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Ruthenium-catalyzed alkoxylation of a hydrodisilane without Si−Si bond cleavage

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ABSTRACT

Transition metal-catalyzed synthesis of alkoxydisilanes via dehydrogenative coupling of a hydrodisilane with alcohols is reported. During the reaction, the Si−Si bond is preserved effectively when $[RuCl_2(p\text{-cymene})]_2$ is used as a catalyst. Various alcohols can be used in this alkoxylation.

Hydrosilanes are versatile compounds in organic synthesis. The Si−H bond can be transformed into a variety of other functional groups such as alkyl groups, halogen atoms, and alkoxy groups. Recently, functional group transformation of hydrooligosilanes is more and more important because hydrooligosilanes are essential precursors in the synthesis of organosilicon clusters.[1] Furthermore, modification of Si−H functions of hydrogen-terminated silicon surface[2] and silicon nanosheets[3,4] has attracted considerable attentions to improve their chemical and physical properties. The modification has expanded their remarkable potentials of application to novel functional materials.

The functional group transformation of hydrooligosilanes is based on radical reactions,[5,6] Lewis acid catalysis,[7] and organomercury-mediated reactions.[8,9] Although the functional group transformation of hydro*mono*silanes with transition metal catalysts has extensively been used, examples of hydro*oligo*silanes are limited[10] because Si−Si bonds have high reactivity to transition metal complexes to lead to the cleavage of the Si−Si bonds.[11,12] For example, numbers of transition metal catalysts have so far been found to show activity for the dehydrogenative coupling of hydromonosilanes with O−H functions.[13,14] However, the reactions of hydrooligosilanes with alcohols in the presence of transition metal catalysts gave the degradation products via Si−Si bond cleavage.[12] To the best of our knowledge, there has been no report on the transition metal-catalyzed alkoxylation of hydrooligosilanes. The most crucial point to develop functionalization of organosilicon compounds having Si−Si bonds is how to preserve the Si−Si bonds during the transformation.

We report herein ruthenium-catalyzed dehydrogenative alkoxylation of a hydrodisilane with preservation of the Si−Si bond. Realization of this reaction could expand the scope of the functionalized oligosilane synthesis.[15]

A series of transition metal catalysts was examined for the dehydrogenative alkoxylation of 1,1,2,2-tetramethyl-1-phenyldisilane (**1**) with methanol (Table 1). Among these catalysts, $[RuCl_2(p\text{-cymene})]_2$ gave the best result (entry 1). The starting material was consumed within 2 h to afford the desired methoxydisilane **2** in 89% yield along with a small amount of $PhMe_2SiOMe$ (**3**, 4%).

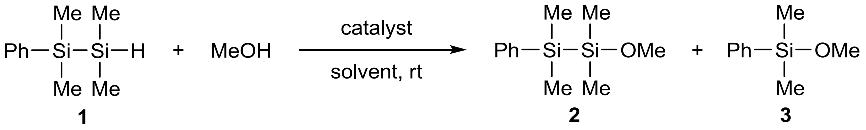
The effects of solvents and reaction temperature were studied. Toluene is also a suitable solvent for the reaction, and even at lower temperature, the reaction proceeded similarly (entries 2 and 3). When the reaction was carried out in THF, a complex mixture was obtained, and GC analysis showed that only a small amount of **2** was formed (entry 4). The reactions in hexane and dichloromethane proceeded smoothly, but the yields of **2** were lower than that in toluene (entries 5 and 6).

Other ruthenium complexes such as $[Cp^*RuCl_2]_n$, $Ru_3(CO)_{12}$, and $[Ru(cod)Cl_2]_n$ also gave unsatisfactory results (entries 7−9). In these cases, both of the desired reaction and the undesired Si−Si bond cleavage occurred simultaneously. When $Ru_3(CO)_{12}$ was used, the reaction was slow, and a large amount of **1** remained (entry 8). These results show that the choice of ligands is important in this reaction.

Transition metal catalysts other than ruthenium were also attempted. When $CoCl_2$ or $NiCl_2$ was used, no reaction took place (entries 10 and 11). The reactions with the transition metal complexes such as $[Rh(cod)_2]BF_4$, $PdCl_2$, and $Pd[P(t\text{-Bu})_3]_2$ gave undesired monosilane **3** as the major product via Si−Si bond

Table 1

Reactions of **1** with methanol in the presence of various transition metal catalysts



Entry	Catalyst[a]	Solvent	MeOH (equiv)	Reaction time (h)	**1**[b] (%)	**2**[b] (%)	**3**[b] (%)
1	$[RuCl_2(p\text{-cymene})]_2$	Benzene	1.5	2	0	89	4
2	$[RuCl_2(p\text{-cymene})]_2$	Toluene	1.5	2	3	83	6
3[c]	$[RuCl_2(p\text{-cymene})]_2$	Toluene	1.4	2	8	77	1
4	$[RuCl_2(p\text{-cymene})]_2$	THF	1.8	2	4	8	18
5	$[RuCl_2(p\text{-cymene})]_2$	Hexane	1.2	2	17	64	2
6	$[RuCl_2(p\text{-cymene})]_2$	CH_2Cl_2	1.1	2	0	62	0
7[c]	$[Cp^*RuCl_2]_n$	Toluene	1.5	48	5	10	39
8[c]	$Ru_3(CO)_{12}$	Toluene	1.5	24	69	12	2
9[c]	$[Ru(cod)Cl_2]_n$	Toluene	1.5	24	22	33	13
10	$CoCl_2$	Benzene	1.0	2	100	0	0
11	$NiCl_2$	Benzene	0.86	2	100	0	0
12	$[Rh(cod)_2]BF_4$	Benzene	1.0	48	0	2	42
13	$PdCl_2$	Benzene	0.92	2	2	0	84
14	$Pd[P(t\text{-Bu})_3]_2$	Benzene	1.0	48	0	0	42
15[c]	$[ReBr(CO)_3(thf)]_2$	Toluene	1.5	24	22	40	2
16[c]	$[CpMo(CO)_3]_2$	Toluene	1.5	24	88	1	0

[a] 5 mol% on the employed metal. [b] Yields were determined by GC. [c] The reaction was conducted at 0 °C.

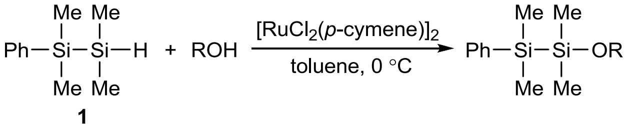
cleavage (entries 12−14). The reaction with $[ReBr(CO)_3(thf)]_2$ afforded **2** in moderate yield, but the prolonged reaction time showed no improvement of the yield of **2** (entry 15). The catalytic activity of $[CpMo(CO)_3]_2$ is very weak, and most of **1** remained unreacted (entry 16).

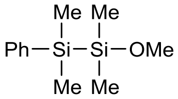
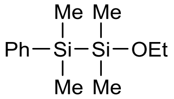
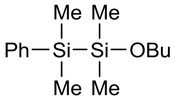
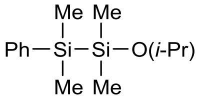
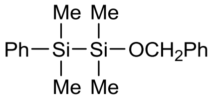
Thus obtained optimized conditions were applied to alkoxylation with various alcohols (Table 2). The reactions with primary alcohols such as ethanol and 1-butanol gave the corresponding alkoxydisilanes in high yields (entries 2 and 3). When these reactions were carried out at room temperature, the yields were decreased due to formation of a large amount of the alkoxydimethylphenylsilanes. The reaction with 2-propanol was more sluggish than those with primary alcohols. Therefore, a large excess amount of 2-propanol was used to reduce the reaction time, and the desired (isopropoxy)disilane was obtained in good yield (entry 4). The reaction was applicable to benzyl alcohol to furnish benzyloxydisilane in high yield (entry 5). However, the isolated yield was low due to its more susceptible nature to moisture than the other alkoxydisilanes and difficulty in separation from benzyl alcohol. The reactions with 2-methyl-2-propanol and neopentyl alcohol, however, gave no desired products, probably due to the steric congestion of the employed alcohols.

To obtain information on the reaction mechanism, the stoichiometric reactions were carried out (Scheme 1). When $[RuCl_2(p\text{-cymene})]_2$ was mixed with **1** in toluene-d_8 at room temperature, the monohydrido-diruthenium complex **4** was formed in 33% NMR yield along with chlorodisilane **5** (54%) based on the starting diruthenium complex (maximum 200% yield). Complex **4** was identified by comparison of the ^{1}H NMR spectrum with the reported data.[16] The characteristic signal of the bridged hydride is observed at −10.2 ppm, and two pairs of aromatic protons and isopropyl methyl protons of the η^6-*p*-cymene ligands are observed. The formation of **5** was also confirmed by the ^{29}Si NMR spectrum. The similar results have been reported in the reaction of $[RuCl_2(p\text{-cymene})]_2$ with triethylsilane to afford **4** and the mononuclear ruthenium complex, $(p\text{-cymene})Ru(SiEt_3)_2H_2$ (**6**) along with chlorotriethylsilane.[17]

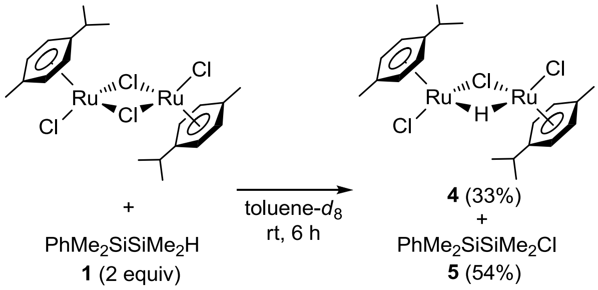
Table 2

Reactions of **1** with various alcohols in the presence of $[RuCl_2(p\text{-cymene})]_2$



Entry	Alcohol (equiv)	Reaction time (h)	Product	Yield[a] (%)
1	MeOH (1.4)	2	 $Ph-SiMe_2-SiMe_2-OMe$	63
2	EtOH (1.5)	24	 $Ph-SiMe_2-SiMe_2-OEt$	78
3	BuOH (1.5)	24	 $Ph-SiMe_2-SiMe_2-OBu$	87
4	*i*-PrOH (5.6)	24	 $Ph-SiMe_2-SiMe_2-O(i\text{-}Pr)$	80
5	$PhCH_2OH$ (1.5)	24	 $Ph-SiMe_2-SiMe_2-OCH_2Ph$	29 (73)

[a] Isolated yield. A GC yield was given in parentheses.



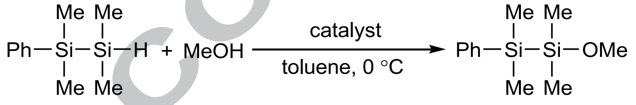
Scheme 1. Reaction of [RuCl$_2$(*p*-cymene)]$_2$ with **1**.

The catalytic activity of **4** and **6** (prepared in situ from [RuCl$_2$(*p*-cymene)]$_2$ and triethylsilane in toluene according to the literature[17]) was examined. The reactions of **1** with methanol in the presence of **4** and **6** in toluene at 0 °C afforded **2** in 77 and 57% yields, respectively. This result suggests that not only **4** but also mononuclear ruthenium complexes such as **6** are candidates for the real catalysts in this reaction. A possible mechanism may include disilanyl-substituted ruthenium hydride species generated by oxidative addition of the Si−H bond of **1**. Of course, the present results are not enough to exclude other possible mechanisms, where a Si−H σ-complex intermediate is included.[18,19]

In contrast, when [RuCl$_2$(*p*-cymene)]$_2$ was added to methanol in benzene-d_6, no reaction was observed by the ^{1}H NMR spectrum. This seems natural since hot alcohol is used as a solvent in the preparation of [RuCl$_2$(*p*-cymene)]$_2$.[20]

As the results described here strongly suggest the superiority of the (η^6-arene)ruthenium complex for dehydrogenative coupling without Si−Si bond cleavage, other (η^6-arene)ruthenium complexes were also examined (Table 3). The benzene complex is effective similarly to the *p*-cymene complex (entry 1). When the mesitylene complex was employed, the reaction rate was slow, but **2** was formed in high yield after prolonged reaction time (entries 2 and 3). In contrast, the reaction with the hexamethylbenzene complex was very slow at 0 ºC, and a complex mixture was formed when heated at 50 ºC. The Tsdpen complex was not effective in this reaction (entry 5). The reduced reactivity of the mesitylene and Tsdpen complexes can be explained by the steric hindrance of the η^6-arene ligands.

Table 3
Reactions of **1** with methanol in the presence of various (η^6-arene)ruthenium catalysts



1 **2**

Entry	Catalyst[a]	Reaction time (h)	**2**[b] (%)
1	[RuCl$_2$(benzene)]$_2$	2	76
2	[RuCl$_2$(mesitylene)]$_2$	2	14
3	[RuCl$_2$(mesitylene)]$_2$	72	85
4	[RuCl$_2$(C$_6$Me$_6$)]$_2$	96	14
5	RuCl[(*S*,*S*)-Tsdpen](*p*-cymene)	24	14

[a] 5 mol% on the ruthenium atom. [b] Yields were determined by GC.

In conclusion, we have developed the efficient transition metal-catalyzed functionalization of the Si−H bond of **1** with preservation of the Si−Si bond. Studies on the scope of the reactions with various types of hydrooligosilanes and alcohols, and further confirmation of the reaction mechanism are now in progress.

Acknowledgments

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2016.xx.xxx.

Graphical Abstract

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Ruthenium-catalyzed alkoxylation of a hydrodisilane without Si−Si bond cleavage

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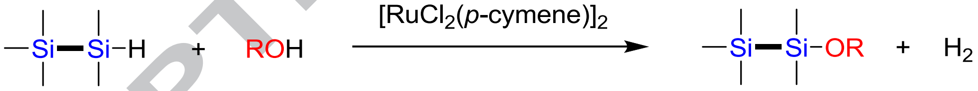
Ken-ichiro Kanno, Yumi Aikawa, Soichiro Kyushin



Highlights

1) Alkoxylation of a hydrooligosilane has been accomplished without Si−Si bond cleavage.
2) $[RuCl_2(p\text{-cymene})]_2$ is the most effective catalyst.
3) Various alcohols can be used in this alkoxylation.