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Regio- and Stereoselective Dehydrogenative Silylation and Hydrosilylation of Vinylarenes Catalyzed by Ruthenium Alkylidenes

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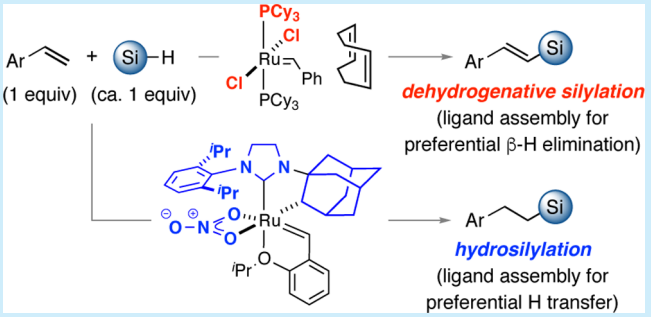
Supporting Information

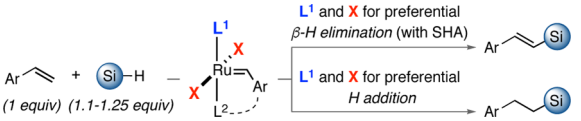
ABSTRACT: Development of regio- and stereoselective dehydrogenative silylation and hydrosilylation of vinylarenes with alkoxysilanes, catalyzed by ruthenium alkylidenes, is described. Varying L- and X-type ligands on ruthenium alkylidenes permits selective access to either (*E*)-vinylsilanes or *β*-alkylsilanes with high regio- and stereocontrol. *cis,cis*-1,5-Cyclooctadiene was identified as the most effective sacrificial hydrogen acceptor for the dehydrogenative silylation of vinylarenes, which allows use of a nearly equimolar ratio of alkenes and silanes.



Vinylsilanes and alkylsilanes are important building blocks in the synthesis of small molecules and polymers, based, in part, on their relatively high stability and virtually nontoxic nature.[1] These organosilanes have been extensively exploited as useful synthetic intermediates whose silicon functional groups can be directly converted to many other useful moieties through further reactions.[1c,2] Regio- and stereoselective dehydrogenative silylation[3−5] to provide vinylsilanes are challenging,[6,7] owing to either competitive hydrosilylation to afford alkylsilanes or alternative *β*-hydride elimination to furnish allylsilanes.[8] Because alkenes are more readily accessible than alkynes and serve as one of the most important starting materials, more direct silylation methods to afford vinylsilanes are highly attractive. For example, Falck[4] and Hartwig[5] recently reported Ir-catalyzed regio- and stereoselective dehydrogenative silylation of terminal alkenes with norbornene as a stoichiometric sacrificial hydrogen acceptor (SHA). Watson demonstrated a Pd-catalyzed silyl Heck reaction utilizing terminal alkenes and silyl triflates.[9] Although there are a number of developments in the dehydrogenative silylation to afford vinylsilanes utilizing metal catalysts,[3d,f,g−i,l,n−p] such methods generally require either excess alkene substrates or silanes albeit employing excess SHA, air- and moisture-sensitive catalysts, or more reactive alkylsilanes in lieu of more useful alkoxysilanes for further manipulations. Chirik and co-workers recently demonstrated highly selective Co-catalyzed dehydrogenative silylation of alkenes for preparation of allylsilanes where, for catalytic turnover, half of the alkenes served as sacrificial hydrogen acceptors to furnish simple alkanes as byproducts.[8]

In a previous study, we first demonstrated that the preferential Si−H activation over alkene activation utilizing Ru alkylidene complexes was feasible to achieve intramolecular alkene hydrosilylation. In contrast to a generally accepted Chauvin-type silylation mechanism of addition of Si−H across the *π*-bond of a Ru benzylidene,[6b,d,10] a mechanism involving direct Si−H activation by RuCl was proposed on the basis of a series of spectroscopic and isotope-labeling experiments.[11] However, there are no examples of this type of Si−H activation by metal alkylidenes (i.e., catalytic deprotonative silyl metalation) for dehydrogenative silylation to afford vinylsilanes (Scheme 1).[8,12]

Scheme 1. Ru Alkylidene Catalyzed Dehydrogenative Silylation and Hydrosilylation of Vinylarenes



We now report regio- and stereoselective dehydrogenative silylation to afford only (*E*)-vinylsilanes and hydrosilylation of vinylarenes by altering the ruthenium alkylidene catalysts (L^1 and X ligand). Notably, preparation of both alkylsilanes and vinylsilanes was achieved using a nearly equimolar ratio of alkenes and silanes with a new sacrificial hydrogen acceptor.

We first investigated the optimal reaction parameters for the dehydrogenative silylation depicted in Table 1. The results revealed that a ratio of products (alkylsilane **2a**, vinylsilane **3a**, stilbene **4a**, and ethylbenzene **5a**) was highly dependent upon catalyst structure and silanes. The reaction of styrene **1a** (1 equiv) and alkyl- or alkoxysilanes (1.1 equiv) with **Ru-1**, constituting phosphine L-type ligand and dichloride X-type ligands, afforded a mixture of products with low to moderate conversion (entries 1−5). Gratifyingly, the use of HSiMe(OSiMe$_3$)$_2$ provided (*E*)-vinylsilane **3a** as a major silylation product with excellent product selectivity of dehydrogenative silylation vis-à-vis hydrosilylation as well as regio- and stereoselectivity (only *E*, of note, previously known metal-catalyzed

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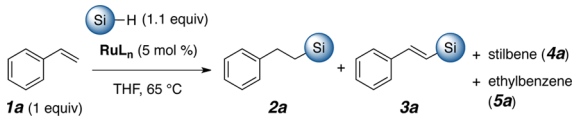
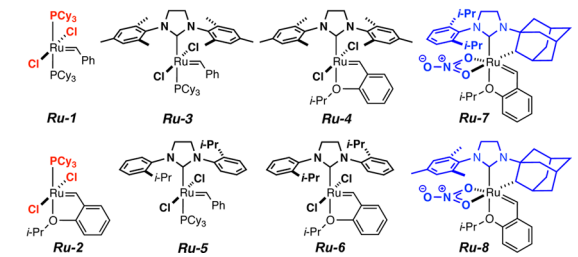
Table 1. Evaluation of Catalysts and Silanes[a]



entry	RuL_n	solvent	conversion (%)[b]	2a:3a:4a:5a[c]
1	**Ru-1**	$HSiEt_3$	77	1:6:0:4
2	**Ru-1**	H_2SiPh_2	94	1.5:1:0:1.5
3	**Ru-1**	H_2SiEt_2	32	nd
4	**Ru-1**	$H_2Si^iPr_2$	25	nd
5	**Ru-1**	$HSi(OEt)_3$	91	1:1:0:1
6	**Ru-1**	$HSiMe(OSiMe_3)_2$	100	1:16:0:10
7	**Ru-2**	$HSiMe(OSiMe_3)_2$	100	1:3:0:1
8	**Ru-3**	$HSiMe(OSiMe_3)_2$	100	1:5:14:2
9	**Ru-4**	$HSiMe(OSiMe_3)_2$	100	1:8:25:1
10	**Ru-5**	$HSiMe(OSiMe_3)_2$	100	1:3:12:3
11	**Ru-6**	$HSiMe(OSiMe_3)_2$	100	1:4:5:1
12	**Ru-7**	$HSiMe(OSiMe_3)_2$	100	5:1:0:1
13	**Ru-8**	$HSiMe(OSiMe_3)_2$	100	4:1:0:1

a) preferential dehydrogenative silylation catalysts — b) preferential olefin metathesis catalysts in the precence of silane — c) preferential hydrosilylation catalysts

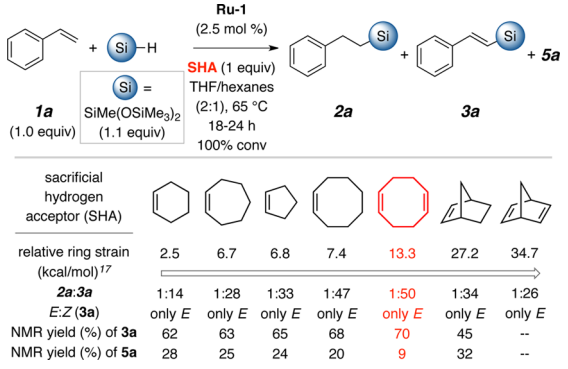


[a]Conditions: **1a** (0.4 mmol), silane (0.44 mmol), THF (0.2 M). [b]Determined by GC/MS analysis. [c]Determined by GC/MS analysis and ^{1}H NMR spectroscopy utilizing an internal standard (CH_2Br_2).

alkyne hydrosilylations or dehydrogenative silylations typically afford *Z*-vinylsilanes as major) (entry 6). In contrast, **Ru-7** and **Ru-8**, best known for *Z*-selective olefin metathesis catalysts containing an NHC L-type and bidentate nitrate X-type ligands, as well as chelating adamantyl ligand,[13] furnished alkylsilanes **2a** as a major product (entries 12 and 13). Interestingly, NHC/dichloride-containing catalysts including **Ru-3**, **Ru-4**, **Ru-5**, and **Ru-6** produced olefin metathesis product stilbene **4a** as a major product, even in the presence of silane (entries 8−11). These results are summarized in Table 1 (bottom), which comprises three modes of Ru alkylidene reactivity toward dehydrogenative silylation, olefin metathesis in the presence of silane, and hydrosilylation.

The issue of simple reduction of the starting alkenes **1** was addressed by employing a sacrificial hydrogen acceptor (SHA, 1 equiv) (Scheme 2). When well-known strained bicyclic alkenes [e.g., norbornene (nbe), norbornadiene (nbd)] were tested, we observed noticeable ring-opening metathesis polymerization (ROMP) activity of **Ru-1** in the presence of nbe or nbd. We quickly discovered that moderately ROMP-active cycloalkenes [including cyclopentene, cyclohexene, cycloheptene, *cis*-cyclooctene, and *cis,cis*-1,5-cyclooctadiene (cod)] not only afforded good yields by diminishing the alkene reduction product **5a** [use of 2 equiv of SHA (i.e., cod) eventually further improved yields (<5% of **5a**)] but also exhibited excellent selectivity of dehydrogenative silylation over hydrosilylation. The trend of corresponding yield and the ratio of **2a** and **3a** were well correlated with the ring strain of cycloalkenes, whereupon with

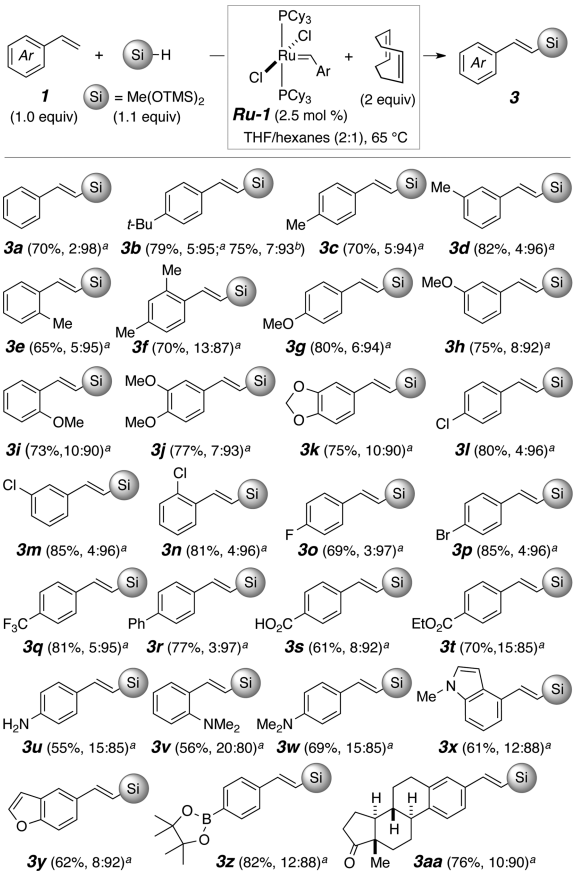
Scheme 2. Evaluation of Sacrificial Hydrogen Acceptors



increasing ring strain[14] the corresponding ratio as well as yield (**3a**) proportionally increased.

Having established the optimized conditions, we explored the scope of Ru alkylidene catalyzed dehydrogenative silylation of **1** with **Ru-1** (X = Cl and $L^1 = PCy_3$) to afford (*E*)-**3** (Scheme 3).

Scheme 3. Substrate Scope of Ruthenium Alkylidene (Ru-1)-Catalyzed Dehydrogenative Silylation of Vinylarenes[a,b]



[a]A ratio of **2** and **3** was determined by GC/MS and ^{1}H NMR spectroscopy. [b]Reaction of **1b** on 7 mmol (1.12 g) scale.

Electron-rich and -deficient styrenes afforded vinylsilanes (**3a**−**r**) in moderate to good yields with excellent stereoselectivity (only *E*) and a good to excellent ratio of dehydrogenative silylation and hydrosilylation. The reaction of **1b** on a 7 mmol (1.12 g) scale provided **2b** in 75% yield with good product selectivity (**2b**/**3b** = 7:93). Notably, carboxylic acid, ester, unprotected amine,

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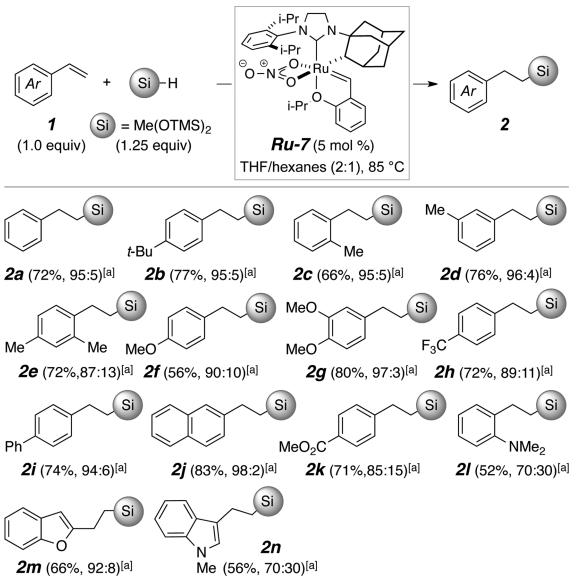
protected *o*-amino group (potential chelation group to Ru), indole, benzofuran, and boronate ester (**3s**-**z**) tolerated the reaction conditions. Finally, structurally complex, C3-vinyl estrone derivative afforded vinylsilane **3aa** in 76% yield with good product selectivity. Ru alkylidene catalytic systems unfortunately did not effect the reaction of aryl-substituted alkenes with an alkyl side chain.

We then continued to investigate the scope of Ru alkylidene-catalyzed hydrosilylation of **1** and $HSiMe(OTMS)_2$ with **Ru-7** (Scheme 4). When **Ru-7** (X = NO_3 and L^1 = NHC bearing

Scheme 4. Substrate Scope of Ruthenium Alkylidene (Ru-7)-Catalyzed Hydrosilylation of Vinylarenes[a]

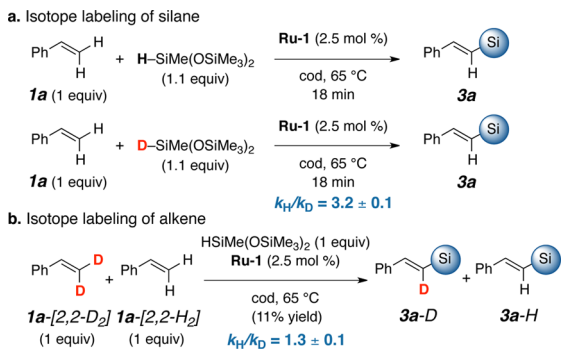


[a]A ratio of **2** and **3** was determined by GC/MS and ^{1}H NMR spectroscopy.

adamantly moiety) was used, diverse mono- and disubstituted styrenes provided alkylsilanes **2a**−**j** with moderate to good yields and a synthetically useful level of product selectivity. Again, ester-, amino-, benzofuran-, and indole-containing styrenes underwent hydrosilylation to provide **2k**−**n** in good yields.

In order to gain insight into the reaction mechanism of the Ru alkylidene catalyzed dehydrogenative silylation, we conducted two KIE experiments (Scheme 5). In the first experiment, parallel KIE experiments with $HSiMe(OTMS)_2$ and $DSiMe(OTMS)_2$ were carried out (Scheme 5.a). Analysis of the products established a significant KIE (k_H/k_D = 3.2). Second, the

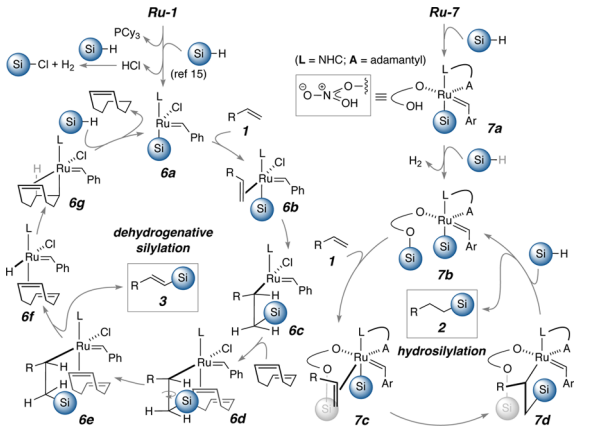
Scheme 5. Preliminary Mechanistic Studies



intermolecular KIE experiment using **1a**-[2,2-D_2] and **1a**-[2,2-H_2] displayed minimal isotopic selectivity (k_H/k_D = 1.3), suggesting that direct C−H activation/silylation to afford vinylsilane is unlikely (Scheme 5b). Taken together, the observed significant KIE in the parallel isotope experiments indicates that the Si−H bond cleavage to generate the putative ruthenium silyl complex and HCl is the turnover-limiting step, which is consistent with observation of Ru alkylidene as the resting state.[6b,15]

The catalytic mechanisms of these interesting processes involving catalysts such as **Ru-1** and **Ru-7** have not been yet fully elucidated. Based on discoveries from our current studies, coupled with previous studies regarding Ru alkylidene catalyzed intramolecular alkene hydrosilylation,[11] we propose mechanisms for the Ru alkylidene catalyzed dehydrogenative silylation and hydrosilylation of alkenes (Scheme 6). First, dehydrogenative

Scheme 6. Proposed Mechanisms



silylation begins with the Si−H activation by Ru catalyst after dissociation of phosphine ligand to afford putative Ru silyl complex **6a** and HCl. The resulting HCl can further react with silane to give Si−Cl and H_2, which were observed by GC−MS and ^{1}H NMR spectroscopy. A similar type of a bond-exchange reaction has been seen in Noyori's asymmetric hydrogenation, where early activation of H_2, by $Ru(II)Cl_2$, provided HRu(II)Cl and HCl.[16] An alkene coordination and olefin migratory insertion then give rise to **6c** via **6b**. When the catalyst contains phosphine/dichloride ligands (e.g., **Ru-1**), **6d**, produced by coordination of moderately ROMP-active and bulky cycloalkene cod (Scheme 2) to Ru metal, could dictate the product selectivity by facilitating the C−C single-bond rotation (to **6e**) and subsequent β-hydride elimination to give a thermodynamic product (*E*)-vinylsilane **3** and Ru−H (**6f**). The catalytically responsible Ru−Si (**6a**) is regenerated by a sequence of olefin migratory insertion of cod into ruthenium hydride (to **6g**) and reaction with silane by releasing cyclooctene (observed in ^{1}H NMR spectroscopy and GC−MS spectrometry).

Activation of the Si−H bond with hydrosilylation catalyst **Ru-7**, which includes NHC, nitrate, and adamantyl ligands, furnishes the putative Ru silyl complex **7a**. The resulting monobound nitrate can quickly react with additional silane to afford bis-silyl Ru complex **7b**. Because of this dehydrogenative Si−O coupling, as shown in Scheme 4, the hydrosilylation process necessitates the use of a slight excess of silane. Otherwise, diminished product selectivity was generally observed. Side-bound olefin in **7c** then undergoes olefin migratory insertion to provide **7d**. Finally, reaction of **7d** with silane releases alkylsilanes **2** and produces the

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active bis-silyl complex **7b**. We observed that this hydrosilylation is nearly four times slower compared to dehydrogenative silylation ($t_{1/2}$ = 30 min for dehydrogenative silylation of **1d** and $t_{1/2}$ = 120 min for hydrosilylation of **1d**), presumably resulting from added steric hindrance with the Ru complex. Moreover, we conjecture that bulky 2,6-diisopropyl groups in the NHC ligand and other moieties in the metal−ligand sphere such as adamantyl and silylated nitrate likely impede the propensity of β-hydride elimination (cf., **6e** to **6f** and **3**) by restricted conformational change for requisite *syn*-elimination within **7e**. A structurally similar catalyst **Ru-8** holding the smaller mesityl group in NHC reduces product selectivity as shown in Table 1, entry 8.

In summary, we have developed regio- and stereoselective dehydrogenative silylation and hydrosilylation of vinylarenes and alkoxysilanes by exploiting ruthenium alkylidene catalysts to access vinylsilanes and alkylsilanes. Notably, variation of catalyst structure, specifically both L- and X-type ligands at ruthenium, greatly altered the reaction pathways to dehydrogenative silylation and hydrosilylation. The readily accessible catalysts, with a *cis,cis*-1,5-cyclooctadiene hydrogen acceptor for the dehydrogenative silylation, exhibited relatively broad functional group tolerance and high regio- and stereoselectivity. Although a variety of nonmetathetical synthetic applications of Grubbs-type ruthenium alkylidenes are known, including silylation reactions, a mechanistic understanding of nonmetathetical catalytic function of such catalysts is still limited. Our preliminary studies on dehydrogenative silylation showed that the turnover-determining step is the Si−H cleavage by Ru alkylidene. The origin of such ligand-controlled selectivity regarding dehydrogenative silylation and hydrosilylation as well as their detailed mechanism are currently under investigation.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b02642.

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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