## EDGE ARTICLE

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# Nickel-catalyzed decarbonylative addition of acylsilanes across alkynes *via* the cleavage of a carbon–silicon bond

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While hydrosilylation, the formal insertion of alkenes or alkynes into an H–Si bond, has been widely developed, analogous transformations involving inert C–Si bonds are rare due to their high bond dissociation energies. Herein, we report a nickel-catalyzed decarbonylative insertion of alkynes into the C–Si bond of acylsilanes, representing a formal insertion into an Ar–Si bond, which has not been previously achieved. Using a bulky N-heterocyclic carbene ligand (IPr*), this reaction enables the stereoselective formation of (Z)-alkenylsilanes from a range of acylsilanes and internal alkynes. This transformation not only expands the synthetic utility of acylsilanes but also illustrates a strategy for structural reprogramming through carbonyl group replacement.

## Introduction

Given the broad utility of organosilicon compounds across diverse fields, including synthetic,[1] materials,[2] and medicinal[3] chemistry, the development of efficient methods for their synthesis remains an active area of research. Hydrosilylation of alkenes or alkynes is one of the most valuable methods for the synthesis of organosilicon compounds, both in academic and industrial settings, owing to its intrinsically high atom economical nature *via* formal insertion into an H–Si bond (Fig. 1A, top).[4] If analogous insertion into a C–Si bond of readily available organosilicon compounds could be achieved, it would offer a powerful strategy to access structurally complex organosilicon molecules from simple precursors with perfect atom economy (hereafter referred to as C–Si insertion; Fig. 1A, bottom). However, in contrast to the relatively weak H–Si bonds in hydrosilanes, C–Si bonds are generally much stronger, posing a significant challenge to the development of such insertion reactions. To date, successful examples of C–Si insertion have been limited to highly reactive organosilicon species, such as strained silacycles,[5] allylsilanes,[6] silyl cyanides,[7] and acylsilanes[8] (Fig. 1B). Only a few examples of insertion into unactivated C–Si bonds have been reported, but they are restricted to intramolecular processes.[9] A key transformation that remains elusive is the intermolecular C–Si insertion of arylsilanes, which would enable the simultaneous introduction

of both an aryl and a silyl group into a C2 unit.[10] While silicon substitution reactions of arylsilanes, wherein the silyl group acts as a leaving group, are well documented,[1c,11] insertion into
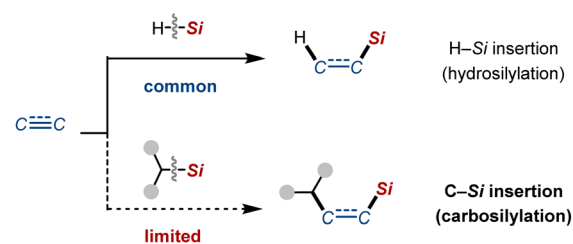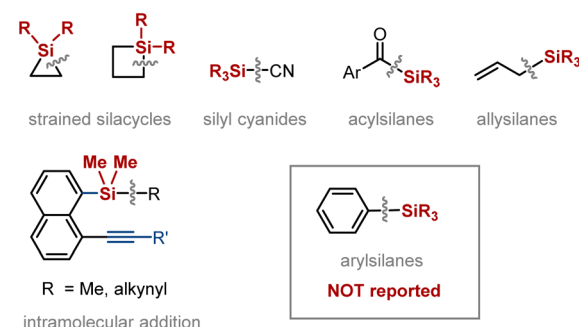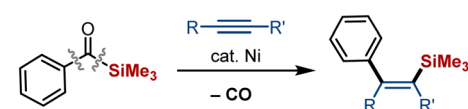


Fig. 1 C–Si insertion: background and this work.

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an Ar–Si bond has not been previously achieved. Herein, we report that this transformation can be formally realized using acylsilanes as arylsilane surrogates via a nickel-catalyzed decarbonylative insertion of alkynes (Fig. 1C).

## Results and discussion

We previously demonstrated that acylsilanes undergo oxidative addition under palladium catalysis, enabling subsequent
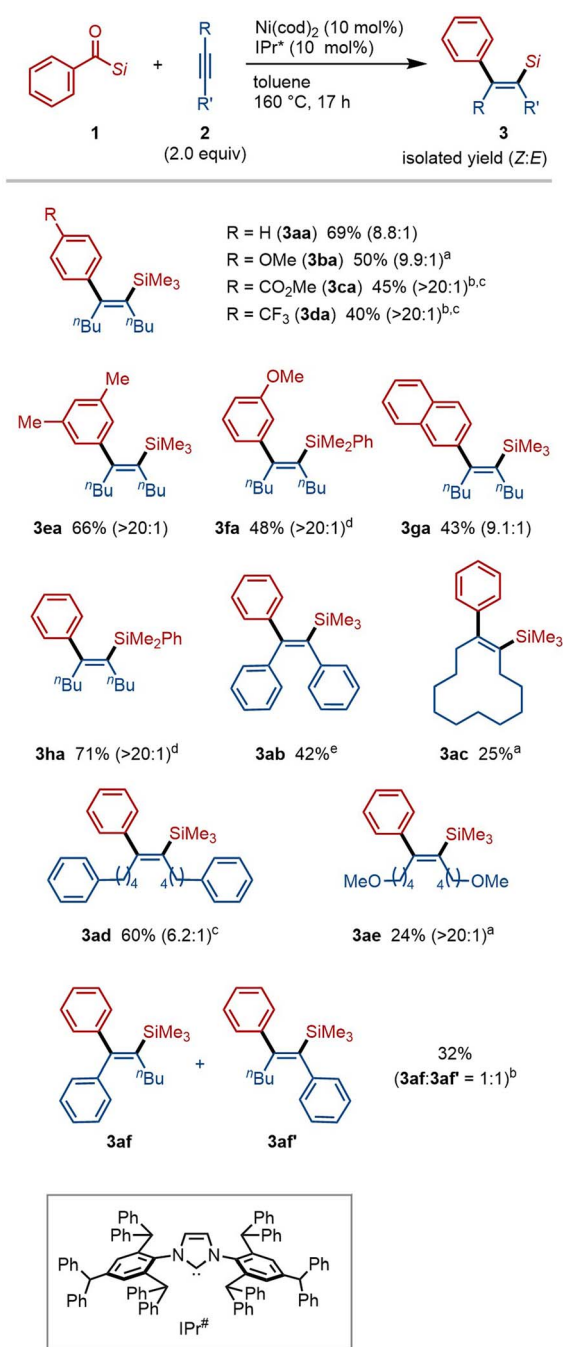


Fig. 2 Scope of Ni-catalyzed decarbonylative addition of acylsilanes across alkynes. [a]IPr[#] was used instead of IPr*. [b]1a (3 equiv.) was used. [c]For 24 h. [d]2a (3 equiv.) was used. [e]1a (5 equiv.) was used.

insertion of allenes[8b] and alkynes,[8c] and that nickel catalysts can promote decarbonylation of acylsilanes.[12] Building on these findings, we hypothesized that nickel catalysis could facilitate decarbonylative C–Si bond insertion upon reaction of acylsilanes with alkenes or alkynes. To evaluate this hypothesis, we first examined the reaction of benzoylsilane (1a, 1.5 equiv.) with 5-decyne (2a) in the presence of Ni(cod)$_2$ (10 mol%) and IPr (10 mol%)—a ligand previously identified as effective for catalytic decarbonylation of 1a (ref. 12a)—in toluene at 160 °C (Table 1). While the decarbonylated product 4 was obtained in 40% yield, the desired C–Si insertion product 3aa was not detected (entry 1). After extensive ligand screening, we found that the use of the more sterically demanding IPr* enabled the formation of 3aa in 26% yield with excellent Z-selectivity (entry 2). In this reaction, byproducts including 4 (11%) and the indene derivative 5aa (ca. 5%)[8c] were also observed. Gratifyingly, the yield of 3aa increased significantly to 69% when the reaction was carried out with 2 equiv. of 2a using IPr* as the ligand (entry 3). These conditions were subsequently employed for exploration of the substrate scope. Notably, the Pd/IPr* catalytic system, which is effective for C–Si insertion without decarbonylation, proved completely ineffective for the formation of 3aa (entry 4).

Having established effective catalyst systems, we next explored the scope of the decarbonylative C–Si insertion of acylsilanes (Fig. 2). A variety of electron-donating and electron-withdrawing groups on the aryl ring of benzoylsilanes were well tolerated, affording the corresponding insertion products with excellent Z-selectivity (3aa–3fa). In addition to aryl groups, a naphthyl substituent could also be employed, enabling the rapid synthesis of π-extended alkenylsilane 3ga. The silicon substituent was not limited to trimethylsilyl (TMS); the more derivatizable dimethylphenylsilyl group was also compatible
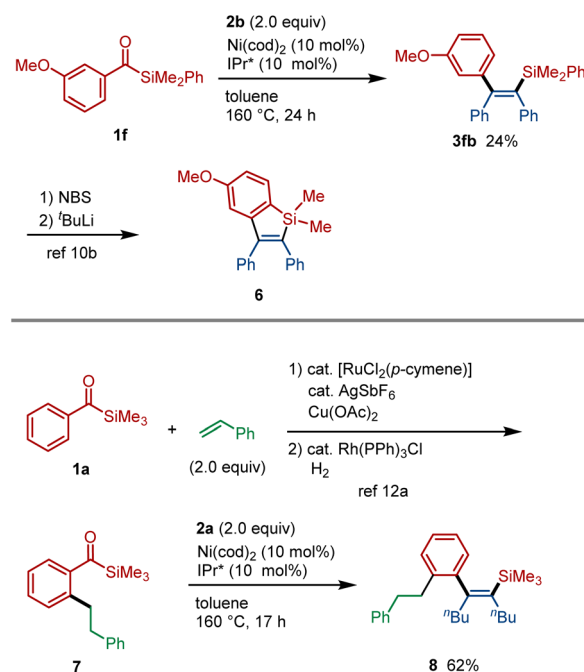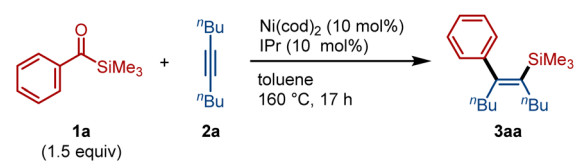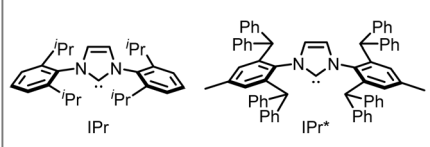


Fig. 3 Synthetic applications.

**Table 1** Ni-catalyzed decarbonylative addition of acylsilane **1a** to alkyne **2a**

| Entry | Deviation from the above conditions | NMR yield[a] (%) | |
|---|---|---|---|
| | | **3aa**[b] | **4** |
| 1 | None | Trace | 40 |
| 2[c] | IPr* instead of IPr | 26 (>20 : 1) | 11 |
| 3[c] | IPr* instead of IPr **1a/2a** = 1/2 | 69 (8.8 : 1)[d] | Trace |
| 4[c] | Pd$_2$(dba)$_3$ instead of Ni(cod)$_2$ IPr* instead of IPr | 0 | 0 |

[a] The yield was determined by $^1$H NMR analysis using 1,1,2,2-tetrachloroethane as an internal standard. [b] The ratio in parentheses refers to the *Z/E* ratio determined by $^1$H NMR. [c] **5aa** was also formed in 3–5% yield. [d] Isolated yield.

(**3fa**, **3ha**). While diphenylacetylene (**2b**) exhibited lower reactivity toward this C–Si insertion reaction, the corresponding product **3ab** was obtained in 42% isolated yield by employing an excess amount (5 equiv.) of **1a**. Various substituted alkynes, including cyclic (**2c**), phenyl-substituted (**2d**), and oxygen-containing aliphatic alkynes (**2e**), successfully underwent the C–Si insertion to furnish the corresponding trisubstituted alkenylsilanes **3ac–3ae**. In the case of the unsymmetrical alkyne **2f**, bearing phenyl and butyl substituents at the termini, a 1 : 1 mixture of regioisomers **3af** and **3af'** was obtained, indicating that aryl and alkyl groups are not distinguished in this nickel-mediated insertion process. Terminal alkynes such as phenylacetylene and 1-octyne did not furnish the desired C–Si insertion products under the current conditions.

The alkenylsilane derivatives synthesized through this C–Si insertion reaction serve as versatile intermediates for further structural elaboration. For instance, alkenylsilane **3fb**, obtained from the nickel-catalyzed reaction of acylsilane **1f** with alkyne **2b**, could be transformed into benzosilole **6**,[10b] a scaffold of interest in organic optoelectronic materials (Fig. 3, top).[2c,d] Beyond enhancing the reactivity of the C–Si bond, the use of acylsilanes as arylsilane surrogates offers notable synthetic advantages. Specifically, the carbonyl group in benzoylsilanes is known to act as an effective directing group for ortho C–H functionalization.[13] For example, simple benzoylsilane **1a** can be converted into the ortho-substituted derivative **7** *via* acylsilane-directed C–H functionalization (Fig. 3, bottom).[14] This intermediate **7** can then undergo the C–Si insertion reaction, enabling the rapid and atom-economical construction of a densely functionalized alkenylsilane **8**.

Several mechanistic experiments were conducted. First, the nickel-catalyzed reaction of phenylsilane **4** with alkyne **2a** under the standard conditions was examined to assess the possible involvement of **4** as an intermediate, since it was observed as a byproduct in the reaction with acylsilane **1a** (Table 1). However, no C–Si insertion product was detected, confirming that **4** cannot act as a substrate in this transformation. Second, a crossover experiment was carried out using two acylsilane derivatives bearing different aryl and silyl groups. As a result, only the two expected C–Si insertion products were obtained, with no evidence of aryl or silyl group scrambling (see the SI for details). These findings indicate that each acylsilane reacts specifically with one alkyne molecule and ligand (aryl or silyl) exchange between nickel intermediates is slow under the present conditions.

## Conclusions

In summary, we have developed a nickel-catalyzed decarbonylative insertion of alkynes into the C–Si bond of acylsilanes, enabling the simultaneous introduction of aryl and silyl groups into unactivated C–C triple bonds. This reaction demonstrates that acylsilanes can serve as surrogates for arylsilanes, thereby formally achieving an otherwise challenging Ar–Si bond insertion. From another perspective, this transformation represents a form of chemical structure reprogramming,[15] in which the carbonyl group of an acylsilane is replaced by a C=C unit. Further studies aimed at expanding this concept of carbonyl group replacement are currently underway in our laboratory.

## Author contributions

Y. M., T. A., T. I., H. F. and M. T. conceived the project. Y. M., T. A., and T. I. performed the experiments. H. F. and M. T. wrote the manuscript. All authors discussed the results and reviewed the final manuscript.

## Conflicts of interest

There are no conflicts to declare.

## Data availability

Additional data and NMR spectra can be found in the supporting information (SI). Supplementary information is available. See DOI: https://doi.org/10.1039/d5sc07524f.

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