Nickel-Catalyzed [4+1] Sila-Cycloaddition: A Divergent Synthesis of Silacarbocycles from Trichlorosilanes

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Abstract: Cyclic chlorosilane transformations present a valuable opportunity for the divergent synthesis of silacarbocycles, but their low availability has hindered this potential. This study presents a direct approach to producing structurally diverse five-membered cyclic chlorosilanes, utilizing trichlorosilanes as a novel Si–1 synthon for catalytic sila-cycloaddition reactions. The method employs a nickel-catalyzed [4+1] cycloaddition reaction between 1,3–dienes and trichlorosilanes, facilitated by upgraded phosphine-nitrogen ligands. This approach accommodates a broad range of 1,3–dienes and trichlorosilanes, yielding cyclic chlorosilanes that act as versatile platform molecules. These intermediates can be readily transformed into advanced silicon reagents and connected with various carbon and heteroatom functionalities through a one-pot reaction.

Keywords: Organosilanes, Silylation, Nickel, Cycloaddition, Reductive coupling

Transition metal-catalyzed sila-cycloaddition offers an efficient route for constructing silacarbocycles,[1-4] which have shown considerable promise in developing pharmaceuticals, pesticides, and advanced materials.[5-7] A key driver of progress in this area is the development of new sila-synthons, as shown by the success of Si–4 and Si–3 synthons, such as silacyclobutanes[8-15] and 2–silylaryls,[16-19] which have enabled innovative synthetic strategies. However, a strong demand remains for new and readily accessible silyl synthons, particularly Si–1 synthons. Although promising results have been achieved with silacyclopropanes,[20-23] HMe$_2$Si–SnBu$_3$,[24] HR$_2$Si–SiMe$_3$,[25] (Et$_2$N)R$_2$Si–Bpin,[26-29] R$_2$SiH$_2$,[30-32] and

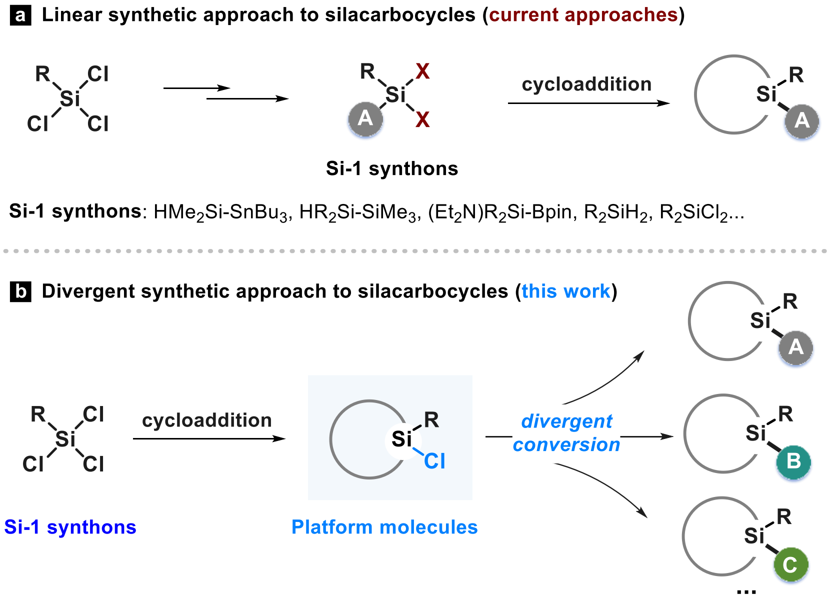
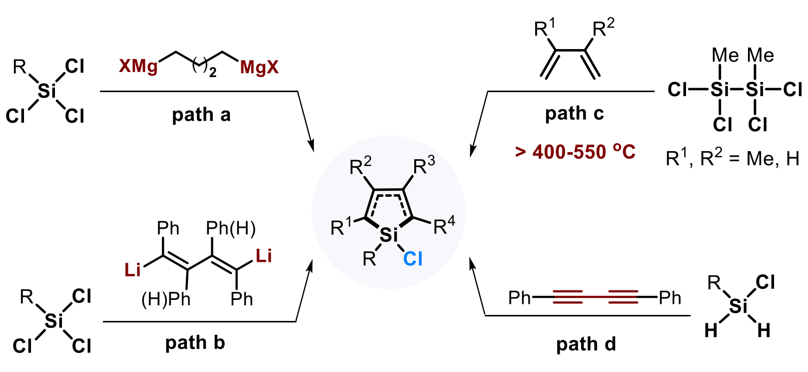


Figure 1. Linear and divergent synthetic approaches to silacarbocycles

R_2SiCl_2[33] in [2+1], [4+1], and [2+2+1] cycloadditions, current approaches rely on linear synthetic pathways, requiring the preinstallation of carbon fragment into $RSiCl_3$ before cycloaddition (Scheme 1a). In this manuscript, we demonstrated that $RSiCl_3$ can directly serve as a Si–1 synthon in catalytic cycloaddition reactions to generate cyclic chlorosilanes (Scheme 1b). These cyclic chlorosilanes act as platform molecules, enabling subsequent reactions with various nucleophiles and facilitating a divergent synthetic approach to diverse silacarbocycles, thus improving both efficiency and synthetic flexibility.

Monochlorosilanes are key precursors for synthesizing organosilicon compounds in medicinal chemistry and materials science,[1-4] and they can also be converted into advanced reagents like hydrosilanes and silylmetallic species. While acyclic chlorosilanes are readily accessible, methods for producing cyclic chlorosilanes remain limited.[34-37] Currently, the most reliable approach for synthesizing five-membered chlorosilanes still relies on the nucleophilic substitution of trichlorosilanes with Grignard or lithium reagents, a method developed over half a century ago (Scheme 2a, path a-b).[38-41] However, this method requires harsh conditions and is applicable to a limited set of molecules. Although alternative approaches, including the cycloaddition of $(MeCl_2Si)_2$ with 1,3-dienes (Scheme 2a, path c),[42,43] double hydrosilylation of diacetylenes (Scheme 2a, path d),[44] and intramolecular hydrosilylation of alkenes,[45] have led to advancements, similar limitations always persist. Herein, we present a nickel-catalyzed [4+1] sila-cycloaddition reaction between readily available trichlorosilanes and 1,3-dienes, providing a mild and efficient method for synthesizing five-membered chlorosilanes with improved efficiency and molecular diversity (Scheme 2b).

(a) General approaches for preparing 5-membered cyclic chlorosilanes (known)



(b) Reductive [4+1] sila-cycloaddition of $RSiCl_3$ with 1,3-dienes (this work)

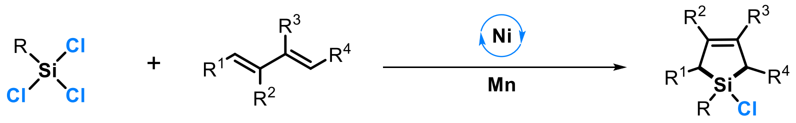
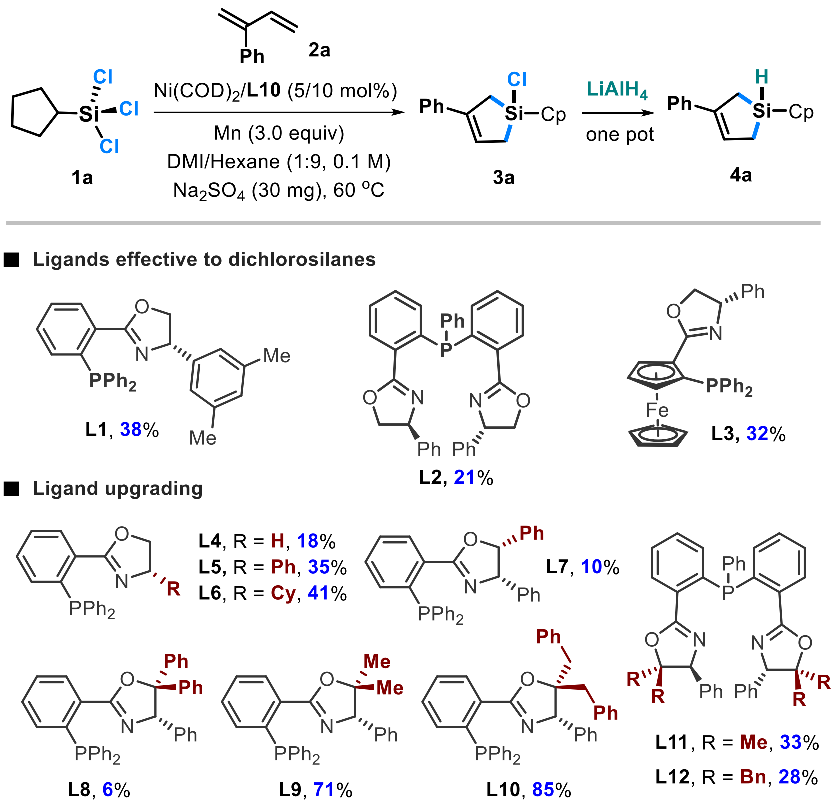


Figure 2. General approaches for synthesis of five-membered chlorosilanes

Nickel-catalyzed reductive C–Si bond-forming reactions of chlorosilanes have recently emerged as a promising strategy for constructing organosilanes.[46-51] A crucial step in advancing this area is to broaden the scope of chlorosilane substrates. Significant progress has been made with mono-chlorosilanes, such as vinyl chlorosilanes,[52-57] chlorohydrosilanes,[58,59] and cyclobutyl chlorosilanes,[60] all of which have proven effective in C–Si coupling reactions. Furthermore, dichlorosilanes have shown potential for forming silacyclopent-3-enes through reductive cycloaddition with 1,3 – dienes.[33] With these advancements in mind, we investigated the reactivity of trichlorosilanes, hypothesizing that their cycloaddition with 1,3–dienes could offer a route to cyclic chlorosilanes, which could serve as versatile intermediates for divergent silacarbocycle synthesis. In this study, we present our findings using newly upgraded phosphine-oxazoline ligand, which not only facilitate the reaction but also address the key limitations of earlier dichlorosilane cycloadditions, restriction to 1-aryl substituted dienes.[33] This catalytic system expands the substrate scope to include a wider range of 1,3–dienes, including non-, mono-, di-, and tri-substituted aliphatic and aryl 1,3–dienes, albeit the reaction efficiency is still to be improved in some cases.

Table 1. Optimization of the reaction conditions[a]



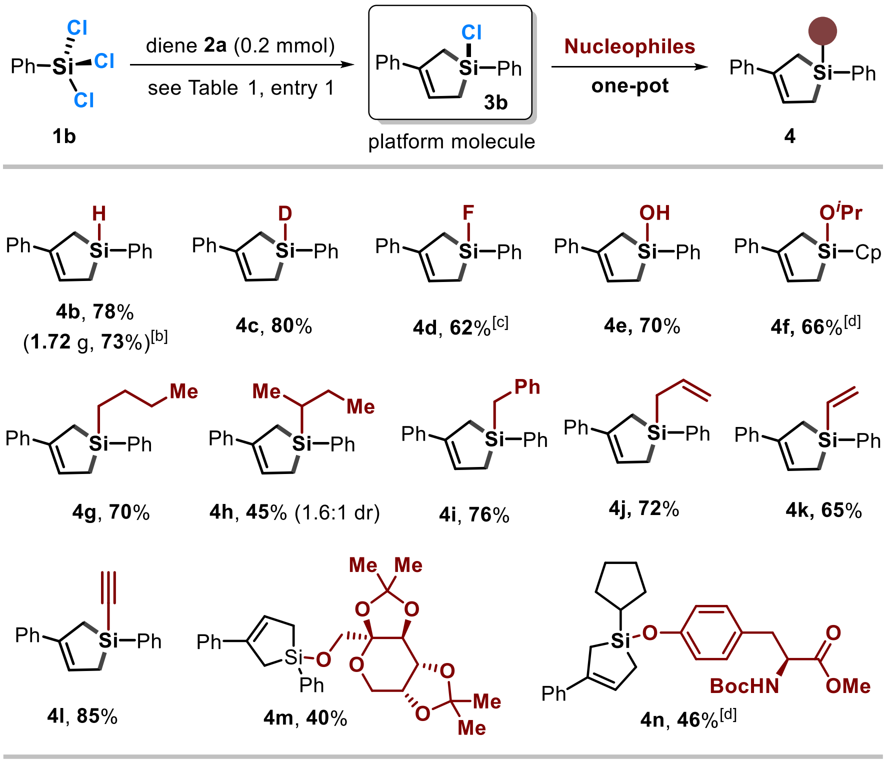
entry	change of conditions	**4a** (%)
1	none	85 (83)[b]
2	$NiBr_2$ instead of Ni(0)	73
3	DMF instead of DMI	0
4	DMI[c]	40
5	no Na_2SO_4	66
6	no Ni, L, or Mn	0 or trace

[a] Reaction of **2a** (0.1 mmol) and **1a** (0.3 mmol) for 48 h, then $LiAlH_4$ (60 mg) was added at 0 °C followed by hexane (1 mL) and DCM (2 mL); after stirring at rt for 2 h, yields of **4a** were determined by NMR analysis with CH_2Br_2 as an internal standard. [b] Isolated yield for the reaction of **2a** (0.2 mmol) and **1a** (0.6 mmol). [c] DMI is 1,3-dimethyl-2-imidazolidinone.

We began our investigation by exploring the reaction of trichlorosilane **1a** with diene **2a** under previously established conditions optimized for dichlorosilanes, using the ligands **L1**–**L3** (Table 1). To simplify the purification, the resulting chlorosilane **3a** was converted to hydrosilane **4a** through a one-pot reaction with $LiAlH_4$. Although hydrosilane **4a** was obtained, all reactions gave low yields, with a substantial recovery of unreacted diene (**L1**–**L3**). This prompted us to enhance the ligand structure through modification. Replacing the 3,5-dimethylphenyl group with hydrogen (**L4**) or phenyl/cyclohexyl groups (**L5**–**L6**) resulted in comparable or inferior yields. When phenyl (**L7**) or diphenyl (**L8**) groups were installed at adjacent positions to increase steric hindrance, yields remained low. However, significant improvement in reaction efficiency was achieved by using ligands with dialkyl substituents (**L9**–L**10**), with dibenzyl-substituted ligand **L10** affording the best result. Notably, compound **L10** has not been previously reported in the literature. Attempts to modify the N–P–N ligands in a similar manner were unsuccessful (**L11**–**L12**).

Using $NiBr_2$ as the precatalyst resulted in a slight decrease in the yield of **4a** to 73% (Table 1, entry 2). Solvent screening revealed that reactions in DMF or hexane did not produce the desired product, while using DMI resulted in a moderate yield of 40% (entries 3 and 4). Interestingly, a combination of hexane and DMI (9:1) significantly improved the yield, providing **4a** in 83% isolated yield (entry 1). The inclusion of Na_2SO_4 as an additive also marginally increased the yield of chlorosilane **3a** (entry 5). Without nickel, ligand, or Mn reductant, the reactions gave no desired product and only a trace of **4a** (entry 6).

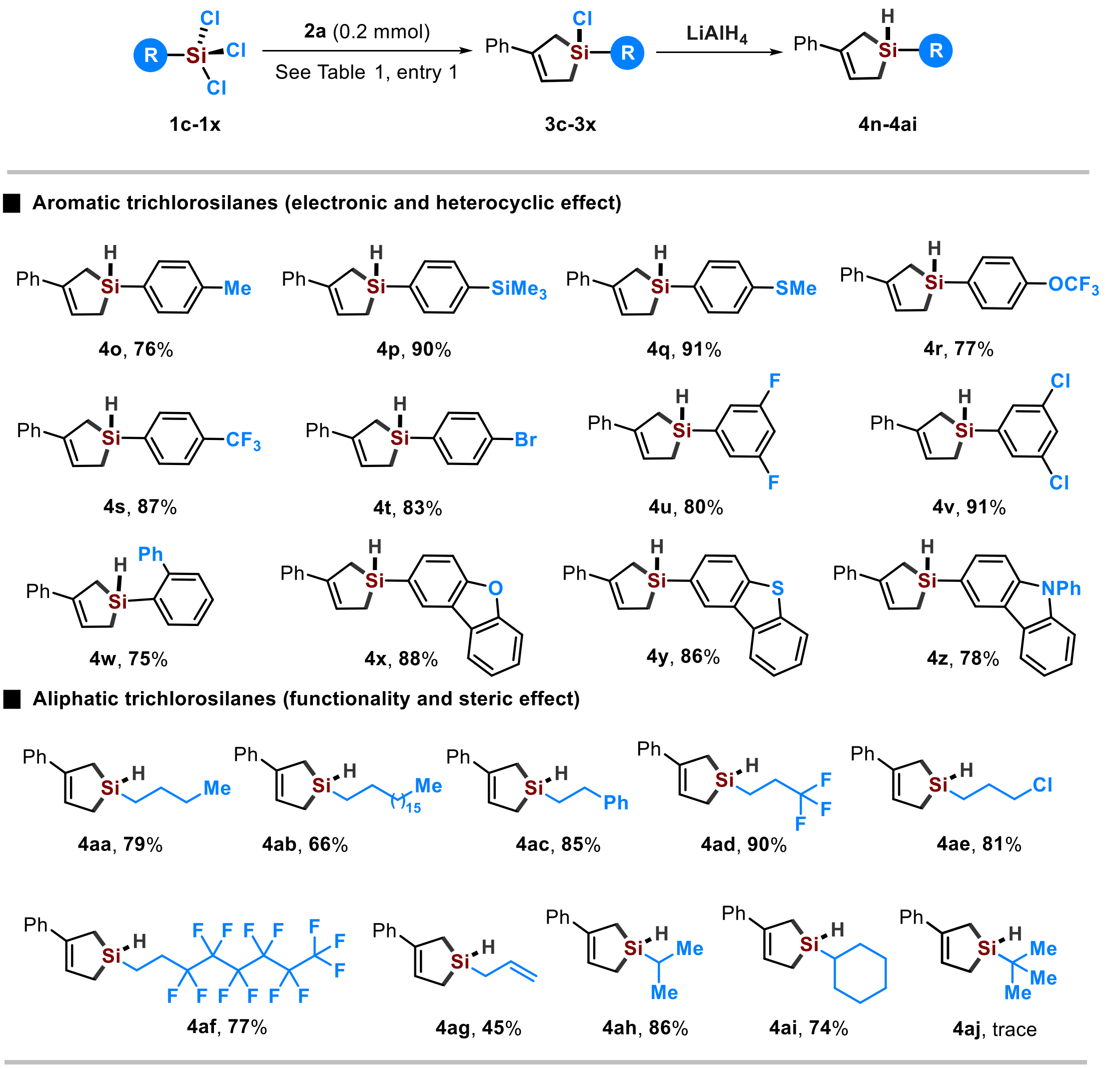
Table 2. Divergent synthesis of silacyclopentanes^{a}



^{a}The cycloaddition reaction conditions are as shown in table 1, entry 1 with dienes **2a** (0.2 mmol) and **1b** (0.6 mmol) used; isolated yields of **4** for two steps are given; after stirring for 48 h, the resulting mixture of 3b was treated with nucleophiles directly (please see Supporting Information for details). ^{b}Diene **2a** (10 mmol) was used. ^{c}Purified chlorosilane **3b** was used. ^{d}Cyclopentyl trichlorosilane **1a** was used.

The resulting cyclic chlorosilane could react with nucleophilic species directly, enabling divergent synthesis of silacarbocycle derivatives, with many of them are difficult to access through traditional linear sila-cycloaddition procedures (Table 2).[8-33] For example, treatment of the reaction mixture with $LiAlH_4$ or $LiAlD_4$ afforded hydrosilane **4b** and deuterated compound **4c** in 78% and 80% yields, respectively.[61-65] The reaction can be scaled up to yield **4b** in 73% (1.72 g). Additional nucleophilic reactions yielded fluorosilane (**4d**, 62%), silanol (**4e**, 70%), and silyl ether **4f** (66%). Reactions involving lithium (**4g**, **4h**) and Grignard reagents (**4i**–**4l**) allowed for integration of silacarbocycles into sp^3, sp^2, and sp carbon frameworks. The presence of alkene (**4j** and **4k**) and alkyne (**4l**) functionalities in these products offers potential for further derivatization. Silacarbocycle could be incorporated into fructose (**4m**) tyrosine (**4n**) derivatives, underscoring their potential applications, including in sila-peptide synthesis.[66]

Table 3. Scope of the reaction with trichlorosilanes[a]

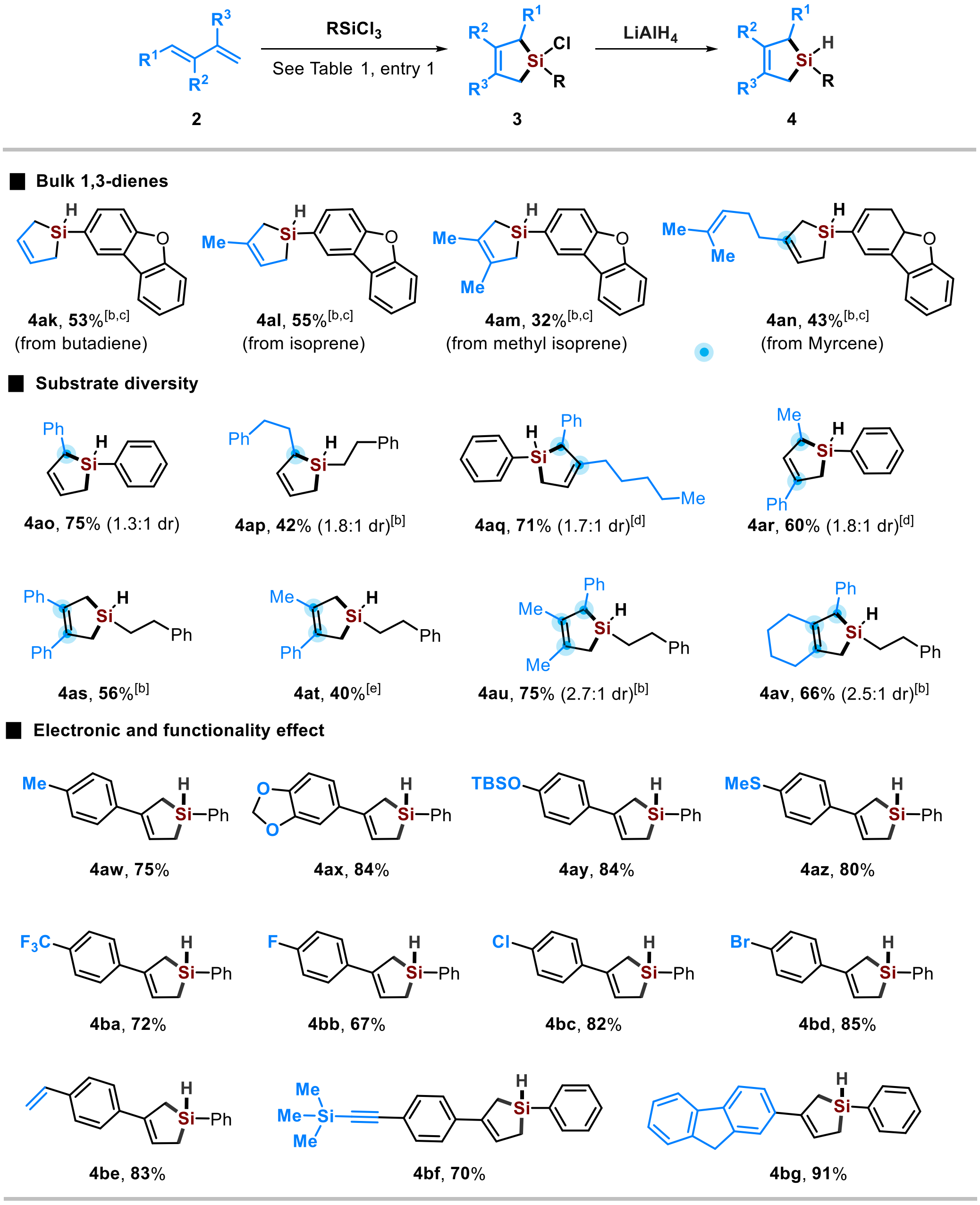


[a]The reaction conditions are as shown in table 1, entry 1; **2a** (0.2 mmol), **1** (0.6 mmol), $LiAlH_4$ (120 mg), hexane (2 mL), and DCM (4 mL) were used; isolated yields of **4** are given.

The substrate scope of trichlorosilanes was evaluated using 2-phenyl substituted 1,3–diene **2a** as a model substrate (Table 3). Trichlorosilanes featuring both electron-rich and electron-deficient aryl groups cyclized well under standard conditions, yielding a diverse array of aromatic hydrosilacarbocycles **4o – 4v** in good yields after treatment with $LiAlH_4$. The reactions exhibited selectivity for transferring trichlorosilanes over traditional coupling-active groups such as Ar–$SiMe_3$ (**4p**), Ar – Br (**4t**), and Ar – Cl (**4v**). Trichlorosilanes conjugated to polyarenes such as biphenyl (**4w**), dibenzofuran (**4x**), dibenzothiophene (**4y**), and dibenzopyrrole (**4z**) maintained high reactivity, offering a potential for producing structurally diverse silicon-based materials.

In addition to aryl substitution, a wide range of alkyl substituted trichlorosilanes reacted with **2a** efficiently, resulting in hydrosilanes **4aa–4ai** with good yields (Table 3). Trichlorosilanes bearing perfluoroalkyl chains respectively yielded **4ad** and **4af** in 90% and 77%, indicating potential applications in the design of hydrophobic fluorinated organosilicon materials. Additionally, chloroalkyl (**4ae**) and allyl substituted (**4ag**) trichlorosilanes were tolerated, which could be used for further derivatization. Both acyclic (**4ah**) and cyclic (**4ai**) secondary alkyl trichlorosilanes worked well, delivering the target products with high conversion rates, ranging from 74% to 86%. High sterically hindered tertiary alkyl trichlorosilane is presently ineffective (**4aj**).

Table 4. Scope of the reaction with 1,3-dienes[a]



[a]The reaction conditions are as shown in table 1, entry 1; **2** (0.2 mmol), **1b** (0.6 mmol), $LiAlH_4$ (120 mg), hexane (2 mL), and DCM (4 mL) were used; isolated yields of **4** are given. [b]$Ni(COD)_2$ (30 mol%) was used. [c]Trichlorosilane

1l (0.8 mmol) was used. [d]Ni(COD)$_2$ (10 mol%) was used. [e]Ni(COD)$_2$ (20 mol%) was used.

The primary limitation in our previous cycloaddition of dichlorosilane was the restricted scope of 1,3–dienes, which was largely confined to 1-aryl-substituted variants.[33] In the current catalytic system, we demonstrate the inclusion of a broader range of 1,3-dienes, as detailed in Table 4. Industrial feedstocks, such as butadiene (**4ak**), isoprene (**4al**), methyl isoprene (**4am**), and myrcene (**4an**) show promise for cycloaddition with trichlorosilanes, although the catalytic efficiency requires further enhancement. This method accommodates a diverse array of substituted 1,3-dienes, including non-substituted (**4ak**), monosubstituted (**4an–4ap**), 1,2-/1,3- and 2,3-disubstituted (**4aq–4at**), and 1,2,3-trisubstituted (**4au** and **4av**) diene substrates. Both aromatic and aliphatic 1,3–dienes reacted effectively under standard conditions, with cyclic dienes yielding bicyclic carbocycle **4av** at a 66% yield.

The influence of electronic effects and functional group tolerance was examined using 2-aryl-substituted 1,3-dienes as substrates (**4aw–4bg**). The electronic effects appeared to have little impact, as both electron-donating (**4aw–4az**) and electron-withdrawing (**4ba–4bd**) substituents on aromatic 1,3-dienes yielded comparable results, with hydrosilane yields ranging from 67% to 85%. Functionalities, such as thioether (**4az**), aryl chloride (**4bc**) and bromo (**4bd**), terminal styrene (**4be**), and TMS alkyne (**4bf**), were tolerated, enabling opportunities for further derivatization. The 1,3–diene bearing a conjugated fluorenyl fragment yielded the target product in 91% (**4bg**).

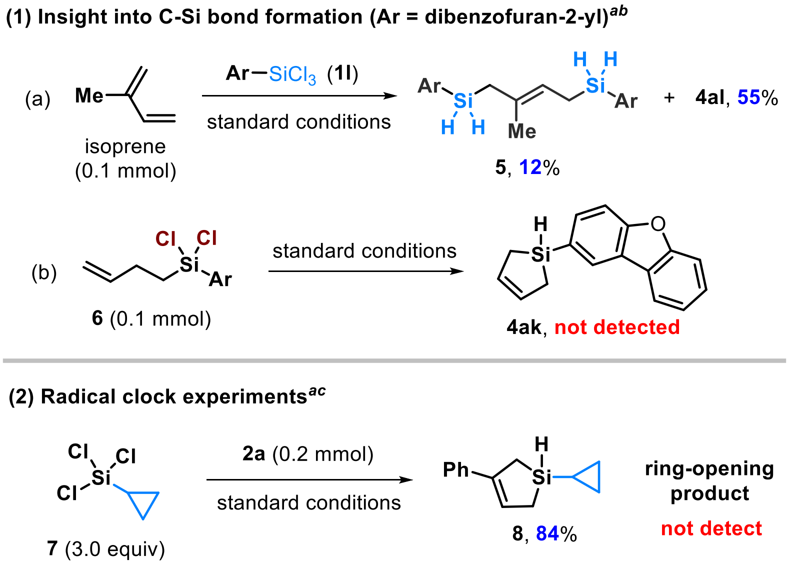


Figure 3. Mechanistic experiments. [a]The reaction conditions are as shown in table 1, entry 1; isolated yields are given. [b]Ni(COD)$_2$ (30 mol%) was used. [c]1,3–Diene **2a** (0.2 mmol) was used.

In addition to the cyclization product, the reaction of isoprene produced a significant amount of disilylation product **5** (Scheme 3, 1a). This result aligns with a mechanism where the Si–Ni intermediate undergoes migratory insertion into the 1,3–diene, followed by intermolecular silylation of the resulting allyl–Ni species with trichlorosilane.

When dichlorosilane **6** was subjected to the same conditions, no cyclization product (**4ak**) was obtained (Scheme 3, 1b), whereas butadiene and trichlorosilane produced the desired product in 53% yield (Table 4). These results rule out the possibility that the desired product forms through a tandem reductive silylation of trichlorosilanes with 1,3–dienes followed by intramolecular sila-Heck cyclization of the resulting alkene-tethered dichlorosilanes.[67]

Additionally, the reaction of cyclopropyl chlorosilane **7** yielded the cycloaddition product **8** in 84%, with no ring-opening derivatives detected (Scheme 3, 2a). This result suggests that the Si–Cl bond may not activated through a radical pathway.

Based on these findings and previous reports, we propose a catalytic cycle as illustrated in Scheme 4. The oxidative addition of trichlorosilane to Ni(0) generates the Ni(II) intermediate **A**.[33] Under reductive conditions, the migratory insertion of the Si–Ni intermediate with the diene produces the π–allylnickel(I) intermediate **B**.[68-70] This intermediate then undergoes intramolecular oxidative addition with Si–Cl, followed by reductive elimination to produce the desired cyclization product.

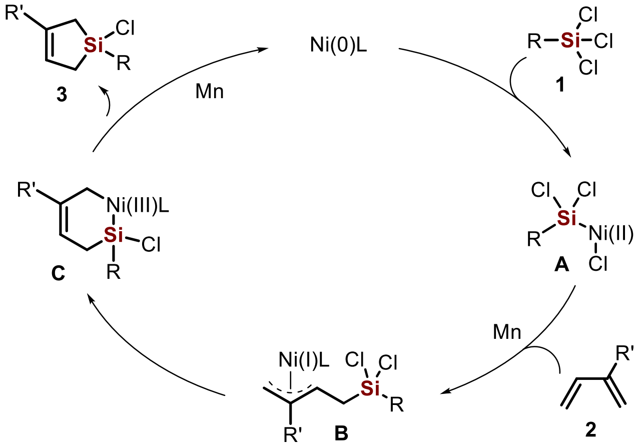


Figure 4. Proposed mechanism

In conclusion, we have established a nickel-catalyzed [4+1] cycloaddition reaction of 1,3–dienes with trichlorosilanes, demonstrating a novel use of trichlorosilanes as Si – 1 synthons in catalytic sila-cycloaddition reactions. This method provides a new pathway for constructing five-membered cyclic chlorosilanes with improved efficiency and high molecular diversity, which has proven challenging in organosilicon and synthetic chemistry. The reaction is facilitated by newly upgraded phosphine-nitrogen ligand, accommodating a wide range of 1,3–diene and trichlorosilane substrates. The resulting cyclic chlorosilanes serve as versatile platform molecules, allowing for further reactions with various nucleophiles and paving the way for a divergent synthetic strategy toward diverse silacarbocycles. The exploration of new reductive C–Si bond-forming reactions of chlorosilanes is ongoing in our laboratory.

Methods

General Procedure. The procedure was conducted in an argon-filled glove box. To a reaction tube equipped with a magnetic stir bar was charged with Ni(COD)$_2$ (2.8 mg, 0.01 mmol), **L10** (20 mol %, 0.02 mmol, 11.7 mg), Mn (-325) (33.6 mg, 3.0 equiv), and Na_2SO_4 (1.9 equiv, 60 mg). Trichlorosilane **1** (0.6 mmol), diene **2** (0.2 mmol), and DMI/hexane (1:9, 2 mL, 0.1 M) were then added in sequence. The reaction tube was sealed and removed from the glove box. The reaction mixture was stirred at 60 °C for 48 h. $LiAlH_4$ (120 mg), hexane (2 mL), and DCM (4 mL) were added at 0 °C. The reaction mixture was stirred at 25 °C for 2 hours. The solvent was removed, and the residue was purified by flash chromatography on silica gel to afford the desired product **4**.

Data availability. The authors declare that all the data supporting the findings of this work are available within the article and its Supplementary Information files or from the corresponding author upon request.

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Competing interests

The authors declare no competing financial interests

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