



Silylation reactions of olefins with monosilane and disilane in the presence of a transition metal complex, metal hydride, and radical initiator

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Abstract

The catalytic reactions between monosilane or disilane and 1-hexene or 1,5-hexadiene were studied. The reactions with monosilane gave the silylated compounds in the presence of a platinum complex, LiAlH_4 and a radical initiator. In the reactions with disilane, the same silylated compounds were produced in the presence of a platinum complex as in the reaction with monosilane, and disilanylated compounds were obtained using LiAlH_4 and a radical initiator. The reaction mechanisms are discussed. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Silylation; Olefins; Transition metal complex

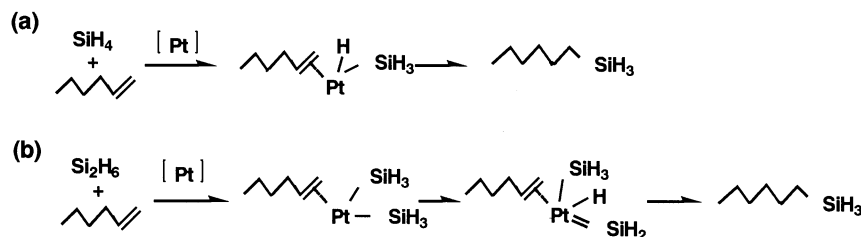
1. Introduction

The hydrosilylations of olefins with HSiCl_3 , $\text{CH}_3\text{SiHCl}_2$ or $(\text{CH}_3)_3\text{SiH}$, which are easily obtainable by Rochow's direct process, have been extensively investigated using many transition metal complexes as catalysts [1]. However the reports on the hydrosilylations with H_2SiCl_2 , $(\text{CH}_3)_2\text{SiH}_2$, $\text{C}_6\text{H}_5\text{SiH}_3$, SiH_4 or Si_2H_6 , which have some Si–H bonds in the molecule, are few [2]. The pyrolytic reactions and photo reactions were carried out between monosilane (SiH_4) or disilane (Si_2H_6) and ethylene or acetylene at an elevated temperature in the gas phase with very low yields and selectivities [3]. SiH_4 was alkylated in the presence of NaAlR_4 (R is alkyl) at an elevated temperature [4]. We have briefly reported that some silylated compounds (RSiH_3 , R_2SiH_2) were selectively

obtained by the hydrosilylation of olefins with SiH_4 in the presence of transition metal complexes [5] and LiAlH_4 [6]. On the other hand, double silylation reactions and dehydrogenative single silylation reactions of unsaturated hydrocarbons with disilane compounds ($\text{XR}_2\text{SiSiR}_2\text{X}$; X is alkyl or halogen), which were accompanied by the cleavage of the Si–Si bond, were investigated in the presence of transition metal complexes [7]. But reports on the hydrosilylation reactions and the double silylation reactions of olefins with Si_2H_6 are rare.

A large quantity of SiH_4 and Si_2H_6 has recently been produced and used for polysilicon and amorphous silicon. We can now use SiH_4 and Si_2H_6 as new raw materials in the organosilicon industry. In this paper, we report the hydrosilylation and double silylation reactions of olefins with SiH_4 and Si_2H_6 using transition metal complexes, metal hydrides and radical initiator as catalysts, and discuss the reaction mechanisms.

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Scheme 1. Mechanisms of the hydrosilylation of 1-hexene with (a) SiH_4 and (b) Si_2H_6 in the presence of PtL_4 .

2. Experimental

2.1. Reaction procedures

All experiments were performed in an autoclave. 1-Hexene or 1,5-hexadiene and a small amount of catalyst, that is, PtL_4 (L: PPh_3), LiAlH_4 , AIBN (2,2-azobis(isobutyronitrile), or DTBP (di-*t*-butylperoxide) were charged into the autoclave. A sample of SiH_4 or Si_2H_6 was then added under pressure, and the reaction was carried out under high pressure. The details of the reaction conditions are shown in Table 1 and Table 2.

After the reaction, all gases in the autoclave were replaced with nitrogen and passed through a solution of lithium in ethanol. Unreacted SiH_4 and Si_2H_6 , which were converted into silicon tetraethoxide in the solution, was analyzed by GC. The liquid products (hexylsilane and dihexylsilane) were separated by distillation under reduced pressure, and assigned based on the GC-Mass, IR, and ^1H -, ^{13}C - and ^{29}Si -NMR. They were compared with the spectra of the compounds which were prepared by the LiAlH_4 reduction of hexyltrichlorosilane and dihexyldichlorosilane [8]. The amounts of unreacted olefin and some liquid products were determined by GC using *n*-eicosan as an internal standard.

2.2. Product characterization

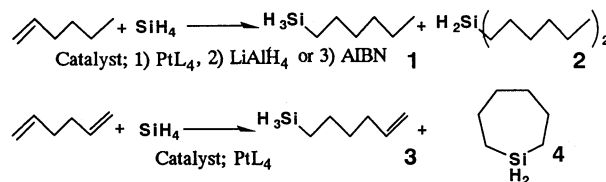
(a) Hexylsilane (**1**) and dihexylsilane (**2**): see ref. [6]. (b) *n*-5-hexenylsilane (**3**): ^1H -NMR(CDCl_3/TMS); δ 5.6–6.0 (m, 1H, $\text{CH}=\text{CH}_2$), 4.8–5.1 (m, 2H, $\text{CH}=\text{CH}_2$), 3.50 (t, 3H, $J = 4.1$ Hz, SiH_3), 1.9–2.2 (m, 2H, $\text{CH}_2-\text{CH}=\text{CH}_2$), 1.3–1.7 (m, 4H, $\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2$), 0.6–1.0 (m, 2H, CH_2-SiH_3). IR (neat); $\nu(\text{Si}-\text{H})$ 2150 cm^{-1} , $\nu(\text{C}=\text{C})$ 1641 cm^{-1} , $\nu(\text{C}-\text{H})$ 3075, 2925, 2851 cm^{-1} , $\delta(\text{Si}-\text{H})$ 922 cm^{-1} . MS (m/z); 114 (M^+), 113 ($(\text{M}-\text{H})^+$, base peak). (c) SilacycloHeptane (**4**): ^1H -NMR (CDCl_3/TMS); δ 3.8 (m, 2H, $J = 3.3$ Hz, SiH_2), 1.2–1.9 (m, 8H, $\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2$), 0.5–1.1 (m, 4H, $\text{CH}_2-\text{SiH}_2-\text{CH}_2$). IR (neat); $\nu(\text{Si}-\text{H})$ 2140 cm^{-1} , $\nu(\text{C}-\text{H})$ 2925, 2860 cm^{-1} , $\delta(\text{Si}-\text{H})$ 948, 923 cm^{-1} . MS (m/z); 114 (M^+), 113 ($(\text{M}-\text{H})^+$, base peak). (d) Hexyldisilane (**5**): ^1H -NMR ($\text{CDCl}_3/\text{CDCl}_3$, 7.26 ppm); δ 3.6–3.7 (m, 2H, SiH_2), 3.1–3.2 (m, 3H,

SiH_3), 1.2–1.5 (m, 8H, $\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$), 0.8–1.0 (m, 5H, $\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$). ^{13}C -NMR ($\text{CDCl}_3/\text{CDCl}_3$, 77.1 ppm); δ 32.5, 31.6, 27.1, 22.7 ($\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$), 14.2 (CH_3), 7.6 (SiH_2-CH_2). ^{29}Si -NMR (CDCl_3/TMS); δ -64.3(t, SiH_2), -102.0 (q, SiH_3). IR (neat); $\nu(\text{Si}-\text{H})$ 2150 cm^{-1} , $\nu(\text{C}-\text{H})$ 2970, 2940, 2860 cm^{-1} , $\delta(\text{Si}-\text{H})$ 919 cm^{-1} . MS (m/z); (EI mode) 146 (M^+), 145 ($(\text{M}-\text{H})^+$, base peak). (e) Dihexyldisilane (**6**): ^1H -NMR ($\text{CDCl}_3/\text{CDCl}_3$, 7.26 ppm); δ 3.5–3.6 (m, 4H, $\text{SiH}_2-\text{SiH}_2$), 1.2–1.5 (m, 16H, $\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$), 0.8–1.0 (m, 10H, $\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$). ^{13}C -NMR ($\text{CDCl}_3/\text{CDCl}_3$, 77.1 ppm); δ 32.5, 31.6, 27.4, 22.7 ($\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$), 14.2 (CH_3), 7.4 (SiH_2-CH_2). ^{29}Si -NMR (CDCl_3/TMS); δ -63.5(t, SiH_2). IR (neat); $\nu(\text{Si}-\text{H})$ 2120 cm^{-1} , $\nu(\text{C}-\text{H})$ 2950, 2910, 2850 cm^{-1} , $\delta(\text{Si}-\text{H})$ 938 cm^{-1} . MS (m/z); 230(M^+), 229 ($(\text{M}-\text{H})^+$, base peak).

3. Results and discussion

3.1. The reaction of olefins with SiH_4

The results are shown in Table 1. In the presence of PtL_4 , hexylsilane (**1**) and dihexylsilane (**2**) were obtained by the reaction of SiH_4 with 1-hexene, and 1-hexenylsilane (**3**) and silacycloheptane (**4**) were obtained by the reaction with 1,5-hexadiene [5].



The presumed reaction mechanism is shown in Scheme 1(a). The reaction rapidly took place during the first 30 min, but the catalyst was immediately destroyed as we previously reported [5]. Complete conversion of SiH_4 was not achieved. Therefore, the turnover numbers of the reactions (TN) were low compared with those for HSiCl_3 , which was completely transformed to the trichlorosilylated compound and no catalyst poisoning was observed under the same reaction condi-

Table 1
Reaction of 1-hexene and 1,5-hexadiene with SiH_4

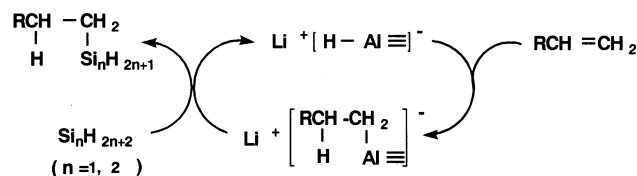
Reaction condition			Product yield (%) ^a						
Run no.	1-Hexene (mmol)	SiH ₄ (mmol)	Catalyst (mmol)	Temperature (°C)	Time (h)	Pressure (kg cm ⁻²)	Main compound	Others ^b	TN ^c (mol mol ⁻¹ cat)
1	42	14	PtL ₄	80	3	10	(1) 37.4 (2) 4.7	1.5	139
2	42 ^d	14	PtL ₄	80	3	10	(3) 16.0 (4) 15.3	6.3 ^e	20
3	89	100	LiAlH ₄	120	20	30-40	(1) 34 (2) 6		9
4	42	50	AIBN	100	3	10	(1) 10.6 (2) 1.8	3.0	19

^a The mole percent ratio of the product versus the charged SiH_4 . ^b Other products detected by gas chromatography. ^c The ratio of the amount of the two main products versus catalyst used. ^d 1,5-Hexadiene was used instead of 1-hexene. ^e The component was di-5-hexenylsilane.

Table 2
The reaction of 1-hexene and 1,5-hexadiene with Si_2H_6

Reaction condition			Product yield (%) ^a						
Run no.	1-Hexene (mmol)	Si ₂ H ₆ (mmol)	Catalyst (mmol)	Temperature (°C)	Time (h)	Pressure (kg cm ⁻²)	Main compound	Others ^b	TN ^c (mol mol ⁻¹ cat.)
1	42	14	PtL ₄	80	3	6	(1) 35.8 (2) 9.5	0.8	153
2	42 ^d	14	PtL ₄	80	3	6	(3) 8.5 (4) 6.6	1.9	53
3	99	99	LiAlH ₄	120	20	13	(5) 21.6 (5) 4.2	5.7	5
4	80	71	DTBP	150	1	9	(5) 15.1 (5) 29.6 ^e	46.7 ^f	289

^a The mole percent ratio of the product versus the charged Si_2H_6 . ^b Other products detected by gas chromatography. ^c The ratio of the amount of the two main products versus its of used catalyst. ^d 1,5-Hexadiene was used instead of 1-hexene. ^e Some isomers of $\text{C}_{12}\text{H}_{30}\text{Si}_2$ were included. ^f The main component was trihexylsilane.



Scheme 2. Mechanisms of the hydrosilylation of 1-hexene with SiH_4 and Si_2H_6 in the presence of LiAlH_4 .

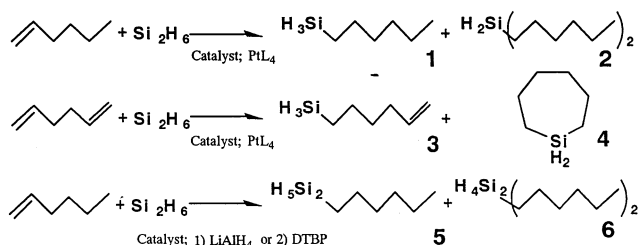
tions. Perhaps SiH_4 and the produced alkyl and alkenylsilanes would decompose to form the Si–metal bond, and would polymerize involving the intermolecular dehydrogenative coupling on the catalyst, followed by catalyst reduction. This presumption is supported by the fact that the solid compounds, which probably contain platinum and silicon, are deposited after the reaction. Molnar et al. reported that alkylhydrosilanes (Et_3Si , Pr_2SiH_2 , AmSiH_3) were observed to exert strong poisoning effects on the hydrogenation of 1-hexene on Cab-O-Sil[®]-supported Pt, and the poisoning activity of these silanes increased with increasing number of Si–H bonds in the molecules [9]. The TN value of 1,5-hexadiene was lower than that of 1-hexene (see run nos. 1 and 2). Though there is no experimental evidence, perhaps it may be would by the hydrosilylative coupling polymerization of 5-hexenylsilane (3), which would induce the catalyst poisoning.

The hydrosilylation reactions also proceeded using LiAlH_4 without a decrease in catalyst reactivity [6]. The presumed mechanism of this reaction is shown in Scheme 2. It is well known that the alkyl anion is formed by the interaction between LiAlH_4 and olefins (hydroalumination) above 110°C [10]. The complex SiH_4 may react with these anions to produce the silylated compounds, and LiAlH_4 would be regenerated.

The hydrosilylation reaction also proceeded using a radical initiator. The silyl radical would easily be produced by the cleavage of the Si–H bond (Scheme 3).

3.2. The reaction of olefins with Si_2H_6

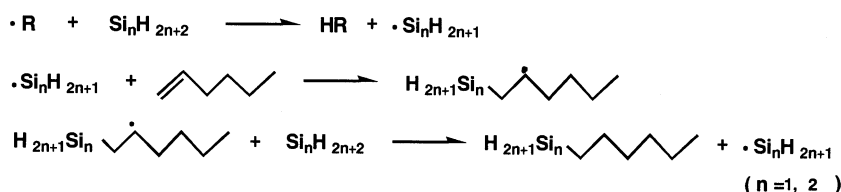
These results are shown in Table 2. In the presence of PtL_4 , the cleavage of the Si–Si bond occurred and the products were quite same as the reaction of SiH_4 . Hexylsilane (1) and dihexylsilane (2) were obtained by the reaction of Si_2H_6 with 1-hexene, and 5-hexenylsilane (3) and silacycloheptane (4) were obtained from Si_2H_6 and 1,5-hexadiene.



The turnover numbers of the reactions (TN) of Si_2H_6 , as well as SiH_4 , are much smaller than those of HSiCl_3 . The Si–Si bond would be cleaved from the catalyst to form a H_3Si metal bond, and then react with the olefin. A similar reaction mechanism would be considered for the silylation reaction (Scheme 1(b)) and the catalyst poisoning as in the case of SiH_4 . In the reaction of $\text{XMe}_2\text{Si}-\text{SiMe}_2\text{X}$ with an olefin ($\text{R}-\text{CH}=\text{CH}_2$) using PtL_4 , the double silylation reaction and/or dehydrogenative monosilylation occurred to produce $\text{XMe}_2\text{Si}-\text{C}(\text{R})\text{H}_2-\text{CH}_2-\text{SiMe}_2\text{X}$ or $\text{R}-\text{CH}=\text{CH}-\text{SiR}_2\text{X}$ ([7]b, [7]c). In the case of Si_2H_6 , no double silylated compounds, dehydrogenative monosilylated compounds and disilanylated compounds (RSi_2H_5) were detected. One of two SiH_3 groups bonded to platinum would easily decompose to SiH_2 and H, then the SiH_3 and H would be attached to the olefin. Perhaps some by-products such as polysilane would also be produced, though we have no experimental evidence.

Using LiAlH_4 , Si–Si bond cleavage did not occur and hexyldisilane (5) and 1,2-dihexyldisilane (6) were obtained. The hexylaluminum anion would be formed, then react with Si_2H_6 . Usually the cleavage of the Si–Si bond and the double silylation reaction occurs between the disilane compounds and the unsaturated hydrocarbons using transition metal complexes [7], so LiAlH_4 is a new catalyst for the disilanylation of unsaturated hydrocarbons.

In the presence of a radical initiator, the disilanyl compounds are mainly produced. Hexyldisilane (5) and 1,2-dihexyldisilane (6) were produced (Scheme 3). Hsiao and Waymouth also reported that the hydrosilylation reaction of olefins with poly(phenylsilane), which contains many Si–Si and Si–H bonds in the molecule, proceeded with little polymer degradation in the presence of a radical initiator. These results suggest that the cleavage of the Si–H bond by a radical would be much easier than that of the Si–Si bond [11].



Scheme 3. Mechanisms of the hydrosilylation of 1-hexene with SiH_4 and Si_2H_6 in the presence of the radical initiator.

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