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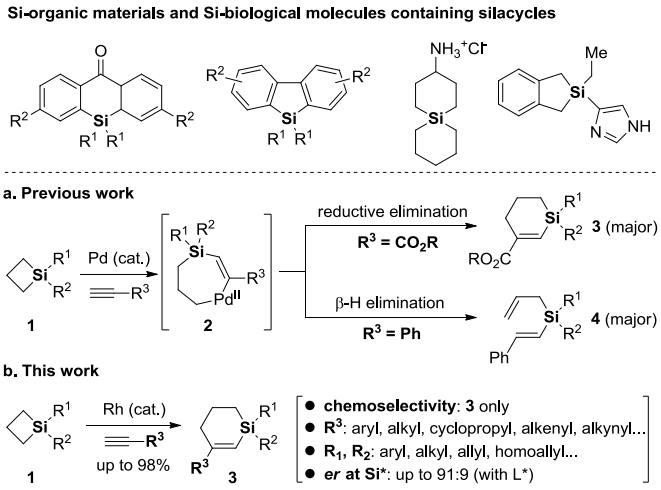
Rhodium-catalyzed Reaction of Silacyclobutanes with Unactivated Alkynes to Afford Silacyclohexenes**

*Hua Chen, Yi Chen, Xiaoxiao Tang, Shunfa Liu, Runping Wang, Tianbao Hu, Lu Gao, and Zhenlei Song**

Abstract: *A Rh-catalyzed reaction of silacyclobutanes (SCBs) with unactivated alkynes has been developed to form silacyclohexenes with high chemoselectivity. Good enantioselectivity at the stereogenic silicon center was achieved using a chiral phosphoramidite ligand. The resulting silacyclohexenes are useful scaffolds for synthesizing structurally attractive silacyclic compounds.*

Silacycles[1] are attractive organosilanes because they are widely used in developing π-conjugated organic materials with unique optical and electronic properties.[2] Lately they have become the focus of efforts to develop silicon-containing bioactive molecules of interest.[3] Silacycles are typically synthesized by cyclization of chain-like substrates,[4] but some desirable products cannot be produced in this way. Instead, they can be obtained using an alternative approach in which small, strained silacycles such as silacyclobutane (SCB) are expanded into larger rings. Ever since Kipping pioneered the synthesis of SCB,[5] a series of SCB ring-expansion reactions have been developed that exploit its high ring strain and Lewis acidity.[6]

In 1975, Sakurai and Imai reported the first Pd-catalyzed reaction of SCB **1** with alkynes substituted with electron-withdrawing groups, giving silacyclohexenes **3**.[7] Revisiting this reaction in 1991, Oshima and Utimoto observed formation of a large amount of allylsilane **4** as a by-product.[8] They proposed that **3** formed via reductive elimination of pallada-silacycloheptene **2**, while β-H elimination of **2** would generate **4**. Recently, Shintani and Hayashi made an important breakthrough at developing an asymmetric version of this approach based on a Pd-catalyzed desymmetrization of SCB.[9] Using a sterically demanding chiral phosphoramidite



Scheme 1. (a) Si-organic materials and Si-biological molecules containing silacycles. (b) Pd-catalyzed reaction of SCB with unactivated alkyne leading to non-cyclic allylsilane. (c) Rh-catalyzed reaction of SCB with unactivated alkyne leading to silacyclohexenes.

ligand facilitated the reductive elimination step, leading to **3** with high chemoselectivity and ultimately to high enantioselectivity at the stereogenic silicon center[10]. Despite these progresses, this reaction requires electron-deficient alkynes to generate silacyclohexenes effectively. Using unactivated alkynes such as phenylacetylene leads in many intermolecular reactions to severe β-H elimination with SCBs, giving allylsilanes **4** as single or major products.[7, 8] To the best of our knowledge, only Shintani and Hayashi have succeeded in forming silacyclohexenes, for which they used an intramolecular approach involving an aryl-substituted alkyne and SCB tethered by a phenyl ring.[11] Therefore, it would be beneficial to develop general processes that generate silacyclohexenes intermolecularly from unactivated alkyne and SCBs. Such approaches would largely expand the structural diversity of the resulting silacyclohexenes. Here we report such a reaction in the presence of Rh catalyst that generates silacyclohexenes with high chemoselectivity. The good enantioselectivity at the stereogenic silicon center was also achieved using a newly synthesized chiral phosphoramidite ligand.

First we revisited the Pd-catalyzed reaction of SCB **1a**[12] with phenylacetylene.[13] In most cases, we obtained a mixture of **3a** and **4a**, with **4a** as the major product, similar to Sakurai and Imai[7] as well as Oshima and Utimoto.[8] Shintani and Hayashi's conditions[9] generated predominantly **3a** but in only 17% yield. These failures led us to focus on other transition metals such as monomeric and dimeric Rh catalysts possessing CO or alkene ligands (Table 1, entries 1-8), but all reactions provided complex mixtures without desired **3a**. We were delighted to find that Wilkinson's catalyst $[Rh(PPh_3)_3Cl]$[14] significantly improved efficiency, affording **3a** in

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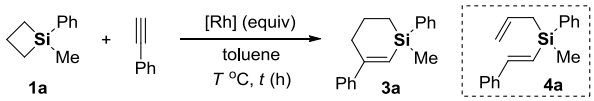
83% yield without formation of the by-product **4a** (entry 9). This result implies that the phosphine ligand is crucial for catalysis, consistent with the different results obtained in entries 8 and 10. Premixing $[Rh(CH_2{=}CH_2)_2Cl]_2$ with PPh_3 for 1.0 h facilitated ligand transfer from alkene to PPh_3, giving **3a** in 91% yield (entry 10). Decreasing $Rh(PPh_3)_3Cl$ loading from 0.1 to 0.02 equiv. improved the yield from 83% to 97% (entry 11). Further decreasing the loading of $Rh(PPh_3)_3Cl$ to 0.01 equiv lowered the yield (entry 12). Increasing the temperature from 25 to 60 °C accelerated the reaction (entry 13). The reaction also proceeded well in non-anhydrous toluene under air, giving **3a** in 98% yield (entry 13).

Table 1. Screening of Reaction Conditions[a]

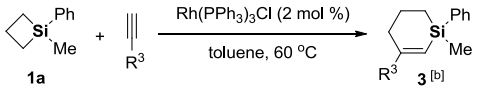


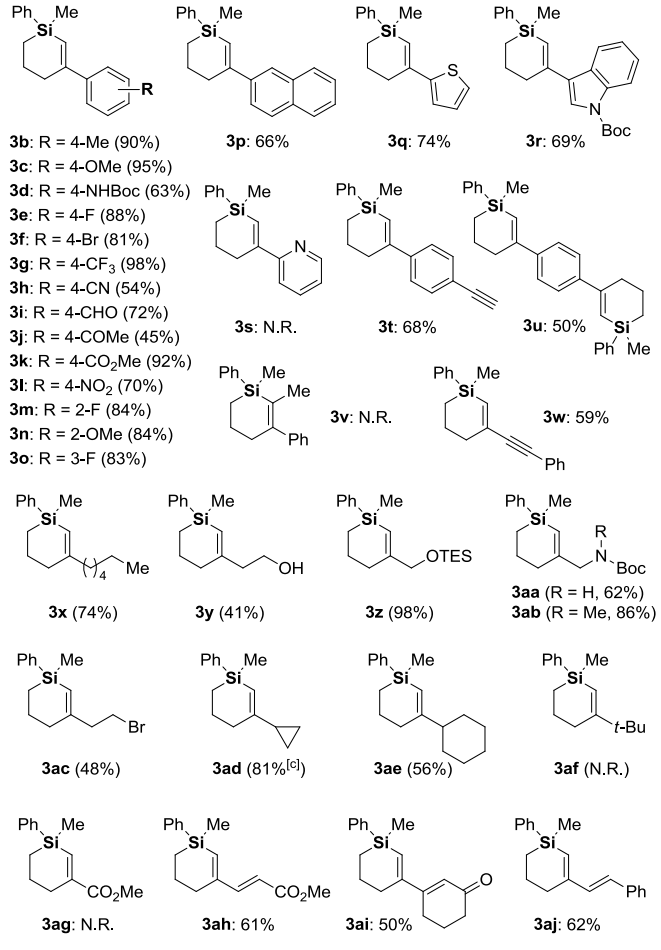
Entry	[Rh] (mol %)	equiv.	*T* (°C)	*t* (h)	Yield (%)[c]
1	$Rh(CO)_2(acac)$	0.1	60	3 h	N.D.
2	$[Rh(CO)_2Cl]_2$	0.1	25	3 h	N.D.
3	$Rh(cod)_2BF_4$	0.1	60	3 h	N.D.
4	$Rh(cod)_2OTf$	0.1	25	3 h	N.D.
5	$[Rh(cod)Cl]_2$	0.1	25	3 h	N.D.
6	$Rh(nbd)_2BF_4$	0.1	60	3 h	N.D.
7	$[Rh(nbd)Cl]_2$	0.1	25	3 h	N.D.
8	$[Rh(CH_2{=}CH_2)_2Cl]_2$	0.1	60	3 h	N.D.
9	$Rh(PPh_3)_3Cl$	0.1	25	4 h	83
10	$[Rh(CH_2{=}CH_2)_2Cl]_2$/ PPh_3 (0.2)	0.1	60	4 h	91
11	$Rh(PPh_3)_3Cl$	0.02	25	4 h	97
12	$Rh(PPh_3)_3Cl$	0.01	25	4 h	83
13	$Rh(PPh_3)_3Cl$	0.02	60	2 h	98(98[c])

[a] Reaction conditions: **1a** (0.20 mmol), phenylacetylene (0.24 mmol), 1.0 mL of toluene. [b] Isolated yields. [c] The yield was obtained using non-anhydrous toluene under air.

Next the scope of alkynes was examined using SCB **1a** as the model scaffold. The reaction worked well with aryl alkynes in which the 4-position of the phenyl ring was substituted with electron-donating or -withdrawing groups (Table 2), giving **3b**-**3u** in high yields. Moderate yields were observed only for **3h** containing a -CN group and **3j** containing a -COMe group. Changing the position of the phenyl ring substitution did not reduce efficiency, providing **3m**-**3o** in yields exceeding 80%. The reaction also afforded **3p**-**3r** possessing naphthaline or the heterocycles. In contrast, 2-ethynylpyridine did not react to give **3s**, probably because the pyridine's strong Lewis basicity inactivated the catalyst. Reaction of 2,4-diacetylide benzene with 0.5 equiv. of **1a** delivered mono-cyclized **3t** in 68% yield, in which the alkyne left can be further functionalized. Repeating this reaction with 2.0 equiv. of **1a** afforded **3u**, in which two silacyclohexenes are linked symmetrically to a phenyl ring. The reaction proved unsuitable for preparing **3v** from more sterically demanding internal alkynes. The reactivity difference between internal and terminal alkynes allowed us to synthesize enyne-type silacyclohexene **3w** from the corresponding diynes. The reaction was suitable for functionalized alkyl alkynes. The yield differences between **3y** and **3z** or between **3aa** and **3ab** indicate that the free hydroxyl and amide groups interfere with the reaction, probably by interacting with the catalyst or by partially opening the SCB ring. The cyclopropyl group did not interfere with the catalytic process, giving **3ad** in 81% yield. The bulky *t*-Bu group inhibited the reaction to give **3af**. Surprisingly, methyl propiolate, which functions well in Pd-catalyzed silacyclohexene formation, was ineffective in our Rh-catalyzed

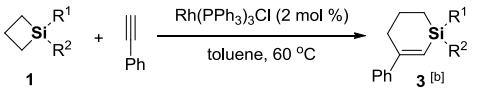
Table 2. Scope of Alkynes [a]

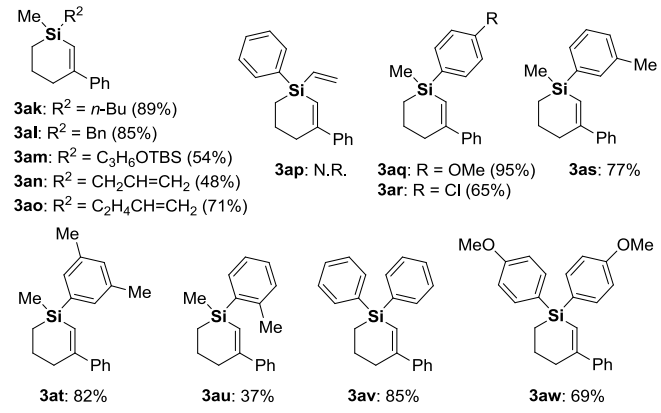




[a] Reaction conditions: **1a** (0.20 mmol), alkyne (0.24 mmol), $Rh(PPh_3)_3Cl$ (2 mol %), 1.0 mL of toluene, 60 °C. [b] Isolated yields. [c] **1a** (1.0 mmol), cyclopropyl acetylene (2.4 mmol).

Table 3. Scope of Silacyclobutanes [a]





[a] Reaction conditions: **1** (0.20 mmol), phenylacetylene (0.24 mmol), $Rh(PPh_3)_3Cl$ (2 mol %), 1.0 mL of toluene, 60 °C. [b] Isolated yields.

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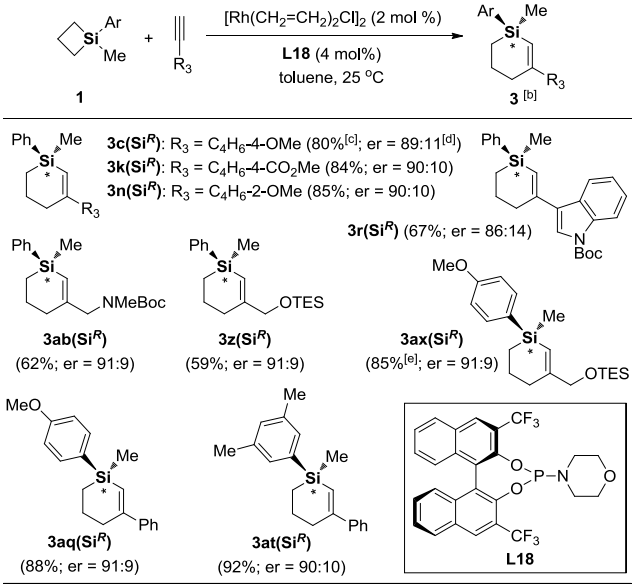
approach. However, the vinylogous propargyl methyl ester was effective to form **3ah** in 60% yield. The process also provided **3ai** and **3aj** containing a similar diene moiety.

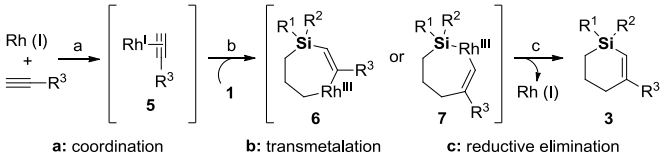
The scope of substitution on silicon was examined (Table 3). Suitable substituents included *n*-butyl, benzyl and C_3H_6OTBS groups, giving **3ak-3am** in good yields. The reaction proceeded well in the presence of allyl and homoallyl groups, affording **3an-3ao**. However, introducing a vinyl group onto the silicon inhibited the reaction to give **3ap**. The silicon can be mono- or diaryl substituted, leading to **3aq-3aw** in high yields. The electron-donating and -withdrawing groups on the phenyl ring were tolerated. A methyl group at the 2-position was sterically disfavored, such that **3au** was generated in only 37% yield.

Table 4. Scope of the Asymmetric Process[a]



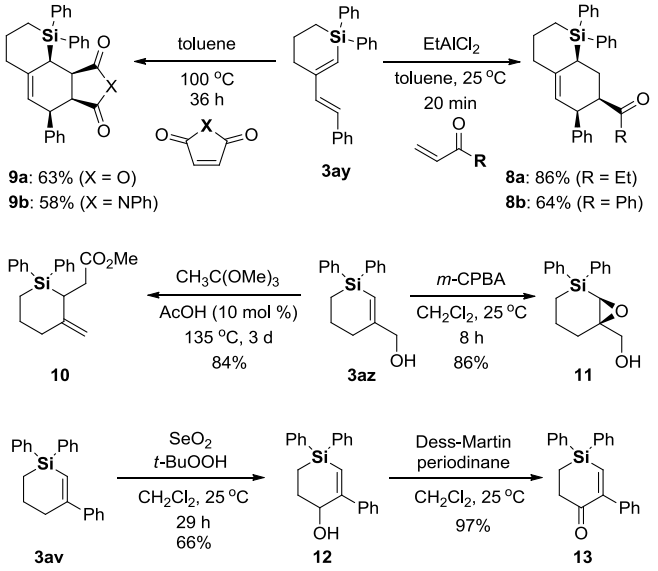
[a] Reaction conditions: **1** (0.20 mmol), alkyne (0.240 mmol), $[Rh(CH_2=CH_2)_2Cl]_2$ (2 mol %), **L18** (4 mol %), 1.0 mL of toluene, 25 °C, 10 h. [b] The configuration at Si was determined by transformation of **3ax** into the known compound. [c] Isolated yields. [d] Determined by HPLC analysis using a chiral stationary phase. [e] The yield was obtained on 1.0 mmol scale.

Inspired by the success of using $[Rh(CH_2=CH_2)_2Cl]_2$ and PPh_3 to synthesize racemic **3a** (Table 1, entry 10), we screened a range of chiral phosphine ligands to enantioselectively construct the silicon stereocenter in silacyclohexenes.[15] The binaphthyl phosphoramidite **L18**, containing 3,3'-trifluoromethyl groups,[16] most efficiently generated **3** with high *er* (Table 4). Increasing the bulkiness of the 3, 3'-groups in binaphthyl ligands typically improves enantioselectivity, but in our case, it severely reduced the *er* for **3**. This unusual steric bias implies that the bulkier 3, 3'-substituents might simultaneously increase the steric interaction with both the aryl and methyl groups on silicon when interacting with two prochiral Si-CH_2 bonds in silacyclobutanes **1**, therefore decreasing the efficiency of desymmetrization. In addition, the morpholine ring in **L18** was better than traditional nitrogen moieties such as NMe_2, $N(i\text{-}Pr)_2$ or NBn_2.



Scheme 2. Proposed catalytic cycle.

Oshima and Utimoto[8] proposed that oxidative addition of Pd to SCB initiates silacyclohexene formation from activated alkynes. Subsequent control experiments by Shintani and Hayashi[9] led them to favor a mechanism starting with Pd coordination of alkynes. When we mixed SCB **1a** with 1.0 equiv. of $Rh(PPh_3)_3Cl$ in $CDCl_3$ for 1 h at 60 °C, most **1a** remained unchanged. But the signal of the alkynyl proton in phenylacetylene shifted up-field from 3.0 to 2.0 ppm by mixing with 1.0 equiv. of $Rh(PPh_3)_3Cl$.[17] These results suggest that our reaction may proceed via a mechanism similar to Shintani and Hayashi's model. We propose the pathway in Scheme 2: the coordination of Rh with alkyne (**5**) promotes transmetalation with SCB to give Rh-silacycloheptene **6**. Reductive elimination of **6** proceeds preferentially to β-H elimination, giving silacyclohexene **3**. Formation of the Rh-silacycloheptene **7,** which cannot undergo β-H elimination, could be also possible because we did not observe the by-product **4**.



Scheme 3. Functionalization of silacyclohexenes.

Silacyclohexenes **3** could be further transformed into structurally attractive silacyclic compounds. For example, **3ay** participated in an *endo*-type Diels-Alder reaction to construct the silabicyclic **8** in the presence of $EtAlCl_2$ and silatricyclic **9** under heating. **3az** generated from selective *O*-desilylation of the corresponding silylether was subjected to Johnson-Claisen rearrangement to give cyclic allylsilane **10** in 84% yield, and to epoxidation to give 3-silyl-2,3-epoxy alcohol **11** in 86% yield. Allylic oxidation of **3av** with SeO_2 afforded silacyclohexenol **12**, which was further oxidized to silacyclohexenone **13** in 97% yield.

In summary, we have developed a Rh-catalyzed reaction of SCBs with unactivated alkynes. The reaction chemoselectively generates a wide range of silacyclohexenes. Using a chiral binaphthyl phosphoramidite bearing 3,3'-trifluoromethyl- and *N*-morpholino-substitutions provided good enantioselectivity at the stereogenic silicon center. The resulting silacyclohexenes serve as versatile synthons to generate diverse silacyclic compounds. More detailed studies and application of this approach for the synthesis of Si-biological molecules are underway.

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[17] Reaction of **1a** with phenylacetylene in $CDCl_3$ under otherwise identical conditions provided **3a** in 70% yield.

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Organosilanes

Hua Chen, Yi Chen, Xiaoxiao Tang, Shunfa Liu, Runping Wang, Tianbao Hu, Lu Gao, and Zhenlei Song*

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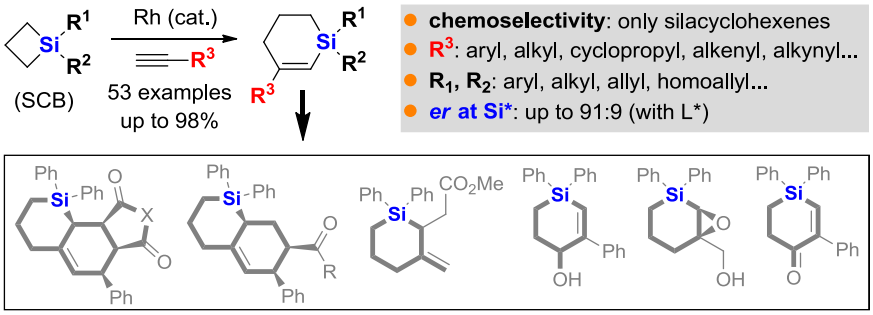
Rhodium-catalyzed Reaction of Silacyclobutanes with Unactivated Alkynes to Afford Silacyclohexenes**



A Rh-catalyzed reaction of silacyclobutanes (SCBs) with unactivated alkynes has been developed to form silacyclohexenes with high chemoselectivity. The approach tolerates a range of functionalities on the alkynes and silicon of SCBs. Good enantioselectivity at the stereogenic silicon center was achieved using a newly synthesized chiral phosphoramidite ligand. The resulting silacyclohexenes are useful scaffolds for synthesizing structurally attractive silacyclic compounds.