, the reaction could be selectively stopped at the mono-methylation stage. On the other hand, controlled experiments using $PhMeSiCl_2$ and MeLi (or MeMgBr) in the absence of Ni catalyst gave a non-selective mixture of $PhMe_2SiCl$ and $PhSiMe_3$. The reaction with Me_2AlCl resulted in no reaction. Some aluminum reagents, such as Et_3Al, $(C_8H_{17})_3Al$, and Ph_3Al

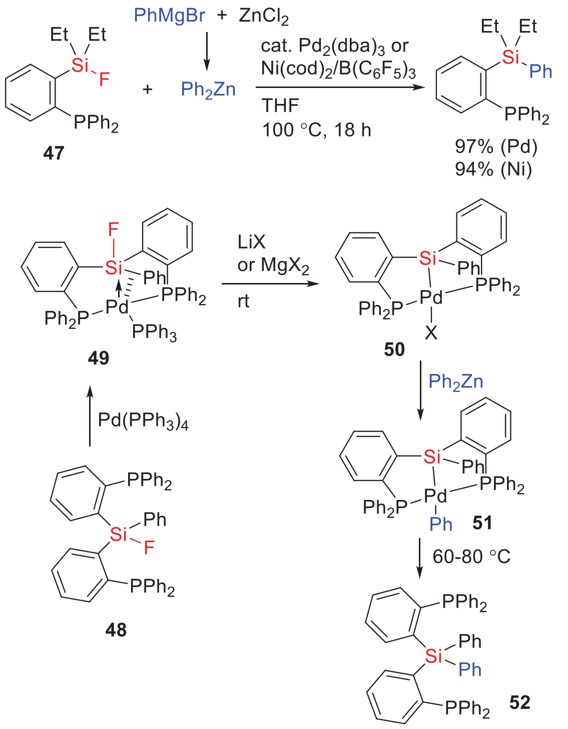
gave the corresponding products in good yields. The reaction was also applicable to the selective di-methylation of $PhSiCl_3$ to $PhMe_2SiCl$, which is converted into the alkoxysilane **44** by treatment with cyclohexanol.

The catalytic cycle is proposed to proceed through an oxidative addition/transmetalation/reductive elimination sequence. The oxidative addition of the unreactive Si—Cl bond could be assisted by Lewis acidic trialkylaluminium reagents, similar to the case shown in Scheme 6.[29]

The previous work shown in Scheme 15a had limitations. Thus, chlorosilanes required an aryl group on the silicon atom. In 2021, the same group successfully extended the protocol to the mono-methylation of dialkyldichlorosilanes with Me_2AlCl using Pd as a catalyst (Scheme 15b).[45] The reaction was also applicable to the di-methylation of alkyltrichlorosilanes, as in **45**. Remarkably, the selective tri-methylation of $SiCl_4$ was also achieved under lower reaction temperature to give **46**. In sharp contrast, the Ni-catalyzed reaction of $SiCl_4$ with Me_3Al under the reaction conditions shown in Scheme 15a gave $MeSiCl_3$ in 21% and Me_4Si in 7% yields without Me_2SiCl_2 or Me_3SiCl being formed. The lower Lewis acidity of the silicon center in the monochlorosilanes suppress the oxidative addition of a Si—Cl bond to a Pd center. This could be the reason why monochlorosilanes did not react further and were selectively obtained.

In 2022, Kameo and the above authors later carried out theoretical studies on the Pd-catalyzed cross-coupling reaction of chlorosilanes with Me_2AlCl, which focused on how Si—Cl bond activation proceeds.[46] It was found that the activation of a Si—Cl bond in Me_2SiCl_2 to $Pd(PCy_3)_2$ proceeds through a trans-oxidative addition or S_N2-type oxidative addition assisted by the Lewis acid (Me_2AlCl). On the other hand, the activation of a Si—Cl bond in $MeSiCl_3$ or $SiCl_4$ was found to prefer trans-oxidative addition due to their higher Lewis acidities, in which Pd→Si-Cl interaction enables the facile activation of a Si—Cl bond. It was also found that the Lewis acid (Me_2AlCl) has no acceleration effect in the transmetalation and reductive elimination steps. In the reaction of Me_2SiCl_2 with $Ni(PCy_3)_2$, trans-oxidative addition was found to be the favorable pathway.

A Si—F bond is the strongest single bond for any pair of atoms due to the strong affinity between silicon and fluorine atoms. Hence, the formation of a Si—F bond is a driving force in many organic reactions with organosilicon reagents. In 2020, Kameo, Bourissou, and coworkers reported the Pd- and Ni-catalyzed silyl-Negishi coupling of **47**, which was the first example of a cross-coupling reaction involving a Si—F bond activation (Scheme 16).[47] The presence of a Ph_2P moiety at the ortho-position in the fluorosilane **47** was found to be crucial for the reaction to proceed, suggesting that a PPh_3 moiety functions a directing group. Although the reaction with **47** with Ph_2Zn resulted in no reaction, the use of the in situ formed Ph_2Zn by the reaction of $ZnCl_2$ with PhMgBr dramatically increased the product yield, suggesting that the generated MgX_2 plays a key role. In addition, the use of both in situ generated Ph_2Zn and $B(C_6F_5)_3$ as an additive was also effective in the Ni-catalyzed reaction. These results suggest that the presence of a Lewis acid significantly accelerates the reaction.

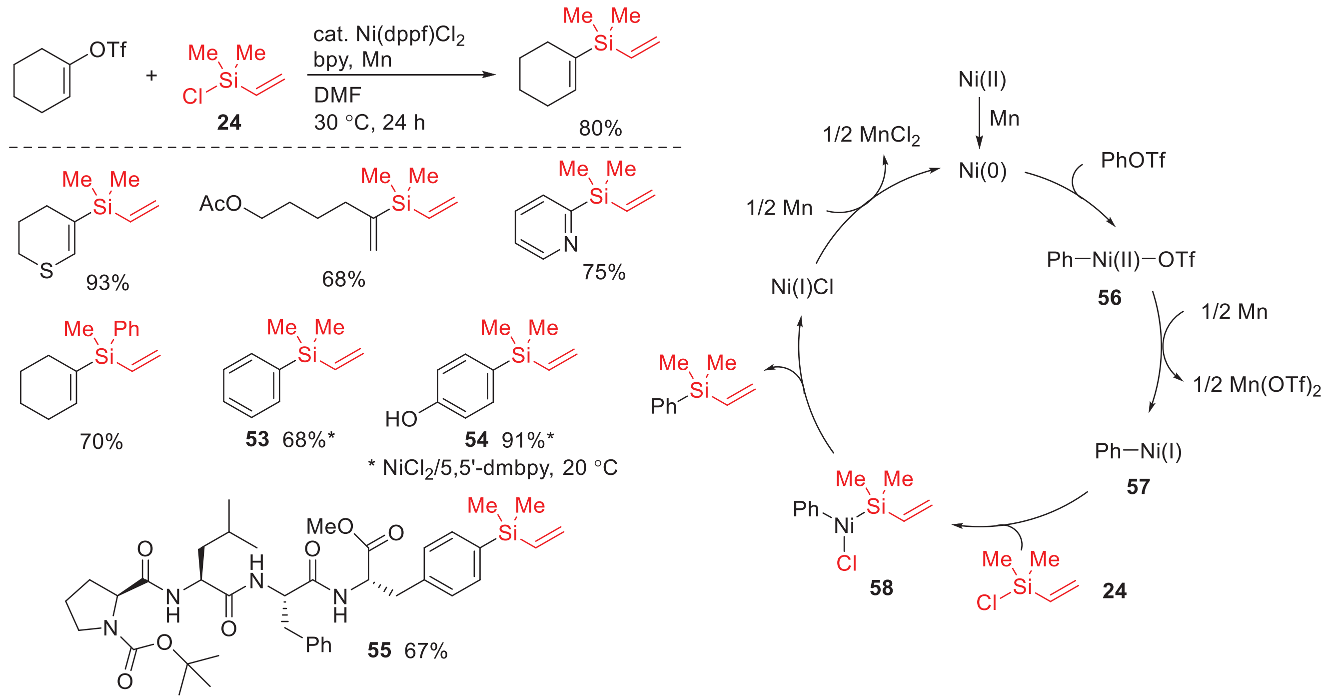


Scheme 16. Pd- or Ni-catalyzed silyl-Negishi coupling involving Si—F bond activation.

To gain additional information regarding the reaction mechanism, stoichiometric reactions using **48**, which consists of two coordinating PPh_2 moieties, were conducted. The reaction of **48** with $Pd(PPh_3)_4$ resulted in ligand exchange to give **49** in 91% yield. The presence of a Pd→Si-F interaction in **49** was supported by X-ray diffraction analysis, ^{29}Si NMR spectroscopy, and DFT calculations. The addition of LiX (X = Cl, Br, and I) or MgX_2 (X = Cl, Br) to **49** at room temperature gave square–planar Pd(II) complexes **50**. The reaction of **50** with Ph_2Zn resulted in transmetalation to give **51**, which was heated at 60–80 °C to give the final coupling product **52**. The structure of all key complexes was confirmed by spectral or X-ray diffraction analyses. These results of stoichiometric experiments and DFT calculations provided support that a Si—F bond is activated by Pd→Si-F→Lewis acid interactions. The proposed mechanism for the catalytic reaction of **47** with Ph_2Zn involves the coordination of a PPh_2 moiety in **47** to a Pd center, the cleavage of a Si—F bond promoted by Pd→Si-F→Lewis acid interactions, transmetalation by Ph_2Zn, and reductive elimination.

6. Cross-Electrophile Coupling Reaction

Cross-electrophile coupling in which two different electrophiles are coupled under reductive conditions have recently seen rapid development as a viable alternative to conventional cross-coupling reactions between nucleophiles and electrophiles.[48] This strategy avoids the need for the preparation of occasionally unstable nucleophiles. To avoid the formation of homo-electrophile coupling products, a significant difference in the

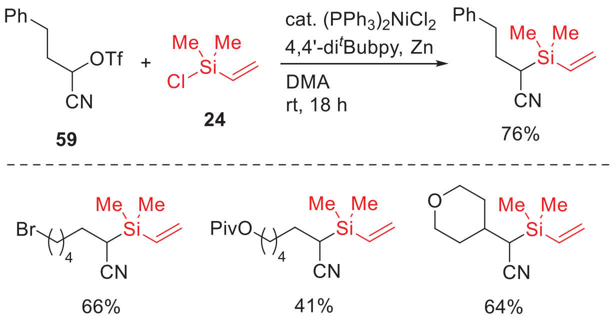


Scheme 17. Ni-catalyzed cross-electrophile coupling between chlorovinylsilanes and vinyl/aryl triflates.

reactivity of the two electrophiles or a different activation mode between the two electrophiles is required. In this regard, the cross-electrophile coupling between a C–halogen bond and Si–halogen bond could ideally be successful, because the mechanism of the activation of Si-halogen bonds and C–halogen bonds would be totally different.

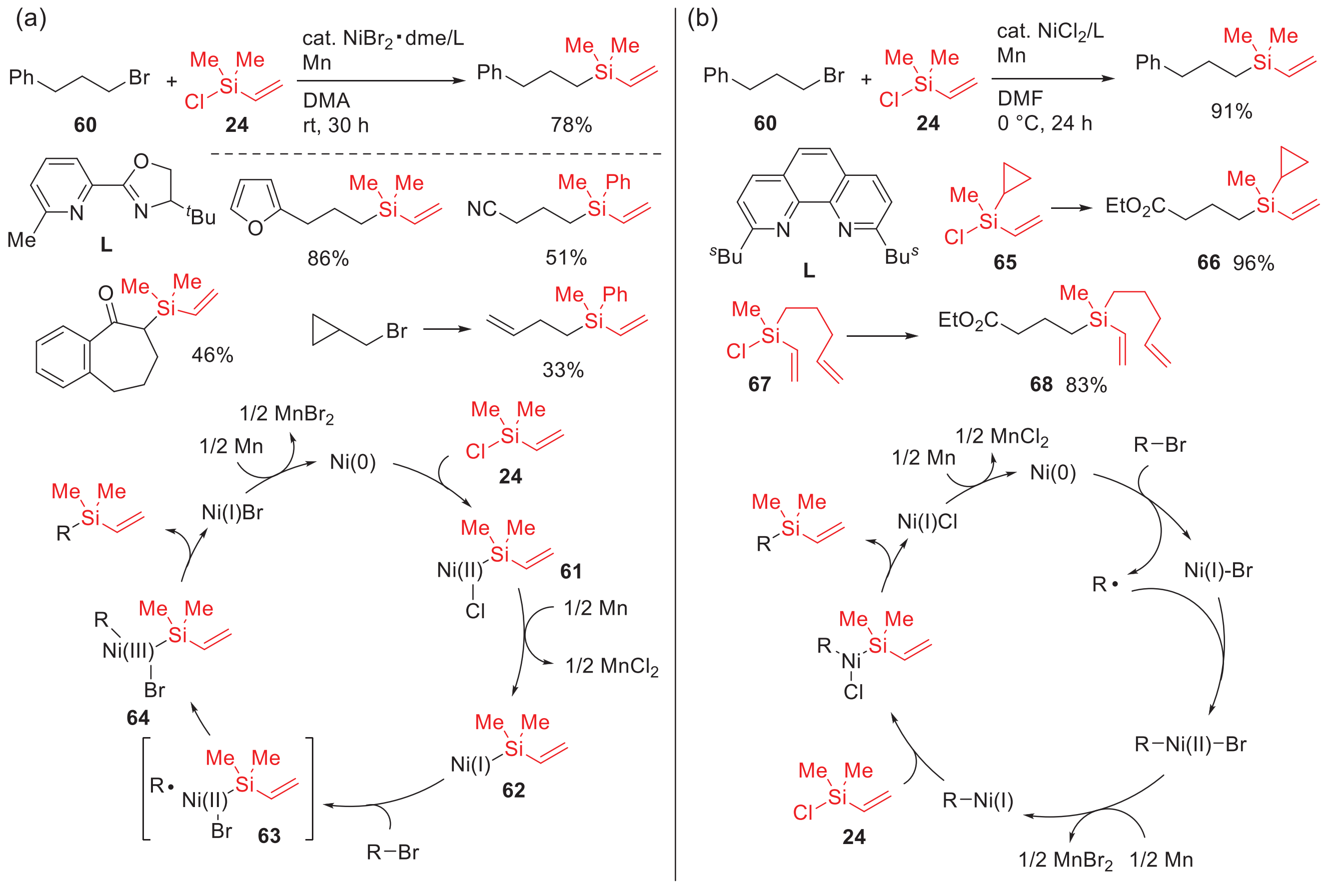
In 2020, Shu and coworkers reported the reductive cross-electrophile coupling between chlorovinylsilanes and aryl or vinyl triflates in the presence of Ni(dppf)Cl_2/bipyridine as a catalyst and a stoichiometric amount of Mn as a reducing reagent (Scheme 17).[49] Curiously, simple chlorosilanes, such as Me_3SiCl, $^tBuMe_2SiCl$, $Me_2PhSiCl$, $MePh_2SiCl$, and $(EtO)_3SiCl$ and even Me_3SiI were ineffective, with no C-Si coupling products being formed. The reaction of chlorovinylsilanes with vinyl triflates proceeded under mild reaction conditions (30 °C) and showed a wide scope for vinyl triflates and chlorovinylsilanes. The functional group compatibility was also found to be high. In the reaction of aryl triflates, the combination of $NiCl_2$ and 5,5′-dmbpy was an effective catalyst precursor even at 20 °C, as in **53** and **54**. In addition, the reaction was applicable to the late-stage transformation of pharmaceuticals and natural products, as shown in a tetra-peptide derivative **55**. In addition, aryl(vinyl)silanes were shown, for the first time, to be used in Hiyama–Denmark cross-coupling reagents.

Based on some mechanistic studies and literature reports, the oxidative addition of PhOTf to the in situ generated Ni(0) complex leading to the generation of a Ph-Ni(II) species **56** is proposed to initiate the catalytic cycle. The one electron reduction of **56** by Mn gives a Ph–Ni(I) species **57**. The oxidative addition of a Si—Cl bond in the chlorovinylsilane **24** to **57** gives the Ni(III) species **58**. Subsequent reductive elimination from **58** gives the final product and a Ni(I) species, which eventually undergoes reduction by the Mn reductant to complete the catalytic cycle. Thus, the reaction is proposed to proceed via Ni(0)→Ni(II)→Ni(I)→Ni(III)→Ni(I)→Ni(0) catalytic cycle. The reaction was limited to vinyl-substituted chlorosilanes. The role of the vinyl group is currently unclear, but it is proposed that the coordination of the vinyl group in chlorovinylsilane **24** to **57** brings the Ni(I) center into close proximity to the Si—Cl bond, which facilitates the oxidation addition of a Si—Cl bond in **24** to generate **58**.



Scheme 18. Ni-catalyzed cross-electrophile coupling between chlorovinylsilanes and α-cyanoalkyl triflates.

In 2021, Oestreich and coworkers reported a Ni-catalyzed cross-electrophile coupling reaction between chlorovinylsilane **24** and α-cyanoalkyl triflates in the presence of 3 equiv. of Zn as a reducing reagent (Scheme 18).[50] The use of Mn in place of Zn resulted in a dramatic decrease in product yield. Simple chlorosilanes, such as Me_3SiCl and $EtMe_2SiCl$ also reacted with **59** to give the corresponding products, albeit in slightly lower yields (40% and 33% yields, respectively). The reaction of **59** with **24** in the presence of TEMPO (2.5 equiv.) did not affect the reaction (75% product yield). While a radical-probe



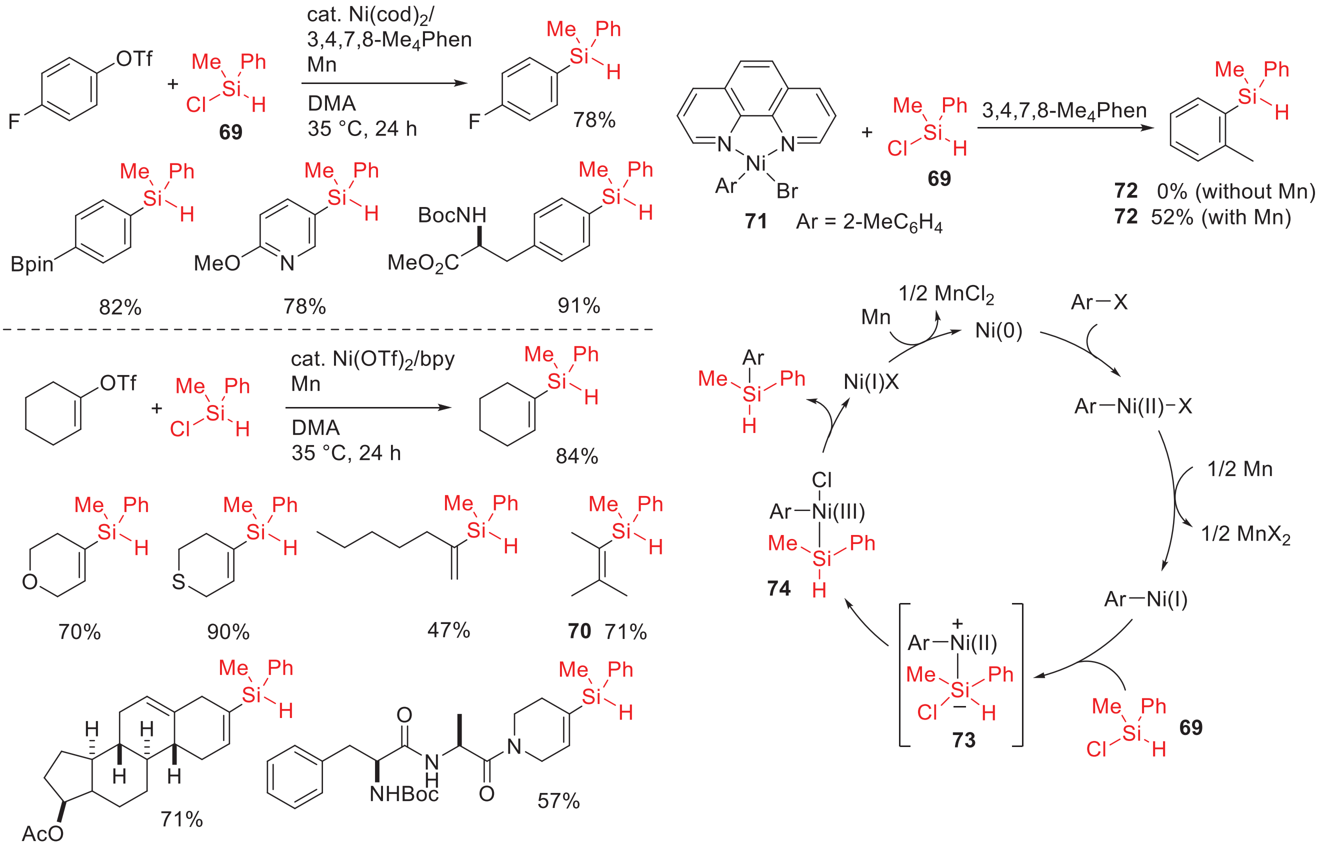
Scheme 19. a) Ni-catalyzed cross-electrophile coupling between chlorovinylsilanes and alkyl bromides. b) Ni-catalyzed cross-electrophile coupling between chlorovinylsilanes and alkyl bromides.

experiment by the reaction of α-(cyano)cycopropylmethyl triflate with **24** gave the expected product in a low yield, no ring-opened product was obtained. Based on these results, the authors concluded that a radical species is likely not involved in the reaction. Nevertheless, the reaction of a chiral substrate (*R*)-**59** (99% ee) led to complete racemization. This is probably due to non-stereospecific reductive elimination. The proposed mechanism is essentially the same as that shown in Scheme 17. Thus, the catalytic cycle involves the oxidative addition of α-cyanoalkyl triflates to Ni(0), one-electron reduction by Zn, the oxidative addition of a Si—Cl bond in **24**, and reductive elimination. However, the authors concluded that the oxidative addition of a chlorosilane to Ni(0) prior to that of a triflate cannot be ruled out.

Chlorovinylsilanes were also found to undergo cross-electrophile coupling with simple alky bromides in the presence of Mn as a reducing reagent and a Ni catalyst, which was reported by Zhang and coworkers in 2021 (Scheme 19a).[51] No reaction took place in the absence of Mn. Various alkyl bromides including primary and secondary alkyl bromides reacted. The reaction showed a good functional group tolerance. The reaction of **60** with **24** under the standard reaction conditions in the presence of TEMPO (2.5 equiv.) completely inhibited the reaction. The reaction of cyclopropylmethyl bromide in place of **60** selectively gave the ring-opening product in 33%. These results clearly indicate that a radical intermediate is involved in the reaction.

Curiously, unlike the reactions shown in Schemes 17 and 18, the reaction is proposed to be initiated by the oxidative addition of a Si—Cl bond in **24** to a Ni(0) center, leading to the generation of a silyl-Ni(II) species **61**. The one-electron reduction of **61** by Mn gives an alkyl-Ni(I) species **62**, which then results in the oxidative addition of an alkyl bromide to afford the Ni(III) species **64** via a carbon-radical process, as shown in **63**. The following reductive elimination gives the final product and Ni(I) being generated. The Ni(I) species is reduced by Mn to regenerate Ni(0) to complete the catalytic cycle.

At almost the same time, Shu and coworkers reported essentially the same transformation as the reaction shown in Scheme 19a (Scheme 19b).[52] It was found that the reaction of **60** with **24** proceeded even at 0 °C and the reaction showed a high functional group compatibility. The product, a vinylsilane was immobilized onto a silica surface by the Ir(I)-catalyzed coupling reaction of vinylsilanes with the surface hydroxyl groups. A radical clock experiment using cyclopropylmethyl bromide gave only the ring-opening product, the same as the result obtained in Scheme 19a. However, the use of chloro(cyclopropyl)vinylsilane **65** did not result in the production of a ring-opening product, but the unrearranged product **66** was obtained in 96% yield. In addition, the reaction of chlorovinyl-



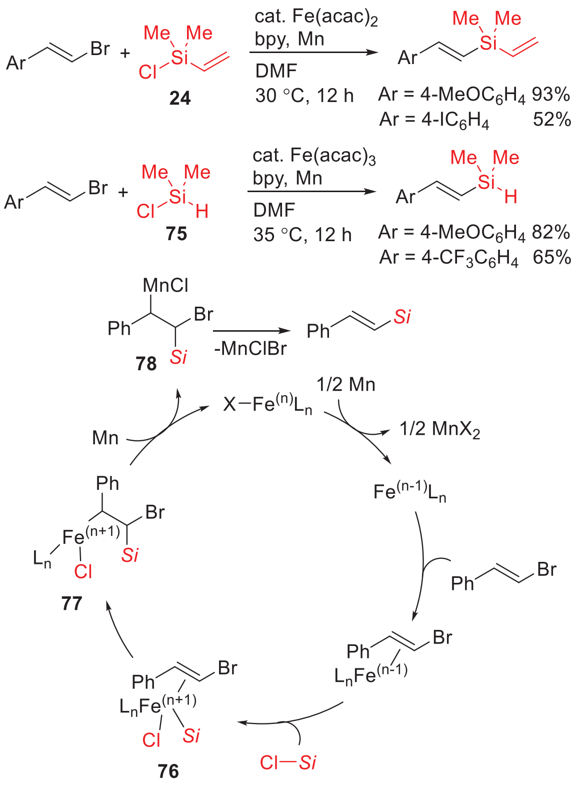
Scheme 20. Ni-catalyzed cross-electrophile coupling between chlorohydrosilanes and aryl/vinyl triflates.

silane **67** with ethyl 3-bromopropionate gave **68** without the formation of any ring-closing product. These results indicate that the activation of a Si-Cl bond in chlorovinylsilanes does not proceed via a radical process, but, rather, a radical process appears to be involved during the cleavage of a C(sp^3)—Br bond in an alkyl bromide.

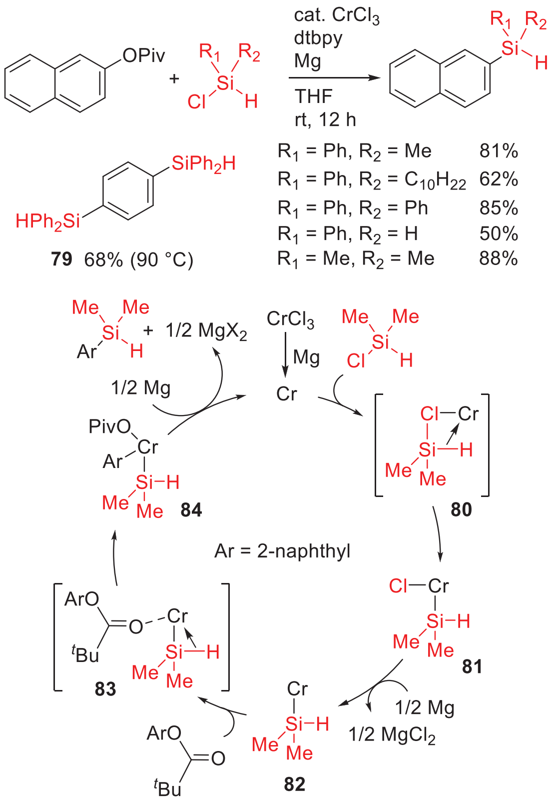
Based on the results obtained by these mechanistic experiments, a different reaction mechanism from that shown in Scheme 19a is proposed for the present reaction. Thus, the reaction starts with the oxidative addition of a C–Br in an alkyl bromide via a radical process to generate an alkyl Ni(II) species, which is then reduced by Mn to give an alkyl Ni(I) species. The oxidative addition of **24** followed by the reductive elimination provides the final product, along with Ni(I).

Chlorovinylsilanes, such as **24** were found to be suitable as an electrophilic counter partner in cross-electrophile coupling, as shown above, although the reason for this is not clear. In 2022, Shu and coworkers reported that chlorohydrosilane **69** also act as silyl electrophiles in cross-electrophile coupling reactions with aryl triflates, alkenyl triflates, and aryl bromides (Scheme 20).[53] Remarkably, a reactive Si–H moiety remains intact, even in the presence of a Ni catalyst. Thus, the presence of a Si-H bond appears to play a crucial role for the reaction to proceed, although its exact role was not discussed. Not only cyclic alkenyl triflates but acyclic alkenyl triflates also gave the corresponding coupling products in good yields. Silylation took place even in the reaction of trimethyl-substituted vinyl triflate to give tetra-substituted vinylsilane, as in **70**. A hydrosilyl moiety could be introduced into biologically active compounds, such as testosterone and dipeptide compounds. Aryl bromides in place of aryl triflates also participated in the reaction. A hydrosilyl moiety of the products was demonstrated to be useful for further transformations, such as hydrosilylation, hydration, dimerization, and cross-coupling reactions. While the authors showed one example of the enantioselective reaction using a chiral ligand, the enantiomeric excess was only 50%. To gain insights into the reaction mechanism, the authors prepared the 2-MeC_6H_4-Ni(II)—Br complex **71**, which is similar to the proposed key intermediate. A stoichiometric reaction of **71** with 3 equiv. of **69** in the presence of Mn (1 equiv.) gave the desired silylation product **72** in 52% yield. In sharp contrast, **72** was not produced in the absence of Mn. These results suggest that a Ni(I) species is generated from the Ni(II) complex **71** by the one-electron reduction with Mn under the reaction conditions and serves as a key catalytic species. In addition, following the time dependent product formation in the reaction of 2-isopropylphenyl triflate with HBuPhSiCl in the presence of **71** as the catalyst, it was found that the aryl group on the Ni catalyst **71** was first silylated to give the corresponding coupling product, and the substrate triflate then reacted, indicating that the Ar-Ni(II)—X species **71** is a key intermediate.

Based on these results, the reaction is proposed to be initiated by the oxidative addition of Ar–X to Ni(0) to give Ar-Ni(II)—X, followed by a one-electron reduction by Mn to give a



Scheme 21. Fe-catalyzed cross-electrophile coupling between chlorovinylsilanes/chlorohydrosilanes and (E)-β-bromostyrenes.



Scheme 22. Cr-catalyzed cross-electrophile coupling between chlorohydrosilanes and aryl pivalates.

more nucleophilic Ar–Ni(I) species. The oxidative addition via S$_N$2 type reaction of **69** gives the Ni(III) species **74** through a five-coordinated Ni intermediate **73**. The reductive elimination from **74** gives a final cross-coupling product. The oxidative addition of a Si—H bond to transition metal complexes is a well-known process that occurs in a variety of catalytic reactions, such as hydrosilylation because the bond dissociation energy of a Si—H (90 kcal/mol for Me$_3$Si—H) is much lower than a Si—Cl (113 kcal/mol for Me$_3$Si—Cl).[7] However, a Si—H bond remains intact in the present catalytic reaction. Consequently, the authors propose that the oxidative addition of a Si—Cl bond in **69** occurs through an S$_N$2 type reaction because the Si—Cl bond is much more polarized than the Si—H bond.

In addition to Ni, other metal catalysts have also been reported to catalyze cross-electrophile coupling reactions using chlorovinylsilanes and chlorohydrosilanes. In 2023, Ye, Xie, Ye, and coworkers reported that cross-electrophile coupling between chlorovinylsilane **24** and (E)-β-bromostyrenes proceeds in the presence of Fe(acac)$_2$ as the catalyst (Scheme 21).[54] The use of Ni(cod)$_2$ and Ni(dppf)Cl$_2$ also gave the desired products, but these catalysts were less active than Fe(acac)$_2$. It was found that β-alkyl-substituted alkenyl bromides and vinyl triflates do not participate in the reaction to produce silylated products. The reaction shows excellent functional group compatibility. Even iodide on the aromatic ring remained intact under the reaction conditions. Curiously, the reaction was also applicable to chlorohydrosilanes, such as HPhMeSiCl **69** and HMe$_2$SiCl **75** in place of chlorovinylsilanes as silyl electrophiles when Fe(acac)$_3$ was used as a catalyst. When the reaction of (E)-β-bromostyrene was carried out in the absence of chlorovinylsilane **24**, (E)-β-bromostyrene was recovered even in the presence of a stoichiometric amount of Fe(acac)$_2$ and Mn, suggesting that the oxidative addition of a C(sp^2)—Br bond to a low valent Fe complex is less likely. In addition, it was found that the addition of TEMPO and activated alkenes, such as 1,1-diphenylethlene and ethyl acrylate had no negative effect on the reaction.

Based on the mechanistic studies, a reaction mechanism different from that for the Ni-catalyzed reaction is proposed for the Fe-catalyzed reaction. In this proposal, the reaction does not begin with the oxidative addition of β-bromostyrene with a low valent Fe complex, which is clear from the experimental results presented above. Instead, the coordination of bromostyrene to a low valent Fe species followed by the oxidative addition of chlorosilanes gives the Fe intermediate **76**. Silylmetalation then proceeds via a syn-manner to give an alkyl-Fe species **77**, which undergoes the further reduction by Mn to afford the carbanion **78**. The elimination of MnClBr from **78** gives the final product.

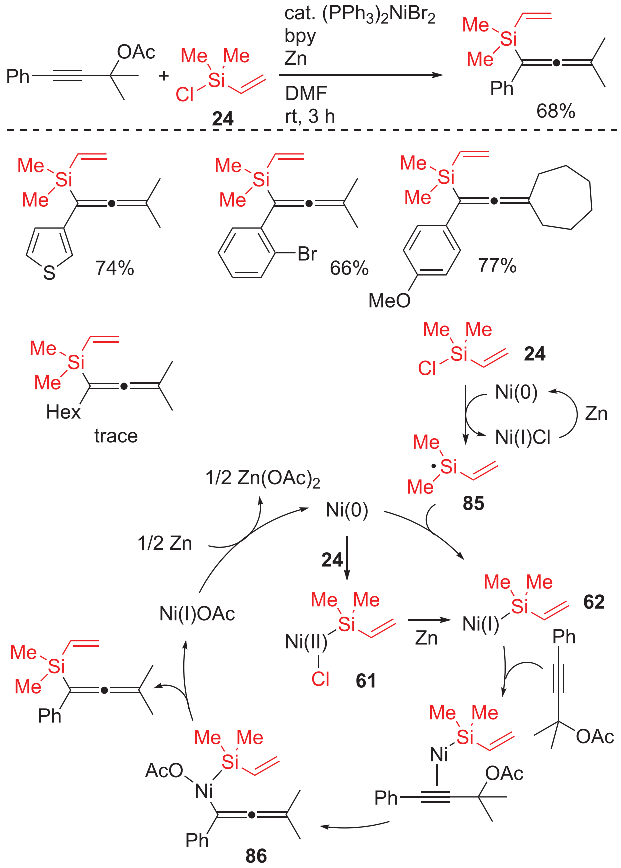
Zeng and coworkers reported the Cr-catalyzed cross-electrophile coupling between hydrochlorosilanes and aryl pivalates, in which both the activation of Si—Cl and C—O bonds is involved as a key step (Scheme 22).[55] The reaction of 2-napthyl pivalate with HPhMeSiCl **69** in THF at room temperature gave the cross- electrophile coupling product in 5% yield, along with the reduction product, naphthalene in 3%. The addition of a bpy ligand dramatically increased the desired product yield to 70%, but the yield of naphthalene, a byproduct, was also increased to 26%. After screening a series of ligands, it was found that dtbpy gives a high yield of the desired product. The scope of substrates including aryl and heteroaryl pivalates, and the functional group compatibility was found to be high. In addition, the reaction was applicable to various hydrochlorosilanes. A double silylation with two C—OPiv bonds was achieved to give disilylated product, as in **79** at an elevated reaction temperature. It was found that a radical species and the related silyl Grignard reagent are not involved as silylation reagents. Kinetic studies suggest that the reaction displays first-order for a catalyst, half-order for hydrochlorosilane, and an inverse first-order for pivalate. The results of DFT studies suggested that the α-agostic interaction of a Si-H σ-bond to Cr stabiles the related intermediates and transition states of the cleavage of both Si-Cl in chlorosilanes and C-O bonds in aryl pivalates.

Based on information obtained from DFT calculations, a plausible mechanism is shown in Scheme 22. An active Cr species is formed in situ by the reduction of $CrCl_3$ with Mg. The reaction of the active low-valent Cr species with HMe_2SiCl generates **81** via **80**, which is thermodynamically stabilized by α-agostic Si-H→Cr interaction. Due to the agnostic interaction, the cleavage of a Si-Cl bond in **80** with Cr proceeds to give **81** with a relatively low energy barrier. The one-electron reduction of **81** by Mg gives a silyl-Cr species **82**, which undergoes oxidative addition to a pivalate to give **84**. The reductive elimination from **84** affords the final product.

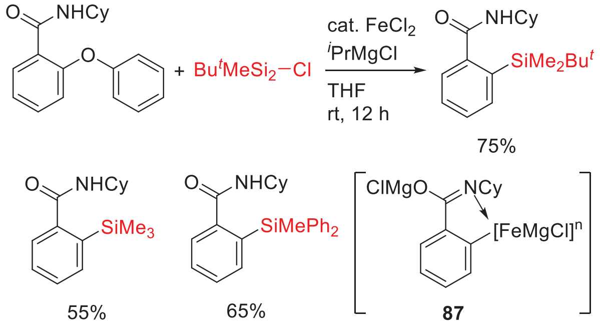
In 2023, Qin, Li and coworkers reported the Co-catalyzed cross-electrophile coupling between chlorovinylsilanes and propargyl acetates under electro-conditions, leading to the production of tetra-substituted vinylsilylallenes.[56] The reaction required 50 mol% of CoI_2 as a promoter. The reaction is proposed to be initiated by the addition of a Si-centered radical species, which is generated by the cathodic reduction of **24** followed by the reaction with Mg^{2+}, across an alkyne in propargyl acetates to generate a vinyl radical intermediate. It therefore appears that the activation of a Si—Cl bond is not involved in this process.

In a subsequent report, the same authors reported that a Ni catalyst also shows a high catalytic activity for this transformation (Scheme 23).[57] The reaction was only applicable to chlorovinylsilanes, and chlorosilanes without a vinyl group, such as Et_3SiCl, $^iPr_3SiCl$, $Me_2PhSiCl$, and $MePh_2SiCl$ were found to show no reactivity. The use of OBoc or OPiv in place of OAc as leaving groups also gave the corresponding allenylsilanes, but OBz or OH showed no reactivity. The use of an alkyl group in place of an aryl group at a terminal alkyne carbon did not give the desired product. The reaction was completely inhibited by the addition of radical scavengers, such as TEMPO and BHT.

The reaction is proposed to begin with the generation of a Si-centered radical species **85** by the Ni-mediated reaction of chlorovinylsilane **24** with the Zn reductant. The reaction of the silyl radical **85** to Ni(0) catalyst gives Si—Ni(I) species **62**, which then coordinates with a propargyl acetate followed by the oxidative addition of a propargyl acetate to give an allenyl Ni intermediate **86**. A subsequent reductive elimination affords the final product. An alternative path to generate **62** from **61** through the oxidative addition of **24** with Ni(0) followed by one-electron reduction by Zn cannot be excluded.

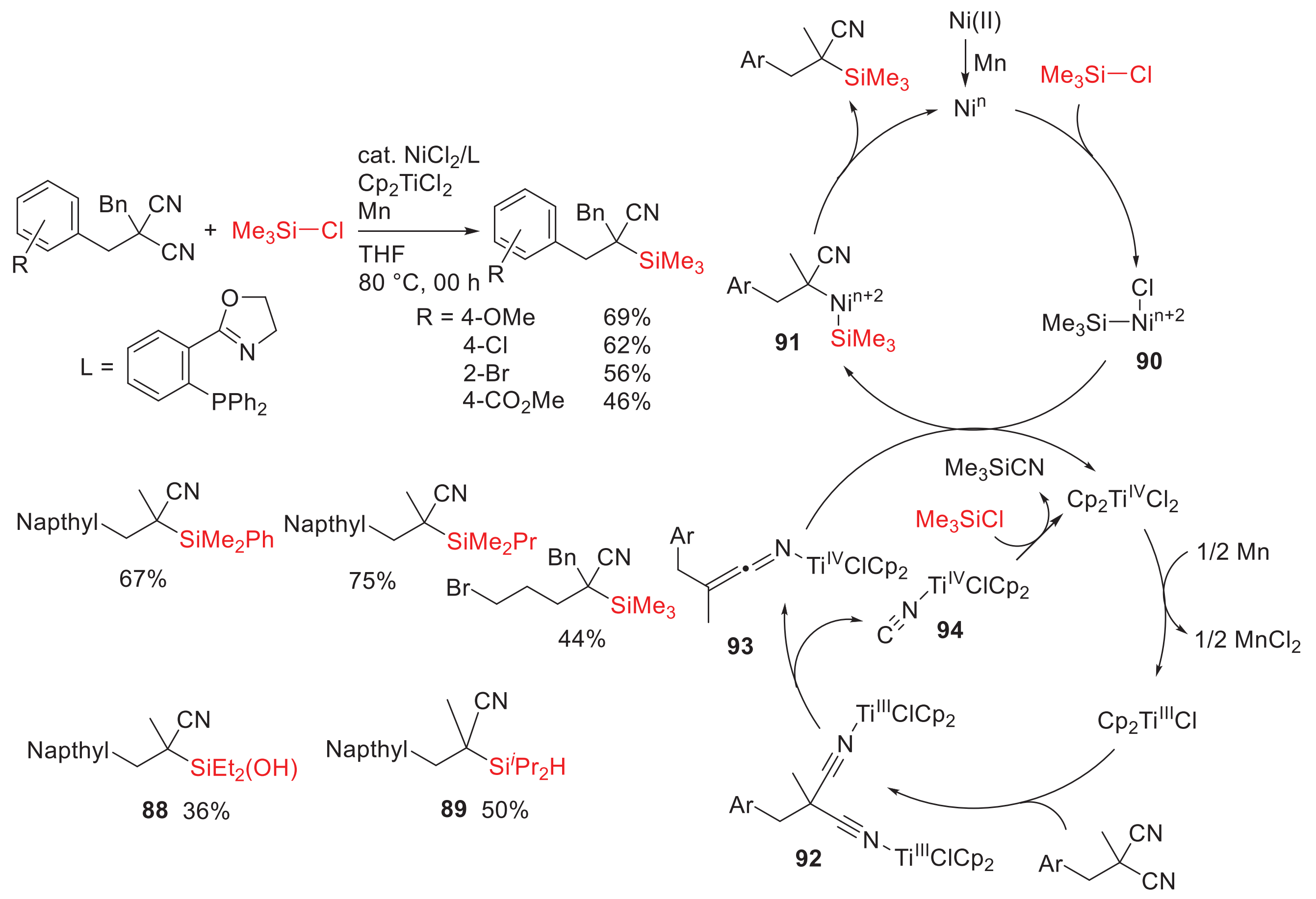


Scheme 23. Ni-catalyzed cross-electrophile coupling between chlorovinylsilanes and propargyl acetates.



Scheme 24. Fe-catalyzed chelation-assisted cross-electrophile coupling between unactivated chlorosilanes and phenoxy ethers.

Liu, Cong, Kong, and coworkers reported the Fe-catalyzed cross-electrophile coupling between and Si—Cl and C(aryl)—O bonds by using chelation assistance of an amide group (Scheme 24).[58] Curiously, the reaction was only applicable to simple chlorosilanes, such as Me_3SiCl, $EtMe_2SiCl$, $BuMe_2SiCl$, $(CF_3CH_2CH_2)PhMeSiCl$, $PhMe_2SiCl$, and $Ph_2MeSiCl$. In fact, $(CH_2{=}CH)Me_2SiCl$ **24** and HMe_2SiCl **75**, which are specifically reactive silylation reagents in various cross-electrophile coupling reactions, as shown above, were ineffective for the present reaction. The use of methoxy and ethoxy groups as leaving groups gave the desired silylation products, but only in yields of 10%. The reaction of meta-phenoxybenzamide did not



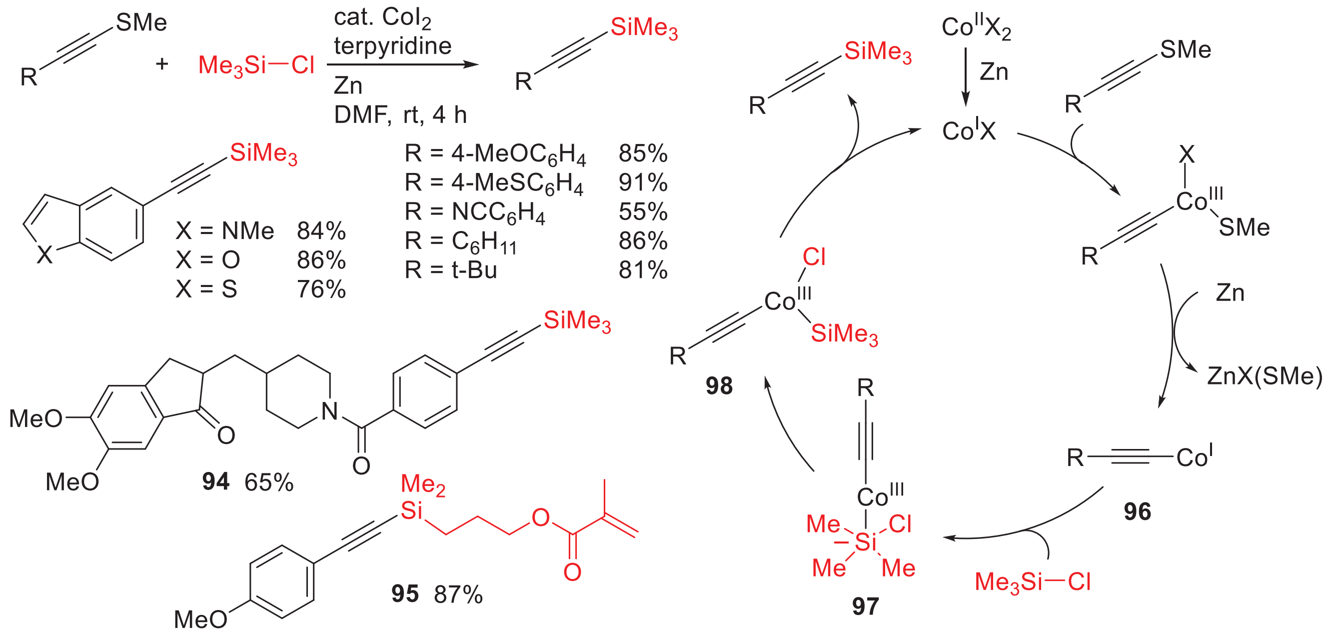
Scheme 25. Ni/Ti-catalyzed cross-electrophile coupling between chlorosilanes and malononitriles.

undergo the silylation indicating that an amide group at the ortho-position functions as a chelating group to activate a C—O bond. It was also found that a radical process is not involved in the reaction, based on radical probe experiment. After generating the Fe intermediate in situ, which is expected to exist in the system, the desired product was obtained by adding $PhMe_2SiCl$. The addition of D_2O in place of $PhMe_2SiCl$ resulted in deuteration at the ortho-position. These results suggest that the Fe intermediate **87** is generated in the reaction as a key intermediate, although its exact structure is not clear.

The reaction is proposed to proceed through the oxidative addition of a C—O bond to a low-valent Fe species, which is generated by the reaction of $FeCl_2$ with an excess amount of $^{i}PrMgCl$, with aid of an amide directing group to give an ortho Fe intermediate, **87** which undergoes the oxidative addition of a Si—Cl followed by reductive elimination. However, the authors stated that direct nucleophilic silylation of the Fe intermediate **87** cannot be ruled out.

Liu and coworkers reported the Ni/Ti dual catalytic system for cross-electrophile coupling involving the activation of the $C(sp^3)$-CN bond of a malonate (Scheme 25).[59] The reaction was limited to α,α-dialkyl-substituted malonates. A wide variety of monochlorosilanes, such as Me_3SiCl, $BuMe_2SiCl$, $^{i}PrMe_2SiCl$, Et_3SiCl, (allyl)Me_2SiCl, $PhSiMe_2Cl$, $Ph_2MeSiCl$, $(CH_2{=}CH)Me_2SiCl$ **24**, and $HPr^{i}{}_2SiCl$ was applicable to the reaction. Various functionalized chlorosilanes were also found to participate in the reaction. The product was demonstrated to be a suitable organosilicon reagent for use in the Hiyama-Denmark cross-coupling reaction. Dichlorosilanes were also tolerated in this reaction. Thus, the reaction with Et_2SiCl_2, followed by workup gave the alkylsilanol **88**. The use of chlorohydrosilane $H^{i}Pr_2SiCl$ under the standard reaction conditions gave the expected hydrosilane **89**. The results of radical clock experiments using 4-pentenyl- or cyclopropyl-substituted malonates suggest that a radical species is not generated in the reaction.

The activation of a Si—Cl bond is proposed to be promoted by Ni complex. On the other hand, the activation of a C-CN bond is proposed to be promoted by the Ti complex, although the activation of a C—CN bond by a Ni(0) complex is well-known. A catalyst precursor $NiCl_2$ is reduced by Mn to generate a low valent Ni species, in which the exact oxidation state is not clear. The generation of the low valent Ni species initiates the main catalytic cycle, which involves the oxidative addition of a Si-Cl bond to the Ni species generating a silyl-Ni—Cl species **90**, transmetalation with a keteimine-Ti complex **93**, and the reductive elimination from **91** to afford the final product. The keteimine-Ti complex **93** is generated through Steruff's mechanism.[60] Thus, the one-electron reduction of $Cp_2Ti(IV)Cl_2$ by a Mn reductant generates $Cp_2Ti(III)Cl$, which then coordinates to the malonate to give **92**. A C—CN bond cleavage in **92** takes place to generate



Scheme 26. Co-catalyzed cross-electrophile coupling between unactivated chlorosilanes and alkynyl sulfides.

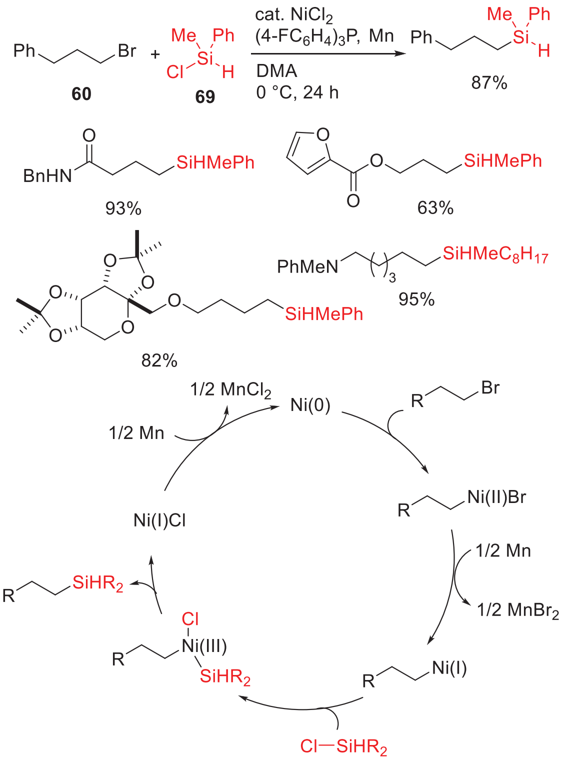
the keteimine-Ti complex **93** and Ti isocyanide complex **94**. The transmetalation of **90** with **93** gives **91**, followed by the reductive elimination to give the final product, along with the regeneration of Cp_2TiCl_2 to complete the bottom catalytic cycle. The reaction of **94** with Me_3SiCl also leads to the regeneration of Cp_2TiCl_2. Even in the absence of the Ni catalyst, the desired product was obtained (17% yield), suggesting that the route possibly involves the direct silylation of **93** with Me_3SiCl exists. However, a dual catalytic system was found to be more effective. The reaction was found to be applicable to chlorogermanes to give the corresponding organogermane compounds. The results of a competition experiment between Me_3SiCl and Me_3GeCl showed that Me_3GeCl is much more reactive than Me_3SiCl due to its lower bond dissociation energy. In fact, the energy barrier of the oxidative addition of a Ge—Cl bond to Ni was calculated to be lower than that of a Si—Cl bond by 6.7 kcal/mol.

Jiang, Huang, and coworkers reported the Co-catalyzed cross-electrophile coupling between chlorosilanes and alkynyl sulfides a (Scheme 26).[61] Remarkably, a broad range of unacitivated chlorosilanes, such as Me_3SiCl, $EtMe_2SiCl$, $BuMe_2SiCl$, $^iPrMe_2SiCl$, Et_3SiCl, $PhMe_2SiCl$, and $Ph_2MeSiCl$ were applicable to the reaction. Not only aryl-substituted alkynes, but also alkyl-substituted alkynes were found to participate in the reaction to give corresponding silyl-substituted alkynes in good to high yields. The reaction tolerated a broad range of functional groups. The reaction was also shown to be applicable to late-stage functionalization, as in **94**. The reaction was extended to the synthesis of germyl-substituted alkynes by using Me_3GeCl. When several radical acceptors, such as ethyl acrylate, acrylonitrile, phenyl vinyl sulfone, and 1,1-diphenylethylene were added to the standard reaction conditions, the desired product was obtained in 69%–82% yields with no sign of the side reaction product from radical trapping. The reaction of radical clock experiment did not give any cyclized product, as in **95**. The results of cyclic voltammetry experiments using the related Co(II) complex and a stoichiometric reaction with the in-situ formed Co(I) complex with alkynyl sulfide suggested that Co(I) species is the active intermediate. Additional experiments suggest that the generation of an alkynyl-Zn intermediate is not involved.

The catalytic cycle is proposed to be initiated by the generation of a low-valent Co(I) species via the in-situ reduction of CoI_2 with Zn. The oxidative addition of alkynyl sulfide followed by a two-electron reduction by Zn gives a more nucleophilic alkynyl Co(I) intermediate **96**. The S_N2-type oxidative addition of Me_3SiCl through an intermediate **97** gives an alkynyl-Co(III) **98** intermediate. The reductive elimination from **98** gives a final product and Co(I) species is regenerated to start the next catalytic cycle.

Shen, Zhou, Luo, and coworkers reported the Ni-catalyzed reaction of aryl fluorosulfates with chlorovinylsilanes, leading to the production of aryl(vinyl)silanes.[62] Although other metals, such as $FeCl_2$, $FeCl_3$, and $CoCl_2$ also showed catalytic activity, Ni complexes exhibited a higher activity. As a result of a competition experiment, it was found that an electron-withdrawing group in the aryl group accelerates the reaction compared to an electron-donating group. The reaction is proposed to proceed through essentially the same mechanism of the reaction of aryl triflates shown in Scheme 17.[49]

Shu and coworkers previously reported the Ni-catalyzed cross-electrophile coupling of unactivated alkyl bromides with chlorovinylsilanes, as shown in Scheme 19b.[52] The authors successfully expanded the reaction to cross-electrophile coupling with chlorohydrosilanes (Scheme 27).[63] The reaction exhibited a high functional group tolerance. Thus, the reaction was found to be applicable to the synthesis of various highly functionalized alkylsilanes. However, secondary alkyl bromides failed to react. The reaction of cyclopropylmethyl bromide as an alkyl bromide with **69** gave a ring-opening product, indicating that a radical



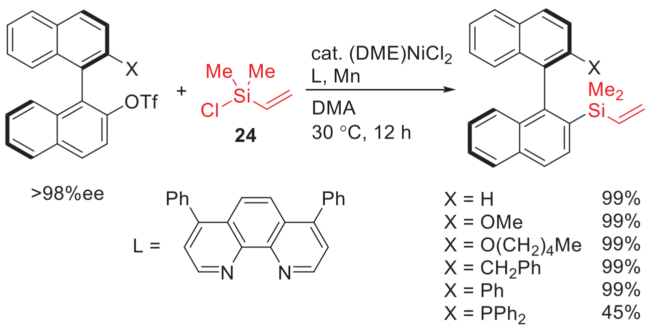
Scheme 27. Ni-catalyzed cross-electrophile coupling between chlorohydrosilanes and alkyl bromides.

process is involved in the reaction of an alkyl bromide with the Ni species. On the other hand, the cyclopropyl moiety in chlorosilane remained intact to afford the desired product in 70% yield in the case of using cyclopropyl(phenyl)chlorohydrosilane in place of **69**, indicating that the reaction with chlorohydrosilane proceeds through a non-radical process.

Based on these results, a different catalytic cycle from that previously reported (Scheme 19b) is proposed. Thus, the oxidative addition of an alkyl bromide with Ni(0) via a radical pathway gives an alkyl-Ni(II)Br species which does not undergo β-hydride elimination, instead a one-electron reduction by Mn takes place to give an alkyl-Ni(I) species. The oxidative addition of a Si—Cl bond via a nonradical pathway followed by reductive elimination gives the desired alkylhydrosilane, along with Ni(I), which is reduced by Mn to regenerate an active catalytic species Ni(0).

Chang, Bai, and coworkers reported the synthesis of axially chiral organosilicon compounds by the Ni-catalyzed cross-electrophile coupling of chiral 1,1′-(binaphthalen)-2-yl trifluoromethansulfonates with chlorovinylsilanes (Scheme 28).[64,65] In all cases, the reaction proceeded without a loss of enantioselectivity. Although the reaction with HMe_2SiCl **75** also gave the corresponding products in high yields, the use of Me_3SiCl gave a complex mixture.

Qin, Li and coworkers previously reported the Ni-catalyzed cross-electrophile coupling between chlorovinylsilanes and propargyl acetates (Scheme 23).[57] In 2025, Deng and coworkers found that the reaction successfully proceeds when hydrochlorosilanes **69** are used.[65] In addition,

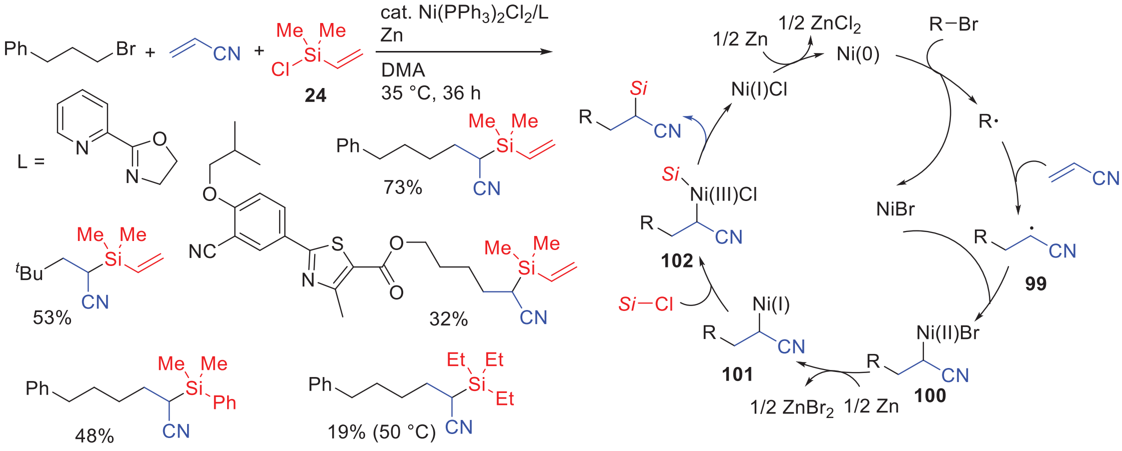


Scheme 28. Ni-catalyzed cross-electrophile coupling between chlorovinylsilanes and chiral 1,1′-(binaphthalen)-2-yl trifluoromethansulfonates.

Me_3SiCl, $^iPrMe_2SiCl$, and Et_3SiCl also gave the corresponding allenylsilanes, but in slightly lower yields. In sharp contrast to the results shown in Scheme 23,[57] in which the reaction was completely inhibited by the addition of radical inhibitors, such as TEMPO and BHT, the addition of TEMPO completely inhibited the reaction but BHT and 1,1-diphenylethytlene did not show any negative effects in the present reaction. The authors concluded that this result is probably not due to the generation of a radical species but rather, to the oxidative capacity of TEMPO, which inhibits the initiation of the reaction. The reaction could be extended to Me_3GeCl and Me_3SnCl. The proposed reaction mechanism involves the oxidative addition of propargyl acetate with Ni(0), a one-electron reduction with Mn, the oxidative addition of chlorohydrosilane, and reductive elimination.

7. Three-Component Cross-Electrophile Coupling Reactions

In 2003, Kambe and coworkers reported the Ni-catalyzed reaction of 1,3-butadines with chlorosilanes and Grignard reagents, in which dimerization and the carbosilylation of 1,3-butadines are involved.[38] However, the reaction appears not to involve the oxidative addition of Si—Cl bond, as described above. As described in Section 3, some examples of Pd-catalyzed three-component coupling reactions had been already reported. These reactions apparently proceed through the silylmetalation of a Si-Pd species to an alkyne, leading to vinyl-Pd intermediates, which are trapped by nucleophiles. In contrast, three-component coupling reactions based on electrophilic coupling have been reported only recently. In 2022, Zhang and coworkers reported the first successful example of the Ni-catalyzed three-component, cross-electrophile coupling reaction of chlorosilanes, alkyl bromides, and acrylonitrile under reductive conditions with broad substrate scope including primary, secondary, and tertiary alkyl bromides under mild reaction conditions (Scheme 29).[66] The reaction was not limited to chlorovinylsilanes, but simple chlorosilanes, such as Me_3SiCl, $^iPrMe_2SiCl$, Ph_3SiCl, and Et_3SiCl were also found to react to give the corresponding products. In the presence of TEMPO (3 equiv.), the reaction was completely shut down. The reaction of cyclopropylmethyl bromide resulted in the ring-opening product



Scheme 29. Ni-catalyzed three-component coupling reaction of chlorosilanes, alkyl bromides, and acrylonitrile.

in 72% yield. These results indicate that an alkyl radical is generated under the reaction conditions.

Based on some mechanistic experimental results, a catalytic cycle is proposed as follows. The reaction of Ni(0) with alkyl bromide gives an alkyl radical, which is trapped by acrylonitrile to generate the alkyl radical **99**, which recombines with the Ni(I) species to give the alkyl Ni(II) intermediate **100**. One-electron reduction by Zn gives an alkyl—Ni(I) species **101**, which undergoes the oxidative addition of a Si—Cl bond to give alkyl silyl Ni(III) intermediate **102**. Reductive elimination affords a desired three-component coupling product.

In a series of studies on cross-electrophile coupling reactions, in 2023, Shu and coworkers reported the discovery of the Ni-catalyzed three-component coupling reaction of chlorosilanes, aryl bromides, and 1,3-butadienes, which undergoes the 1,2-silyl-arylation of 1,3-butadienes (Scheme 30a).[67] A silyl group was selectively introduced at the terminal position of 1,3-butadienes. While other aryl electrophiles, such as aryl triflates, iodides, and chlorides also gave the corresponding products, the product yields were poor. The scope of chlorosilanes were also examined and it was found use of Me_3SiCl, $PhMe_2SiCl$, (thiophenyl)Me_2SiCl, (naphtyl)Me_2SiCl, and Ph_3SiCl gave the corresponding 1,2-silyl-arylation products in good yields, and no direct silylation byproducts being produced with aryl bromides via reductive cross-electrophile coupling were formed in all cases. In sharp contrast, the use of HPhMeSiCl **69** gave only a trace amount of the expected 1,2-silyl-arylation product, but a simple silylation product via reductive cross-electrophilic coupling with PhBr was obtained in a high yield. The authors concluded that a silyl radical species is not generated because the desired products were obtained in good yields even in the presence of radical scavengers (2 equiv.), such as BHT and TEMPO. In the reaction of 1-phenyl-1,3-butadiene with PhBr in the absence of $PhMe_2SiCl$ under the standard reaction conditions, 98% of the butadiene was recovered and a significant amount of Ph–Ph dimer was obtained. In the reaction of 1-phenyl-1,3-butadiene with $PhMe_2SiCl$ in the absence of PhBr under the standard reaction conditions, a 1.4:1 mixture of silyl-protonation product and silyl-Mizoroki–Heck type product was obtained in a total yield of 70%. The results of these controlled experiments suggest that butadiene and chlorosilane react first and PhBr then reacts. In the reaction of 1-phenyl-1,3-butadiene with $PhMe_2SiCl$ in the absence of PhBr and Mn, a 1.6:1 mixture of silyl-protonation product and silyl-Mizoroki–Heck type product was obtained only in 15% yield and 81% of butadiene was recovered, suggesting that Mn acts as a reducing reagent to generate a low-valent Si-Ni species.

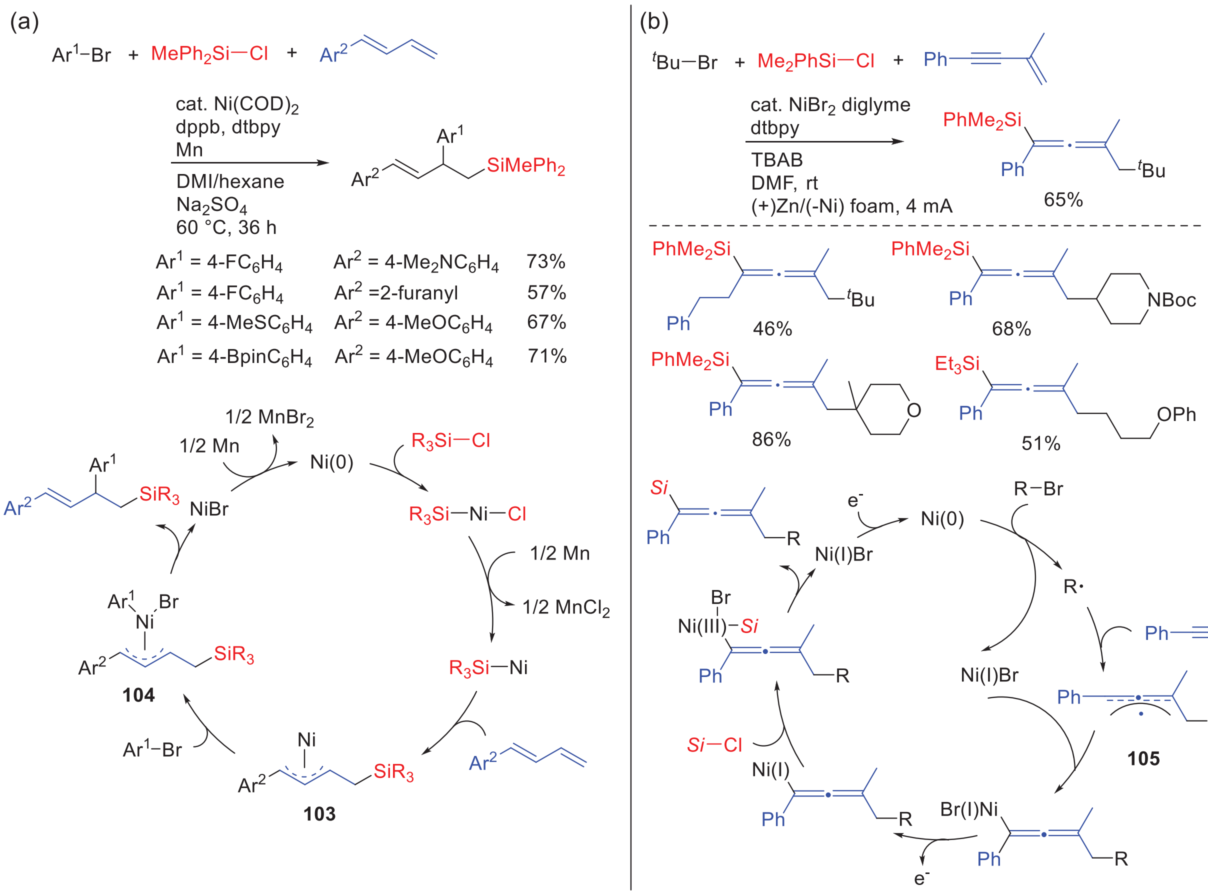
Based on some mechanistic studies, the following catalytic cycle is proposed. The reaction proceeds through the oxidative addition of a Si—Cl bond to Ni(0) followed by one-electron reduction to give Si—Ni(I) species, which undergoes silylnickelation with 1,3-diene to give π-ally Ni(I) intermediate **103**. The oxidative addition of aryl bromides to **103** gives the π-ally Ni(III) intermediate **104**, which then undergoes reductive elimination to give the desired product, along with Ni(I) species, which is reduced by Mn to regenerate an active catalytic species Ni(0).

Yue, Rueping, and coworkers reported the Ni-catalyzed reductive three-component coupling of chlorosilanes, alkyl bromides, and 1,3-enynes under electrochemical conditions, leading to the production of highly substituted allenylsilanes (Scheme 30b).[68] Various alkyl bromides including primary, secondary, and tertiary alkyl bromides were found to participate in the reaction. It was also found that Sn—Cl and Ge—Cl bonds participate in the reaction to give the corresponding tetra-substituted allenystannaes and germanes.

The proposed mechanism is essentially the same as that proposed in Scheme 29. Thus, the generation of an alkyl radical followed by the addition of an enyne moiety to generate an allenyl radical species **105** initiates the catalytic cycle.

8. Summary and Outlook

This review article provides an overview of the current state of our knowledge regarding transformations involving the oxidative addition of Si–halogen and Si–pseudohalide bonds as a key step. It is well known that the oxidative addition of C–halogen bonds of aryl halides or alkyl halides can initiate a



Scheme 30. a) Ni-catalyzed three-component coupling reaction of chlorosilanes, aryl bromides, and 1,3-dienes. b) Ni-catalyzed three-component coupling reaction of chlorosilanes, alkyl bromides, and 1,3-enynes.

wide variety of useful transition metal-catalyzed reactions. In fact, this step is recognized as the most important fundamental reaction involved in a variety of transition metal-catalyzed reactions. In comparison with these reactions, the development of transformations involving the oxidative addition of Si–halogen bonds as key steps has not advanced. Only limited types of transformations have been reported thus far, as shown above. However, this review shows that the oxidative addition of Si–halogen bonds has considerable potential and promise with respect to designing the synthesis of useful silicon-containing compounds, which cannot be prepared by the existing methods.

Although there are some possible activation paths of Si–halogen bonds, concerted cis-oxidative addition, trans-oxidative addition, S_N2-type oxidative addition, and σ-bond metathesis, only a few theoretical calculations focusing on how to activate a Si-halogen bond have been reported thus far.[14,46,69–71] In addition, only a few theoretical studies on overall catalytic reactions have been performed.[14,46,47,55] The use of chiral chlorosilanes would provide important information to gain insights into the mode of how a Si-halogen bond is activated. Given the fact that there is still much that is unknown, completely different reaction mechanisms have been proposed, even for similar reactions. For example, in some cases, the oxidative addition of a Si–halogen bond to Ni(0) is proposed to occur first while, in other cases, the oxidative addition of a C–halogen bond is proposed to occur first. More detailed mechanistic studies including DFT calculations and stoichiometric reactions using related isolable complexes are needed if we are to develop a better understanding of the reaction mechanism.

In early studies of transformations involving the oxidative addition of Si–halogen bonds, Pd complexes were mainly used as catalysts but more recently Ni complexes have been recognized as a promising catalyst for activating Si-halogen bonds, similar to that for Ni complexes which are known to activate various strong chemical bonds, such as C—OMe, C—F, C—CN, and related bonds.[72] However, other base metals, such as Fe, Co, and Cr have recently been found to activate Si-halogen bonds, as shown above. New types of transformations are expected to be developed using metals contained by these metal complexes. The scope of chlorosilanes is still limited to vinylchlorosilanes and hydrochlorosilanes in many cases. Expansion of the substrate scope will be needed if such protocols are to become of practical use.

Over the past decade, the combination of transition metal catalysis and photocatalysis to explore valuable transformations has gained significant attention due to their unique activation modes. Dual Ni/photoredox catalysis provide a new method for cross-electrophile couplings under reductive conditions.[73]

In some of the reactions shown above, it was proposed that Ni(I) species play an important role in the oxidative addition of Si-halogen bonds. In this sense, a dual Ni- and photoredox-catalyzed reaction has the potential for developing interesting new types of transformations involving the activation of Si–halogen bonds.

Various types of asymmetric reactions in which the oxidative addition of C–halogen bonds of an aryl halide is a key step, have been reported. In contrast, the development of asymmetric reactions involving the oxidative addition of Si–halogen bonds has not yet been achieved.

Although it is not within the scope of this review, catalytic reactions involving the oxidative addition of Ge–halogen,[59,61,65,68,74–80] Sn–halogen,[65,68,81] and B–halogen bonds[82] have recently appeared in the literature.

The goal of this review is that this review will attract more researchers to this fascinating field, and that this will lead to a substantial expansion of this field that will lead to further significant developments in this fascinating field.[83]

Acknowledgments

The authors have nothing to report.

Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.

Keywords: Halosilanes · Oxidative addition · Silylmetalation · Cross-Coupling · Cross-Electrophile Coupling

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