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PII: S0040-4039(16)31554-4
DOI: http://dx.doi.org/10.1016/j.tetlet.2016.11.073
Reference: TETL 48359

To appear in: *Tetrahedron Letters*

Received Date: 17 September 2016
Revised Date: 14 November 2016
Accepted Date: 17 November 2016

Please cite this article as: Kanno, K-i., Aikawa, Y., Kyushin, S., Ruthenium-catalyzed alkoxylation of a hydrodisilane without Si−Si bond cleavage, *Tetrahedron Letters* (2016), doi: http://dx.doi.org/10.1016/j.tetlet.2016.11.073

Tetrahedron Letters
journal homepage: www.elsevier.com

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

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ARTICLE INFO

Article history:
Received
Received in revised form
Accepted
Available online

Keywords:
Alkoxylation
Dehydrogenative coupling
Hydrooligosilane
Silicon−silicon bond

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