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$B(C_6F_5)_3$-Catalyzed Hydrosilylation of Vinylcyclopropanes

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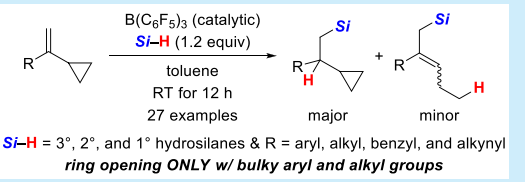
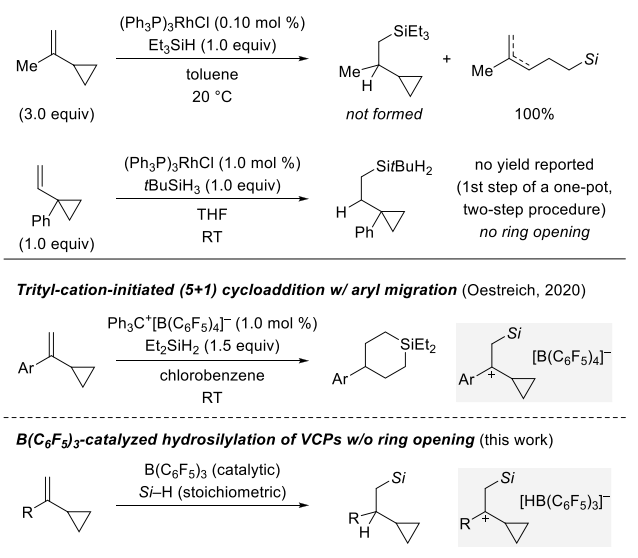
ABSTRACT: A hydrosilylation of vinylcyclopropanes (VCPs) catalyzed by the strong boron Lewis acid $B(C_6F_5)_3$ is reported. For the majority of VCPs, little or no ring opening of the cyclopropyl unit is observed. Conversely, for VCPs with bulky R groups, such as ortho-substituted aryl rings or branched alkyl residues, ring opening is the exclusive reaction pathway. This finding is explained by the thwarted hydride delivery to a sterically shielded, β-silicon-stabilized cyclopropylcarbinyl cation intermediate.



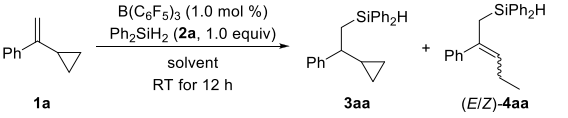
The rhodium-catalyzed hydrosilylation of vinylcyclopropanes (VCPs)[1] typically results in the opening of the cyclopropyl group[2] with the exception of an isolated example[3] (Scheme 1, top). A recent report on an iron-catalyzed hydrosilylation also includes a VCP with an internal double bond where the cyclopropyl unit has remained intact (not shown).[4] We recently found that VCPs undergo an unusual (5 + 1) cycloaddition when subjected to trityl-cation-initiated and subsequent silylium-ion-propagated hydrosilylation (Scheme 1, middle).[5] The reaction commences with the formation of the corresponding β-silicon-stabilized[6] cyclopropylcarbinyl cation (gray box). Because the hydrosilane is a poor hydride donor, this intermediate engages in various bond reorganizations. We wondered whether that same carbenium ion could be captured by a different hydride source and therefore turned toward the known $B(C_6F_5)_3$-catalyzed hydrosilylation of alkenes[7] (Scheme 1, bottom).[8] We report here an ionic[9] hydrosilylation of VCPs that predominantly affords the conventional products, that is, with little or no ring opening.[10]

Scheme 1. Rhodium-Catalyzed Hydrosilylation of VCPs and Planned $B(C_6F_5)_3$-Catalyzed Hydrosilylation



A brief optimization of a model reaction showed that the $B(C_6F_5)_3$-catalyzed hydrosilylation indeed proceeds with hardly any opening of the cyclopropyl ring (Table 1). With 1.0 mol % of $B(C_6F_5)_3$ at room temperature, VCP **1a** reacted with dihydrosilane **2a** to mainly give product **3aa** in various solvents. Arene solvents as well as polar aprotic solvents worked well (entries 1–4), whereas the yield was low in a hydrocarbon solvent (entry 5). The amount of ring-opened **4aa** was usually <10%, and the highest yield of **3aa** was

Table 1. Selected Examples of the Optimization[a]



entry	solvent	yield of **3aa** (%)[b]	yield of (*E*)-**4aa** (%)[b]	yield of (*Z*)-**4aa** (%)[b]
1	benzene	85	7	<5
2	toluene	93	7	<5
3	chlorobenzene	73	6	<5
4	CH_2Cl_2	89	11	<5
5	*n*-hexane	23	<5	<5

[a]All reactions were performed on a 0.15 mmol scale. [b]Yields were determined by ^1H NMR spectroscopy using CH_2Br_2 as an internal standard.

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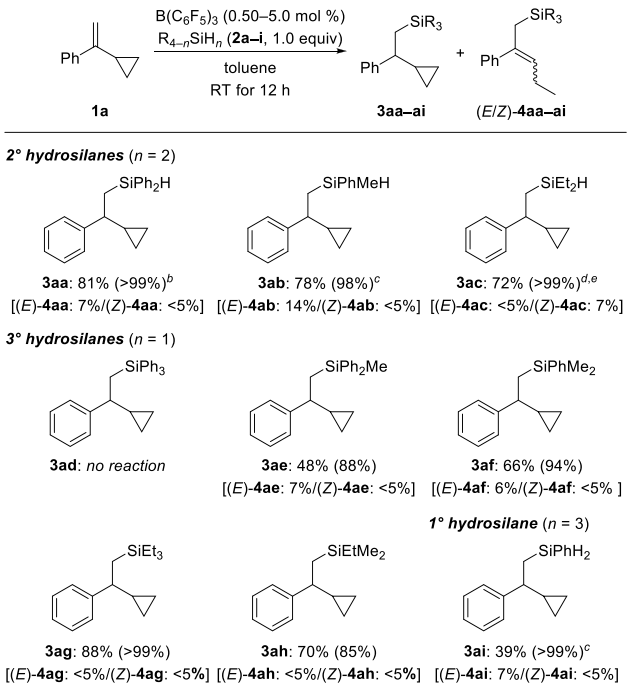
obtained in toluene. A catalyst loading of 0.50 mol % resulted in a decreased yield (76% instead of 93%).

A broad range of hydrosilanes could be employed in this reaction (Scheme 2). Other dihydrosilanes reacted in good

Scheme 2. Scope I: Variation of the Hydrosilane[a]

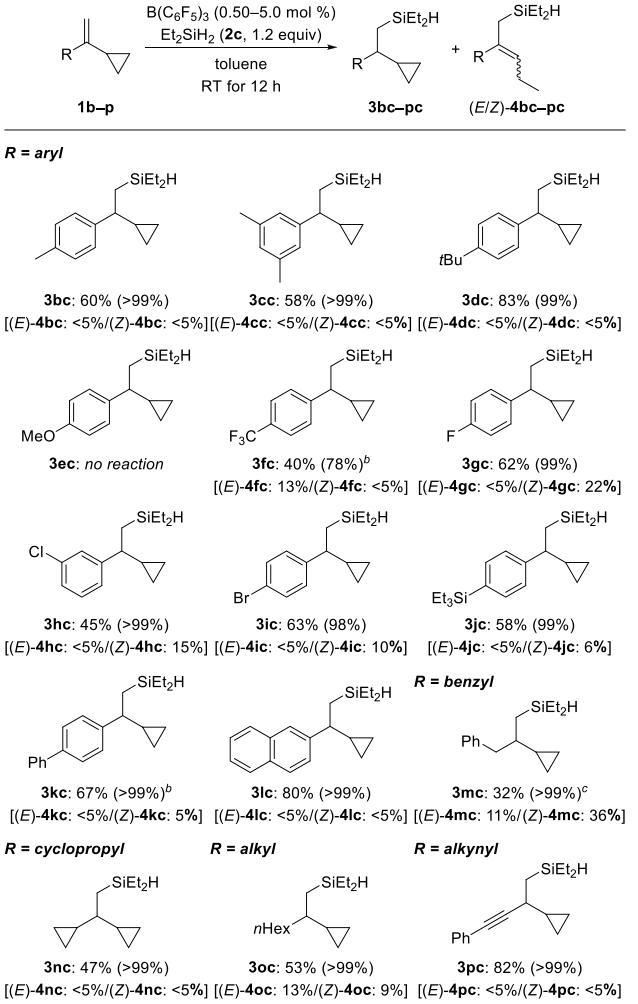


[a]Unless otherwise noted, reactions were performed using 5.0 mol % of $B(C_6F_5)_3$. The conversion in parentheses and the distribution of ring-opened byproducts in square brackets were determined by NMR analysis. Yields are of analytically pure material obtained after flash chromatography on silica gel. [b]1.0 mol % of $B(C_6F_5)_3$. [c]2.0 mol % of $B(C_6F_5)_3$. [d]0.50 mol % of $B(C_6F_5)_3$. [e]75% (99%) along with <5% of ring-opened products obtained on a 1.0 mmol scale.

yields: 81% for Ph_2SiH_2 (**2a**), 78% for $MePhSiH_2$ (**2b**), and 72% for Et_2SiH_2 (**2c**). In turn, the success with monohydrosilanes was dependent on their steric demand. No reaction was seen with Ph_3SiH (**2d**), but mixed alkyl/aryl-substituted derivatives did convert; isolated yields were 48 and 66% with $MePh_2SiH$ (**2e**) and Me_2PhSiH (**2f**), respectively. According to this trend, fully alkyl-substituted Et_3SiH (**2g**) and $EtMe_2SiH$ (**2h**) brought about even higher yields. The trihydrosilane $PhSiH_3$ (**2i**) furnished the product in 39% yield.

We continued the study with Et_2SiH_2 (**2c**) to assess the substrate scope (Scheme 3). Aside from a few exceptions, electronically modified aryl-substituted VCPs **1b–l** reacted in moderate to good yields. Electron-rich **1e** with an OMe group in the para position did not participate, likely because of Lewis pair formation with the catalyst. Yields were generally lower for VCPs with electron-deficient aryl groups, and the CF_3-substituted congener **1f** did not fully convert, even with an increased catalyst loading of 5.0 mol %. We attribute this to the poorer stabilization of the carbenium-ion intermediate. Also, the formation of the ring-opened product became competitive in these cases. Several other R groups were tolerated: benzyl, as in **1m**, cyclopropyl, as in **1n**, primary alkyl, as in **1o**, and alkynyl, as in **1p**, underwent the hydrosilylation in reasonable yields. However, the hydrosilylation of benzyl- and *n*-hexyl-substituted VCPs **1m** and **1o** was accompanied by substantial

Scheme 3. Scope II: Variation of the VCP in the Hydrosilylation with Et_2SiH_2[a]



[a]Unless otherwise noted, reactions were performed using 0.50 mol % of $B(C_6F_5)_3$. The conversion in parentheses and the distribution of ring-opened byproducts in square brackets were determined by NMR analysis. Yields are of analytically pure material obtained after flash chromatography on silica gel. [b]5.0 mol % of $B(C_6F_5)_3$. [c]3.0 mol % of $B(C_6F_5)_3$.

ring opening (32% of **3mc** along with 47% **4mc** and 53% of **3oc** along with 22% **4oc**, respectively). VCPs with internal double bonds did not react.

The above substrate selection is biased in the sense that it does not include any sterically hindered VCPs. The reason for this is that these do exclusively follow the ring-opening pathway (Scheme 4). VCPs having an ortho-substituted aryl or an α-naphthyl group, as in **1q–s**, as well as a branched alkyl group, as in **1t**, do not produce any of the conventional hydrosilylation product **3**. The ring-opening products **4** were formed in moderate yields throughout. Moreover, the same observation was made for VCP **1u** with a quaternary carbon atom ($R' \neq H$). We think that steric shielding of the β-silicon-stabilized cyclopropylcarbinyl cation intermediate thwarts the hydride delivery from the borohydride.

To support the assumed intermediacy of a β-silicon-stabilized cyclopropylcarbinyl cation (cf. Scheme 1, gray box), we conducted deuterium-labeling experiments with two representative VCPs (Scheme 5, top). With Et_3SiD (**2g**-d_1),

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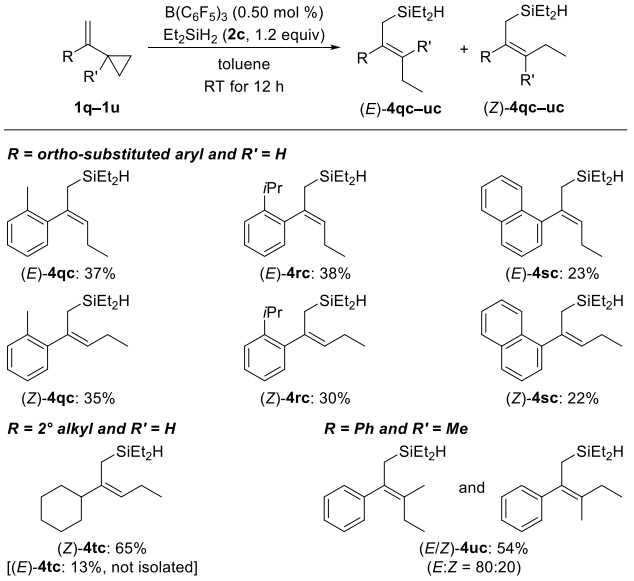
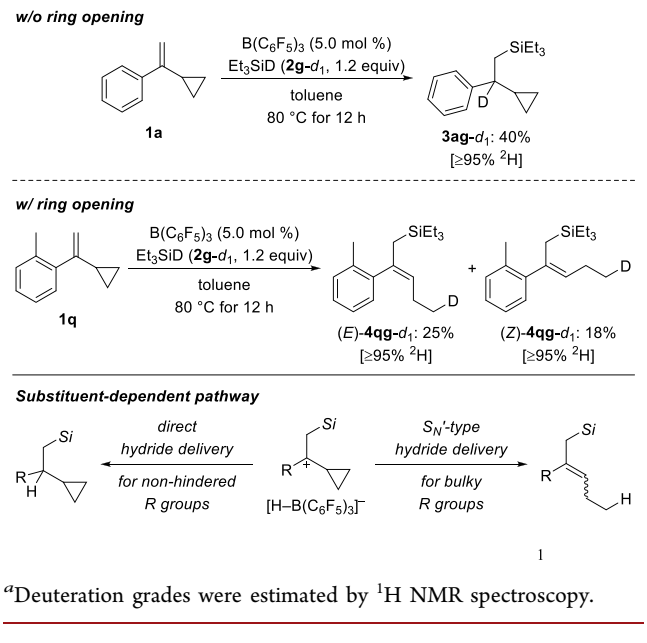
Org. Lett. XXXX, XXX, XXX–XXX

Scheme 4. Scope III: VCPs Undergoing Ring Opening in the Hydrosilylation with Et_2SiH_2[a]



[a]Yields are of analytically pure material obtained after flash chromatography on silica gel. Unless otherwise noted, alkene isomers have been quantitatively separated.

Scheme 5. Deuterium-Labeling Experiments and Simple Mechanistic Picture[a]



[a]Deuteration grades were estimated by ^{1}H NMR spectroscopy.

nonhindered **1a** converted cleanly to **3ag**-d_1 in 40% yield, and ortho-substituted **1q** afforded **4qg**-d_1 as a mixture of diastereomers in 43% overall yield. The low yields indicate significant kinetic isotope effects in these reactions,[7,11] and k_H/k_D was determined to be 2.85 for the former (see the Supporting Information for details). These outcomes are in agreement with the assumed reaction mechanism where the steric demand of the R group governs the hydride delivery (Scheme 5, bottom).

In summary, we have described here a reliable protocol for the hydrosilylation of VCPs with little or no opening of the cyclopropyl ring. The limitations of the new method have been gauged, and the functional-group tolerance is acceptable, given that catalysis with $B(C_6F_5)_3$/hydrosilane combinations is often not compatible with oxygen Lewis-basic sites.[8]

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c02751.

General procedures, experimental details, characterization, and spectral data for all new compounds (PDF)

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Notes

The authors declare no competing financial interest.

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