Ruthenium-Catalyzed Dehydrogenative Silylation of Aryloxazolines with Hydrosilanes via C–H Bond Cleavage

Fumitoshi Kakiuchi, Kimitaka Igi, Mitsutaka Matsumoto, Naoto Chatani, and Shinji Murai*
Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565-0871

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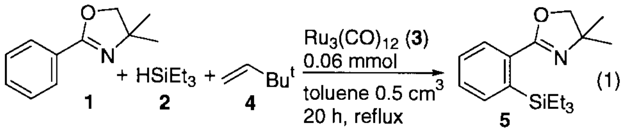
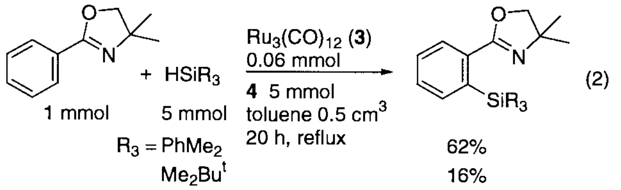
The reaction of aryloxazolines with trialkylhydrosilanes using $Ru_3(CO)_{12}$ or $Ru(H)_2(CO)(PPh_3)_3$ complex as a catalyst resulted in dehydrogenative silylation to form *ortho* silylated aryloxazolines in good to excellent yields. This reaction can be applied to aryloxazolines having either electron-donating (NMe_2, OMe, and CH_3) or -withdrawing (CF_3 and F) groups.

Since the transition metal-catalyzed dehydrogenative silylation of olefins is a useful method for obtaining synthetically versatile vinylsilanes, numerous studies have been reported in this area.[1] If this type of dehydrogenative silylation could be extended to the dehydrogenative silylation of arenes via C–H bond cleavage, this protocol would represent a powerful synthetic tool for the preparation of arylsilanes. To date, however, only a few examples have been reported.[2–7] These can be classified into three categories: one being silylation with hydrosilanes,[2–4] the second one, silylation with disilanes,[5,6] and the last one, silylation with vinylsilanes.[7] For the first procedure, the silylation of arenes with trialkylhydrosilanes catalyzed by $IrCl(CO)(PPh_3)_2$,[2] $(\eta^5\text{-}C_5Me_5)Rh(H)_2(SiEt_3)_2$,[3] $(\eta^6\text{-arene})Ru(H)_2(SiEt_3)_2$,[3] and $Pt_2(dba)_3$[4] (dba = *trans,trans*-dibenzylideneacetone) complexes is neither selective nor efficient. In the case of silylation with disilanes, $1/2Pt_2(dba)_3$-$5/3P(OCH_2)_3CEt$[5] and $Ni(PEt_3)_4$[6] catalyst systems have been found to be effective, but only a limited number of substrates can be used in this type of reaction. For the last procedure, only heteroaromatic compounds which contain directing groups, e.g., acetylthiophene, are able to react with vinylsilanes with the aid of $Ru_3(CO)_{12}$ catalyst.[7] In this communication, we describe a ruthenium-catalyzed site-selective silylation of a variety of aryloxazolines with hydrosilanes via chelation-assisted C–H bond cleavage. This is the first example of the direct silylation at a C–H bond using a hydrosilane as the source of the silyl group. The key to this success is the use of an olefin as the scavenger of the two hydrogen atoms, which effectively concludes the catalytic cycle.

When the reaction of 4,4-dimethyl-2-phenyl-2-oxazoline (**1**) with triethylsilane (**2**) with the aid of the $Ru_3(CO)_{12}$ (**3**) catalyst was carried out, the expected *ortho* silylation product **5** was obtained in only 7% yield (eq 1). We attributed the reason for this low yield to the failure in the reductive elimination of molecular hydrogen, which should be generated by the reaction of phenyloxazoline **1** with silane **2**, from the ruthenium center. It has been reported that this reductive elimination is thermally unfavorable and requires high reaction temperature, since this step is usually endothermic.[8] After intensive efforts, we discovered that *tert*-butylethylene (**4**) functions as a hydrogen scavenger. When the reaction was conducted using 2 equivalents of hydrosilane and the olefin, the yield of **5** was improved to 21% (eq 1). The use of a large amount (5 equivalents) of silane **2** and olefin **4** has led to a further improvement in the yield to 93%.[9] These results prompted us to examine dehydrogenative silylation described herein using several triorganohydrosilanes (eq 2). Dimethylphenylsilane can also be used for this reaction, but the yield is slightly decreased. Even in the case of the reaction with bulky silane, i.e., *tert*-butyldimethylsilane, silylation took place, albeit in low yield. The use of triethoxysilane, triisopropylsilane, and ethoxydimethylsilane failed to give the desired product under the reaction conditions shown in eq 2. Triethylsilane (**2**) provided the best result and, as a result, was used for further investigations.



1	2	4	5
1 mmol	5 mmol	0 mmol	7%
1 mmol	2 mmol	2 mmol	21%
1 mmol	5 mmol	5 mmol	93%

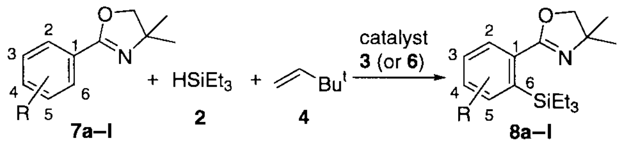


A variety of aromatic oxazolines are applicable to the present reaction. In some cases, the ruthenium carbonyl catalyst **3** exhibited only low activity and, as a result, both complex **3** and $Ru(H)_2(CO)(PPh_3)_3$ (**6**) were used as catalysts in all runs. Some representative results are listed in Table 1.

Substituents at the *ortho* position appeared to decrease the reactivity compared with **1**. Carbon–fluorine bond is known to be reduced to C–H bonds with hydrosilane using a transition metal-catalyst,[10,11] but the silylation of oxazolines which contain a fluoro group (**7b**, **7g**, and **7k**) took place without affecting the functional group. In the cases of 3-substituted aryloxazolines **7d**–**f**, the use of catalyst **6** resulted in better yields. Both catalysts showed a high level of activity for the reaction of 4-substituted oxazolines **7i**–**l**. Electron-donating substituents, such as Me, NMe_2, and OMe groups, improve the reactivity of the substrates, compared to the electron-withdrawing CF_3 group. In some cases, catalyst **3** and **6** showed different activities, and the reason of this difference is not clear at present.

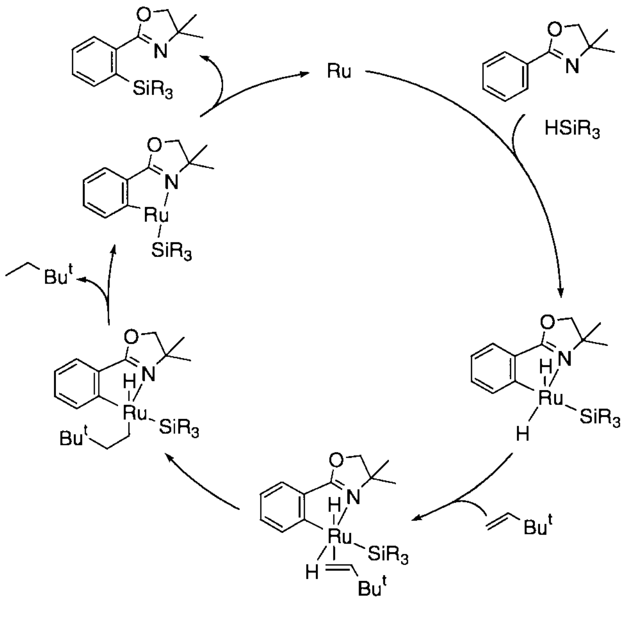
A plausible reaction pathway is shown in Scheme 1. In this proposal, an oxidative addition of the hydrosilane to the Ru(0) center occurs to give the corresponding $Ru(H)(SiR_3)$ intermediate, followed by the addition of C–H bond to the Ru(II) species, resulting in the formation of the Ru(IV)

Table 1. Ruthenium-catalyed dehydrogenative silylation of aryloxazolines **7** with triethylsilane **2**[a]



Aryloxazoline	R =	Time	Yield of 8 For Catalyst 3	(For Catalyst 6)
7a:	2-Me	20 h	49%	(72h 56%)
7b:	2-F	48 h	85%	(72h 0%)
7c:	2-CF_3	48 h	26%	(72h trace)
7d:	3-NMe_2	48 h	25%	(60 h 97%)
7e:	3-OMe	20 h	33%	(60 h 95%)[b]
7f:	3-Me	20 h	39%	(65 h 97%)
7g:	3-F	48 h	12%[c]	(72 h 8%)[d]
7h:	3-CF_3	48 h	20%	(72 h trace)
7i:	4-OMe	24 h	92%	(48 h 97%)
7j:	4-Me	24 h	94%	(48 h 98%)
7k:	4-F	48 h	79%	(72 h 65%)
7l:	4-CF_3	20 h	30%	(72 h 32%)

[a]Reaction conditons: aryloxazoline (1 mmol), triethylsilane (5 mmol), *tert*-butylethylene (5 mmol), $Ru_3(CO)_{12}$ (**3**)(0.06 mmol) or $Ru(H)_2(CO)(PPh_3)_3$ (**6**)(0.06 mmol), toluene 0.5 cm^3, reflux. [b]The silylation also occurred at the 2-position, more hindered site, giving 4,4-dimethyl-2-(3-methoxy-2-triethylsilylphenyl)-2-oxazoline in 5% yield. [c]The silylation also occurred at the 2-position giving 4,4-dimethyl-2-(3-fluoro-2-triethylsilylphenyl)-2-oxazoline (**9**) in 6% yield. [d]The product **9** was also obtained in 4% yield.



Scheme 1. A plausible reaction pathway.

species,[12] i.e., the $Ru(H)_2(SiR_3)(Ar)$ intermediate. Alternatively, the addition of the C–H bond to the Ru(0) center prior to the oxidative addition of H–Si bond cannot be excluded. At present, we have no experimental evidence that allows us to distinguish between these pathways. Since the yields of the silylation products were increased by the co-presence of the olefin as a hydrogen scavenger, the hydrogen atoms which are generated by the oxidative addition of Si–H and C–H bonds to the ruthenium center are transferred to the olefin. The resulting (silyl)(aryl)ruthenium intermediate would then undergo reductive elimination to give the corresponding silylation product. However, alternative mechanisms involving a σ bond metathesis mechanism[13] cannot be excluded at present.

A new synthetic pathway for arylsilanes via C–H bond cleavage by the reactions of aromatic oxazolines with hydrosilanes using $Ru_3(CO)_{12}$ or $Ru(H)_2(CO)(PPh_3)_3$ complex as a catalyst is described herein. This coupling reaction proceeds in the presence of both electron-donating and -withdrawing groups. The corresponding products were obtained in high yield, in many cases, by choosing the optimal catalyst. Broadening the scope of this protocol for the synthesis of arylsilanes under neutral reaction conditions and an elucidation of the reaction mechanism for this reaction are future topics to be addressed in our laboratories.

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