

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

Sergio Mata, Luis A. López,* and Rubén Vicente*

Dedication

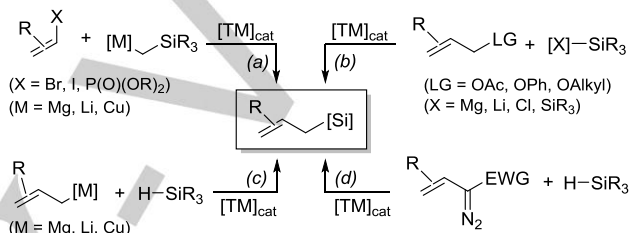
Abstract: Allylsilanes have long been recognized as valuable building blocks for organic synthesis. In this investigation, we report that zinc-catalyzed reaction of cyclopropenes and hydrosilanes represents a convenient route to these versatile unsaturated organosilanes. In this transformation, ZnBr_2 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.^[1] Among them, allylsilanes hold a prevalent position due to an assorted reactivity as alkenes or metal-allyl reagents, among others.^[2] Allylsilanes are employed in well-known reactions such as Hiyama^[3] or Hosomi-Sakurai reactions,^[2,4] and proved useful in complex synthetic targets.^[5] Owing to this significance, a variety of methods for the synthesis of allylsilanes have been reported.^[6] 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^[8] or allene hydrosilylations.^[9] 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 vinyldiazo 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.

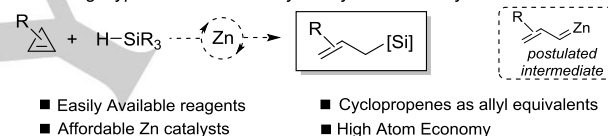
In the course of our studies focused on the development of *zinc-catalyzed transformations involving carbenoid intermediates*,^[11] we recently reported the ZnCl_2 -catalyzed alkene cyclopropanation through zinc vinyl carbenoids generated from cyclopropenes.^[11c,12] Continuing with our interest in the 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.

Transition metal-catalyzed syntheses of allylsilanes



Working Hypothesis: Zinc-catalyzed synthesis of allylsilanes

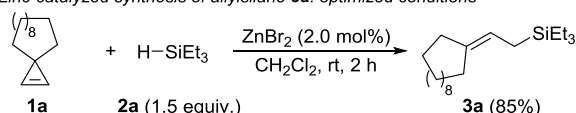
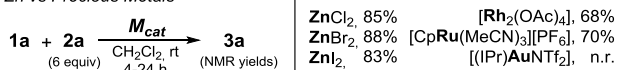


Scheme 1. Common synthetic routes to allylsilanes (top) vs Zinc-catalyzed coupling of cyclopropenes and hydrosilanes (bottom).

The feasibility of the planned reaction was tested with 3,3-disubstituted cyclopropene **1a**, triethylsilane (**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 ZnCl_2 (10 mol%) (0.1 M, CH_2Cl_2 , 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 ZnBr_2 as catalyst at a remarkably low catalyst loading (2 mol%) (0.1 M CH_2Cl_2 , 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 complementary reactivity to PtCl_2 , which led to hydrosilylation products as previously reported by Gevorgyan and coworkers.^[15]

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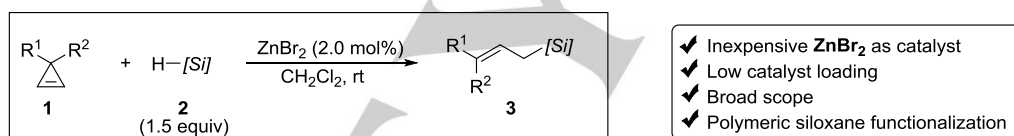
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■ Zinc-catalyzed synthesis of allylsilane **3a**: optimized conditions■ Zn vs Precious Metals ^[a]

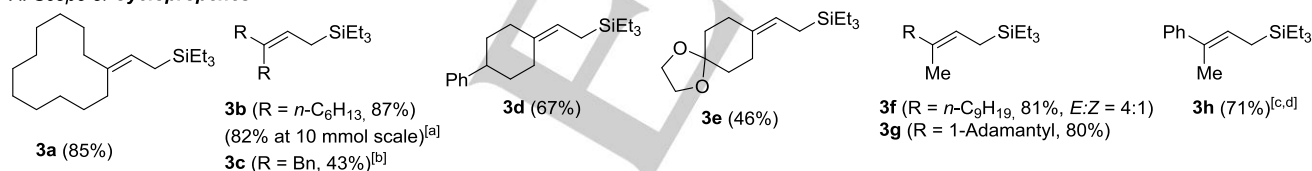
Scheme 2. Zinc-catalyzed synthesis of allylsilane **3a** using cyclopropene **1a** and triethylsilane (**2a**): Optimized conditions and reactivity comparison with precious metals. ^[a] See the Supporting Information for details. (IPr = [1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene]).

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.^[16, 17] Notably, catalyst loading could be reduced to 0.2 mol% without significant erosion in yield for a 10 mmol reaction with cyclopropene **2b** ($R^1 = R^2 = n\text{-C}_6\text{H}_{13}$), thus demonstrating the scalability of this protocol. Cyclopropene **1f** with two different alkyl groups ($R^1 = \text{C}_9\text{H}_{19}$; $R^2 = \text{Me}$) installed at the C-3 carbon afforded allylsilane **3f** in good

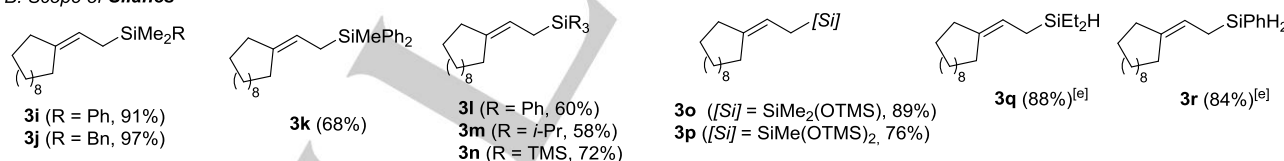
yield (71%) but in moderate selectivity (4:1 mixture of *E/Z* isomers). In contrast, allylsilane **3g** decorated with a bulky adamantyl group was obtained in 80% yield as single *E*-isomer. Similarly, 3-phenyl-3-methylcyclopropene (**3h**) was converted into (*E*)-allylsilane-**3h** in 71% yield, albeit 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 benzyldimethylsilane (**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 triisopropylsilane (**2f**), respectively. Moreover, synthetically valuable supersilane, (TMS)₃SiH (**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.



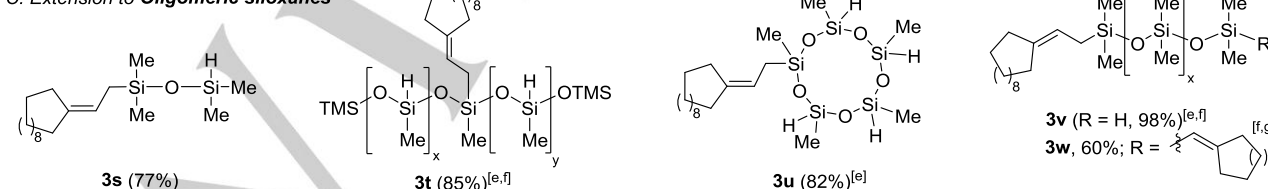
A. Scope of Cyclopropenes



B. Scope of Silanes



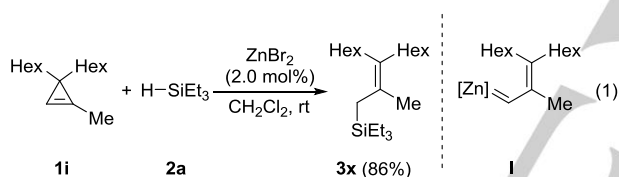
C. Extension to Oligomeric siloxanes



Scheme 3. Zinc-catalyzed reaction of cyclopropenes **1** and silanes **2**: Scope. Values are referred to isolated yields. d.r. was determined by ¹H NMR. ^[a] Using 0.2 mol% of ZnBr₂. ^[b] Reaction run at 50 °C. ^[c] Using 20 equiv. of the **2a**. ^[d] The formation of a cyclopropene dimer side-product was also observed (See Supporting Information). ^[e] With 6 equiv. of the corresponding silane. ^[f] Yields estimated by ¹H NMR using CH₂Br₂ as internal standard. ^[g] Using 2.2 equiv. of **1a** with respect to the siloxane.

Silicon-based materials and polymers are relevant commodities.^[18] 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 monoallylated **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 **1i** 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**.^[19]

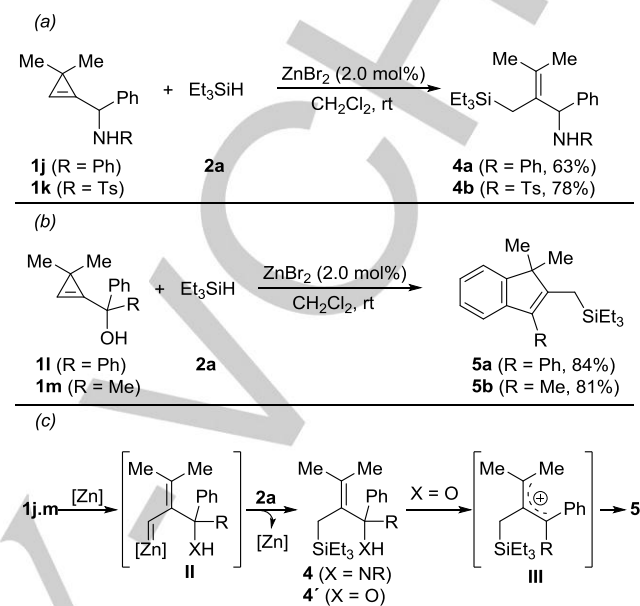


With this result in hand, we extended the study to cyclopropene derivatives with additional functionalities (Scheme 4). First, we found that amino functionalities were well-tolerated by this protocol. Indeed, zinc-catalyzed reaction of amino-substituted cyclopropene derivatives **1j,k** with triethylsilane (**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 allylamine moieties is remarkable, offering interesting synthetic opportunities.

Next, cyclopropenylcarbinols were evaluated (Scheme 4, b). Unexpectedly, treatment of cyclopropenylcarbinol **1l** ($\text{R} = \text{Ph}$) under the above reaction conditions (**2a**, 1.5 equivalents, ZnBr_2 2 mol%, CH_2Cl_2 , 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** ($\text{R} = \text{Me}$) furnished indene **5b** also in good isolated yield (81%). Again, the combination of indene and allylsilane moieties makes compounds **5** attractive for subsequent transformations.

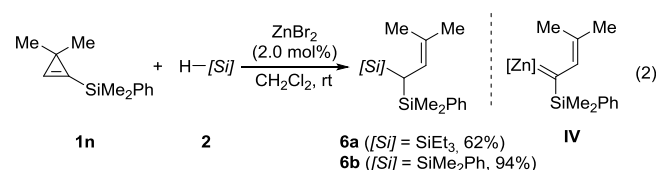
A mechanistic rationale (Scheme 4, c) for the formation of compounds **4** and **5** should involve the regioselective generation of zinc carbenoid intermediate **II**.^[19] Then, insertion into the Si–H bond would afford allylsilane derivatives **4** ($\text{X} = \text{NR}$) and **4'** ($\text{X} = \text{O}$).

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.



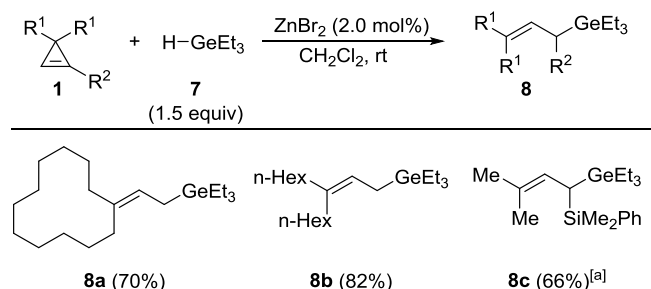
Scheme 4. Zinc-catalyzed reactions of functionalized cyclopropenes **1j-m** with triethylsilane (**2a**) and mechanistic proposal. (Values are referred to isolated yields).

Notably, a divergent regiochemical outcome was found when using silyl-substituted cyclopropene derivative **1n** (Eq. 2). Indeed, its reaction with triethylsilane (**2a**) and dimethylphenylsilane (**2b**) led to geminal bis(silane) products **6a** and **6b** in 62 and 94% yield, respectively. This process is believed to proceed through zinc silylcarbenoid intermediate **IV**.^[20] Compounds **6** seem particularly well suited for the development of new synthetic applications based on allylsilane chemistry.



Finally, we also studied the reactivity of cyclopropenes toward heavier group 14 hydrides (Scheme 5). Unfortunately, reactions with $(n\text{-Bu})_3\text{SnH}$ did not proceed, the starting material being recovered unchanged. In contrast, we found that 3,3-disubstituted cyclopropenes **1a,b** ($\text{R}^2 = \text{H}$) 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.



Scheme 5. First zinc-catalyzed allylation of germanium hydrides via Ge–H bond insertion. (Values are referred to isolated yields). ^[a] Reaction run in 1,2-dichloroethane at 70 °C using 10 equivalents of **7**.

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 carbenoid 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.

Acknowledgements

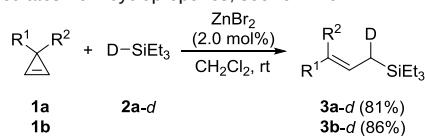
Financial support from Ministerio de Economía y Competitividad (MINECO), Agencia Estatal de Investigación (AEI) and Fondo Europeo de Desarrollo Regional (FEDER) (grants CTQ2013-41511-P, CTQ2016-76840-R and “Ramón y Cajal” Grant to R.V.) and Principado de Asturias (grant GRUPIN14-013 and Severo Ochoa PhD grant to S. M.) is gratefully acknowledged. We thank Prof. J. M. González for his support.

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

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computational studies supporting the generation of zinc vinyl carbenoid intermediates from cyclopropenes, see ref. 11c.



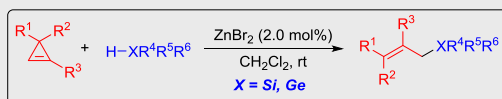
- [17] Reaction of cyclopropene derivative **1b** with Et₃SiH/Et₃SiD (1:1) afforded an almost equimolecular mixture of **3b** and **3b-d** (*k_H/k_D* = 1.08). This result is in agreement with KIE values reported in Rh- and Cu-catalyzed Si-H insertions of carbenes generated from diazoacetates. For example, see: L. A. Dakin, P. C. Ong, J. S. Panek, R. J. Staples, P. Stavropoulos, *Organometallics*, **2000**, 19, 2896).
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- [19] This regiochemistry has been found in other transition metal-catalyzed transformations of cyclopropenes (see ref. [14] for specific examples).
- [20] 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.

Entry for the Table of Contents (Please choose one layout)

COMMUNICATION



- ✓ Inexpensive ZnBr_2 as catalyst
- ✓ High regioselectivity
- ✓ Broad scope
- ✓ Polymeric siloxane functionalization

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

The zinc-catalyzed reaction of cyclopropenes and hydrosilanes represents an efficient, regioselective and atom-economical 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.