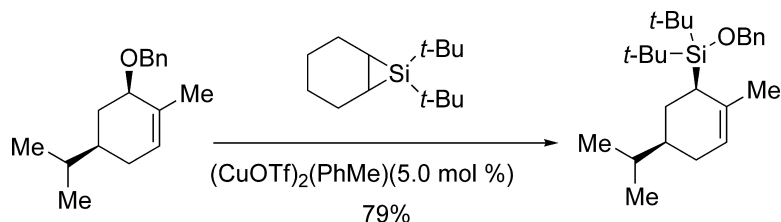


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Metal-Catalyzed Silylene Insertions of Allylic Ethers: Stereoselective Formation of Chiral Allylic Silanes

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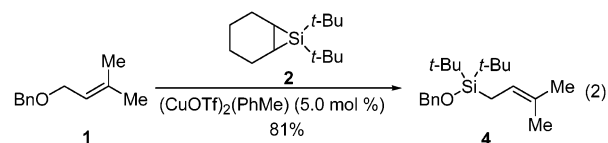
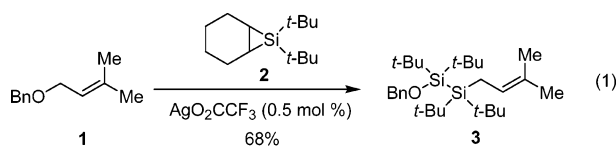
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Because silylenes (SiR_2) are highly reactive low-oxidation state intermediates, they insert readily into σ -bonds to form tetravalent silanes.¹ The most common examples of silylene insertions involve O–H bonds,^{2–5} Si–H bonds,^{3,6} S–H bonds,⁷ C–Cl bonds,^{4,8–10} and metal–hydrogen bonds.¹¹ More recent examples include silylene insertions into activated C–H bonds.^{12–14} Metal-catalyzed silylene insertions have not been reported.^{15,16}

In this Communication, we describe metal-catalyzed silylene insertion reactions into allylic and benzylic C–O bonds. Stereochemical studies indicate that it should be possible to prepare optically active allylic silanes by insertion into optically active allylic alcohols. Consequently, this transformation may be useful in stereoselective synthesis because chiral allylic silanes are synthetically valuable,¹⁷ but they are challenging to prepare.^{18–23}

The insertion of a silylene into an allylic C–O bond was first observed during investigations of silylene transfer to alkenes containing protected hydroxyl groups.²⁴ Treatment of allylic ether **1** with 2 equiv of cyclohexene silacyclopropane **2** and a catalytic amount of AgO_2CCF_3 yielded a product where two di-*tert*-butylsilylene (*t*- Bu_2Si) groups were inserted into the allylic C–O bond to form allylic disilane **3** (eq 1).²⁵ A screen of metal salts known to catalyze silylene transfer to alkenes²⁶ showed that copper(I) triflate promoted the insertion of a single *t*- Bu_2Si moiety to give allylic silane **4** (eq 2). The longer reaction times and lower reactivity associated with this catalyst suggest that the proposed copper–silylenoid intermediate²⁷ operated in a manner distinct from its silver counterpart.²⁶



A variety of protected allylic alcohols were subjected to the reaction conditions to provide silylene insertion products (eq 3, Table 1). The silylene C–O insertion reaction tolerated 1,2-disubstituted and trisubstituted alkenes, substitution at the allylic position of the substrate, and a variety of protecting groups on the alcohol functionality. Secondary allylic alcohols inserted a single silylene unit, even with a silver catalyst (Table 1, entry 1). Geminally disubstituted terminal alkenes underwent insertion followed by a [2,3]-sila-Wittig rearrangement,^{21,28} probably because of significant steric effects at the allylic carbon (entry 4). When the substrate had no alkene moiety, the *t*- Bu_2Si fragment inserted into the C–O bond of the benzyl protecting group instead (entry

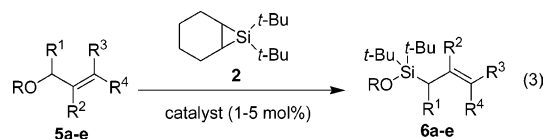
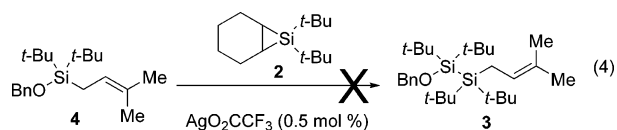


Table 1. Silylene Insertion into C–O Bonds

Entry	Substrate (5)	Product (6)	Catalyst	Yield
1			AgO_2CCF_3	74%
2			$(\text{CuOTf})_2(\text{PhMe})$	72%
3			$(\text{CuOTf})_2(\text{PhMe})$	67%
4			$(\text{CuOTf})_2(\text{PhMe})$	63%
5			AgO_2CCF_3	65%

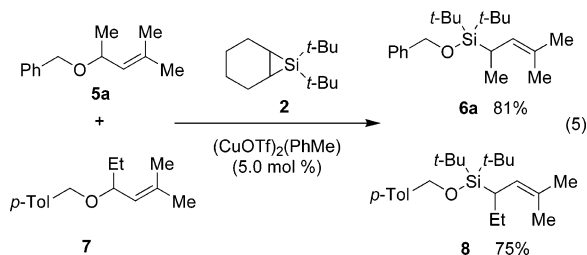
5). The reactions of monosubstituted alkenes did not result in silylene insertion but instead led to formation of silacyclopropane products.²⁹

Control experiments determined that the formation of allylic disilane **3** did not proceed by two sequential insertions. When the single *t*- Bu_2Si insertion product **4** was subjected to the reaction conditions (eq 4), the starting material was recovered unchanged after 12 h. This experiment suggests that sequential insertion of two *t*- Bu_2Si units cannot be responsible for the generation of allylic disilane **3**.

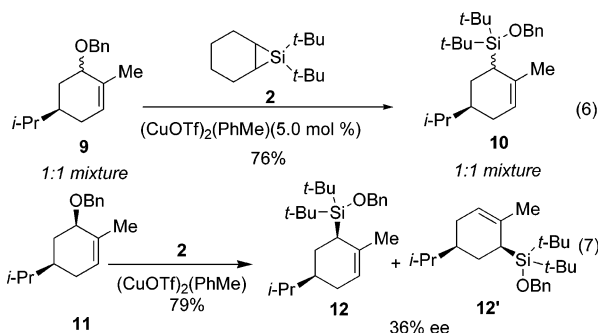


A crossover experiment demonstrated that silylene insertion is intramolecular with respect to the allylic ether. Treatment of a mixture of benzyl-protected allylic ether **5a** and *p*-tolyl-protected allylic ether **7** to the reaction conditions did not provide crossover products (eq 5).³⁰ The results of this experiment indicate that little or no dissociation of the alkoxy group from the unsaturated carbon framework occurred.

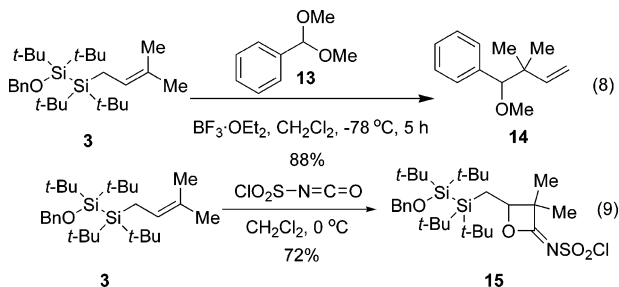
Stereochemical studies provided insight into the mechanism of silylene insertion. Silylene insertion into a 1:1 mixture of *cis* and *trans* diastereomers of allylic ether **9** led to a 1:1 mixture of allylic silane products (eq 6). The reaction of *cis* allylic ether **11** resulted in the sole formation of a *cis*-substituted allylic silane (eq 7).³¹ X-ray



crystallography and analysis of chiral esters demonstrated that the product was enantiomerically enriched, but it was a mixture of enantiomeric silanes **12** and **12'**.³² The observation of only cis products indicates that formation of the new C–Si bond occurs exclusively on the same face as the C–O bond that is broken. The loss of enantiomeric purity shows that some, but not complete, allylic transposition occurred. The retention of facial selectivity, the evidence of some allylic transposition, and the intramolecularity of the insertion are all consistent with a [1,2]-Stevens rearrangement of an oxonium ylide.^{33–35} These observations, along with the lack of allylic transposition in several cases (such as entries 1 and 3 of Table 1), are inconsistent with a [2,3]-sila-Wittig reaction, which would require retention of enantiopurity.^{36,37}



Although the reactivity of the allylic silanes has been thoroughly investigated,¹⁷ the reactivity of allylic disilanes such as those formed in eq 1 are not well-documented.^{38,39} Our results show that these disilanes react with electrophiles just as allylic silanes do. Allylic disilane **3** reacted with benzaldehyde dimethyl acetal (**13**) to afford allylated product **14** (eq 8). The annulation of allylic disilane **3** and *N*-chlorosulfonyl isocyanate⁴⁰ provided *N*-chlorosulfonyl β -iminolactone **15** (eq 9).



In summary, allylic ethers undergo metal-catalyzed silylene insertion to provide allylic silanes and disilanes. This transformation occurs on the same face of the allylic alcohol, leading to the formation of enantiomerically enriched products from optically pure allylic alcohols. Allylic disilanes exhibit similar reactivity to allylic silanes, undergoing allylation and annulation reactions.

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Supporting Information Available: Experimental procedure, spectroscopic, analytical, and X-ray data for the products (PDF, CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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