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New Si–C bond forming reactions over solid-base catalysts

Toshihide Baba, Akiko Kato, Hiroko Yuasa, Fumihiko Toriyama,
Haruhisa Handa, Yoshio Ono*

Department of Chemical Engineering, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152, Japan

Abstract

The reactions of silanes with carbanions generated on the surface of solid bases bring about the nucleophilic substitution at the Si atom to form Si–C bonds. The reaction of alkynes with silanes afforded alkynylsilanes. For example, the reaction of *tert*-BuC$\equiv$CH or *n*-BuC$\equiv$CH with Et_2SiH_2 in the presence of KNH_2/Al_2O_3 gave *tert*-BuC$\equiv$CSiEt$_2$H and *n*-BuC$\equiv$CSiEt$_2$H in a 77% and 67% yield, respectively, at 329 K. Toluene also reacted with Et_2SiH_2 at 329 K to yield benzyldiethylsilane in a 85% yield. The reactions of 1-alkynes with $Me_3SiC\equiv CH$ in the presence of KNH_2/Al_2O_3 or KF/Al_2O_3 resulted in a novel type of metathesis reaction between the two alkynes. For example, the reaction of PhC$\equiv$CH with $Me_3SiC\equiv CH$ afforded $PhC\equiv CSiMe_3$ and HC$\equiv$CH in a high yield. These new types of base-catalyzed reactions provide new synthetic routes for Si–C bond formation. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Solid-base catalysts; Si–C bond; Alkynylsilanes; Benzylsilanes; Alkynes

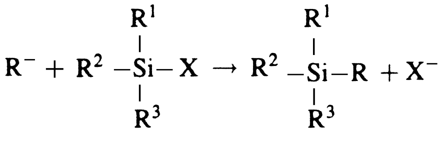
1. Introduction

The reaction of carbanions with silanes is one of the most important methods for achieving Si–C bond forming synthetic sequences [1–5]. The most common sources of carbanions are alkyllithium and Grignard reagents. The detailed mechanism of the nucleophilic substitution has also been extensively discussed.

Carbanions can be generated from various sources by the action of bases, but this method has rarely been used for Si–C bond formation. Ito et al. [6] reported that dehydrogenative coupling occurred between phenylsilanes and 1-hexyne to directly afford Si–C bonds. For example, the reaction of diphenylsilane and 1-hexyne proceeds in the presence of MgO to give 1-diphenylsilylhex-1-yne. The reaction mechanism proposed involves the formation of alkynyl anions, which were formed by the abstraction of a proton from an alkyne molecule by the basic sites on MgO.

In this work, we will report on the three types of Si–C bond forming reactions with use of solid bases, where carbanions are generated on their surface. The general scheme of the reaction is expressed as follows.

$$RH + B^- \rightarrow R^- + BH$$



$$R^- + R^2-\overset{\displaystyle R^1}{\underset{\displaystyle R^3}{\overset{|}{\underset{|}{Si}}}}-X \rightarrow R^2-\overset{\displaystyle R^1}{\underset{\displaystyle R^3}{\overset{|}{\underset{|}{Si}}}}-R + X^-$$

$$X^- + BH \rightarrow B^- + HX$$

Here, B^- and X^- denote the basic sites of catalysts and the group leaving from the Si atom, respectively.

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*Corresponding author. Tel.: 00 81 3 5734 2625; fax: 00 81 3 5734 2878; e-mail: tbaba@o.cc.titech.ac.jp

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Catalysts used in this work are KNH_2/Al_2O_3 and KF/Al_2O_3. We have reported that KNH_2, which is supported on alumina from its ammoniacal solution and heated under vacuum at 573 K, is a very strong base [7]. The catalyst showed very high catalytic activities for the isomerization of alkenes [7,8]. For example, 2,3-dimethylbut-1-ene is readily converted to 2,3-dimethylbut-2-ene even at 201 K in the presence of KNH_2/Al_2O_3.

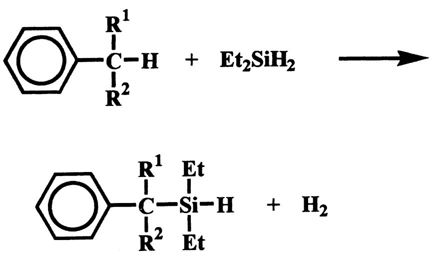
KF supported on alumina has been used as a convenient base for many organic reactions [9–19]. Recently, Hattori and coworkers [20] have reported that KF/Al_2O_3 shows a high activity for the isomerization of 1-pentene only when it was treated around 623 K under vacuum. We have also reported that KF/Al_2O_3 showed high activity for self-condensation of benzaldehyde to benzyl benzoate when heated around 670 K under vacuum [21]. Here, KF/Al_2O_3 was heated under vacuum at 673 K and then used as a catalyst.

Types of reactions studied and typical examples studied in this work are as follows:

(I) Dehydrocoupling of 1-alkyne and Et_2SiH_2

$$RC \equiv CH + Et_2SiH_2 \rightarrow RC \equiv CSi(Et)_2H + H_2 \qquad (1)$$

(II) Reaction of alkylbenzene with Et_2SiH_2



(2)

(III) Metathesis of 1-alkyne and $Me_3SiC{\equiv}CH$

$$\begin{aligned} &RC \equiv CH + Me_3SiC \equiv CH \\ &\rightarrow RC \equiv CSiMe_3 + HC \equiv CH \qquad (3) \end{aligned}$$

These novel types of reactions over solid bases may offer new routes for Si–C bond formation.

2. Experimental

2.1. Catalyst preparation

Alumina used as a support had a surface area of 131 $m^2\,g^{-1}$ and an average diameter of 15 nm. KNH_2 loaded on alumina (KNH_2/Al_2O_3) was prepared by impregnation from its ammoniacal solution as follows; alumina and a small amount of Fe_2O_3 (2 wt% per g-alumina) was placed in a quartz reactor and then heated under vacuum at 673 K for 3 h. Fe_2O_3 was a catalyst for converting K metal into KNH_2 in liquid ammonia. A piece of K metal (2.6 mmol per g-alumina) was added into the reactor under nitrogen. After evacuation, ammonia was liquefied into the reactor cooled with a dry-ice-ethanol, to dissolve the K metal. The blue color due to solvated electrons disappeared in about 10 min, indicating the formation of KNH_2. After 1 h, the reactor was warmed to room temperature to remove liquid ammonia and then heated under vacuum at 573 K for 1 h.

KF-loaded alumina was prepared by an impregnation method from their aqueous solutions followed by drying in air at 393 K for 12 h. Prior to the reactions, the catalysts were evacuated under 10^{-3} Pa at 673 K for 3 h.

2.2. Reaction procedures

Silanes such as $Me_3SiC{\equiv}CH$ and Et_2SiH_2 obtained from Shin-etsu Chemical were used without further purification. 1-Alkynes such as $PhC{\equiv}CH$ were distilled under reduced pressure. Benzene and heptane were refluxed with Na metal for 5 h before distillation.

The mixture of the purified reactants placed in a glass tube, which was then attached to the side arm of the quartz reactor, was degassed with a freeze-thaw method. The reaction was started by transferring the mixture into the reactor containing a catalyst prepared as described above. The products were identified with ^{1}H NMR and GS-MAS. The conversion and the yields of the products were determined with a gas-chromatograph (a OV 101 glass column) using propylbenzene as an internal standard. The yields of products were calculated based on the starting silanes.

3. Results and discussion

3.1. Dehydrocoupling of 1-alkyne with silane

Alkynylsilanes are versatile reagents in organic synthesis. They are usually synthesized by the reactions of chlorosilanes with alkynylmetals derived from organometallic reagents such as alkyl lithium or Grignard reagents. In addition, several procedures for synthesizing alkynylsilanes have been reported [22–25]. Liu and Harrod [22] reported that CuCl catalyzed the dehydrocoupling between silanes and 1-alkynes such as phenylacetylene. Hiyama and co-workers [23] have reported that the reaction of 1-alkynes with chlorosilanes takes place around 390 K in the presence of metallic zinc or metallic samarium and zinc(II) chloride [24]. However, the reaction is not catalytic. It has been reported that dehydrocondensation of trialkylsilanes with 1-alkynes by using transition metal complexes such as H_2PtCl_6–metal halide catalysts [25]. In this case, hydrosilylation occurs as a side reaction.

Alkynyl anions can be generated from alkynes by base catalysts [26]. Therefore, the reaction of the carbanions thus generated with silanes may lead to the formation of new Si–C bonds. The scheme of the reaction between an alkyne and Et_2SiH_2 can be expressed as follows:

$$\begin{aligned} &RC \equiv CH + B^- \rightarrow RC \equiv C^- + BH \\ &RC \equiv C^- + Et_2SiH_2 \rightarrow RC \equiv CSi(Et)_2H + H^- \\ &H^- + BH \rightarrow B^- + H_2 \end{aligned} \tag{4}$$

The overall reaction is expressed by

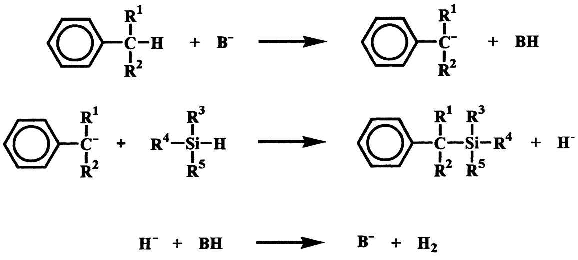
$$RC \equiv CH + Et_2SiH_2 \rightarrow RC \equiv CSi(Et)_2H + H_2 \tag{5}$$

The reactions of alkynes with Et_2SiH_2 were carried out in the presence of KNH_2/Al_2O_3 at 329 K. The results are listed in Table 1. When *tert*-BuC≡CH (3.0 mmol) was stirred with Et_2SiH_2 (1.5 mmol) in the presence of KNH_2/Al_2O_3 at 329 K for 20 h, *tert*-BuC≡CSi$(Et)_2$H was obtained in a 77% yield (based on the silane). A secondary product, (*tert*-BuC≡C)$_2$Si$(Et)_2$ was also obtained in a 3% yield. Under the same reaction conditions, the reaction of 1-hexyne (*n*-BuC≡CH) with Et_2SiH_2 gave *n*-BuC≡CSi$(Et)_2$H and (*n*-BuC≡C)$_2$-SiEt$_2$ in 67% and 9% yields, respectively. In this case, the isomerization of 1-hexyne to 2-hexyne also took place.

In the case of PhC≡CH, however, the dehydrocoupling between the two alkynes occurred only slightly. Instead, the dimerization of the alkyne extensively proceeded to give (*Z*)-1,4-diphenylbut-1-ene-3-yne. We have already reported that KNH_2/Al_2O_3 is the regio- and stereo-selective catalyst for the dimerization of phenylacetylene [26].

3.2. *Reactions of alkylbenzene with silane*

Benzyl anions can be generated from alkylbenzenes such as toluene. Therefore, the nucleophilic substitution at a Si atom of silane molecules may proceed to afford benzylsilanes. The general reaction scheme can be expressed as follows



(6)

In the case of the reaction between toluene and Et_2SiH_2, the overall reaction is expressed by Eq. (7)

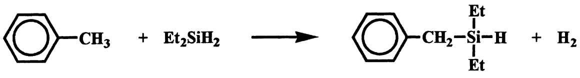


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Table 1
Reaction of Et_2SiH_2 with RC≡CH

R	Yield (%)		Other products	
	RC≡CSi$(Et)_2$H	(RC≡C)$_2$SiEt$_2$		
Me$_3$C-	77	9	None	
C_4H_9-	67	9	2-Hexyne	49^a%
Ph-	0.5	0	(*Z*)-1,4-Diphenylbut-1-ene-3-yne	60^a%
			(*E*)-1,4-diphenylbut-1-ene-3-yne	2.4^a%

Conditions: 329 K, 20 h, RC≡CH: 3.0 mmol, Et_2SiH_2: 1.5 mmol, 0.20 g KNH_2/Al_2O_3, solvent: hexane 2 cm^3.
^{a}The yield was calculated based on RC≡CH.

Table 2
Reaction of toluene with alkylsilanes over KNH_2/Al_2O_3

Reactant	Amount of reactant (mmol)	Reaction temperature (K)	Yield of alkylbenzylsilane (%)
Et_2SiH_2	1.5	329	74
Et_3SiH	3.2	363	22
$(Me)_2PhSiH$	3.2	353	4
$(C_4H_9)(Me)_2SiH$	3.0	329	3
$PhSiH_3$	4.2	373	1 (Ph_2SiH_2 40%)

Conditions: 20 h, 0.20 g of KNH_2/Al_2O_3, toluene 28 mmol. Amount of K metal 2.6 mmol per 1.00 g of Al_2O_3.

3.2.1. *Reactions of toluene with alkylsilanes*

When Et_2SiH_2 was stirred in excess toluene in the presence of KNH_2/Al_2O_3 at 329 K for 20 h, benzyldiethylsilane was obtained in a 74% yield (Table 2). The yield was increased to 40% by increasing the reaction time to 40 h. Though not shown in Table 2, $RbNH_2/Al_2O_3$ was as active as KNH_2/Al_2O_3 for this reaction.

Reactions of toluene with alkylsilanes other than Et_2SiH_2 were also carried out in the presence of KNH_2/Al_2O_3 and the results are also listed in Table 2. Toluene reacted with Et_3SiH to afford a 22% yield of benzyltriethylsilane at 363 K. In the case of $(Me)_2PhSiH$ and n-$Bu(Me)_2SiH$, the yields of the corresponding benzylsilanes were very low.

3.2.2. *Reactions of alkylbenzenes with Et_2SiH_2*

Reactions of various alkylbenzenes with Et_2SiH_2 were carried out in the presence of KNH_2/Al_2O_3 at 329 K for 20 h (Table 3). Ethylbenzene gave a 23% yield of diethyl-1-phenylethylsilane. Propylbenzene and isopropylbenzene also reacted with Et_2SiH_2 to give diethyl(1-phenylethyl)silane and diethyl(1-phenyl-1-methylethyl)silane in 7% and 2% yields, respectively. Thus, the reactivity towards Et_2SiH_2 are in the order of toluene > ethylbenzene > propylbenzene > isopropylbenzene. This reactivity order seems to agree with the acidity of these alkylbenzenes [27].

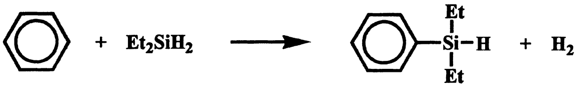
Table 3
Reactivates of alkylbenzenes with Et_2SiH_2 over KNH_2/Al_2O_3

Reactant (mmol)	pK_a	Amount of reactant	Yield (%)
Toluene	35[a]	28	74
Ethylbenzene		25	23
Propylbenzene		21	7.0
Isopropylbenzene	37[a]	29	2.0

Conditions: 0.20 g of KNH_2/Al_2O_3, 329 K, 20 h, Et_2SiH_2: 1.5 mmol. Amount of K metal 2.6 mmol per 1.00 g of Al_2O_3.
[a] From [27].

3.2.3. *Reaction of benzene with Et_2SiH_2*

Benzene has a pK_a value of 37, which is almost same as that of isopropylbenzene [27], reacted with Et_2SiH_2. Therefore, the reaction of benzene with Et_2SiH_2 was examined. When Et_2SiH_2 (3.1 mmol) was stirred with excess benzene in the presence of KNH_2/Al_2O_3 at 329 K for 20 h, diethylphenylsilane was obtained in a 7.5% yield.



(8)

3.2.4. *Metathesis between 1-alkyne and $Me_3SiC{\equiv}CH$*

If nucleophilic attack of an alkynyl anion ($RC{\equiv}C^-$) generated from an alkyne molecule at a Si atom of $Me_3SiC{\equiv}CH$ should result in the metathesis between alkynes. In this case, $HC{\equiv}C^-$ is a leaving group. The scheme over base catalysts is expressed as

$$\begin{aligned} &RC \equiv CH + B^- \rightarrow RC \equiv C^- + BH \\ &RC{\equiv}C^- + Me_3SiC{\equiv}CH \rightarrow RC{\equiv}CSiMe_3 + HC{\equiv}C^- \\ &HC \equiv C^- + BH \rightarrow B^- + HC \equiv CH \end{aligned} \tag{9}$$

The overall reaction between phenylacetylene and $Me_3SiC{\equiv}CH$ is expressed by Eq. (10).

$$\begin{aligned} &RC{\equiv}CH + Me_3SiC{\equiv}CH \\ &\quad \rightarrow RC{\equiv}CSiMe_3 + HC{\equiv}CH \end{aligned} \tag{10}$$

When $Me_3SiC{\equiv}CH$ was stirred in the presence of KNH_2/Al_2O_3 at 298 K for 30 min, $Me_3SiC{\equiv}CSiMe_3$ was obtained in a 77% yield, indicating that metathesis occurred between two molecules of $Me_3SiC{\equiv}CH$ (Table 4).

$$\begin{aligned} &2Me_3SiC{\equiv}CH \\ &\quad \rightarrow Me_3SiC{\equiv}CSiMe{\equiv}3 + HC{\equiv}CH \end{aligned} \tag{11}$$

KF/Al_2O_3 was also very effective as the catalyst for this metathesis.

Table 4
Reaction of $\mathrm{Me_3SiC{\equiv}CH}$ with 1-alkynes ($\mathrm{RC{\equiv}CH}$)

Catalyst	Reactants		Reaction temperature	Reaction time (h)	Main product	Other products
$\mathrm{KNH_2/Al_2O_3}$ 0.125 g	—	$\mathrm{Me_3SiC{\equiv}CH}$ 13.5 mmol	298 K	0.5	5.2 mmol (77%)	$\mathrm{Me_3SiC{\equiv}CSiMe_3}$
$\mathrm{KNH_2/Al_2O_3}$ 0.25 g	$\mathrm{PhC{\equiv}CH}$ 18.0 mmol	$\mathrm{Me_3SiC{\equiv}CH}$ 9.4 mmol	318 K	2	$\mathrm{PhC{\equiv}CSiMe_3}$ 8.5 mmol (91%)	(*Z*)-$\mathrm{PhC{\equiv}C{-}CH{=}CHPh}$ 0.24 mmol $\mathrm{PhCH{=}CH{-}C{\equiv}CSiMe_3}$ 0.03 mmol
$\mathrm{KF/Al_2O_3}$ 0.25 g	$\mathrm{PhC{\equiv}CH}$ 18.2 mmol	$\mathrm{Me_3SiC{\equiv}CH}$ 9.4 mmol	318 K	2	$\mathrm{PhC{\equiv}CSiMe_3}$ 9.0 mmol (96%)	(*Z*)-$\mathrm{PhC{\equiv}C{-}CH{=}CHPh}$ 0.10 mmol $\mathrm{Me_3SiC{\equiv}CSiMe_3}$ 0.04 mmol $\mathrm{PhCH{=}CH{-}C{\equiv}CSiMe_3}$ 0.01 mmol
$\mathrm{KF/Al_2O_3}$ 0.25 g	*tert*-$\mathrm{BuC{\equiv}CH}$ 17.3 mmol	$\mathrm{Me_3SiC{\equiv}CH}$ 8.1 mmol	303 K	20	*tert*-$\mathrm{BuC{\equiv}CSiMe_3}$ 6.3 mmol (78%)	$\mathrm{Me_3SiC{\equiv}CSiMe_3}$ 0.12 mmol
$\mathrm{KF/Al_2O_3}$ 0.25 g	*n*-$\mathrm{BuC{\equiv}CH}$ 17.3 mmol	$\mathrm{Me_3SiC{\equiv}CH}$ 8.1 mmol	318 K	20	*n*-$\mathrm{BuC{\equiv}CSiMe_3}$ 6.3 mmol (78%)	$\mathrm{Me_3SiC{\equiv}CSiMe_3}$ 0.12 mmol 2-hexyne 0.35 mmol

Numbers in parentheses are the yields on the basis of $\mathrm{Me_3SiC{\equiv}CH}$.

When the reaction of $\mathrm{Me_3SiC{\equiv}CH}$ (9.4 mmol) with $\mathrm{PhC{\equiv}CH}$ (18.0 mmol) was carried out in the presence of $\mathrm{KNH_2/Al_2O_3}$ at 318 K for 2 h, $\mathrm{PhC{\equiv}CSiMe_3}$ was selectively obtained (91% yield based on silane) (Table 4). Metathesis between $\mathrm{Me_3SiC{\equiv}CH}$ molecules occurred only slightly. Dimerization of $\mathrm{PhC{\equiv}CH}$ also occurred slightly. Without $\mathrm{Me_3SiC{\equiv}CH}$, the dimerization of $\mathrm{PhC{\equiv}CH}$ proceeds smoothly in the presence of $\mathrm{KNH_2/Al_2O_3}$ [26]. $\mathrm{KF/Al_2O_3}$ also selectively catalyzed the metathesis reaction. The catalytic activity was as high as $\mathrm{KNH_2/Al_2O_3}$, the yield of $\mathrm{PhC{\equiv}CSiMe_3}$ being 96% under the same reaction conditions.

Metathesis between $\mathrm{Me_3SiC{\equiv}CH}$ and *tert*-$\mathrm{BuC{\equiv}CH}$ or 1-hexyne (*n*-$\mathrm{BuC{\equiv}CH}$) also proceeded in the presence of $\mathrm{KNH_2/Al_2O_3}$ to selectively give *tert*-$\mathrm{BuC{\equiv}CSiMe_3}$ or *n*-$\mathrm{BuC{\equiv}CSiMe_3}$, respectively (Table 4).

4. Conclusions

Carbanions generated on the surface of solid bases effectively bring about nucleophilic attack on the Si atom of silanes to form Si–C bonds. Three types of Si–C bond forming reactions were demonstrated. (I) Dehydrocoupling of 1-alkyne and silane. (II) Reactions of alkylbenzene with silane. (III) Metathesis of 1-alkyne with $\mathrm{Me_3SiC{\equiv}CH}$. $\mathrm{KNH_2/Al_2O_3}$ was an effective catalyst for all of the three types of reactions. For the last class of reactions, $\mathrm{KF/Al_2O_3}$ was also very effective. These new classes of reactions will provide novel synthetic methods for Si–C bond formation.

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