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Metathesis of Silylalkynes and Cross-Metathesis of Silylalkyne and 1-Alkyne over Solid-Base Catalysts

Toshihide Baba,*,[1] Akiko Kato,* Hidetaka Takahashi,* Fumihiko Toriyama,* Haruhisa Handa,* Yoshio Ono,* and Hisashi Sugisawa†

**Department of Chemical Engineering, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152, Japan; and †Analytical Instrument Division, JEOL Ltd., 1-2 Musashino 3-Chome, Akishima-shi, Tokyo 196, Japan*

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KF loaded on alumina (KF/Al_2O_3) catalyzed the metathesis of $Me_3SiC{\equiv}CH$ to $Me_3SiC{\equiv}CSiMe_3$ and $HC{\equiv}CH$. The catalytic activity of KF/Al_2O_3 depended strongly on the heat-pretreatment temperature under vacuum and the loading amount of KF on alumina. An 87% yield of $Me_3SiC{\equiv}CSiMe_3$ was obtained by the reaction of $Me_3SiC{\equiv}CH$ in 30 min at 298 K in the presence of KF/Al_2O_3 (5 mmol KF/g-Al_2O_3), which had been pretreated at 673 K for 3 h. KF/Al_2O_3 also catalyzed the cross-metathesis of $Me_3SiC{\equiv}CH$ and 1-alkynes. When $Me_3SiC{\equiv}CH$ was reacted with $PhC{\equiv}CH$ in the presence of KF/Al_2O_3 at 318 K for 2 h, $PhC{\equiv}CSiMe_3$ was obtained in a 96% yield. The reactions of $Me_3SiC{\equiv}CH$ with *tert*-$BuC{\equiv}CH$ and *n*-$BuC{\equiv}CH$ gave *tert*-$BuC{\equiv}CSiMe_3$ and *n*-$BuC{\equiv}CSiMe_3$, respectively, in high yields. © 1998 Academic Press

INTRODUCTION

Silylalkynes are important in synthetic chemistry. They are used to mask the potentially acidic ethynyl proton and to afford a degree of chemical protection to the triple bond or to activate regioselectively the triple bond towards electrophilic attacks (1). They are also used to prepare vinylsilanes. Silylalkynes are commonly prepared from alkynes through the reaction of the alkynide anion or its equivalent with a suitable silyl chloride. For example, $PhC{\equiv}CSiMe_3$ is prepared as follows:

$$PhC{\equiv}CH \xrightarrow{n\text{-BuLi}} PhC{\equiv}CLi \xrightarrow{Me_3SiCl} PhC{\equiv}CSiMe_3. \quad [1]$$

Obviously, the reactions are not catalytic and require a stoichiometric amount of an organometallic compound. Besides the classical methods, several procedures for synthesizing silylalkynes have been reported (2–5). Lermontov *et al.*, reported that the reaction of $PhBF_3$ and $Me_3SiC{\equiv}CH$ to $PhC{\equiv}CSiMe_3$ proceeded in the presence of CuCl (2). However, the main product was $PhC{\equiv}CPh$. Hiyama and co-workers reported that the silylation of 1-alkynes with chlorosilanes took place around 390 K in the presence of zinc powder (3) or an equimolar mixture of samarium powder and Zn(II) chloride (4). In this method, the stoichiometric amounts of metals are required. It has been reported dehydrocondensation of trialkylsilanes with 1-alkynes by using transition metal complexes such as H_2PtCl_6-metal halide catalysts (5). In this case, hydrosilylation occurs as a side reaction.

Here, we will report the novel method for the catalytic preparation of silylalkynes; namely, metathesis of silylalkynes,

$$2R_3SiC{\equiv}CH \rightleftarrows R_3SiC{\equiv}CSiR_3 + HC{\equiv}CH, \quad [2]$$

and cross-metathesis of silylalkynes and 1-alkynes,

$$R^1C{\equiv}CH + R^2_3SiC{\equiv}CH \rightleftarrows R^1C{\equiv}CSiR^2_3 + HC{\equiv}CH. \quad [3]$$

Here, alkynide ions are generated by the interaction of alkyne molecules and basic sites on solid surfaces. A proposed reaction scheme is as follows:

$$\begin{gathered} R^1C{\equiv}CH + B^- \rightarrow R^1C{\equiv}C^- + BH \\ R^1C{\equiv}C^- + R^2_3SiC{\equiv}CH \rightarrow R^1C{\equiv}CSiR^2_3 + HC{\equiv}C^- \\ HC{\equiv}C^- + BH \rightarrow B^- + HC{\equiv}CH. \end{gathered} \quad [4]$$

Here, B^- stands for a basic site on solid surfaces. The solid bases effective for this new class of reactions are KF/Al_2O_3 and KNH_2/Al_2O_3.

KF loaded on alumina has been used as a convenient base in synthetic organic chemistry (6–16). Recently, Hattori and co-workers reported that treating KF-loaded alumina (KF/Al_2O_3) at high temperature (573–673 K) under high vacuum was essential for obtaining the high catalytic activity for double-bond isomerization of 1-pentene (17). We have also reported that KF/Al_2O_3 is a highly efficient catalyst for a self-condensation of benzaldehyde to benzyl benzoate when it is preheated under vacuum around 670 K (18), while KF/Al_2O_3 pretreated under vacuum around

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[1] Corresponding author. E-mail: tbaba@o.cc.titech.ac.jp.

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620 K shows the highest catalytic activity for the isomerization of 2,3-dimethylbut-1-ene to 2,3-dimethylbut-2-ene (18). These results suggest that there are two kinds of active sites of KF/Al_2O_3 catalyst as reported in Ref. (17).

The activation of carbonyl group of benzaldehyde and the abstraction of a proton from 2,3-dimethylbut-1-ene seem to be key steps for the self-condensation of benzaldehyde to benzyl benzoate and the isomerization of 2,3-dimethylbut-1-ene to 2,3-dimethylbut-2-ene, respectively. There is a possibility that the two different active sites such as F^- and O^{2-} on the surface of KF/Al_2O_3 are effective for these reactions; however, the definitive supporting evidence is lacking at this stage.

We have also reported that KNH_2/Al_2O_3 which is prepared by loading KNH_2 on Al_2O_3 from the ammoniacal solution, followed by heating under vacuum at 573 K, is a strongly basic catalyst (19). KNH_2/Al_2O_3 showed very high catalytic activities for the isomerization of various alkenes (19) and olefinic amines (20). KNH_2/Al_2O_3 also catalyzed the dehydrocoupling of toluene with Et_2SiH_2 to benzyldiethylsilane (21). The catalytic activities of KNH_2/Al_2O_3 for these reactions strongly depended on the heating temperature under vacuum as in the case of KF/Al_2O_3 (18–19). Moreover, Al_2O_3 was a unique support for KNH_2 and KNH_2/Al_2O_3 had a very high catalytic activity, while KNH_2 supported on SiO_2 and TiO_2 were totally inactive. For example, KNH_2/Al_2O_3 heated under vacuum at 573 K readily isomerized 2,3-dimethylbut-1-ene to 2,3-dimethylbut-2-ene even at 201 K, the yield of 2,3-dimethylbut-2-ene being 95% in 30 min (19). Thus, the high temperature treatment (573 K) for KNH_2/Al_2O_3 is essential for obtaining the super-active catalyst. KNH_2 supported on CaO and MgO which were evacuated at 998 and 873 K, respectively, showed much lower catalytic activities than that of KNH_2/Al_2O_3 for the isomerization of alkenes.

We also reported that the exchange reaction between KNH_2 and D_2 occurred on an alumina surface and that the NH_2 groups in KNH_2/Al_2O_3 reacted even with methane. Thus, the exchange reaction between KND_2/Al_2O_3 and CH_4 and C_2H_6 proceeded at room temperature (22). The rate of the exchange of KND_2 with CH_4 was faster than with C_2H_6 in conformity with the difference in their acidities:

$$\begin{aligned} KND_2 + CH_4 &\leftrightarrows KNDH + CDH_3 \\ KNDH + CH_4 &\leftrightarrows KND_2 + CDH_3. \end{aligned} \qquad [5]$$

Moreover, when the sample which showed the bands due to the KND_2, was exposed to 3-methylbut-1-ene at room temperature for 10 min, the bands due to ND_2 groups disappeared and the bands due to NH_2 groups reappeared, besides the bands due to C–H stretching and bending. This shows the NH_2 groups are involved in the isomerization of alkenes (21). It is confirmed that D atoms are contained in the reaction products in the gas phase. Therefore, the active sites of KNH_2/Al_2O_3 seem to be NH_2^- ions. However, the possibility that the active sites are O^{2-} ions, is not always contradicted, because Al_2O_3 as a support is essential to show the high catalytic activities for various reactions.

In this work, we will apply the solid base catalysts, KF/Al_2O_3 and KNH_2/Al_2O_3, to the metathesis of $Me_3SiC\equiv CH$:

$$2Me_3SiC\equiv CH \rightarrow Me_3SiC\equiv CSiMe_3 + HC\equiv CH. \qquad [6]$$

The preparation conditions of highly active KF/Al_2O_3 for this reaction will be explored. The relation between the catalytic activity of KF/Al_2O_3 for the metathesis of $Me_3SiC\equiv CH$ and the surface property of KF/Al_2O_3 will be examined. We also wish to report the cross-metathesis between $Me_3SiC\equiv CH$ with 1-alkynes where $R^1 =$ Ph, *tert*-Bu, *n*-Bu and $R^2 =$ Me in Eq. [3].

EXPERIMENTAL

Catalyst Preparation

Alumina used as a support had a surface area of 131 $m^2\,g^{-1}$ and an average diameter of 15 nm. KF, KOH, and K_2CO_3 supported on alumina were prepared by an impregnation method from their aqueous solutions, followed by drying under air at 393 K for 12 h. Prior to the reactions, the catalysts were evacuated under 10^{-3} Pa at a prescribed temperature for 3 h. In the case of KF/Al_2O_3 catalysts, the loading amount of KF was 5 mmol/g-alumina and the evacuation temperature was 673 K, if not otherwise mentioned. The amounts of KOH and K_2CO_3 were 5 mmol/g-alumina and 2.5 mmol/g-alumina, respectively.

KNH_2 loaded on alumina was prepared by impregnation from its ammoniacal solution as follows; alumina and a small amount of Fe_2O_3 (2 wt% of Al_2O_3) 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/g-Al_2O_3) was added into the reactor under nitrogen. After evacuation, ammonia was liquefied 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 heated under vacuum at 573 K for 1 h.

CaO and MgO were prepared by heating $CaCO_3$ and $Mg(OH)_2$ under vacuum for 3 h at 998 and 873 K, respectively.

Reaction Procedures

Silylethynes such as $Me_3SiC\equiv CH$ obtained from Shin-etsu Chemical Co. Ltd., 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 reactant(s) placed in a glass tube, which is attached to the side arm of the quartz reactor, was(were) degassed with a freeze-thaw method. The reaction was started by transferring the reactant(s) into the reactor containing a catalyst prepared as described above. The products were identified with ^{1}H or ^{13}C NMR and GS-MAS. The yields of the products were determined with a gas-chromatograph (an OV 101 glass column) and were calculated on the basis of silylacetylenes. Propylbenzene was used as an internal standard for quantitative analysis.

Identifications

^{1}H NMR or ^{13}C NMR data of products were good agreement with those which have been already reported as follows;

^{1}H NMR date of products have been already reported. $Me_3SiC{\equiv}CSiMe_3$: Dunogues, J., Bourgeois, P., Pilot, J. P., and Merault, G., *J. Organomet. Chem.* **87**, 169 (1975). GC MAS: m/e 180, 170, 155, 73. $PhC{\equiv}CSiMe_3$: Bulmanpage, P. C., and Rosenthal, S., *Tetrahedron* **46**, 2573 (1990). GC MAS: m/e 174, 159, 129, 105. n-$C_4H_9C{\equiv}CSiMe_3$: Bulman-Page, P. C., and Rosenthal, S., *Tetrahedron* **46**, 2573 (1990). GC MAS: m/e 139, 112, 83. *tert-Bu* $C{\equiv}CSiMe_3$: Zweifel, G., and Vewis, W., *J. Org. Chem.* **43**, 2739 (1978). GC MAS: m/e 154, 139, 97, 73.

^{13}C NMR data. $Et_3SiC{\equiv}CSiEt_3$: Kamienska-Trla, K., Beidrzycka, Z., Machinek, K., Knieriem, B., and Luettke, W., *Org. Magn. Reson.* **22**, 317 (1984).

^{1}H NMR data. $PhCH{=}CH{-}C{\equiv}CPh$ (270 MHz, $CDCl_3$) δ 5.91 (d, J = 11.8 Hz 1H $CH{=}CH$), 6.69 (d, J = 11.8 Hz 1H $CH{=}CH$), 7.23–7.93 (m, 5H, Ph). GC MAS: m/e 204, 101.

$PhCH{=}CH{-}C{\equiv}CSiMe_3$ (270 MHz, $CDCl_3$) δ 0.12 (s, 9H, $SiMe_3$), 5.71 (d, J = 12.0 Hz 1H $CH{=}CH$), 6.66 (d, J = 12.0 Hz 1H $CH{=}CH$), 7.2–7.7 (m, 5H, Ph).

GC MAS data. $Me_2(EtO)SiC{\equiv}CSi(EtO)\ Me_2$: m/e 215, 171, 133, 103, 73. $Me_2(EtO)SiC{\equiv}CSi(Me_2)C{\equiv}CH$: m/e 195. $Me_2(EtO)SiC{\equiv}CSi(Me)_2\ C{\equiv}CSi(EtO)Me_2$: m/e 283, 253, 223, 191, 141, 112, 73.

^{19}F MAS NMR Measurements

The samples for ^{19}F MAS NMR measurements were prepared in a glass tube by the same manner as the case of the catalyst preparation. The glass tube with side arms was connected to a glass capsule used for ^{19}F MAS NMR measurements. After the preparation of the sample, it was transferred into a glass capsule under a vacuum. The neck of the capsule was then sealed, while the sample itself was maintained at 77 K.

^{19}F MAS NMR spectra were recorded at 298 K on a Chemagnetics CMX-Infinity spectrometer operating at 282.4 MHz. A sealed sample in a glass tube was inserted into a zirconia rotor. The spinning rate of the sample was 12 kHz. The chemical shifts were referenced relative to external $CFCl_3$ (0.0 ppm).

RESULTS AND DISCUSSION

Catalytic Activities of Various Solid Bases

The reaction of $Me_3SiC{\equiv}CH$ was carried out at 293 K for 30 min by using various solid-base catalysts. As shown in Table 1, the formation of $Me_3SiC{\equiv}CSiMe_3$ was observed in every case. Although not quantified, the formation of acetylene was confirmed by the analysis of the gas phase with a gas-chromatograph. The pressure of the reactor increased to ca 45 kPa in 30 min, when KF/Al_2O_3 was used as a catalyst. These results suggest that the metathesis of $Me_3SiC{\equiv}CH$ to $Me_3SiC{\equiv}CSiMe_3$ and $HC{\equiv}CH$ proceeds. The reaction is very selective, no other products being observed. KF/Al_2O_3, KNH_2/Al_2O_3, $CsOH/Al_2O_3$, and MgO gave about 77% yields of $Me_3SiC{\equiv}CSiMe_3$. The catalytic activities of KOH/Al_2O_3 and K_2CO_3/Al_2O_3 were lower, the yields being 64 and 11%, respectively. Although CaO is a strong solid base (12), CaO showed a very low catalytic activity.

We reported that the optimum amount of KNH_2 loaded on Al_2O_3 was 2.6 mmol of KNH_2 per g-alumina for the isomerization of 2,3-dimethylbut-1-ene (19) and the dimerization of phenylacetylene to (Z)-1,4-diphenylbut-1-ene-3-yne (23). KNH_2(2.6 mmol/g-alumina)/Al_2O_3 was also used as a catalyst for the metathesis reaction. When the reaction was carried out at 273 K, the yields of $Me_3SiC{\equiv}CSiMe_3$ over KF/Al_2O_3, KNH_2/Al_2O_3, and MgO were 78, 61, and 72% in 30 min, respectively. Thus, KF/Al_2O_3 showed the highest catalyst for this reaction.

TABLE 1

Catalytic Activities of Various Solid Base Catalysts for Metathesis of $Me_3SiC{\equiv}CH$

Catalyst	Pretreatment temperature/ K	Amount of base/ mmol per g-alumina	Yield of $Me_3SiC{\equiv}CSiMe_3$/ %
KF/Al_2O_3	673 K for 3 h	5	77 78[a]
KNH_2/Al_2O_3	573 K for 1 h	2.6	76 61[a]
MgO	773 K for 3 h		74 72[a]
$CsOH/Al_2O_3$	673 K for 3 h	5	74
KOH/Al_2O_3	673 K for 3 h	5	64
K_2CO_3/Al_2O_3	673 K for 3 h	5	11
CaO	998 K for 3 h		2

Note. Reaction conditions: 293 K, 30 min, catalyst weight; 0.25 g, $Me_3SiC{\equiv}CH$: 13.5 mmol.

[a] Reaction temperature was 273 K. The yields were calculated on the basis of $Me_3SiC{\equiv}CH$.

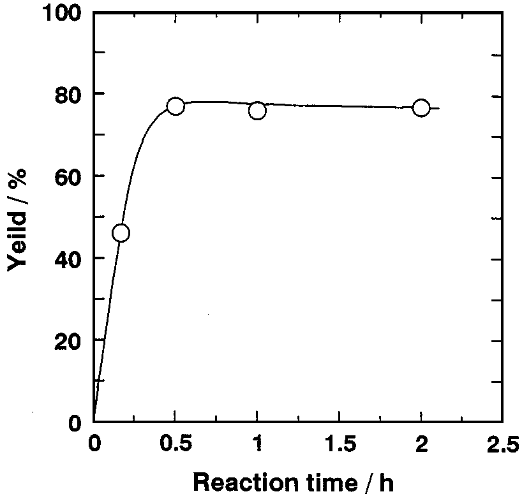

FIG. 1. Yield of $Me_3SiC{\equiv}CSiMe_3$ with reaction time in the metathesis of $Me_3SiC{\equiv}CH$ by KF/Al_2O_3. Reaction conditions: catalyst: 0.125 g of K/Al_2O_3, $Me_3SiC{\equiv}CH$: 13.5 mmol, 293 K. KF/Al_2O_3 was pretreated by heating under vacuum at 673 K for 3 h.

Reaction of $Me_3SiC{\equiv}CH$ over KF/Al_2O_3

Figure 1 shows the change in the yield of $Me_3SiC{\equiv}CSiMe_3$ with reaction time in the reaction of $Me_3SiC{\equiv}CH$ in the presence of KF/Al_2O_3. The reaction was carried out at 293 K in a reactor system whose dead volume was 356 cm^3. The yields of $Me_3SiC{\equiv}CSiMe_3$ were 46 and 77% in 10 and 30 min, respectively. The yield did not change by further expanding the reaction time to 2 h. This indicates that the reaction is reversible and that the equilibrium of Eq. [6] is established in 30 min. Actually, formation of $Me_3SiC{\equiv}CH$ by the reaction of $Me_3SiC{\equiv}CSiMe_3$ with acetylene was confirmed.

When a reactor system with a larger dead volume was used (1350 cm^3), the yield in 30 min increased to 87%. This yield dependence on the volume of the reactor system indicates that the yield depends on the partial pressure of acetylene in the gas phase because of the equilibrium.

Influence of the Loading Amount of KF on Al_2O_3

The effect of the loading amount of KF on Al_2O_3 on the yield of $Me_3SiC{\equiv}CSiMe_3$ was examined at 273 K (Fig. 2). Al_2O_3 showed no catalytic activity. The yield increased with increasing KF content, a maximum yield of 78% being observed at 5 mmol/g-Al_2O_3, or 0.5 mol KF/mol Al_2O_3. Further increase of the loading amount of KF beyond 5 mmol/g-Al_2O_3 led to the decrease of the catalytic activity. The selectivity for $Me_3SiC{\equiv}CSiMe_3$ was always 100% and was independent of the loading amount of KF.

Al_2O_3 and KF heated at 673 K under vacuum, when separately used, showed no catalytic activity. Moreover, KF supported on SiO_2, TiO_2, and activated carbon showed no catalytic activity. Thus, it is essential to support KF on alumina to generate the catalytic activity, indicating that the active sites are generated by the reaction of KF with alumina.

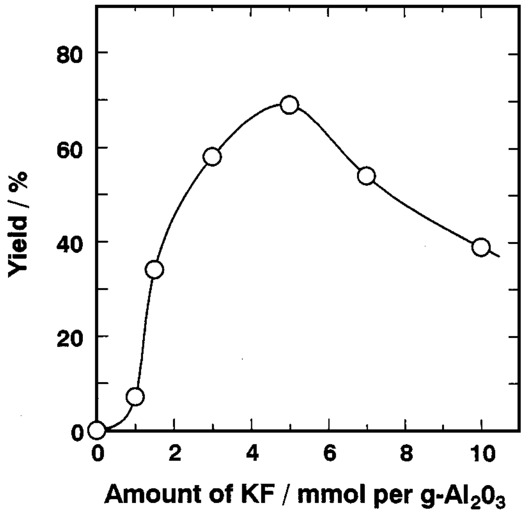

FIG. 2. Effect of the loading amount of KF on alumina on the yield of $Me_3SiC{\equiv}CSiMe_3$. Reaction conditions: catalyst: 0.125 g of KF/Al_2O_3, $Me_3SiC{\equiv}CH$: 13.5 mmol, 273 K, 1 h. KF/Al_2O_3 was pretreated by heating under vacuum at 673 K for 3 h.

Influence of Pretreatment Temperature of KF/Al_2O_3

It has been reported that the catalytic activity of KF/Al_2O_3 depends very much on the drying conditions of alumina after loading KF by impregnation (8). Figure 3 shows the influence of the temperature of pretreatment under vacuum on the catalytic activity of KF/Al_2O_3 at 273 K. KF/Al_2O_3 samples were heated under vacuum for

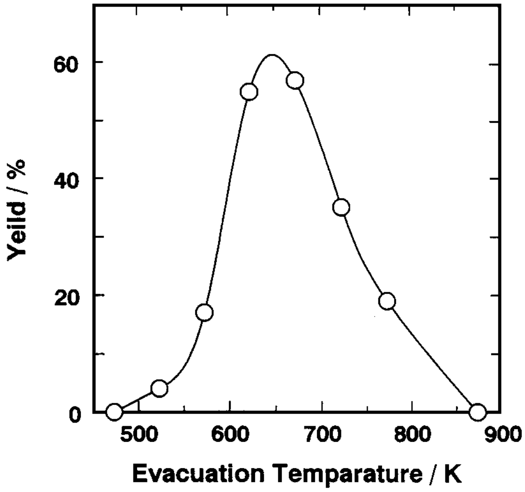

FIG. 3. Influence of evacuation temperature on the catalytic activity of KF/Al_2O_3 for metathesis of $Me_3SiC{\equiv}CH$. Reaction conditions: catalyst: 0.125 g of KF/Al_2O_3, $Me_3SiC{\equiv}CH$: 13.5 mmol, 273 K, 0.5 h. KF/Al_2O_3 was pretreated by heating under vacuum at prescribed temperature for 3 h.

3 h at various temperatures. The catalytic activity strongly depended on the pretreatment temperature. The yield of $Me_3SiC{\equiv}CSiMe_3$ sharply increased with increasing the pretreatment temperatures and reached a maximum around 670 K. At higher pretreatment evacuation temperature than 670 K, the catalytic activity declined and almost disappeared by evacuating the catalyst at 873 K.

The similar dependence of the catalytic activity on the pretreatment temperature has been reported for the isomerization of 1-pentene (17) and the self-condensation of benzaldehyde (18).

The surface area of KF/Al_2O_3 did not change much in the pretreatment temperature range of 523 to 773 K, being constant (ca 90 m^2/g). This result indicates that the decrease in the activity of KF/Al_2O_3 above 673 K, is not caused by the decrease in the surface area and that the surface chemical state of the KF/Al_2O_3 changes with thermal treatment.

Metathesis of Other Silylalkynes

Metathesis of $Et_3SiC{\equiv}CH$ also proceeded over KF/Al_2O_3 or KNH_2/Al_2O_3 to selectively afford the corresponding bisilylethyne, $Et_3SiC{\equiv}CSiEt_3$. When the reaction was carried out in benzene at 333 K, the yields of $Et_3SiC{\equiv}CSiEt_3$ over KF/Al_2O_3 were 53 and 84% in 30 min and 2 h, respectively (Table 2). Selective metathesis of $Et_3SiC{\equiv}CH$ also occurred over KNH_2/Al_2O_3, the yield being 47% in 2 h.

$Me_2(EtO)SiC{\equiv}CH$ also underwent metathesis over these catalysts. Heptane was used as a solvent. The main product was $Me_2(EtO)SiC{\equiv}CSi(EtO)\ Me_2$, I (Table 3). Heptane was used as a solvent. The yields of I were 56 and 61% in 30 min and 1 h, respectively, when KF/Al_2O_3 was used as a catalyst. The $Me_2(EtO)SiC{\equiv}CH$ gave a 77% yield over KNH_2/Al_2O_3 in 1 h. The formation of a small amount of $Me_2(EtO)SiC{\equiv}CSi(Me_2)C{\equiv}CH$, II, and $Me_2(EtO)SiC{\equiv}CSi(Me)_2C{\equiv}CSi(EtO)Me_2$, III, were confirmed by a GC-MS analysis (Table 3). The compound II is formed when the leaving group is EtO^- instead of $CH{\equiv}C^-$:

$$\begin{aligned} &Me_2(EtO)SiC{\equiv}C^- + Me_2(EtO)SiC{\equiv}CH \\ &\quad \rightarrow \underset{\text{II}}{Me_2(EtO)SiC{\equiv}CSi(Me_2)C{\equiv}CH} + EtO^-. \end{aligned} \quad [7]$$

TABLE 2

Metathesis of $Et_3SiC{\equiv}CH$

Catalyst	Reaction time/h	Yield of $Et_3SiC{\equiv}CSiEt_3$/%
KF/Al_2O_3	0.5	53
KF/Al_2O_3	2	84
KNH_2/Al_2O_3	2	47

Note. Reaction conditions: 333 K, catalyst weight: 0.25 g, $Et_3SiC{\equiv}CH$: 2.8 mmol, benzene as solvent: 2 ml. The yields were calculated on the basis of $Et_3SiC{\equiv}CH$.

TABLE 3

Metathesis of $Me_2(EtO)SiC{\equiv}CH$

Catalyst	Reaction time/h	Yield/% I	Yield/% II	Yield/% III
KF/Al_2O_3	0.5	56	3	4
KF/Al_2O_3	1	61	4	7
KNH_2/Al_2O_3	1	77	2	5

Note. I = $Me_2(EtO)SiC{\equiv}CSi(EtO)Me_2$; II = $Me_2(EtO)SiC{\equiv}CSi(C{\equiv}CH)Me_2$; III = $Me_2(EtO)SiC{\equiv}CSiMe_2C{\equiv}CSi(EtO)Me_2$. Reaction conditions: 313 K, catalyst weight: 0.2 g, $Me_2(EtO)SiC{\equiv}CH$: 3.1 mmol, Solvent: heptane 2 ml. The yields were calculated on the basis of $Me_2(EtO)SiC{\equiv}CH$.

The compound III is formed by the further reaction of II with $Me_2(EtO)SiC{\equiv}CH$:

$$\begin{aligned} &Me_2(EtO)SiC{\equiv}CSi(Me_2)C{\equiv}CH + Me_2(EtO)SiC{\equiv}CH \\ &\quad \rightarrow \underset{\text{III}}{Me_2(EtO)SiC{\equiv}CSi(Me)_2C{\equiv}CSi(EtO)Me_2} + CH{\equiv}CH. \end{aligned} \quad [8]$$

The order of the reactivates of silylacetylenes is

$$Me_3SiC{\equiv}CH > Et_3SiC{\equiv}CH > Me_2(EtO)SiC{\equiv}CH.$$

The difference of reactivities of these compounds seems to depend on the steric hindrance of the alkyl groups of silylacetylenes.

Cross-Metathesis between $Me_3SiC{\equiv}CH$ and 1-alkyne

When a mixture of $Me_3SiC{\equiv}CH$ (9.4 mmol) and $PhC{\equiv}CH$ (18.2 mmol) was stirred with 0.25 g of KF/Al_2O_3 at 318 K for 2 h, 9.0 mmol of $PhC{\equiv}CSiMe_3$ was obtained (96% yield on the basis of $Me_3SiC{\equiv}CH$) as shown in Table 4. KNH_2/Al_2O_3 also selectively catalyzed the cross-metathesis, the yield of $PhC{\equiv}CSiMe_3$ being 91% (Table 4). In both cases, the metathesis of $Me_3SiC{\equiv}CH$ to $Me_3SiC{\equiv}CSiMe_3$ and acetylene was almost completely suppressed in the presence of $PhC{\equiv}CH$.

The reaction was carried out by using a mixture of $Me_3SiC{\equiv}CH$ (9.4 mmol) and $PhC{\equiv}CH$ (9.4 mmol) (the ratio of $Me_3SiC{\equiv}CH$ to $PhC{\equiv}CH = 1.0$) with KF/Al_2O_3. The metathesis reaction of $Me_3SiC{\equiv}CH$ was also proceeded, the yield of $Me_3SiC{\equiv}CSiMe_3$ being 19% (Table 4). The selectivity for $PhC{\equiv}CSiMe_3$ decreased by decreasing the ratio of $PhC{\equiv}CH$ to $Me_3SiC{\equiv}CH$, while the selectivity for $Me_3SiC{\equiv}CSiMe_3$ increased.

We have reported that KNH_2/Al_2O_3 catalyzed the selective dimerization of $PhC{\equiv}CH$ to (*Z*)-1,4-diphenylbut-3-ene-1-yne in high yield at 363 K (24). When $PhC{\equiv}CH$ (27.6 mmol) was stirred with 0.25 g of KNH_2/Al_2O_3 at 313 K, the yield of $PhCH{=}CH{-}C{\equiv}CPh$ was 12% in 20 h:

$$2PhC{\equiv}CH \rightarrow PhCH{=}CH{-}C{\equiv}CPh. \quad [9]$$

TABLE 4

Cross-Metathesis between $Me_3SiC\equiv CH$ and $PhC\equiv CH$

Catalyst	KF/Al_2O_3	KF/Al_2O_3	KNH_2/Al_2O_3
Reactant			
$PhC\equiv CH$	18.2 mmol	9.4 mmol	18.0 mmol
$Me_3SiC\equiv CH$	9.4 mmol	9.4 mmol	9.4 mmol
Consumption			
$PhC\equiv CH$	9.3 mmol	8.7 mmol	9.7 mmol
$Me_3SiC\equiv CH$	9.1 mmol (97%)	8.5 mmol (90%)	9.0 mmol (96%)
Products			
$PhC\equiv CSiMe_3$	9.0 mmol (96%)	7.6 mmol (81%)	8.5 mmol (91%)
$Me_3SiC\equiv CSiMe_3$	0.04 mmol	0.89 mmol (19%)	trace
(Z)-$PhC\equiv C{-}CH{=}CHPh$	0.10 mmol	0.06 mmol	0.24 mmol
$PhCH{=}CHC\equiv CSiMe_3$	0.01 mmol	0.02 mmol	0.03 mmol

Note. Reaction conditions: 318 K, 2 h, catalyst 0.25 g. Numbers in parentheses are the yields on the basis of $Me_3SiC\equiv CH$.

The reaction [9] was also suppressed when the two alkynes exist in the system, indicating that the anion $PhC\equiv C^-$ attacks mostly at Si atom in $Me_3SiC\equiv CH$, but not at the terminal carbon atoms in ethynyl groups of $PhC\equiv CH$ and $Me_3SiC\equiv CH$.

The reaction of $Me_3SiC\equiv CH$ (8.1 mmol) and *tert*-$BuC\equiv CH$ (16.0 mmol) at 303 K in the presence of KF/Al_2O_3 gave 58 and 78% yields of *tert*-$BuC\equiv CSiMe_3$ in 2 and 20 h, respectively (Table 5). In this case, the yield of the side-product, $Me_3SiC\equiv CSiMe_3$ was 16% in 2 h, while it decreased to 3% in 20 h, indicating that at least a part of *tert*-$BuC\equiv CSiMe_3$ was formed by a secondary reaction between $Me_3SiC\equiv CSiMe_3$ and *tert*-$BuC\equiv CH$:

$$2Me_3SiC\equiv CH \rightarrow Me_3SiC\equiv CSiMe_3 + HC\equiv CH \qquad [10]$$

$$Me_3SiC\equiv CSiMe_3 + tert\text{-}BuC\equiv CH \rightarrow tert\text{-}BuC\equiv CSiMe_3 + Me_3SiC\equiv CH. \qquad [11]$$

TABLE 5

The Cross-Metathesis between $Me_3SiC\equiv CH$ and *tert*-$BuC\equiv CH$ or n-$C_4H_9C\equiv CH$ over KF/Al_2O_3

$RC\equiv CH$	Reaction temperature/K	Reaction time/h	Yield of product/%	
tert-$BuC\equiv CH$	303	2	*tert*-$BuC\equiv CSiMe_3$	58
			$Me_3SiC\equiv CSiMe_3$	16
	303	20	*tert*-$BuC\equiv CSiMe_3$	78
			$Me_3SiC\equiv CSiMe_3$	3
n-$C_4H_9C\equiv CH$	318	2	n-$C_4H_9C\equiv CSiMe_3$	59
			$Me_3SiC\equiv CSiMe_3$	16
			2-hexyne	0.6
			3-hexyne	0.4
	318	20	n-$C_4H_9C\equiv CSiMe_3$	83
			$Me_3SiC\equiv CSiMe_3$	3
			2-hexyne	2
			3-hexyne	0.5

Note. Reaction conditions: catalyst KF/Al_2O_3 0.25 g, $Me_3SiC\equiv CH$ 8.1 mmol, $RC\equiv CH$ 17.3 mmol. The yields of $RC\equiv CSiMe_3$ and $Me_3SiC\equiv CSiMe_3$ were calculated on the basis of $Me_3SiC\equiv CH$. The yields of hexynes were calculated on the basis of 1-hexyne.

When $Me_3SiC\equiv CH$ (8.7 mmol) was stirred with 0.25 g of KF/Al_2O_3 in the presence of n-$C_4H_9C\equiv CH$ (17.3 mmol) at 318 K for 20 h, n-$C_4H_9C\equiv CSiMe_3$ (7.2 mmol) was obtained in a 83% yield. The yields of $Me_3SiC\equiv CSiMe_3$ were 16 and 3% in 0.5 h and 20 h, respectively. The isomerization of n-$C_4H_9C\equiv CH$ to 2-hexyne and 3-hexyne slightly occurred.

The Si atom in $Me_3SiC\equiv CH$ is more cationic than the carbon atoms of ethynyl groups in $PhC\equiv CH$, n-$C_4H_9C\equiv CH$ and *tert*-$BuC\equiv CH$, while the acidity of protons of $PhC\equiv CH$ may be higher than that of $Me_3SiC\equiv CH$. $PhC\equiv C^-$ ions are more easily generated than $Me_3SiC\equiv C^-$ ions and attack selectively at Si atom in $Me_3SiC\equiv CH$. The acidity of ethynyl protons in n-$C_4H_9C\equiv CH$ and *tert*-$BuC\equiv CH$ may be a little different, as compared with $Me_3SiC\equiv CH$. Therefore, the selectivity of $PhC\equiv CSiMe_3$ is higher, as compared with those of n-$C_4H_9C\equiv CSiMe_3$ and *tert*-$BuC\equiv CSiMe_3$.

Basic Sites of KF/Al_2O_3

As for the basic sites on KF/Al_2O_3, several proposals have been made (8, 24, 25). It is known that K_3AlF_6 is formed by the reaction of aqueous KF and alumina:

$$12KF + Al_2O_3 + 3H_2O \rightarrow 2K_3AlF_6 + 6KOH. \qquad [12]$$

We have also reported that the formation of K_3AlF_6 is confirmed by XRD in the sample upon loading KF by impregnation on Al_2O_3 and that K_3AlF_6 still exists after heating the sample at 673 K (18). To check the catalytic activity of K_3AlF_6, the metathesis reaction of $Me_3SiC\equiv CH$ was carried out by using neat K_3AlF_6 and K_3AlF_6 which had been supported on Al_2O_3 by impregnation and heated under the vacuum at 673 K. Both catalysts showed no catalytic activity. Moreover, the XRD pattern due to K_3AlF_6 was observed after pretreating KF/Al_2O_3 at 873 K, where its catalytic

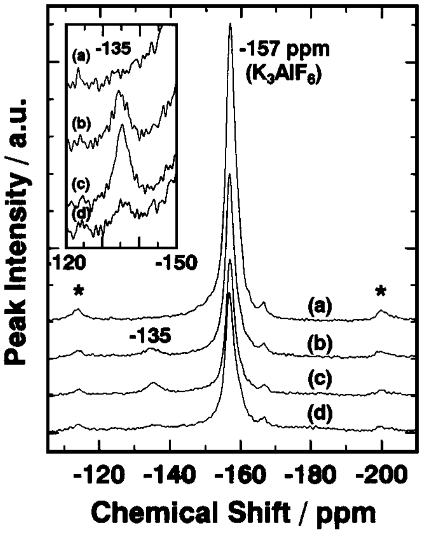

FIG. 4. ^{19}F MAS NMR spectra of KF (5 mmol/g-alumina) recorded at the room temperature. Evacuation temperature: (a) 473 K; (b) 623 K; (c) 673 K; and (d) 773 K. (∗) Spinning side bands.

activity was completely lost. These results may suggest that K_3AlF_6 is not catalytically active species for the metathesis reaction.

Furthermore, the catalytic activity of KOH and that of K_2CO_3 loaded on alumina were lower than that of KF/Al_2O_3 (Table 1), while the surface area of KOH/ Al_2O_3 and that of K_2CO_3/Al_2O_3 were 121 and 132 m^2/g, respectively, which are larger than that of KF/Al_2O_3 (92 m^2/g). These results suggest that F^- ions may be more responsible for the catalytic activity than O^{2-} ions, which may be basic sites on KOH/Al_2O_3 and K_2CO_3/Al_2O_3 for the methasesis reactions. Ando *et al.* stressed the importance of coordinately unsaturated F^- ions as the basic sites, although they did not deny the participation of the hydroxide species (8, 24).

Figure 4 shows the ^{19}F MAS NMR spectrum of KF/Al_2O_3 evacuated at prescribed temperatures. The major band was observed at −157 ppm attributed to K_3AlF_6 (26, 27). The small peak at −166 ppm was also observed, as shown in Fig. 4. The intensities of the peak at −155 and −166 ppm decreased by raising the evacuation temperature. On the other hand, the intensity of the peak at −135 ppm increased with evacuation temperature and through a maximum at 473 K, it decreased. The peak at −135 ppm was not observed when the sample was evacuated at 873 K. The intensity change of the peak at −135 ppm with evacuation temperature almost paralleled with the change in the catalytic activity for the metathesis of $Me_3SiC{\equiv}CH$ with the evacuation temperature as in the case of the self-condensation of benzaldehyde to benzyl benzoate (18). Since the F^- species giving this ^{19}F NMR signal is directly related to the catalytic activity, F^- ions may be the basic sites over KF/Al_2O_3.

CONCLUSION

Metathesis between two molecules of $R_3SiC{\equiv}CH$ (R = Me, Et) proceeds easily in the presence of solid bases, namely KF/Al_2O_3 and KNH_2/Al_2O_3. These solid bases also promote the cross-metathesis between $Me_3SiC{\equiv}CH$ and $RC{\equiv}CH$ (R = Ph, *tert*-Bu, *n*-Bu). These reactions are catalytic and offer a new synthetic pathway for producing alkynylsilanes.

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