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Mechanistic Insights into Grubbs-Type Ruthenium-Complex-Catalyzed Intramolecular Alkene Hydrosilylation: Direct σ-Bond Metathesis in the Initial Stage of Hydrosilylation

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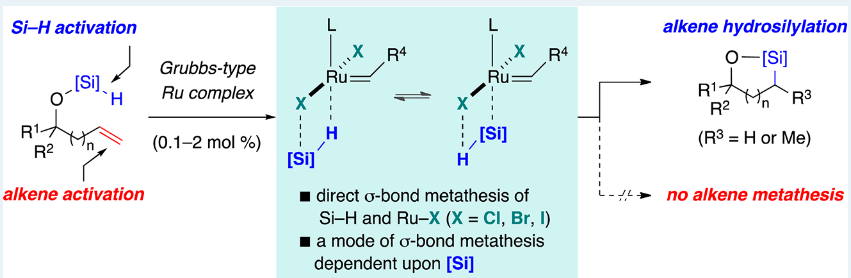
Supporting Information



ABSTRACT: Grubbs-type ruthenium-complex-mediated intramolecular alkene hydrosilylation of alkenylsilyl ethers has been developed to provide cyclic silyl ethers with high regioselectivity. This non-metathetical use of such ruthenium complexes for alkene hydrosilylation via preferential Si−H bond activation over alkene activation is notable, where the competing alkene metathesis dimerization was not detected. In addition to the synthesis of organosilicon heterocycles from readily available olefins, this study provides fundamental mechanistic insights into the non-metathetical function of Grubbs-type ruthenium catalysts. In the initial stage of hydrosilylation within a ruthenium coordination sphere, evidence for activation of a ruthenium complex by direct σ-bond metathesis between Si−H and Ru−Cl via a four-centered transition state is presented. This study counters the traditionally accepted Chauvin-type mechanism, specifically the addition of R_3Si−H across the π-bond of a Ru-benzylidene.

KEYWORDS: *ruthenium, alkene hydrosilylation, metathesis, silane, σ-bond metathesis*

Olefin metathesis is a revolutionary technology for olefin synthesis through a highly efficient C−C bond-forming reaction. In particular, ruthenium-catalyzed olefin metathesis is among the most powerful olefination processes due to the stability of catalysts, high reactivity, and broad functional group compatibility.[1] New discoveries stemming from non-metathetical applications of Grubbs-type ruthenium complexes have led to the development of new synthetic strategies in parallel.[2] The instructive non-metathetical use of Grubbs-type catalysts for intermolecular alkyne hydrosilylation has been reported by the Cox,[3] Lee,[4] and Cossy[5] laboratories. However, Grubbs-type ruthenium-complex-catalyzed alkene hydrosilylation to provide cyclic silyl ethers has not been reported to date.

Metal-catalyzed alkene hydrosilylation,[6] an addition reaction of silicon−metal hydride across a carbon−carbon double bond, is an important homogeneous catalytic process used to produce not only versatile silicon-containing synthetic intermediates[7−9] but also functionalized materials[10] and medicinally useful molecules[11] from readily available hydrocarbon alkene feedstock. We wondered if Grubbs-type ruthenium complexes can effectively promote intramolecular alkene hydrosilylation of alkenylsilyl ethers **1** via preferential Si−H bond activation,[12] over alkene activation, to selectively afford cyclic silyl ethers such as **2** or **3** (Scheme 1). The challenge of such processes would be associated with (i) inferior reactivity of alkenes to alkynes toward ruthenium catalysts, which are largely less reactive toward hydrosilylation than other late transition metal catalysts,[13] and (ii) more importantly the potential cross-metathesis of **1** via alkene activation to afford homocoupled products **4** and **5**. Due to the paucity of mechanistic studies (e.g., isotope-labeling experiments, reaction kinetic studies, and spectroscopic observations), the origin of the reactivity and selectivity of such processes is elusive. The regio- and diastereoselectivity remain uncertain. Nonetheless, the outcome of this process has merit by virtue of silicon functionality, which allows further elaboration.[8,14,15] Herein, we report Grubbs-type ruthenium-complex-catalyzed regioselective intramolecular alkene hydrosilylation of alkenyl silyl ethers, unveiling mechanistic insights into the process.

To demonstrate the feasibility of Grubbs-type ruthenium-complex-catalyzed alkene hydrosilylation and relieve our concern regarding the competing alkene metathesis dimerization, several ruthenium catalysts were examined (Table 1). At ambient temperature, the reaction using **Ru-1** (first-generation Grubbs catalyst) did not proceed, and homoallyl silyl ether **1a**

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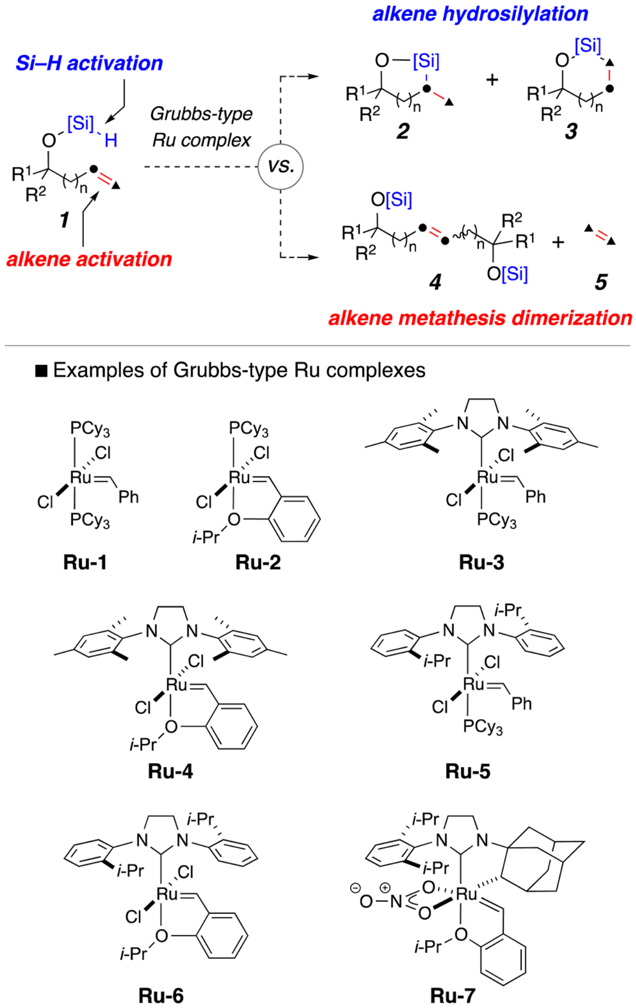
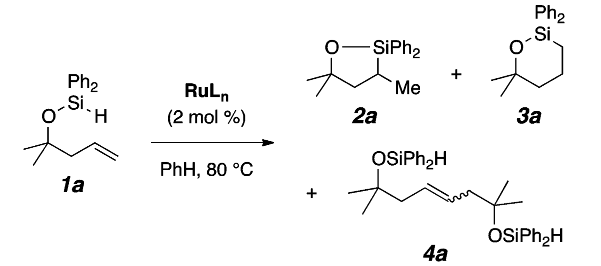
Scheme 1. Intramolecular Alkene Hydrosilylation vis-à-vis Homo-crossed Alkene Metathesis Dimerization Using a Grubbs-Type Ruthenium Complex



was cleanly recovered. However, we were able to observe the formation of oxasilacyclopentane **2a** via a 5-*exo-trig* hydrosilylative cyclization by exploiting **Ru-2** (first-generation Hoveyda–Grubbs catalyst),[16] which indicates the viability of Si–H bond activation (ca. 20% conversion for 7 days). Among the seven ruthenium catalysts examined, **Ru-2** was identified as the most effective catalyst, permitting intramolecular alkene hydrosilylation of **1a** to afford **2a** (73–85% in tetrahydrofuran (THF), entries 5–7). A low catalyst loading of **Ru-2** (0.1 mol %) gave slightly lower yield (73%, entry 7). Catalysts bearing bistricyclohexylphosphine ligands (i.e., **Ru-1**, entry 1), a mono-*ortho*-substituted N-heterocyclic carbene ligand developed for olefin metathesis of hindered alkenes (i.e., **Ru-5** and **Ru-6**, entries 10 and 11),[17] and a bidentate nitrate and adamantyl ligands developed for *Z*-selective olefin metathesis (i.e., **Ru-7**, entry 12)[18] gave yields lower than those of other catalysts (i.e., **Ru-2** to **Ru-5**). Nonetheless, all of the Grubbs-type ruthenium catalysts that we tested exhibited a complete regioselectivity, and regioisomer **3a** was consistently absent upon completion of the reaction. Notably, metathesis activity was not detected in any of these cases; no change to the resonance of a benzylidene proton in ^{1}H NMR was observed nor was the formation of corresponding Ru-alkylidene/methylidene intermediates detected in any of the reactions. Additionally, we were not able

Table 1. Evaluation and Optimization of Grubbs-Type Ruthenium-Catalyzed Intramolecular Alkene Hydrosilylation[a]



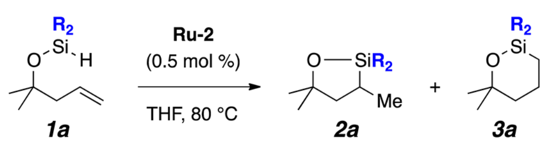
entry	RuL_n	solvent	2a/3a/4a[b]	yield (%)[c]
1	**Ru-1** (2 mol %)	PhMe	100:0:0	27
2	**Ru-2** (2 mol %)	PhMe	100:0:0	75
3	**Ru-2** (2 mol %)	CH_2Cl_2	100:0:0	50
4	**Ru-2** (2 mol %)	PhH	100:0:0	52
5	**Ru-2** (2 mol %)	THF	100:0:0	85
6	**Ru-2** (0.5 mol %)	THF	100:0:0	85
7	**Ru-2** (0.1 mol %)	THF	100:0:0	73
8	**Ru-3** (2 mol %)	PhMe	100:0:0	67
9	**Ru-4** (2 mol %)	PhMe	100:0:0	50
10	**Ru-5** (2 mol %)	PhMe	100:0:0	28
11	**Ru-6** (2 mol %)	PhMe	100:0:0	15
12	**Ru-7** (2 mol %)	PhMe	100:0:0	13

[a]Conditions: silane **1a** (0.1 mmol), solvent (0.2 M). [b]Determined by GC/MS analysis. [c]Determined by ^{1}H NMR spectroscopy utilizing an internal standard (CH_2Br_2).

to detect homo-crossed dimers such as **4a** or the styrene byproduct released by the initial metathesis event in the GC/MS and ^{1}H NMR analyses.[19] These results established that the regioselective synthesis of oxasilacyclopentanes **2** is feasible via hydrosilylative cyclization, exploiting Grubbs-type ruthenium catalysts.

The effect of substituents on silicon was also examined (Table 2). Dimethyl and diphenyl substituents cleanly effected

Table 2. Silyl Substituent Effect on the Intramolecular Alkene Hydrosilylation Catalyzed by Ru-2[a]



entry	R	2a/3a[b]	yield (%)[c]
1	Me	100:0	63
2	Ph	100:0	85
3	*i*-Pr	100:0	20
4	*t*-Bu	100:0	0

[a]Conditions: silane **1a** (0.1 mmol), THF (0.2 M). [b]Determined by GC/MS analysis. [c]Determined by ^{1}H NMR spectroscopy utilizing an internal standard (CH_2Br_2).

the hydrosilylation. However, a substrate possessing diphenyl substituents clearly exhibited a superior yield and conversion over those containing alkyl substituents, suggesting that the silyl substituent plays a critical role in the success of this process.

With the reaction conditions optimized, two other substrates were examined, which successfully produced **2b** (62%) and **2c** (65%), depicted in Scheme 2. Our preliminary results establish

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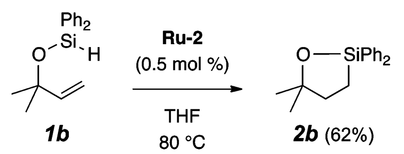
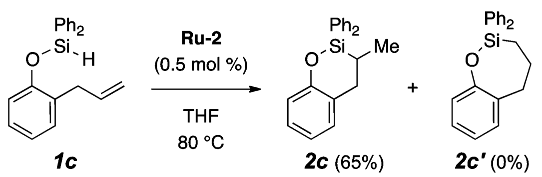
Scheme 2. Selective Synthesis of Either Oxasilacyclopentanes and Oxasilacyclohexanes via Grubbs-Type Ruthenium-Catalyzed Hydrosilylative Cyclization

A. Selective synthesis of oxasilacyclopentane via *5-endo-trig* hydrosilylative cyclization

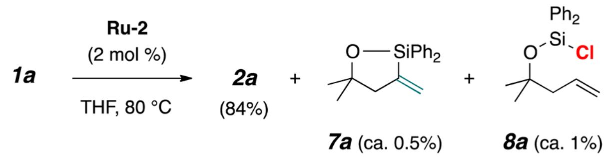


B. Selective synthesis of oxasilacyclohexane via *6-exo-trig* hydrosilylative cyclization

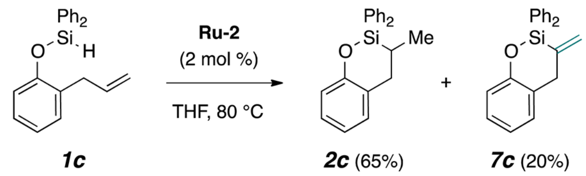


Scheme 3. Insightful Observations of the Formation of Vinylsilanes (7a and 7c) and Chlorosilane (8a)

A. Formation of vinylsilane **7a** and chlorosilane **8a** from diphenylsilane **1a**



B. Formation of vinylsilane **7c** from 2-allylphenoxydiphenylsilane **1c**



that the regioselective synthesis of either oxasilacyclopentanes (e.g., **2a** or **2b**) via a 5-*exo-trig* (for homoallylic silyl ethers) or a 5-*endo-trig* (for allylic silyl ethers) hydrosilylative cyclization or oxasilacyclohexanes (e.g., **2c**) via a 6-*exo-trig* cyclization is feasible.

Several speculative mechanisms of Grubbs-type ruthenium-complex-catalyzed alkyne hydrosilylation have been proposed by Cox and Cossy. Cox proposed either (i) a sequence of an initial addition of R_3Si−H across the π-bond of a Ru-benzylidene (Chauvin mechanism),[20] silylruthenation, α-elimination (to metal alkylidene/hydride),[21] and reductive elimination or (ii) the traditional organometallic route—oxidative addition, migratory insertion, and reductive elimination.[3] Cossy conjectured either hydroruthenation or silylruthenation.[5] However, neither study provided full experimental details regarding any such elemental processes. During our initial study, we made an observation that addressed the initial stage of Grubbs-type ruthenium-complex-catalyzed hydrosilylation within a ruthenium coordination sphere. In detail, upon treatment with **Ru-2**, silane **1a** produced vinylsilane **7a** (ca. 0.5%) and chlorosilane **8a** (ca. 1%),[22] which were detected and characterized by GC/MS analysis (Scheme 3A). We were able to isolate cyclic vinylsilane **7c** (20% isolated yield) from hydrosilylation of **1c** (Scheme 3B). The formation of the vinylsilane suggests that Grubbs-type ruthenium-complex-catalyzed alkene hydrosilylation likely proceeds through a modified Chalk−Harrod mechanism (i.e., silylruthenation)[12b] rather than the Chalk−Harrod (i.e., hydroruthenation) pathway.[12a,23]

The formation of the chlorosilane **8a** offers indirect information for the initial stage of the hydrosilylation. The result suggests two plausible mechanisms (Scheme 4): (i) A two-step sequence, namely, an addition of R_3Si−H across the π-bond of a Ru-benzylidene to give **9b**,[3] followed by HCl elimination[24] to form a putative Ru−Si complex **9d** (productive),[25] could be responsible for alkene hydrosilylation to furnish **2** or reductive elimination to afford the chlorosilane byproduct **8** (e.g., **8a**) and **9c** (unproductive) (path A). (ii) Direct σ-bond metathesis between Si−H and Ru−Cl via a four-centered transition state could be involved in the activation of the ruthenium complex by silanes (path B).[26,27] Based primarily upon a bottom-face olefin coordination mechanism for olefin metathesis,[19] the metathesis of **9a** and silane **1** may furnish either **9g** via **9e** (*metal-out*: unproductive—the silicon never goes to the ruthenium metal center) or **9d** via **9f** (*metal-in*: productive). It could be an analogous situation where the outcome of competitive cross-metathesis (CM) [i.e., productive CM: an ethylene-producing process (cf., **9f** to **9d**) and unproductive CM: a degenerate metathesis (cf., **9e** to **9g**)] is substantially dependent upon the steric hindrance of olefins, as well as the ligand set of the ruthenium catalyst.[28]

To sort out these two mechanistic hypotheses for the initial stage of the catalysis, we first performed a control experiment (Scheme 5A); we speculated that bulkier substituents such as a *t*-Bu group at silicon (i.e., **1a**-*t*-Bu) could be favored for unproductive σ-bond metathesis to yield chlorosilyl ether **8a**-*t*-Bu (via **10a** vis-à-vis **10b**). However, the formation of **2a**-*t*-Bu via the sequential addition of R_3Si−H across Ru═CHAr and reductive elimination is unlikely because an addition of di-*tert*-butylsilane **1a**-*t*-Bu to **Ru-2** is greatly hindered, as seen in a Grubbs' classification of general reactivity patterns of olefins.[29] When **1a**-*t*-Bu was subjected to the reaction conditions employing 100 mol % of **Ru-2**, only **8a**-*t*-Bu (**1a**-*t*-Bu/**8a**-*t*-Bu = 19:81) was observed without any notable cyclization, corroborating our mechanistic hypothesis for the σ-bond metathesis. In an effort to support this hypothesis, a deuterium-labeling experiment was carried out using deuteriosilane **11**-D and **Ru-4** (Scheme 5B). The benzylidene proton within the resulting putative ruthenium complex **12** remained intact; we did not detect deuterium incorporation at this position by ^{2}H NMR spectroscopy. This result suggests that the R_3Si−H addition across the Ru═CHAr and HCl elimination cascade is improbable.

The experiment performed to directly detect a ruthenium silane complex is shown in Figure 1. In this prototype, the use of an essentially equimolar ratio of **Ru-4** and silane **11**-H, which does not bear an alkene moiety, resulted in full conversion to a putative ruthenium silane complex (e.g., **9d** in Scheme 4 or **12** in Scheme 5). Over time, the Si−H bond disappeared, yet benzylidene proton (H^7) and other protons within the catalyst **Ru-4** (H^7 to H^{11}) remained intact; an isopropoxy group was still anchored to the ruthenium center (H^{12}, 4.74 ppm). Interestingly, all protons in substrate **11**-H were shifted downfield, particularly, those at the *ortho*-position of diphenylsilyl substituents (H^1, shifted downfield by 0.12 ppm) and methylene protons (H^3, shifted downfield by 0.063

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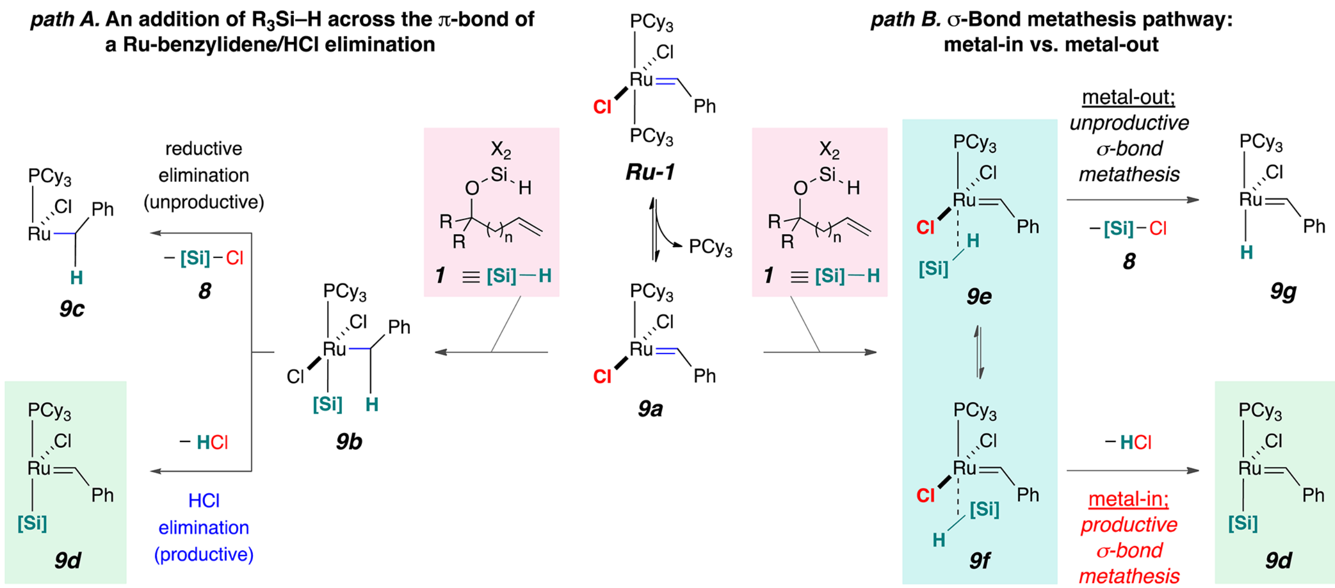
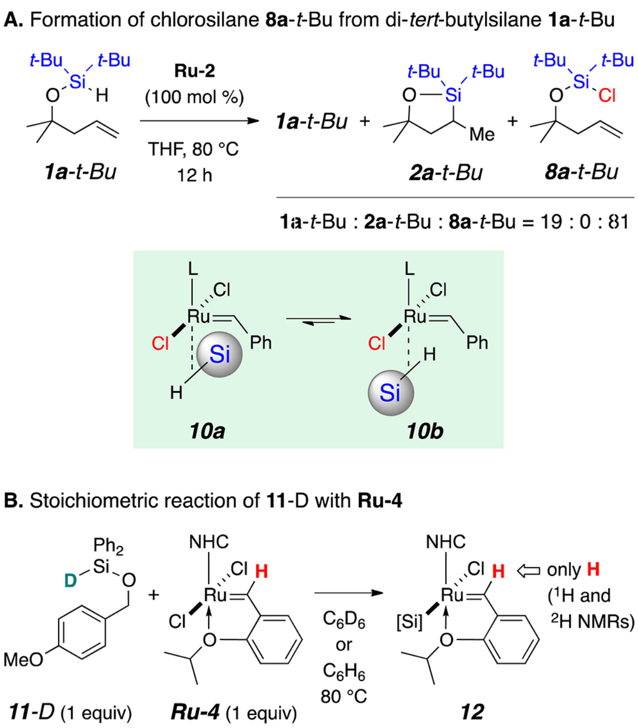
Scheme 4. Activation of Grubbs-Type Ruthenium Catalysts by Silanes



Scheme 5. Stoichiometric Reactions of Alkenylsilyl Ethers (10a-*t*-Bu and 11-D) and Ru-2



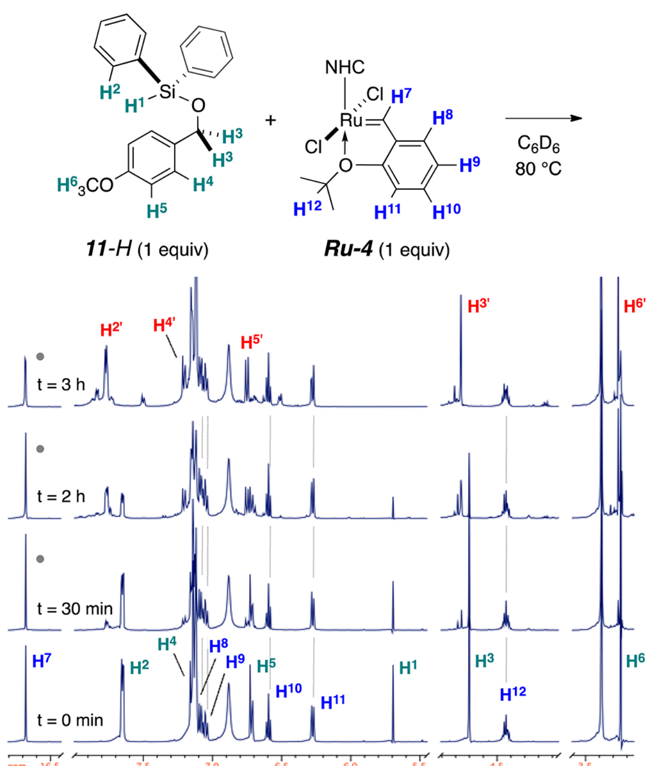


Figure 1. Monitoring the stoichiometric reaction of hydrosilyl ether **11**-H and **Ru-4** by ^{1}H NMR spectra (500 MHz, C_6D_6) over time. Proton resonances colored in red emanate from a newly generated putative Si–Ru complex (for the stoichiometric reaction of **11**-H and **Ru-2** monitored by ^{1}H NMR spectra over time, see Supporting Information).

ppm) within **11**-H. These protons were drawn closer to the ruthenium center. No additional benzylidene or alkylidene resonances were observed during this series of experiments.

Further insights into the reaction mechanism of the hydrosilylation were garnered by examining the impact of the X-type halide ligands within ruthenium catalysts (Scheme 6). The catalytic activity of the hydrosilylation was generally increased by having an electron-withdrawing and smaller halide group from iodide to chloride. This trend is similar to the observed olefin metathesis reactivity of the ruthenium catalyst.[17a] Particularly, the reaction with dichloride catalyst **Ru-2-Cl** was significantly faster than catalysts containing dibromide and diiodide (**Ru-2-Br** and **Ru-2-I**, respectively). The reasons behind the reactivity difference are unclear at this moment, but a sterically less demanding and electron-withdrawing X-type chloride ligand perhaps favors ruthenium binding to Si–H, dictating a facile σ-bond metathesis.

We carried out an additional set of deuterium-labeling studies to further understand the nature of this cyclization (Scheme 7).

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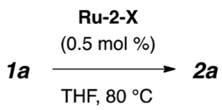
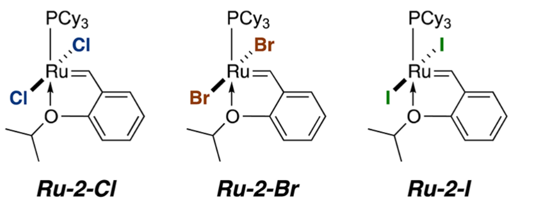
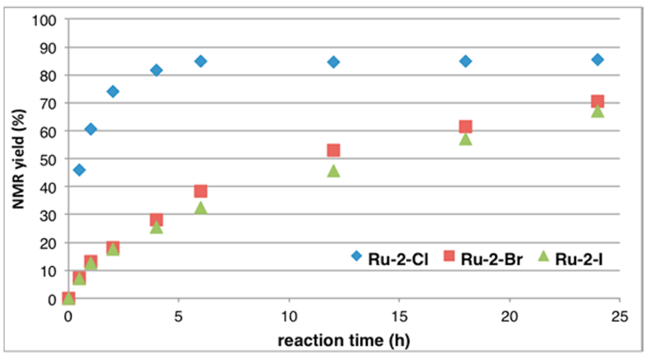
Scheme 6. Catalytic Activities Varying Halides on Ruthenium Catalysts

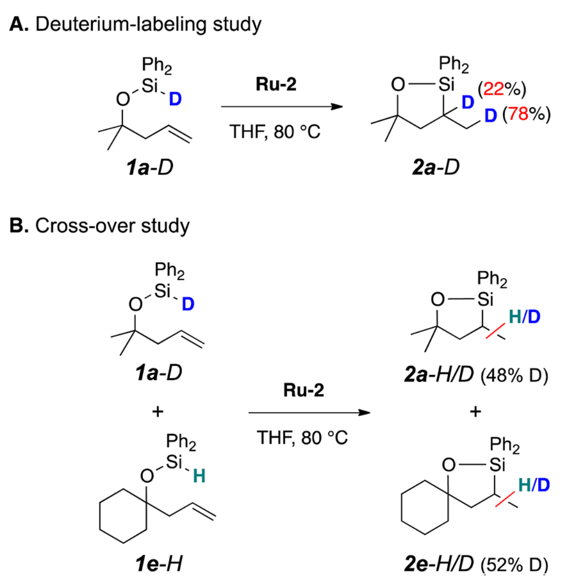


Ru-2-X	X	yield of 2a (%)
Ru-2-Cl	Cl	85
Ru-2-Br	Br	70
Ru-2-I	I	67





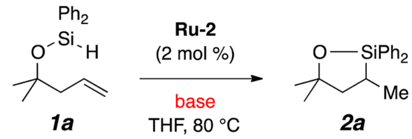
Scheme 7. Intramolecular and Intermolecular Deuterium-Labeling Studies



Under the same reaction conditions, the deuterium of **1a**-D was mainly transferred to two positions of **2a**-D, supporting the modified Chalk–Harrod mechanism (Scheme 7A). Furthermore, the crossover experiment established that the proton transfer occurs intermolecularly (Scheme 7B). The hydrogen and deuterium scrambling, shown as **2a**-H/D and **2e**-H/D, reinforces our mechanistic hypothesis involving the σ-bond metathesis.

Lastly, we examined the reaction of **1a** employing a stoichiometric amount of base [2,6-di-*tert*-butyl-4-methylpyridine (DTBMP) or $NaHCO_3$] (Scheme 8). The rates of two

Scheme 8. Addition of a Proton Scavenger

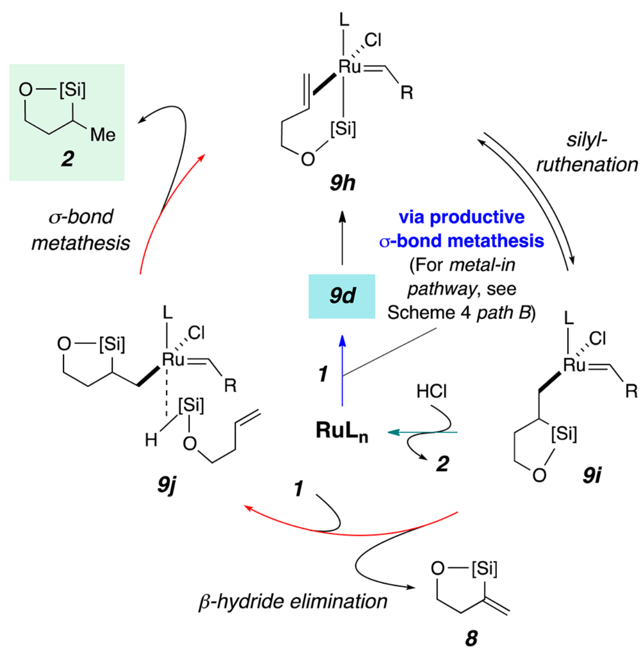


base (1 equiv)	yield of 2a
DTBMP	62%
$NaHCO_3$	63%

reactions with and without base were essentially identical ($t_{1/2}$ = ca. 40 min), albeit resulting in slightly diminished yields of **2a**. This result indicates that the dissociated HCl did not affect the overall reaction efficiency. In addition, a potential mechanism involving heterolysis of a Si–H bond by a ruthenium catalyst can be eliminated.[24,30]

The plausible overall mechanism, based upon our mechanistic studies and observations, is depicted in Scheme 9. The

Scheme 9. Proposed Mechanism



initial productive σ-bond metathesis between a ruthenium catalyst and silyl ether **1** affords ruthenium–silyl complex **9d** (see Scheme 4, path B). Alkene coordination to ruthenium within **9h** followed by silylruthenation affords **9i**. At this stage, either β-hydride elimination (to **8**) or σ-bond metathesis (to product **2**) via **9j** takes place and regenerates **9h**. Alternatively, protonation by HCl would afford **2** and ruthenium catalyst RuL_n.

In light of these new mechanistic insights, we investigated the substrate scope and regio- and stereoselectivity of Grubbs-type ruthenium-complex-catalyzed intramolecular alkene hydrosilylation (Table 3). Homoallylic silyl ethers with 3° alkoxy carbon (**2d–i**) showed good conversions and yields. To understand the impact of relative stereochemistry, substrates **1f–i** were subjected to the reaction conditions. We found that substrates containing a silyl ether and a *syn*-substituent (Ph or *t*-Bu) at the 4-position on a cyclohexyl moiety gave products (**2f** and **2h**) with higher yields when compared with their counterparts (**2g**

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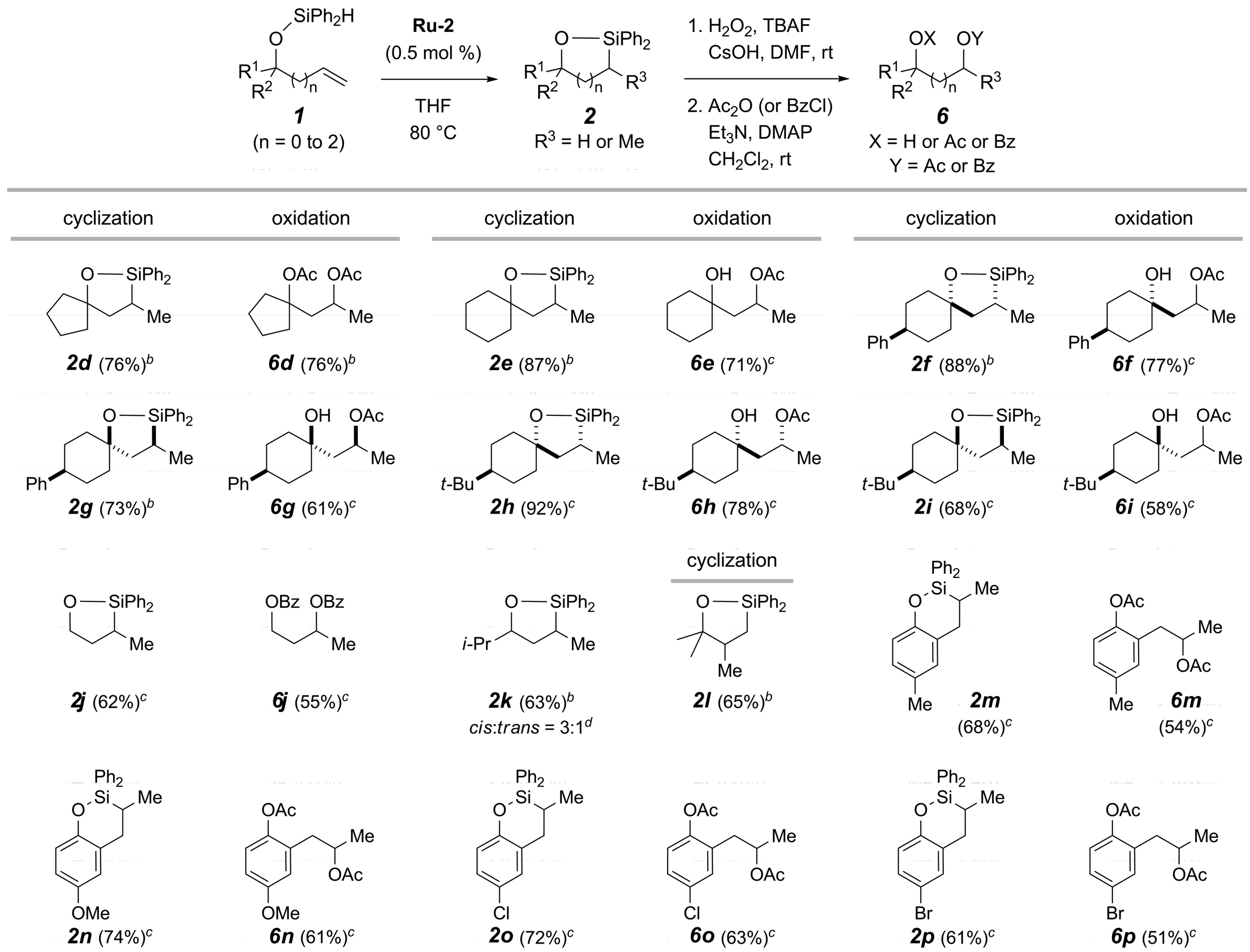
Table 3. Substrate Scope of Grubbs-Type Ruthenium Catalysts for Intramolecular Alkene Hydrosilylation[a]



[a]Conditions: silane **5** (0.3 mmol), THF (0.2 M). [b]Determined by ^{1}H NMR spectroscopy utilizing an internal standard (CH_2Br_2). [c]Isolated yield of oxidation/acetylation or benzoylation products **6**. [d]Diastereomeric ratio was determined by GC/MS analysis and ^{1}H NMR spectroscopy.

and **2i**). Substrates with 1° silyl ether (**1j**) afforded **2j** in modest yield. Substrates with 2° silyl ether (**1k**) yielded **2k** with a 3:1 ratio (*cis*/*trans*) of diastereomers. We also studied allylic sillyl ether **1l**, which provided **2l**. 2-Allylphenoxydiphenylsilanes **1m**−**p** afforded oxasilacyclohexanes **2m**−**p** with respective yields, regardless of electronic nature of the substituents at the *para*-position to the phenoxy group. The resulting organosilicon heterocycles **2** were subjected to oxidation and acylation conditions, which provided diacetates (**6d** and **6m**−**p**), hydroxy acetates (**6e**−**i**), and dibenzoate (**6j**).

In summary, we have developed a Grubbs-type ruthenium-complex-catalyzed intramolecular alkene hydrosilylation of alkenylsilyl ethers to provide cyclic silyl ethers. Preferential Si−H bond activation over alkene activation was observed, where alkene metathesis was effectively suppressed. This study expands our understanding of fundamental mechanistic aspects of non-metathetical function of Grubbs-type ruthenium catalysts for alkene hydrosilylation, with potential implications for other associated transformations such as dehydrogenative condensation between alcohols and silanes,[31] direct arylation,[32] and hydrogenation.[33] Notably, the initial stage of the hydrosilylation involving the σ-bond metathesis between Si−H and Ru−Cl is proposed. The Grubbs-type ruthenium-complex-catalyzed alkene hydrosilylation follows the modified Chalk−Harrod mechanism. Further efforts toward synthetic applications of Grubbs-type ruthenium-catalyzed hydrosilylation are currently underway.

■ ASSOCIATED CONTENT

Supporting Information

The following file is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.5b00431.

Experimental details and spectroscopic characterization data for all compounds (PDF)

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Notes

The authors declare no competing financial interest.

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The authors dedicate this article to Professor Thomas R. Hoye (University of Minnesota) on the occasion of his 65th birthday. We thank UT Arlington Research Enhancement Program and the American Chemical Society Petroleum Research Fund (PRF# 54831-DNI1) for support of our program. The NSF

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