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Thermal hydrosilylation of olefin with hydrosilane. Preparative and mechanistic aspects

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ABSTRACT

The reaction of trichlorosilane (**1a**) at 250 °C with cycloalkenes, such as cyclopentene (**2a**), cyclohexene (**2b**), cycloheptene (**2c**), and cyclooctene (**2d**), gave cycloalkyltrichlorosilanes [$C_nH_{2n-1}SiCl_3$: $n = 5$ (**3a**), 6 (**3b**), 7 (**3c**), 8 (**3d**)] within 6 h in excellent yields (97–98%), but the similar reactions using methyldichlorosilane (**1b**) instead of **1a** required a longer reaction time of 40 h and afforded cycloalkyl(methyl)dichlorosilanes [$C_nH_{2n-1}SiMeCl_2$: $n = 5$ (**3e**), 6 (**3f**), 7 (**3g**), 8 (**3h**)] in 88–92% yields with 4–8% recovery of reactant **2**. In large (**2**, 0.29 mol)-scale preparations, the reactions of **2a** and **2b** with **1a** (0.58 mol) under the same condition gave **3a** and **3b** in 95% and 94% isolated yields, respectively. The relative reactivity of four hydrosilanes [$HSiCl_{3-m}Me_m$: $m = 0–3$] in the reaction with **2a** indicates that as the number of chlorine-substituent(s) on the silicon increases the rate of the reaction decreases in the following order: $n = 3 > 2 > 1 \gg 0$. In the reaction with **1a**, the relative reactivity of four cycloalkenes (ring size = 5–8) decreases in the following order: **2d** > **2a** > **2c** > **2b**. Meanwhile linear alkenes like 1-hexene undergo two reactions of self-isomerization and hydrosilylation with hydrosilane to give a mixture of the three isomers (1-, 2-, and 3-silylated hexanes). In this reaction, the reactivity of the terminal 1-hexene is higher than the internal 2- and 3-hexene. The redistribution of hydrosilane **1** and the polymerization of olefin **2** occurred rarely under the thermal reaction condition.

1. Introduction

It is well known that hydrosilylation reactions, the addition of Si–H unit to a C–C double bond, are useful Si–C bond formation method for the preparation of organosilicon compounds [1–4]. This reaction is induced or catalyzed in numerous ways, including photo-initiated [5,6] and metal compounds [1–4,7–10], in particular, platinum derivatives such as the Speier catalyst (H_2PtCl_6/^{i}PrOH) [1] and the Karstedt catalyst [4]. To our knowledge, a thermal hydrosilylation leading to a discrete organosilane molecule without a catalyst is rare, even though this is a fundamental and simple Si–C bond-forming reaction for the synthesis of organosilicon compounds. From the viewpoint of bond dissociation energy (BDE), the BDE of the H–Si unit of hydrosilane is relatively low. This is especially true for trichlorosilane (**1a**) (~91.3 kcal/mol [11]), which is widely used as a cheap precursor for polycrystalline silicon [12]. It is expected that the Si–H bond of **1a** can be readily activated under thermal conditions. In a test, the thermal reaction of **1a** with a simple cycloalkene, cyclopentene (**2a**) with no catalyst at 150 °C of relatively low temperature gave surprisingly a small amount of cyclopentyltrichlorosilane (**3a**) as a hydrosilylation product. In further study, this reaction at higher temperature of 250 °C afforded **3a** in nearly quantitative yield. Moreover, the reaction works effectively with methyldichlorosilane (**1b**), which is less activated than **1a**. In this paper, we wish to report a basic and simple thermal hydrosilylation of olefin with chlorosilane with a Si–H unit that does not require a catalyst.

2. Results and discussion

2.1. Synthesis of cycloalkylchlorosilanes

The thermal reaction of hydrosilanes $HSiCl_{3-m}Me_m$ [$m = 0$ (**1a**), 1 (**1b**), 2 (**1c**), 3 (**1d**)] with cycloalkenes, such as cyclopentene (**2a**), cyclohexene (**2b**), cycloheptene (**2c**), and cyclooctene (**2d**) at 250 °C gives the corresponding silylated products **3a–h** (Scheme 1). The yields of products were calibrated with the GLC (gas–liquid chromatography) response factor. The results obtained from the reactions of **2a–d** with **1a–b** at 250 °C are summarized in Table 1.

As shown in Table 1, the reaction of **2a–d** with **1a** at 250 °C gave the corresponding silylated products **3a–d** in excellent yield

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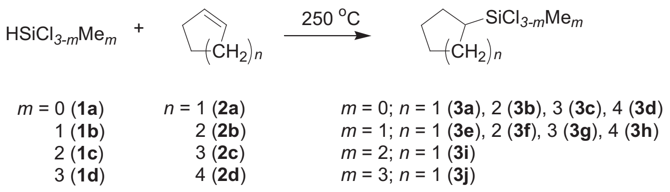


Scheme 1. Hydrosilylation of cycloalkene with hydrosilane.

(97–98%) within 6 h. When the less-activated **1b** was used instead of **1a** at the same temperature, the reactions required a much longer time (40 h) and gave **3e**–**h** in 88–92% yield along with 4–8% of unreacted **2**. Significantly, the reaction of cycloalkene under thermal condition yields the hydrosilylation product in remarkably excellent yield without by-products. Under our reaction conditions, the disproportionation of hydrosilane **1** and the polymerization of olefin **2** did not take place. In large-scale (**2**, 292.1 mmol) preparations, the reactions of **2a** and **2b** with **1a** (583.2 mmol) under the same conditions gave **3a** and **3b** in 95% and 94% isolated yields, respectively. These thermal reactions are surprisingly high-yield approaches to cycloalkylchlorosilanes **3**, which are applicable to composites [13] and external electron-donor additives for polypropylene [14].

2.2. *Effect of the substituent in hydrosilane on hydrosilylation*

To determine the effect of the substituent at the silicon of hydrosilane, an equimolar mixture of a series of hydrosilanes $HSiCl_{3-m}Me_m$ [$m = 0$ (**1a**), 1 (**1b**), 2 (**1c**), 3 (**1d**)] in the same molar ratio was reacted with **2a** as a representative cycloalkene at 250 °C (Scheme 1). In this reaction, the molar ratio of **2a**/sum of **1a**–**d** was 1.1/1. The progress of the reaction was monitored by GLC using an internal standard. The yields of the products (**3a**, **3e**, **3i**, **3j**) obtained from the competitive reaction of **2a** with **1a**–**d** are plotted against reaction time in Fig. 1. The yields of hydrosilylation products (**3a**, **3e**, and **3i**) increase from 21%, 3% and 1% after 1 h to 44%, 7%, and 3% after 2 h to 93%, 16%, and 5% after 4 h, respectively. The reaction with **1a** was almost complete after 6 h to give **3a** in 98% yield, while after 16 h, the reactions with the other hydrosilanes **1b**–**d** provide the corresponding products **3e** (38%), **3i** (12%), and **3j** (trace), respectively. The results show that the reactivities of the hydrosilanes in the thermal hydrosilylation reaction depend on the substituents on silicon, and one or more chlorine-substituent(s) on the silicon for hydrosilylation are required. It seems likely that the reaction proceeds by a free-radical mechanism involving the homolytic cleavage of the Si–H bond under thermal conditions. It is well known that both peroxide and UV light instigate the addition of Si–H bonds to olefinic double bonds [13,15].

Table 1
Hydrosilylation of cycloalkene **2** with **1**.[a]

Reactants **1** ($HSiCl_{3-m}Me_m$)	Reactants **2** (remain %)	Reaction time (h)	Yield of **3** (%)[b]
1a ($m = 0$)	**2a** (1)	6	**3a** (98, 95[c])
1a	**2b** (1)	6	**3b** (98, 94[c])
1a	**2c** (1)	6	**3c** (98)
1a	**2d** (2)	4	**3d** (97)
1b ($m = 1$)	**2a** (5)	40	**3e** (91)
1b	**2b** (6)	40	**3f** (89)
1b	**2c** (8)	40	**3g** (88, 82[c])
1b	**2d** (4)	40	**3h** (92)

[a] The 1:2 reaction of **2** with **1** was carried out at 250 °C.
[b] Yields were determined by GLC using *n*-dodecane as an internal standard.
[c] Isolated yield.

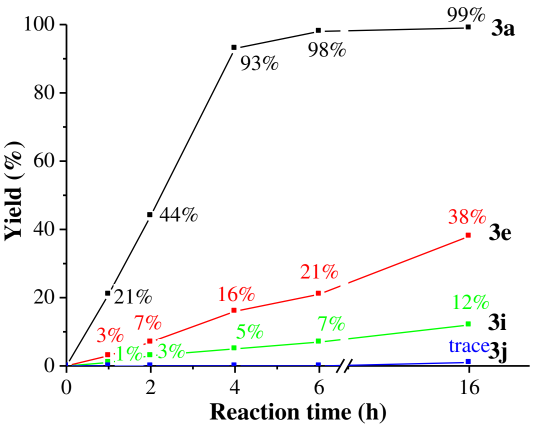


Fig. 1. Yield of **3** *vs.* reaction time.

2.3. *Effect of cycloalkene ring size on the hydrosilylation with **1a***

In order to investigate the effect of ring size on cycloalkene hydrosilylation, a reaction of **1a** with the 1/2 molar ratio an equimolar mixture of cycloalkenes **2a**–**d** was carried out at 250 °C. The yields of products **3a**–**d** obtained from this comparative reaction are plotted against reaction time in Fig. 2. As Fig. 2 shows, the yields of the hydrosilylated products (**3a**, **3b**, **3c**, and **3d**) increase from 21%, 18%, 20%, and 29% after 1 h to 44%, 38%, 42%, and 57% after 2 h, to 93%, 88%, 91%, and 97% after 4 h, respectively. The reactions of **2a**–**d** with **1a** were almost completed after 6 h to give **3a**–**d** in excellent yield (98%). In such a hydrosilylation, the reactivity of **1a** is not very sensitive to the ring size of the cyclic olefins. The hydrosilylation rate of cycloalkenes **2a**–**d** decreases in the following sequence: **2d** > **2a** > **2c** > **2b**, and the relative rates are 1:0.72:0.69:0.62, respectively, for a 1 h reaction. The reactivity of **2a** is slightly lower than **2d** but higher than that of **2c** and **2b**, respectively, suggesting that **2b** (6-membered-ring) has the lowest reactivity for hydrosilylation. The results can be explained on the basis of the "medium ring-size effect", which states that cycloalkenes can exist only in certain conformations due to a number of non-bonded hydrogen–hydrogen repulsive interactions. The order of reactivity in these reactions is similar to that of the bromotrichloromethylation of cyclic olefins with bromotrichloromethane initiated by ^{60}Co irradiation [16].

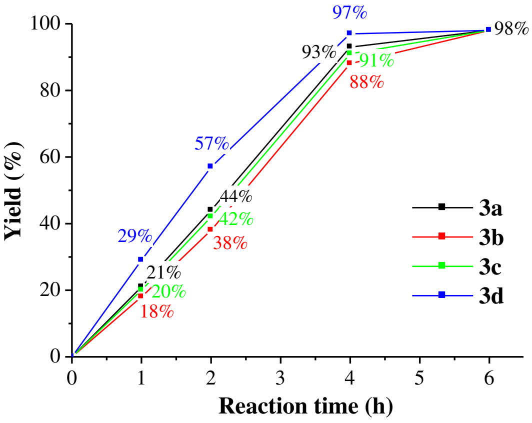


Fig. 2. Relative reactivity of the cycloalkenes **2a**–**d**.

2.4. Effect of temperature on hydrosilylation

In order to get basic information on the thermal hydrosilylation of cycloalkene, the reaction of **2a** as a representative cycloalkene with **1a** was conducted at temperatures ranging from 150 °C to 270 °C. The production of **3a** at each reaction temperature was monitored by GLC and plotted against reaction time in Fig. 3. As shown in Fig. 3, the hydrosilylation occurs at a temperature as low as 150 °C to give **3a** in 11% yield after a long reaction time (3 d), indicating that **1a** can be thermally activated at a relatively low temperature. The same reactions at higher temperatures of 170 °C and 200 °C give **3a** in 35% and 91% yields after 3 d, respectively. Reactions at temperatures higher than 230 °C are completed in shorter times. A reaction at 230 °C affords **3a** in 96% yield after 1 d. The same reactions at the slightly higher temperatures of 250 °C and 270 °C reach 98% yield of **3a** after 4 h and 6 h, respectively. The results show that the reaction rate for the hydrosilylation of **2a** with **1a** increases rapidly as the reaction temperature increases from 150 °C to 250 °C, then slightly again at 270 °C. The reaction at 250 °C would be considered to be suitable for the preparation of **3a** from an economical point of view (saving time and energy).

2.5. Effect of the molar ratio of *1a*/*2a* on hydrosilylation

In order to look for the best molar ratio of reactants for the preparation of **3a**, the reactions were carried out by varying the molar ratio of **1a**/**2a** in the range of 1.2–3.0 at 250 °C. The production of **3a** at each ratio is plotted against reaction time in Fig. 4. As Fig. 4 shows, the two reactions using 2:1 and 3:1 molar ratio of **1a** to **2a** give **3a** in nearly the same yield (93%) after 4 h, but the 1.5:1 reaction of **1a** to **2a** required a slightly longer reaction time and the 1.2: 1 reaction gave 93% yield of **3a** after 8 h. These results show that the reaction rate increases as the molar ratio of **1a** to **2a** increases from 1.2 to 2, but a reaction using a 3 molar ratio of **1a** to **2a** required a slightly longer time, suggesting that the influence of the molar ratio of **1**/**2** on hydrosilylation is relatively low. The optimum molar ratio of **1** to **2** would be approximately 2 for thermal hydrosilylation.

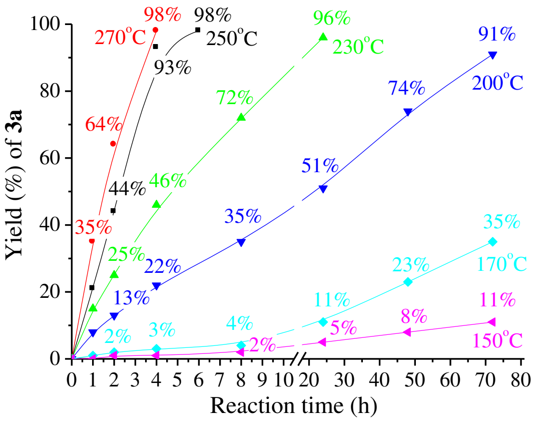


Fig. 3. Effect of temperature on hydrosilylation of **2a** with **1a**.

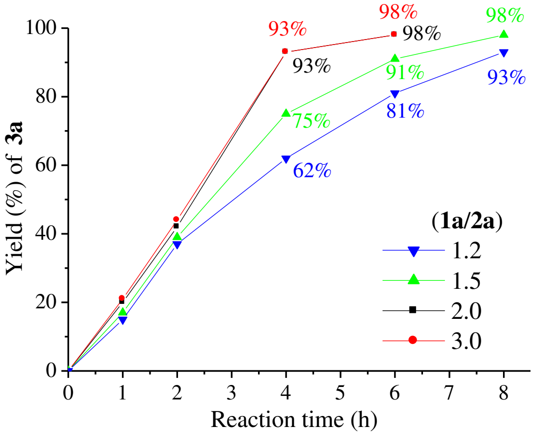


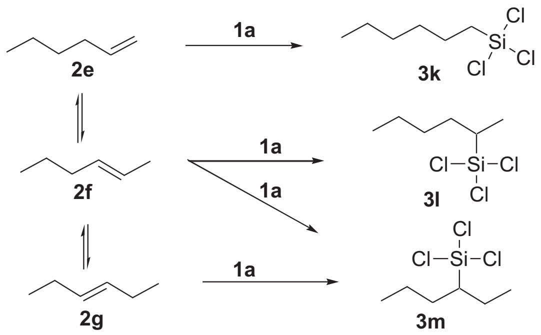
Fig. 4. Effect of molar ratio on hydrosilylation of **2a** with **1a**.

2.6. Thermal reaction of 1-hexene with *1a*

Reactions of **1a** with 1-hexene (**2e**), as a representative linear olefin, were carried out at temperatures ranging from 150 °C to 270 °C. In the reactions, the terminal hydrosilylated compound **3k** was obtained as a major product along with the inner-silylated products **3l** and **3m** as an isomeric mixture. In addition to **3l**–**m**, 2-hexene (**2f**) and 3-hexene (**2g**) were observed among the lower boilers (Scheme 2). **2f** and **2g** can be formed through the double-bond migration of **2e** and react with **1a** to give the internal silylated products **3l** and **3m**.

The yields of **3k**–**m** obtained from each reaction temperature were monitored by GLC and plotted against reaction time in Fig. 5. As shown in Fig. 5, the hydrosilylation occurs at the low temperature of 150 °C for 48 h to give **3k** in 11% yield. At the high temperature of 200 °C, a reaction at the same time affords 72:11:8 mixture of hydrosilylation products (**3k**, **3l** and **3m**) in 91% yield. The rate of reaction increases as the reaction temperature increases. An 8 h reaction at 230 °C lead to 75:10:6 mixture of **3k**, **3l**, and **3m** in 91% yield; a reaction at 250 °C lead to 78:9:5 mixture of the same products in 92% yield within 4 h. In these reactions, only **3k** is obtained at 150 °C, but the ratio of the terminal silylated product **3k** to the internal silylated products **3l** and **3m** increases as the reaction temperatures increase.

In the reaction at 250 °C, the production of the hydrosilylation products (**3k**–**m**) and the olefins (**2f** and **2g**) is plotted against the reaction time, respectively, in Fig. 6. As shown in Fig. 6, as the reaction proceeds, the ratio of the inner hydrosilylated products (**3l** and **3m**) to the terminal hydrosilylated product **3k** increases from 2/25 after 1 h to 6/49 after 2 h, to 14/78 after 4 h. The isomerization of reactant **2e** to the internal olefins **2f** and **2g** occurs after 4 h to give the internal double-bonded hexenes (8%), consisting of a 1:7 mixture of **2f** and **2g** without any **2e** remaining, suggesting that **2e** undergoes both reactions of hydrosilylation with **1a** and self-isomerization to **2f** and **2g** concomitantly. The results indicate that **3k** is produced from **2e** at an early stage in the reaction, but the internally silylated products (**3l** and **3m**) via **2f** and **2g** increase as



Scheme 2. Reaction sequence observed in the hydrosilylation of **2e**.

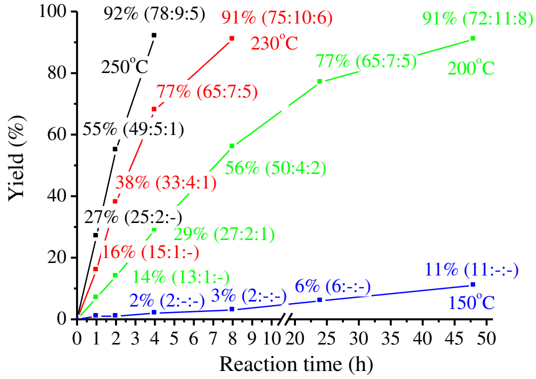


Fig. 5. Effect of temperature on hydrosilylation of **2e** with **1a**.

the reaction proceeds. Generally, an internal olefin is more thermodynamically stable than a terminal olefin [17]. In addition, the isomerization of the double bond of **2e** in neat solvent did not occur at 250 °C [18].

Alternatively, the thermal reaction of the internal olefin **2g** with **1a** was conducted under the same conditions as those of the terminal olefin **2e** with **1a** to compare the distribution of the products. In the reaction at 250 °C, the production of the hydrosilylation products (**3k**–**m**) and olefins (**2f**–**g**) is plotted against the reaction time, respectively, in Fig. 7. As shown in Fig. 7, the yield and distribution of **3k**–**m** from the reaction with **2g** increase from 21% after 1 h to 90% after 16 h. At an early stage of the 1 h reaction, an expected compound (**3m**) is formed in 18% yield as a major product along with **3l** (3%), then the molar ratio of **3l** to **3m** increases from 16/23 after 2 h to 34/45 after 16 h. In addition to **3m** and **3l**, the terminal silylated product **3k** is formed in approximately 1% yield in 2 h and increases to 11% after 16 h. The isomerization of **2g** to **2f** occurs at an early stage to give a 8:71 mixture of **2f** to **2g** after 1 h and reaches a 1:2 mixture after 16 h, but **2e** is not formed in any appreciable amount even though some of **3k** is produced in the 16 h reaction, suggesting that the reactivity of **2e** formed via the double-bond migration of **2g** is much higher than that of **2f** or **2g**. It is known that a terminal alkene is more reactive than an internal alkene in hydrosilylation catalyzed by Pt-complexes [19].

From a mechanistic point of view, it is interesting to note that the thermal reaction of olefins with hydrosilane includes two types of simultaneous reactions, the double-bond migration of olefin and hydrosilylation, suggesting that the results are consistent with a free-radical mechanism.

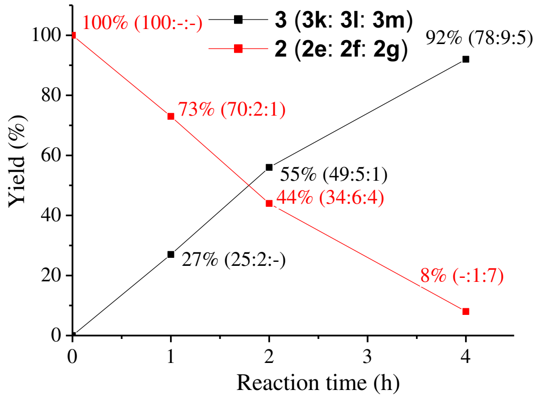


Fig. 6. Distributions of products and reactants in the thermal reaction of **2e** with **1a** *vs.* reaction time.

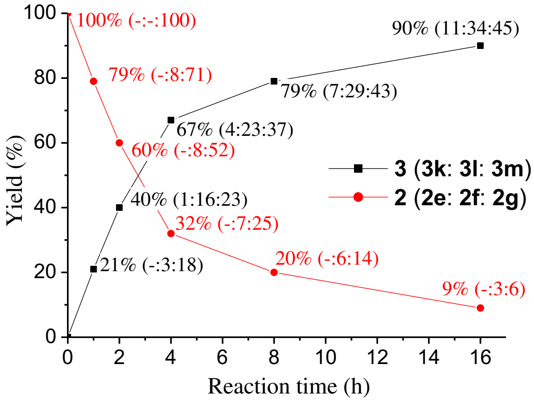


Fig. 7. Distribution of products and reactants in the thermal reaction of **2g** with **1a** *vs.* reaction time.

3. Conclusions

The reaction of hydrosilanes such as **1a** and **1b** with cycloalkenes with 5–8 membered ring size at 250 °C give the corresponding hydrosilylation products in remarkably excellent yields. In the reaction, the reactivity of hydrosilanes [$HSiCl_{3-m}Me_m$] decreases as the number of chlorine-substituents on the silicon decreases in the following order: $n = 3 > 2 > 1 \gg 0$. The effect of ring size on the cyclic olefins was observed in the following order: **2d** > **2a** > **2c** > **2b**. Meanwhile, a linear alkene, such as 1-hexane, undergoes two reactions of self-isomerization and hydrosilylation with hydrosilane to give the three isomeric mixtures of 1-, 2-, and 3-silylated hexanes. Generally, the reactivity of a cycloalkene is higher than a linear internal alkene but not a linear terminal alkene. It was found that side reactions, such as the redistribution of hydrosilanes and the polymerization of olefin, occur rarely under thermal reaction conditions. As a whole, this chemistry will enable the efficient high-yield synthesis of a wide range of cycloalkylchlorosilanes and provides fundamental knowledge to help understanding of thermal hydrosilylation.

4. Experimental section

4.1. General comments

All reactions and manipulations were carried out under nitrogen using cannula techniques. Solvents were dried according to standard procedures. Trichlorosilane, methyldichlorosilane, trimethylsilane, cyclopentene, cyclohexene, cycloheptene, cyclooctene, 1-hexene and 3-hexene were purchased from Aldrich Chem. Co and TCI and used without further purification. The reaction products were analyzed by gas–liquid chromatography (GLC) using a packed column (10% OV-101 on 80–100 mesh Chromosorb W/AW, 1/8 in. × 1.5 m) or a capillary column (30 m, SE-30) with a Varian 3300 gas chromatograph equipped with a thermal conductivity detector. The samples for characterization were purified by a preparative GLC using a packed column (20% OV-101 on 80–100 mesh Chromosorb W/PW, 1/8 in. × 4 m) with a DS 6200 gas chromatograph (Donam Instruments Inc.) with a thermal conductivity detector. NMR spectra were recorded on a Bruker Avance 300 spectrometer (300 MHz for ^{1}H; 75 MHz for ^{13}C) and a Varian Gemini 300 spectrometer (60 MHz for ^{29}Si) using $CDCl_3$ as a solvent. The chemical shifts are given in ppm relative to the residual proton signal of the solvent: $CDCl_3$ 7.25 ppm (^{1}H), $CDCl_3$ 77.0 ppm (^{13}C). In the case of ^{29}Si NMR, the chemical shifts were determined according to standard material: $Si(CH_3)_4$ 0.0 ppm. GC/MS data were obtained with an HP6890/5973 system (70 eV, EI).

4.2. General procedure for synthesis of **3a**

A 25 mL dried stainless steel tube with a valve was charged with **1a** (7.9 g, 58.3 mmol), **2a** (2.0 g, 29.3 mmol), and *n*-dodecane (1.0 g) as an internal standard under a dry nitrogen atmosphere. After the tube was sealed with a cap, the reaction was carried out at 250 °C. The progress of the reaction was monitored by GLC. The yield of **3a** is based on the amount of **2a** used and was determined by GLC with use of an internal standard. In a 10-fold scaled-up reaction, the reaction of **2a** (19.9 g, 292.1 mmol) with **1a** (79.0 g, 583.2 mmol) in a 250-mL dried stainless steel tube with a valve was carried out at 250 °C for 6 h. Then, the reaction mixture was fractionally distilled to give **3a** (56.5 g, 277.5 mmol; CAS no. 14579-03-4) in 95% isolated yield. The results are summarized in Table 1.

4.3. Synthesis of **3b**–**3d**

Following the same procedure and scale described in the general procedure for the synthesis of **3a**, the reactions of cycloalkenes **2b**–**d** with **1a** were carried out. The yields of **3b** (CAS no. 98-12-4), **3c** (CAS no. 135225-23-9) and **3d** (CAS no. 18290-59-0) are based on the amount of **2** used and was determined by GLC with use of an internal standard. These results are summarized in Table 1. In addition, a 10-fold scaled-up reaction of **2b** (24.0 g, 292.1 mmol) with **1a** (79.0 g, 583.2 mmol) was carried out at 250 °C for 6 h in a 250-mL dried stainless steel tube, **3b** (59.8 g, 274.8 mmol) was obtained in a 94% isolated yield.

4.4. Synthesis of **3e**–**3h**

Following the similar procedure and scale described in the general procedure for the synthesis of **3a**, the reactions of cycloalkenes **2a**–**d** with **1b** instead of **1a** were carried out. The yields of **3e** (CAS no. 14579-04-5), **3f** (CAS no. 5578-42-7), **3g**, and **3h** (CAS no. 117314-86-6) are based on the amount of **2** used and was determined by GLC with the use of an internal standard. These results are summarized in Table 1. In addition, a 10-fold scaled-up reaction of **2c** (28.1 g, 292.1 mmol) with **1b** (67.1 g, 583.3 mmol) was carried out at 250 °C for 40 h in a 250-mL dried stainless steel tube, **3g** (50.6 g, 239.5 mmol) was obtained in a 82% isolated yield. Data for **3g**: ^{1}H NMR ($CDCl_3$) δ 0.75 (s; 3H, SiCH_3), 1.08–1.25 (m, 1H, Si*CH*), 1.34–1.70 (m, 8H, $CH_2CH_2CH_2CH_2$), 1.74–1.89 (m, 2H), 1.90–2.05 (m, 2H); ^{13}C NMR δ 3.24 (SiCH_3), 27.17, 28.10, 29.12, 31.14(Si*CH*); ^{29}Si NMR 28.23; mass spectrum (70 eV, EI), *m/z* (rel intensity) 210 (12, M^+), 182 (5), 167 (8), 154 (19), 113 (59, $(Cl_2CH_3Si)^+$), 97 (100), 81 (30), 67 (19), 55 (80). Anal. Calcd for $C_8H_{16}Cl_2Si$: C, 45.49; H, 7.64. Found: C; 45.12, H; 7.68.

4.5. Relative reactivity of **2a** with hydrosilanes

In a typical experiment, reaction of **2a** (19.9 g, 292.1 mmol) with mixture of **1a** (9.0 g, 66.4 mmol), **1b** (7.6 g, 66.0 mmol), **1c** (6.3 g, 66.5 mmol), **1d** (4.9 g, 66.0 mmol) and *n*-dodecane (1.0 g) was carried out. The products **3a**, **3e**, **3i** (CAS no. 73945-55-8), and **3j** (CAS no. 14579-05-6) are plotted against reaction time in Fig. 1.

4.6. Relative reactivity of cycloalkenes with **1a**

Reaction of **1a** (31.6 g, 233.2 mmol) with mixture of **2a** (2.0 g, 29.3 mmol), **2b** (2.4 g, 29.2 mmol), **2c** (2.8 g, 29.1 mmol), **2d** (3.2 g, 29.0 mmol) and *n*-dodecane (1.0 g) in a 100-mL dried stainless steel tube with a valve was carried out at 250 °C. The yields of the products (**3a**–**d**) are plotted against reaction time in Fig. 2. Similar results were obtained when three runs of this reaction were carried out for reproducibility test.

4.7. Effect of temperature on hydrosilylation of **2a** with **1a**

In a typical experiment, the reactions of **1a** (7.9 g, 58.3 mmol) with **2a** (2.0 g, 29.3 mmol) were carried out at temperatures ranging from 150 °C to 270 °C. The progress of the reaction was monitored by GLC. The yields of **3a** obtained at various temperatures are plotted against reaction time in Fig. 3.

4.8. Effect of the molar ratio of reactants on hydrosilylation of **2a** with **1a**

In a typical experiment, reactions were carried out using a variety of molar ratios of **1a** to **2a**: **1a** 11.9 g (87.8 mmol), 8.0 g (58.8 mmol), 6.0 g (44.2 mmol), and 4.8 g (35.4 mmol) were used with respect to **2a** (2.0 g, 29.3 mmol). All reactions were carried out at 250 °C and monitored by GLC. Yields are on the basis of the amount of **2a** used and were determined by GLC with the use of an internal standard and are plotted against reaction time in Fig. 4.

4.9. Thermal hydrosilylation of **2e** with **1a**

In a typical experiment, the reaction of **2e** (2.4 g, 28.5 mmol) with **1a** (7.9 g, 58.3 mmol) was carried out at temperatures ranging from 150 °C to 250 °C. The progress of the reaction was monitored by GLC. Yields are on the basis of the amount of **2e** used and were determined by GLC with the use of an internal standard. The distributions of the products [**3k** (CAS no. 928-65-4), **3l** (CAS no. 18151-52-5), and **3m** (CAS no. 875288-11-2)] and reactants are plotted against reaction time in Figs. 5 and 6.

4.10. Thermal hydrosilylation of **2g** with **1a**

In a typical experiment procedure, the reaction of **2g** with **1a** was carried out. The distribution of products and reactants are plotted against reaction time in Fig. 7.

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References

[1] (a) J.L. Speier, J.A. Webster, G.H. Barnes, J. Am. Chem. Soc. 79 (1957) 974–979;
(b) J.L. Speier, Adv. Organomet. Chem. 17 (1979) 407–447;
(c) I.E. Marko, S. Sterin, O. Buisine, G. Mignani, P. Branlard, B. Tinant, J.-P. Declercq, Science 298 (2002) 204–206;
(d) G. Berthon-Gelloz, J.-M. Schumers, G.D. Bo, I.E. Marko, J. Org. Chem. 73 (2008) 4190–4197.

[2] B. Marciniac, Hydrosilylation: a Comprehensive Review on Recent Advances. Springer, New York, 2008.

[3] (a) M. Tanaka, Y. Uchimaru, H. Lautenschlager, J. Organomet. Chem. 428 (1992) 1–12;
(b) J. Li, J. Peng, D. Wang, Y. Bai, J. Jiang, G. Lai, J. Organomet. Chem. 696 (2011) 263–268.

[4] L.N. Lewis, J. Stein, Y. Gao, R.E. Colborn, G. Hutchins, Platinum Metals Rev. 41 (1997) 66–75.

[5] A. Postigo, S. Kopsov, S.S. Zlotsky, C. Ferreri, Organometallics 28 (2009) 3282–3287.

[6] (a) F. Wang, D.C. Neckers, J Organomet. Chem. 665 (2003) 1–6;
(b) M.G. Steinmetz, R.T. Mayes, B.S. Udayakumar, J. Chem. Soc., Chem. Commun. (1987) 759–761.

[7] S. Schwieger, R. Herzog, C. Wager, D. Steinborn, J. Organomet. Chem. 694 (2009) 3548–3558.

[8] V. Gandon, N. Agenet, K.P.C. Vollhardt, M. Malacria, C. Aubert, J. Am. Chem. Soc. 131 (2009) 3007–3015.

[9] J.J. Peng, J.Y. Li, Y. Bai, W.H. Gao, H.Y. Qiu, H. Wu, Y. Deng, G.Q. Lai, J. Mol. Catal. A 278 (2007) 97–101.

[10] M. Okamoto, H. Kiya, A. Matsumura, E. Suzuki, Catal. Lett. 123 (2008) 72–79.

[11] R. Walsh, J.M. Wells, J. Chem. Soc., Faraday Trans. 72 (1) (1976) 1212–1220.

[12] W.C. O'Mara, R.B. Herring, L.P. Hunt, in Handbook of Semiconductor Silicon Technology. William Andrew Publishing/Noyes, New York, 1990.

[13] (a) M.D. Soucek, D.P. Dworak, R. Chakraborty, J. Coat. Technol. Res. 4 (2007) 263–274;
(b) B.R. Yoo, D.E. Jung, J.S. Han, MRS Proc. 1174 (2009) V06–V08.

[14] R. Hoff, R.T. Mathers, Handbook of Transition Metal Polymerization. John Wiley & Sons, Inc., New Jersey, 2010, 179–184.

[15] (a) S.W. Bennett, C. Eaborn, R.A. Jackson, J. Organomet. Chem. 21 (1970) 79–81;
(b) C. Eaborn, M.R. Harrison, D.R.M. Walton, J. Organomet. Chem. 31 (1971) 43–46.

[16] L.H. Gale, J. Org, Chem. 34 (1969) 81–85.

[17] R.J. Fessenden, J.S. Fessenden, Fessenden Fessenden, sixth ed. Brooks Cole publishing Company, New York, 1998, pp. 449–450.

[18] When 2e was heated at 250°C without 1a, no isomerization reaction was observed.

[19] R.A. Benkeser, W.C. Muench, J. Am. Chem. Soc. 95 (1973) 285–286.