Bissilyl Ketone; A Convenient Method for the Synthesis and Its Pd(0) Catalyzed Reaction with Alkenes and Alkynes

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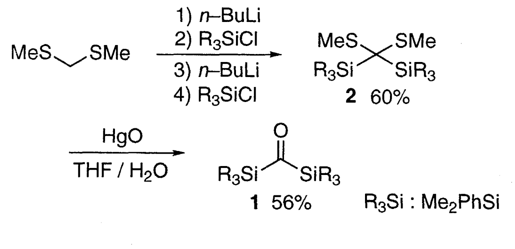
A convenient method for the preparation of a bissilyl ketone is developed via a bissilyl ketone acetal as its precursor. The bissilyl ketone reacts with electron deficient alkynes and alkenes in the presence of Pd(0) catalyst to give bis–silylated products.

Organosilicon compounds have been widely employed in organic synthesis according to their characteristic reactivity and physical property. However, bissilyl ketones are remaining not to be studied well due to the difficulty of their synthesis.

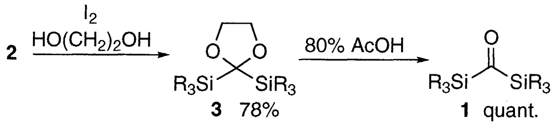
We have reported the synthesis of bis(dimethylphenylsilyl) ketone (**1**) and its reaction with some nucleophiles.[1] Though bis(trimethylsilyl) ketone is readily oxidized in the air, the bissilyl ketone **1** can be isolated as crystals, which is rather stable and gradually decomposed in the air. The X-ray crystallographic analysis of **1** revealed that the Si-C(carbonyl) bond is longer than any other Si-C bond of organosilicon compounds such as acylsilanes.[2] Accordingly, it was supposed that Si-C(carbonyl) bond of the bissilyl ketone **1** would be cleaved by the oxidative addition to Pd(0) compounds. In this paper, we will report a convenient preparative method of the bissilyl ketone **1** and the bis–silylation of electron deficient alkynes and alkenes with **1** using Pd(0) catalysts.

Brook and Ricci have reported the synthesis of bissilyl ketones,[3] however, these synthetic routes involve the oxidation step to generate bissilyl ketones. This makes the yield of bissilyl ketones poor, because bissilyl ketones are readily decomposed by oxidation. Our previous synthetic route of the bissilyl ketone **1** is shown in equation 1. Bis(methylthio)methane was lithiated and silylated successively to give bis(dimethylphenylsilyl) ketone dithioacetal **2**. This dithioacetal **2** was hydrolyzed in the presence of HgO and the bissilyl ketone **1** was obtained in 56% yield. This method, however, is not suitable for multi-gram scale synthesis, because **1** was gradually oxidized even with a weak oxidant such as HgO.



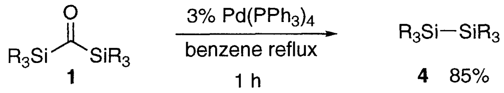
(eq. 1)

To avoid the generation of the bissilyl ketone in the presence of oxidizing reagents, the preparation of **1** was attempted via the corresponding acetal. When bis(methylthio)bis(dimethylphenylsilyl)methane (**2**) was treated with iodine in ethyleneglycol–acetonitrile, an acetal **3** was obtained in 78% yield.[4] The acetal **3** is a stable white solid and is hydrolyzed to the bissilyl ketone **1** quantitatively by treatment with 80% acetic acid (eq. 2).



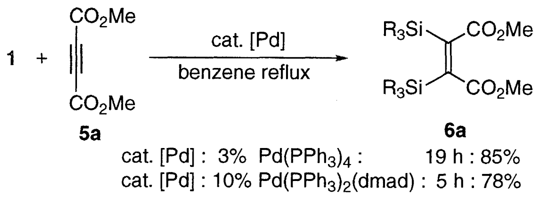
(eq. 2)

Thus, a sufficient amount of the bissilyl ketone **1** could be prepared by the above method, and the reaction of **1** with Pd(0) compounds was examined next. When bis(dimethylphenylsilyl) ketone (**1**) was treated with a catalytic amount of $Pd(PPh_3)_4$ in refluxing benzene, 1,1,2,2-tetramethyl-1,2-diphenyldisilane (**4**) was obtained in 85% yield (eq. 3). The generation of the disilane **4** indicated that the oxidative addition of the Si–C(carbonyl) bond occurred to the Pd(0) catalyst and the reductive elimination presumably proceeded via bissilyl Pd(II) species **7** (*vide infra*) to give the disilane **4**.



(eq. 3)

As it was expected that insertion reaction of acetylenic compounds would proceed to the bissilyl Pd(II) species **7**, bis(dimethylphenylsilyl) ketone **1** was treated in refluxing benzene with a catalytic amount of $Pd(PPh_3)_4$ in the presence of dimethyl acetylenedicarboxylate (DMAD) (**5a**). In fact, bis–silylation proceeded to give dimethyl 1,2-bis(dimethylphenylsilyl)maleate (**6a**) in 85% yield, though it took 19 h to consume the bissilyl ketone **1** (eq. 4). When the disilane **4** was treated with DMAD under the same conditions in the presence of $Pd(PPh_3)_4$, the bis–silylated product **6a** was not obtained and **4** was recovered. Since the oxidative addition of the disilane **4** does not occur under these reaction conditions, bis–silylation of **5a** does not proceed with the disilane **4** but directly with the bissilyl ketone **1**.[5]

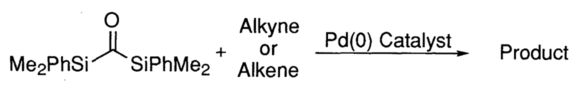


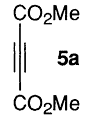
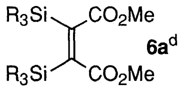
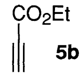
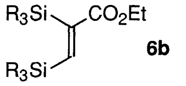
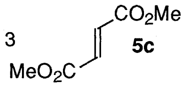
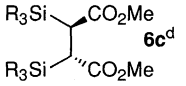
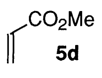
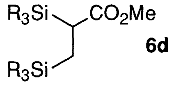
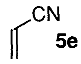
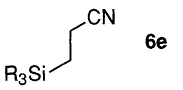
(eq. 4)

Since $Pd(PPh_3)_2(dmad)$ is known to be generated by mixing $Pd(PPh_3)_4$ and DMAD,[6] $Pd(PPh_3)_2(dmad)$ was supposed as the active catalyst of the above bis–silylation reaction. When the reaction was tried by using $Pd(PPh_3)_2(dmad)$ as a catalyst, the bissilyl ketone **1** was disappeared within 5 h and **6a** was obtained in 78% yield.

Results of the Pd(0) catalyzed reactions of **1** with some electron deficient alkynes and alkenes are summarized in Table 1.

Table 1. Pd(0) catalyzed reactions of bissilyl ketone with alkynes and alkenes



Entry	Alkynes or Alkenes	Product (R_3Si : Me_2PhSi)	Catalyst A[a] Yield / % (Time / h)	Catalyst B[b] Yield / % (Time / h)
1	 **5a**	 **6a**[d]	85 (19)	78 (5)
2	 **5b**	 **6b**	27 (20)	25 (5) 41 (5)[c]
3	 **5c**	 **6c**[d]	9 (38)	20 (5)[c]
4	 **5d**	 **6d**	9 (14)	10 (5)[c]
5	 **5e**	 **6e**	40 (14)	28 (5)[c]

[a] Catalyst A: $Pd(PPh_3)_4$. The reactions were carried out by using 3 mol% of $Pd(PPh_3)_4$ and 300 mol% of alkyne or alkene in refluxing benzene.

[b] Catalyst B: $Pd(PPh_3)_2$(dmad). The reactions were carried out by using 10 mol% of $Pd(PPh_3)_2$(dmad) and 300 mol% of alkyne or alkene in refluxing benzene.

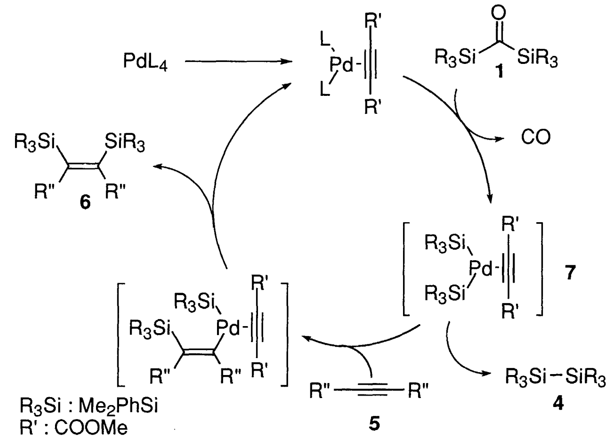
[c] *N,N,N',N'*-tetramethylethylenediamine was added.

[d] When **6a** was hydrolyzed and then treated with trifluoroacetic anhydride, the corresponding acid anhydride was obtained. Thus **6a** was determined as *Z*-form. The relative configuration of **6c** was determined by X-ray crystallographic analysis. The bis-silylation of these unsaturated compounds proceeds by *cis*-addition.

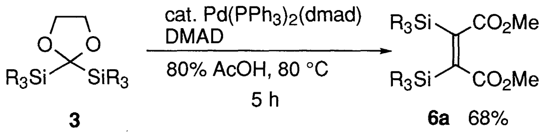
As shown in the entries 1 and 2, the oxidative addition of the bissilyl ketone **1** proceeded more rapidly by the use of $Pd(PPh_3)_2$(dmad) as compared with $Pd(PPh_3)_4$, though the yield of the bis-silylated products was not improved. Only the disilane **4** was isolated as a side product in these reactions. To reduce the reductive elimination of the disilane **4** from the bissilyl Pd intermediate **7**, *N,N,N',N'*-tetramethylethylenediamine was added as an amine ligand.[7] By this modification, the yield of the **6b** was improved considerably (entry 2). In the reactions of **5b-e**, by using $Pd(PPh_3)_2$(dmad) as the catalyst, the bis-silylated product of DMAD **5a** was not detected. That is, the scrambling of DMAD ligand with other alkynes or alkenes **5b-e** does not occur under these reaction conditions.

The proposed mechanism is shown in Scheme 1. Oxidative addition of C–Si bond of the bissilyl ketone **1** to $Pd(PPh_3)_2$(dmad) occurs, then elimination of carbon monoxide gives the bissilyl Pd species **7**. The disilane **4** is obtained by the reductive elimination from the intermediate **7**. By the insertion of an alkyne to **7**, followed by reductive elimination, the bis-silylated product **6** is formed.

Scheme 1. Mechanism of bis-silylation of alkynes and alkenes.



The bis-silylation of alkynes can be also performed with the bissilyl ketone acetal **3**. When bis(dimethylphenylsilyl) ketone acetal **3** was treated with DMAD in the presence of the Pd(0) catalyst in 80% acetic acid, the bis-silylated product **6a** was obtained in 68% yield (eq. 5). This method would be useful, because the isolation of bissilyl ketones, which is susceptible of air-oxidation, is not required.



(eq. 5)

As described above, oxidative addition of bissilyl ketone to Pd(0) occured smoothly as compared with the corresponding disilane and the reaction with electron deficient alkynes and alkenes gave bis-silylated products.

References and Notes

1 K. Narasaka, N. Saito, Y. Hayashi, and H. Ichida, *Chem. Lett.*, **1990**, 1411.

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