Zinc-Catalyzed Synthesis of Allylsilanes via Si–H Bond Insertion of Vinyl Carbenoids Generated from Cyclopropenes

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Abstract: Allylsilanes have long been recognized as valuable building blocks for organic synthesis. In this investigation, we report that zinc-catalyzed reaction of cyclopropenes and hydrosilanes represents a convenient route to these versatile unsaturated organosilanes. In this transformation, ZnBr₂ serves as an efficient catalyst, allowing the generation of a zinc vinyl carbenoid intermediate, which would be subsequently involved in a Si–H bond insertion. The process shows a broad scope, including the use of substituted and functionalized cyclopropenes or the functionalization of polysiloxanes. Moreover, the zinc-catalyzed carbene insertion into a Ge–H bond is reported for the first time.

Organosilanes and siloxanes are widely used as raw chemicals, advanced materials or versatile building blocks in synthetic chemistry. Among them, allylsilanes hold a prevalent position due to their versatile reactivity as alkenes or metal-allyl reagents, among others. Allylsilanes are employed in well-known reactions such as Hiyama[5] or Hosomi-Sakurai reactions,[5,6] and proved useful in complex synthetic targets.[7] Owing to this significance, a variety of methods for the synthesis of allylsilanes have been reported.[8] Among them, metal-catalyzed procedures have emerged as powerful synthetic tools (Scheme 1, top). In particular, transition metal-catalyzed allylic substitutions were found to be very useful.[7] Alternative ways of accessing allylsilanes include palladium-catalyzed silyl-Heck reactions[9] or allene hydroarylations.[10] Although metal-catalyzed insertions of vinyl carbenes into Si–H bonds would enable the synthesis of allylsilanes, to the best of our knowledge, only stabilized vinyldiazoo compounds have been used to access allylsilanes via rhodium(II) vinylcarbenes.[10] Despite these relevant advances, new catalytic methodologies accessing allylsilanes are of great significance.

In the course of our studies focused on the development of zinc-catalyzed transformations involving carbenoid intermediates,[11] we recently reported the ZnCl₂-catalyzed alkene cyclopropanation through vinyl carbenoids generated from cyclopropenes.[11c,12] Continuing with our interest in the catalytic generation of zinc carbenoids and given the relevance of allylsilanes in organic synthesis, we envisioned that zinc-catalyzed reaction of cyclopropenes with hydrosilanes could represent an appealing synthetic route to these versatile building blocks (Scheme 1, bottom). Very likely, this transformation would involve a zinc vinyl carbenoid intermediate, which would evolve to the final products through a Si–H bond insertion, a certainly underexplored process in zinc carbenoid chemistry.[13] Remarkably, this approach makes use of inexpensive catalysts and reagents avoiding by-product formation.

The feasibility of the planned reaction was tested with 3,3-disubstituted cyclopropene 1a, triethylysilane (2a) and various zinc salts as benchmark substrates (Scheme 2). To our delight, treatment of cyclopropene 1a with an excess of silane 2a (6.0 equiv) and ZnCl₂ (10 mol%) (0.1 M, CH₂Cl₂, rt, 4 h) led to β,β-disubstituted allylsilane 3a (85%, NMR yield), thus supporting our initial hypothesis. Subsequent optimization studies showed that the amount of silane could be diminished (1.5 equiv.) when using ZnBr₂ as catalyst at a remarkably low catalyst loading (2 mol%) (0.1 M CH₂Cl₂, rt, 2 h), providing allylsilane 3a in 85% isolated yield (see the Supporting Information for details on the optimization study). Some salient features of this transformation deserve to be highlighted. First, compared with precious metals typically employed in reactions of cyclopropenes involving carbene species (Au, Ru, Rh),[14] inexpensive and low-toxic zinc salts showed superior efficiency. Besides, zinc catalysts exhibited complementarity reactivity to PCl₅, which led to hydroxylation products as previously reported by Gevorgyan and coworkers.[15]
The scope of this reaction was subsequently assessed using optimized reaction conditions as shown in Scheme 3. First, several symmetrical 3,3-dialkylsubstituted cyclopropenes 1a–e were treated with triethylsilane (2a) providing β,β-disubstituted allylsilanes 3a–e in moderate to good yield. Notably, catalyst loading could be reduced to 0.2 mol% without significant erosion in yield for a 10 mmol reaction with cyclopropene 2b (R<sub>1</sub> = R<sub>2</sub> = n-C<sub>6</sub>H<sub>13</sub>), thus demonstrating the scalability of this protocol. Cyclopropene 1f with two different alkyl groups (R<sub>1</sub> = C<sub>9</sub>H<sub>19</sub>; R<sub>2</sub> = Me) installed at the C-3 carbon afforded a allylsilane 3f in good yield (71%) but in moderate selectivity (4:1 mixture of E/Z isomers). In contrast, allylsilane 3g decorated with a bulky adamantyl group was obtained in 80% yield as single E-isomer. Similarly, 3-phenyl-3-methylcyclopropene (3h) was converted into (E)-allylsilane 3h in 71% yield, albeit an excess of silane was required. With respect to hydrosilane partner, the reaction showed a remarkable scope as well (Scheme 3, B). Indeed, the use of cyclopropene 1a along with dimethylphenylsilane (2b) or benzyl(dimethyl)silane (2c) led to the corresponding allylsilanes 3i–j in excellent yields (85% and 97%, respectively). Similarly, diphenylmethylsilane (2d) was converted into allylsilane 3k in a decent 68% isolated yield. Interestingly, the use of sterically encumbered silanes is not a limitation of this protocol as illustrated by the preparation of compounds 3l–m from triphenylsilane (2e) or trisopropylsilane (2f), respectively. Moreover, synthetically valuable supersilane, (TMS)<sub>3</sub>SiH (2g), could also be employed to prepare allylsilane 3n in a remarkable 72% yield. Representative allylsiloxanes 3o–p, which could be used for further functionalization via cross-coupling chemistry, could be obtained with similar efficiency. Dihydro- and trihydrosilanes proved also suitable substrates in this transformation as illustrated by the synthesis of compounds 3q–r, although an excess of the silane was required for selective monoallylation.

Scheme 2. Zinc-catalyzed synthesis of allylsilane 3a using cyclopropene 1a and triethylsilane (2a): Optimized conditions and reactivity comparison with precious metals. See the Supporting Information for details. (IPr = [1,3-bis(2,6-disopropylphenyl)imidazol-2-ylidene]).
Silicon-based materials and polymers are relevant commodities. To highlight the utility of our protocol, we used representative low-molecular weight oligosiloxanes as a demonstration for a feasible polymer functionalization methodology (Scheme 3, C). The simplest substrate (1,1,3,3-tetramethyldisiloxane) was used first, providing the allylsiloxane 3s in 77% isolated yield. More complex commercially available siloxanes were then tested. Representative linear and cyclic polyhydrosiloxanes were functionalized to allylated polymers 3t,u in yields over 80%. Moreover, a hydride-terminated polysiloxane was almost quantitatively converted into the moniallylated 3v (98% NMR yield). Just by controlling the stoichiometry of the reagents, bisallylated polysiloxane 3w could be also prepared in a reasonable yield of 60% (NMR yield). Based on these preliminary results, the functionalization of silicon-based polymers emerges as a promising application of our protocol.

Next, the scope of this transformation was further expanded to 1-substituted cyclopropenes, for which regioselectivity becomes an important issue. As a model, reaction of 1-methyl-substituted cyclopropene 11 with triethylsilane (2a) was studied. Gratifyingly, we found that using an excess of silane (40 equiv), the reaction proceeded in a completely regioselective way affording allylsilane derivative 3x in 86% isolated yield (Eq. 1). The observed regiochemical pattern likely relies on the selective formation of zinc carbenoid intermediate I. Notably, a divergent regiochemical outcome was found when using silyl-substituted cyclopropene derivative 1n with triethylsilane (2a) and mechanistic proposal. (Values are referred to isolated yields).

With this result in hand, we extended the study to cyclopropene derivatives with additional functionalities (Scheme 4). First, we found that amino functionalities were well-tolerated by this protocol. Indeed, zinc-catalyzed reaction of amino-substituted cyclopropene derivatives 1j,k with triethylsilane (2a, 1.5 equiv.) enabled the regioselective synthesis of compounds 4a,b in 63% and 78% yield, respectively (Scheme 4, a). The unusual functionalization of compounds 4 featuring both allylsilane and allylamino moieties is remarkable, offering interesting synthetic opportunities. Next, cyclopropenylcarbinols were evaluated (Scheme 4, b). Unexpectedly, treatment of cyclopropenylcarbinol 11 (R = Ph) under the above reaction conditions (2a, 1.5 equivalents, ZnBr2 2 mol%, CH2Cl2, rt) afforded a complex mixture of products. Gratifyingly, we found that the use of a large excess of triethylsilane (2a, 60 equiv) led selectively to indene derivative 5a in 84% isolated yield. Under similar reaction conditions, cyclopropenylcarbinol 1m (R = Me) furnished indene 5b also in good isolated yield (81%). Again, the combination of indene and allylsilane moieties makes compounds 5 attractive for subsequent transformations.

A mechanistic rationale (Scheme 4, c) for the formation of compounds 4 and 5 should involve the regioselective generation of zinc carbenoid intermediate II. Then, insertion into the Si–H bond would afford allylsilane derivatives 4 (X=NR) and 4’ (X=O).

Whereas allylamines 4 are stable and can be isolated, compounds 4’ would generate allylic cation intermediate III, which in turn would evolve to the final indene derivatives 5 through a Friedel-Crafts-type cyclization.

Notably, a divergent regiochemical outcome was found when using silyl-substituted cyclopropene derivative 1n with triethylsilane (2a) and mechanistic proposal. (Values are referred to isolated yields).

Finally, we also studied the reactivity of cyclopropenes toward heavier group 14 hydrides (Scheme 5). Unfortunately, reactions with (n-Bu)2SnH did not proceed, the starting material being recovered unchanged. In contrast, we found that 3,3-disubstituted cyclopropenes 1a,b (R2 = H) reacted with 1.5 equiv of triethylgermanium hydride (7) to afford the corresponding allylgermanium derivatives 8a,b with an efficiency similar to what was observed in the reaction with silanes. Conversely, the reaction of silyl-substituted cyclopropene derivative 1n with triethylgermanium hydride (7) was more sluggish. Nevertheless, heating a solution of 1n, 7 (10 equiv) and the zinc catalyst (2 mol%) in 1,2-dichloroethane at 70 °C afforded the hybrid
allylgermanesilane 8c in 66% yield. To our knowledge, these results comprise the first zinc-catalyzed carbenoid insertion into Ge–H bonds.

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\begin{align*}
\text{R}^1 \text{R}^1 + \text{HGeEt}_3 & \xrightarrow{\text{ZnBr}_2 (2.0 \text{ mol\% })} \text{CH}_2\text{Cl}_2, \text{rt} \rightarrow \text{R}^1 \text{R}^1 \text{GeEt}_3 \\
(1.5 \text{ equiv})
\end{align*}
\]


In summary, we have developed a catalytic approach to allylsilanes, valuable building blocks in organic synthesis. In this transformation, cyclopropenes serve as the allylic fragment source, via metal vinyl carbeneid intermediates. Relevant features of this protocol are the absence of by-products and the use of an inexpensive zinc salt, which operates at low catalyst loading. The reaction showed a remarkable scope, allowing the development of additional applications such as the functionalization of polymeric siloxanes, the synthesis of highly functionalized allylic derivatives or the synthesis of geminal allyl(bis)silanes. Moreover, the first zinc-catalyzed carbenoid insertion into Ge–H bonds has been herein reported. The potential of zinc catalysis and the use of cyclopropenes as synthetically useful reagents have been highlighted in this work, which might contribute to the development of valuable future applications.

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Keywords: carbenes • cyclopropenes • Si–H bond functionalization • silanes • zinc catalysis


[16] The reaction of cyclopropenes 1a and 1b with deuterated triethysilane (2a–d) under standard conditions afforded the corresponding deuterated products 3a–d and 3b–d with exclusive incorporation of deuterium at the allylic carbon of the allylsilane (>95%). This outcome is consistent with the participation of a zinc vinyl carbeneid, which would be subsequently involved in an insertion reaction. For additional experimental and theoretical discussion, please refer to the Supporting Information.
computational studies supporting the generation of zinc vinyl carbenoid intermediates from cyclopropenes, see ref. 11c.

![Chemical reaction diagram]

1a
1b
2a-d
3a-d (81%)
3b-d (96%)

[17] Reaction of cyclopropene derivative 1b with Et3SiH/Et3SiD (1:1) afforded an almost equimolecular mixture of 3b and 3b-d (kH/kD = 1.08). This result is in agreement with KIE values reported in Rh- and Cu-catalyzed Si-H insertions of carbenes generated from diazoacetates. For example, see: L. A. Dakin, P. C. Ong, J. S. Panek, R. J. Staples, P. Stavropoulos, Organometallics, 2000, 19, 2896.


[19] This regiochemistry has been found in other transition metal-catalyzed transformations of cyclopropenes (see ref. [14] for specific examples). Although this divergent regiochemical outcome deserves further investigations, it could be ascribed to the different ability of alkyl and silyl groups to stabilize the developing partial positive charge on the carbon atoms of the cyclopropene ring in the transition state leading to the corresponding zinc carbene intermediate.
The zinc-catalyzed reaction of cyclopropenes and hydrosilanes represents an efficient, regioselective and atom-economic route to allylsilanes. This Si-H bond functionalization displays a broad scope including functionalized cyclopropenes and oligomeric siloxanes. The process is believed to involve a zinc-vinyl carbenoid species, which would evolve to the final products through insertion into the Si-H bond. This protocol has been successfully extended to the germanium analogs.