Available online at www.sciencedirect.com
ScienceDirect
Journal of Organometallic Chemistry 691 (2006) 4740–4746
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Controlled introduction of allylic group to chlorosilanes

Zhifang Li, Xiaojun Cao, Guoqiao Lai *, Jinhua Liu, Yong Ni, Jirong Wu, Huayu Qiu *

Key Laboratory of Organosilicon Chemistry and Material Technology of Ministry of Educations, Hangzhou Teachers College, Wenyi Road 222, Hangzhou 310012, PR China

Received 10 June 2006; received in revised form 13 July 2006; accepted 18 July 2006
Available online 1 August 2006

Abstract

Allylation of chlorosilanes has been achieved with allylsamarium bromide, especially in a controlled manner. Thus allylation of trisubstituted chlorosilanes (R_3SiCl) afforded a variety of aryl, aralkyl, and alkenyl substituted allylsilanes. Dichlorosilanes (R_2SiCl_2) can either afford monoallylated silanes or diallylated silanes depending on the amount of allylsamarium bromide used. Similarly, trichlorosilanes ($RSiCl_3$) can selectively afford mono-, di-, and tri-allylation products. Finally, perchlorosilane ($SiCl_4$) was allylated stepwise and the corresponding silanes containing one, two, three or four allylic groups, respectively, were obtained in satisfactory yields.

Keywords: Controlled allylation; Allyl samarium bromide; Alkenyl groups; Chlorosilanes

1. Introduction

Substituted allyl or vinylsilanes have become a commonly used class of organosilicon reagents in organic synthesis. Hydrolysis and dehydration of these products yielded polysiloxanes which retained the unsaturated groups, permitting additional polymerization across the double bonds to synthesize the functional polymers [1]. The reactions of Grignard reagents with chlorosilanes and alkoxysilanes offer a convenient route to the synthesis of various industrial useful organosilicon compounds. However, only moderate yields of the products could be obtained in the preparation of unsaturated chlorosilanes with this method [2]. Recently, some modified approaches have been reported for the synthesis of unsaturated organosilicon compounds, such as hydrosilylation and silylmetallation and/or carbosilylation of alkynes or hydrometallation and hydrogenation of alkynylsilanes [3,4]. More recently, ruthenium catalyzed synthesis of vinylsilanes was also described. These methods are useful for the preparation of novel and well-known silicon-containing alkenes, but it did not work well for synthesis of unsaturated chlorosilanes [5,6]. Our recent work in the preparation of polysilanes as functional materials requires unsaturated chlorosilanes (those containing chloro group are most desirable) as monomers. In view of this, we developed a mild, safe, and more efficient method for the controlled introduction of allylic group to several kinds of chlorosilanes.

We previously found that allylsamarium bromide is a versatile reagent for the introduction of allylic group to a variety of substrates such as formanilides, lactones and lactams [7]. Herein we describe the results of our study on the allylation of chlorosilanes with allylsamarium bromide.

2. Results and discussion

2.1. The reaction of trisubstituted chlorosilanes (R_3SiCl) with allylsamarium bromide

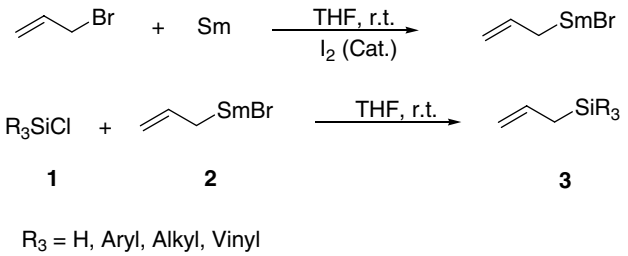
Currently the most practical method for the synthesis of trisubstituted allylsilanes is a Grignard type reaction of chlorosilanes with allylmagnesium chloride, but other

* Corresponding authors. Tel.: +86 571 28868081; fax: +86 571 28865135.
E-mail address: gqlai@hztc.edu.cn (G. Lai).

0022-328X/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2006.07.023

approaches could provide important advantages [8]. For example, the use of more reactive organolithium reagents rather than Grignard reagents, affords the trialkylsilane with bulky substituents [9]; the electrolysis of appropriate chlorosilanes gives the symmetrical difunctional disilanes in good yield [10]; palladium with SmI_2–HMPA system catalyzed stereoselective synthesis of allylsilanes [11]. We found that when trisubstituted chlorosilanes (R_3SiCl) were treated with allylsamarium bromide in THF at room temperature, allyl substituted organosilicons were obtained in good yields (Scheme 1). The chlorosilanes and allylsamarium bromide were used in a ratio of 1:1.1.

The reactions of arylsubstituted chlorosilanes with allylsamarium bromide were completed within 2 h to give the corresponding products in high yield (Table 1, entries 2–5). The product formation was ascertained by TLC monitoring and the product isolation was achieved by quenching the reaction with dilute hydrochloric acid followed by extraction. The aliphatic chlorosilanes such as chlorotrimethylsilane also react with allylsamarium bromide smoothly and the corresponding allyltrimethylsilane was obtained in good yield albeit lower temperature (−10 °C) was required (entry 6).



Scheme 1.

2.2. The reaction of dichlorosilanes (R_2SiCl_2) with allylsamarium bromide

Aryl- and aralkyl-unsaturated chlorosilanes, in which the aryl and aralkyl groups are directly linked with silicon, were widely used in the preparation of functional polysiloxanes with good thermal stability and a rapid cure [12]. It was, therefore, of interest to prepare these silicon derivatives in order to obtain compounds which when mixed with methyl or phenyl polysiloxanes would reduce the cure time of these conventional silicon resins as well as improve certain physical properties of these polymers. These unsaturated chlorosilanes were first reported by Hurd [13]. Pure aryl or aralkyl allyldichlorosilanes were prepared from allyl- and vinyltrichlorosilane and the appropriate Grignard compound [14]. However, in most reactions carried

Table 1
The reaction of trisubstituted chlorosilanes (R_3SiCl) with allylsamarium bromide[a]

Entry	Substrate	Time (h)	Product	Yields[b] (%)
1[c]	Ph_3SiCl	2.5	Ph_3Si **3a**	97
2	$Ph_2MeSiCl$	1.5	Ph_2MeSi **3b**	98
3	$PhMe_2SiCl$	1.5	$PhMe_2Si$ **3c**	99
4	Ph_2HSiCl	1.5	Ph_2HSi **3d**	96
5	AllylMePhSiCl	2	AllylMePhSi **3e**	88
6[d]	Me_3SiCl	2.5	Me_3Si **3f**	78
7	Me_3SiCl	2.5	Me_3Si **3f**	0[e]

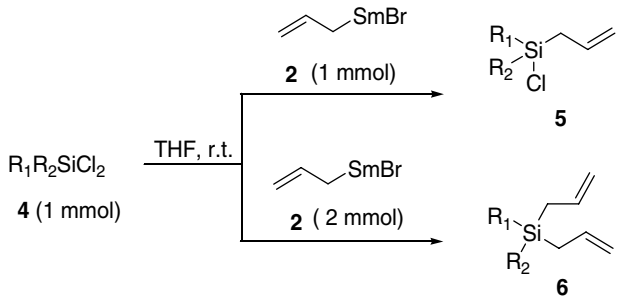
[a] Unless otherwise noted, chlorosilanes (1 mmol) were allowed to react with Sm (1.1 mmol) and allyl bromide (1 mmol) in THF at room temperature for 1.5–2.5 h.
[b] Isolated yields based on **1**.
[c] At 65 °C.
[d] At −10 °C.
[e] Complex mixture.

out between Grignard reagent and chlorosilanes to form partially substituted arylchlorosilanes, successive substitution products were always formed [15]. In our studies for the construction of Si–C bond, we found that the substitution reaction between dichlorosilanes ($R_1R_2SiCl_2$) and allylsamarium bromide could be controlled at the desired mono- or di- substituted manner. When dichlorosilanes ($R_1R_2SiCl_2$) and allylsamarium bromide were used in a ratio of 1:1, the monoallyl substituted organosilicons (**5**) were obtained in excellent yields; while the 1:2 ratio gave the substituted allylsilanes (**6**) (Scheme 2) almost quantitatively. It should be noted that the monoallylation of dichlorosilanes (R_2SiCl_2) were generally clean and no *gem*-diallylated products could be detected in the ^1H NMR spectra of the crude products.

On the basis of the good results obtained with simple dichlorosilanes, it seemed logical to investigate the possibility of extending this methodology to carry out controlled allylation of dichloromethylvinylsilane with an attempt to obtain allylchloromethylvinylsilane or diallylmethylvinylsilane (entry 3). The results and the scope of this reaction are summarized in Table 2, which clearly indicates that the present strategy may afford a general allylation protocol for the synthesis of allylsubstituted chlorosilanes.

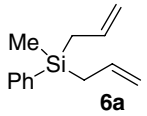
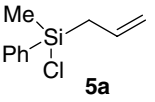
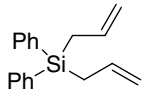
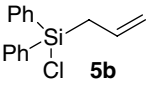
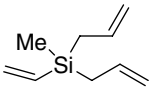
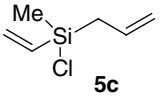
2.3. The reaction of trichlorosilanes ($RSiCl_3$) with allylsamarium bromide

With the success for the synthesis of allyl substituted organosilanes and chlorosilanes, we subsequently investigated the allylation of trichlorosilanes ($RSiCl_3$) with allylsamarium bromide. When trichlorophenylsilane (1 mmol) was treated with allylsamarium bromide (3 mmol), the triallylphenylsilane (**7**) was obtained in excellent yield (99%), where a high chemical selectivity was observed with mono- or diallyl substituted silane contamination. When trichlorophenylsilane and allylsamarium bromide were used in a ratio of 1:2 or 1:1, the diallylchlorophenylsilane (**8**) and allyldichlorophenylsilane (**9**) were obtained, respectively (Scheme 3). Under the similar reaction conditions, trichloromethylsilane also reacted with allylsamarium bromide



Scheme 2.

Table 2
The reaction of dichlorosilanes (R_2SiCl_2) with allylsamarium bromide[a]

Entry	Substrate	Time (h)	Product	Yields[b] (%)
1	$PhMeSiCl_2$	1	 **6a**	97
		1	 **5a**	95
2	Ph_2SiCl_2	1	 **6b**	99
		1	 **5b**	98
		4	 **6c**	90
3[c]	$VinylMeSiCl_2$	4	 **5c**	86

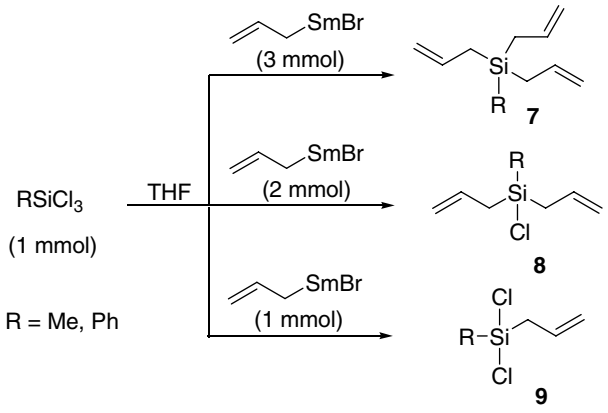
[a] Unless otherwise specified, chlorosilanes (1 mmol) were allowed to react with allylsamariumbromide (1–2 mmol) in THF at room temperature for 1–2 h.
[b] Isolated yields based on **4**.
[c] At −10 to 0 °C.

smoothly, giving the corresponding products in good yields. The results are summarized in Table 3.

2.4. The reaction of perchlorosilane ($SiCl_4$) with allylsamarium bromide

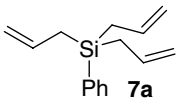
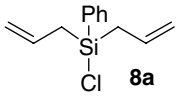
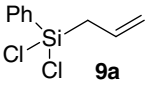
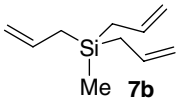
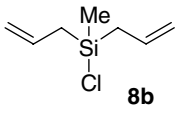
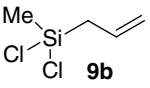
Scott and Frisch reported that the reaction of allyl Grignard reagent with $SiCl_4$ led to a mixture of allyltrichlorosilane (30.5%), diallyldichlorosilane (35.5%) and triallylchlorosilane (25.5%) [13]. Our study here found that the reaction of $SiCl_4$ at room temperature could afford any of them (**10**, **11**, **12** or**13**) as the main product depending upon the amounts of the allylsamarium bromide added, thus having preparative value (Scheme 4).

In conclusion, we present the novel selective allylation of chlorosilanes with allylsamarium bromide. By applying this method, aryl and aralkyl unsaturated chlorosilanes as well as diallyl chlorosilanes containing different allyl groups were prepared conveniently. The new types of allylsubstituted chlorosilanes prepared herein possess unsaturated carbon–carbon bonds and will meet our further requirements to permit additional polymerization across the double bonds so as to synthesize functional polymers.



Scheme 3.

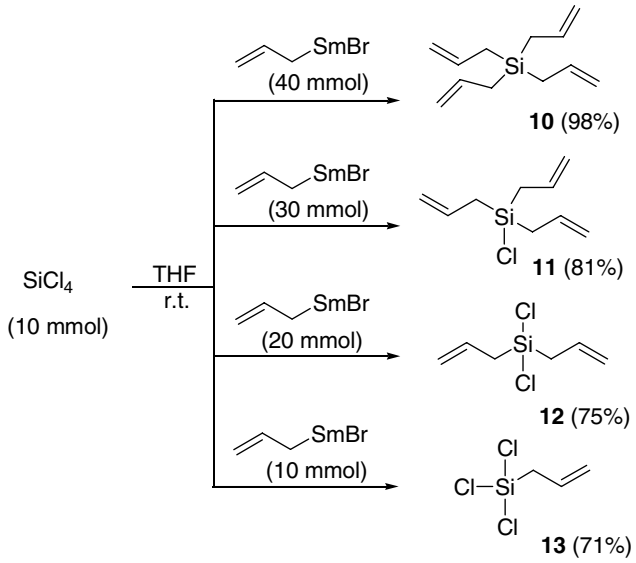
Table 3
The reaction of trichlorosilanes ($RSiCl_3$) with allylsamarium bromide[a]

Entry	Substrate	Time (h)	Product	Yields[b] (%)
1	$PhSiCl_3$	1	 **7a**	97
		1	 **8a**	95
		0.5	 **9a**	99
2	$MeSiCl_3$	1.5	 **7b**	97
		1.5	 **8b**	95
		1.5	 **9b**	99

[a] Chlorosilanes (1 mmol) were allowed to react with allylsamarium bromide for 1–2 h, the respective amounts depending upon the desired allylic silanes.
[b] Isolated yields based on $RSiCl_3$ used.

3. Experimental

Tetrahydrofuran was distilled from sodium-benzophenone immediately prior to use. All reactions were conducted under a nitrogen atmosphere. Melting points are uncorrected. ^1H NMR spectra were recorded on a BRUKER AV-400 MHz instrument as $CDCl_3$ solutions using TMS as an internal standard. Chemical shifts (δ) are reported in ppm and coupling constants J are given in hertz. IR spectra were taken as thin films with a BRUKER TENSOR-27 infrared spectrometer. Elemental analysis



Scheme 4.

was performed on a VARIO EL-3 instrument. Metallic samarium, the starting material chlorosilanes and all solvents were purchased from commercial sources and were used without further purification. Allylsamarium bromide was sensitive to air and water, must be stored in a sealed vessel under nitrogen.

3.1. General procedure for the synthesis of allylaralkyl silanes (*3a–e*)

Allyl bromide (4 mmol) and samarium (2.2 mmol) with a catalytic amount of iodine (0.01 mmol) in dry THF (10 mL) were added to a three-necked flask with stirring at room temperature under a nitrogen atmosphere. The mixture was stirred for about 5 min, and a purple color was formed. Chlorosilanes (2 mmol) were added dropwise, the purple color of the mixture disappeared gradually. The reaction mixture was stirred for 1–2 h and then was quenched with 0.1 M hydrochloric acid (10 mL). The resulting mixture was extracted with diethyl ether (3×15 mL), the diethyl ether solution was washed with saturated NaCl (2×5 mL) and dried over anhydrous $MgSO_4$. The solvent was removed by evaporation under reduced pressure. The crude product was purified by preparative TLC on silica gel (cyclohexane–ethyl acetate (8:1) as eluent).

3.1.1. Allyltriphenylsilane (*3a*)

IR: ν_{max} (KBr) 3066.0, 3041.0, 2996.0, 2923.3, 2863.4, 1628.1, 1427.3, 1112.6 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.34–7.53 (15H, m, ArH), 5.84–5.90 (1H, m, CH), 4.87–4.97 (2H, q, CH_2=), 2.38–2.40 (2H, d, CH_2CH=CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.76, 134.55, 133.82, 129.56, 127.85,115.10, 21.19; MS: m/z (%): 301 ($M^+ + 1$, 2.21), 260 (23.58), 259 (100), 181 (9.92), 105 (3.74). Anal. Calc. $C_{21}H_{20}Si$: C, 83.94; H, 6.71; Si, 9.35. Found: C, 83.89; H, 6.76; Si, 9.38%.

*3.1.2. Allyldiphenylmethylsilane (**3b**)*

IR: ν_{max} (liquid film) 3069.6, 2924.0, 2853.5, 1630.4, 1427.6, 1251.5, 1151.9, 1112.9 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.32–7.36 (10H, m, ArH), 5.74–5.85 (1H, m, CH), 4.85–4.93 (2H, t, CH_2=), 2.06–2.08 (2H, d, CH_2CH=CH_2), 0.55 (3H, s, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.41, 134.41, 133.92, 129.16, 127.70, 114.13, 22.03, −4.95; MS: *m*/*z* (%): 278 (M^+, 4.00), 198 (27.09), 197 (100). Anal. Calc. $C_{16}H_{18}Si$: C, 80.61; H, 7.61; Si, 11.78. Found: C, 80.56; H, 7.57; Si, 11.86%.

*3.1.3. Allyldimethylphenylsilane (**3c**)*

IR: ν_{max} (liquid film) 3070.3, 2998.6, 2957.6, 2915.9, 1630.0, 1426.8, 1249.9, 1155.4, 1114.3 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.33–7.50 (5H, m, ArH), 5.72–5.80 (1H, m, CH), 4.83–4.88 (2H, t, CH_2=), 1.74–1.76 (2H, d, CH_2CH=CH_2), 0.27 (3H, s, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.46, 134.43, 133.43, 128.81, 127.64, 113.19, 23.49, −3.70; MS: *m*/*z* (%): 176 (M^+, 1.00), 161 (0.88), 136 (12.52), 135 (100), 105 (2.97). Anal. Calc. $C_{11}H_{16}Si$: C, 74.93; H, 9.19; Si, 15.93. Found: C, 74.86; H, 9.11; Si, 15.89%.

*3.1.4. Allyldiphenylsilane (**3d**)*

IR: ν_{max} (liquid film) 3069.3, 3003.1, 2972.5, 2920.0, 2125.3, 1629.8, 1427.0, 1155.0, 1114.1 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.32–7.64 (10H, m, ArH), 5.79–5.89 (1H, m, CH), 4.88–4.97 (2H, m, CH_2=), 4.86 (1H, s, SiH), 2.12–2.15 (2H, d, CH_2CH=CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.40, 133.73, 133.57, 129.39, 127.05, 114.79, 19.77; MS: *m*/*z* (%): 224 (M^+, 2.17), 183 (100), 105 (13.62). Anal. Calc. $C_{15}H_{16}Si$: C, 80.30; H, 7.19; Si, 12.52. Found: C, 80.25; H, 7.12; Si, 12.46%.

*3.1.5. Diallylmethylphenylsilane (**3e**)*

IR: ν_{max} (liquid film) 3072.5, 2971.3, 2916.2, 1630.0, 1426.9, 1252.1, 1154.2, 1113.2 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.32–7.50 (5H, m, ArH), 5.73–5.79 (2H, m, 2 × CH), 4.83–4.90 (4H, m, 2 × CH_2=), 1.79–1.81 (4H, d, 2 × CH_2CH=CH_2), 0.28 (3H, s, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.71, 134.05, 133.79, 129.06, 127.62, 113.73, 21.44, −5.98; MS: *m*/*z* (%): 202 (M^+, 4.1), 161 (100), 121 (30.5), 105 (11.9).

*3.2. General procedure for the synthesis of allyltrimethylsilane (**3f**)*

Allyl bromide (20.1 mmol) and samarium (20 mmol) with a catalytic amount of iodine (0.1 mmol) in dry THF (20 mL) were added to a three-necked flask with stirring at room temperature under a nitrogen atmosphere. The mixture was stirred for about 5 min, and a purple color was formed. Then the mixture was stirred for additional 1.5 h. Chlorotrimethylsilane (20 mmol) in THF (5 mL) were added dropwise at −10 °C, and the purple color of the mixture faded gradually. The reaction mixture was stirred for 2.5 h and then was quenched with 0.1 M hydrochloric acid (20 mL). The resulting mixture was extracted with diethyl ether (3 × 20 mL), the diethyl ether solution was washed with saturated NaCl (2 × 20 mL) and dried over anhydrous $MgSO_4$. The solvent was removed by evaporation under reduced pressure. The residual liquid was fractionally distilled.

*3.2.1. Allyltrimethylsilane (**3f**)*

^1H NMR (400 MHz,$CDCl_3$): δ 5.66–5.71 (1H, m, CH), 4.77–4.83 (2H, m, CH_2=), 1.73–1.75 (2H, d, CH_2CH=CH_2), 0.21–0.33 (9H, s, CH_3); MS: *m*/*z* (%): 114 (M^+, 2.56), 74 (29.04), 73(43.76), 9 (46.08), 45(100). Anal. Calc. $C_6H_{14}Si$: C, 63.07; H, 12.35; Si, 24.58. Found: C, 62.89; H, 12.22; Si, 24.46%.

*3.3. General procedure for the synthesis of allyl substituted chlorosilanes (**5a**–**c**)*

Allylsamarium bromide (20.2 mmol) was prepared using the above procedure. Dichlorosilanes (20 mmol) were added dropwise, the purple color of the mixture disappeared slowly. The reaction mixture was stirred for 1–2 h. The inorganic precipitate was filtered off and washed repeatedly with dry ether. The filtrate was then freed from any solvent and the residual liquid fractionally distilled.

*3.3.1. Allylchloromethylphenylsilane (**5a**)*

IR: ν_{max} (liquid film) 3071.2, 2969.5, 1630.5, 1427.8, 1256.2, 1157.0, 1118.3 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.25–7.45 (5H, m, ArH), 5.66–5.71 (1H, m, CH), 4.77–4.83 (2H, m, CH_2=), 1.73–1.75 (2H, d, CH_2CH=CH_2), 0.21–0.33 (3H, s, CH_3);^{13}C NMR (100 MHz, $CDCl_3$): δ 133.7, 133.2, 133.16, 129.36, 127.54, 113.73, 21.43, −1.62; MS: *m*/*z* (%): 161 (100), 155 (21.83), 121 (37.22), 105 (14.01).

*3.3.2. Allylchlorodiphenylsilane (**5b**)*

IR: ν_{max} (liquid film) 3069.9, 3023.2, 2919.9, 1630.0, 1590.6, 1428.0, 1117.5 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.26–7.57 (10H, m, ArH), 5.80–5.89 (1H, m, CH), 4.88–5.01 (2H, m, CH_2=), 2.18–2.22 (2H, m, CH_2CH=CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ 133.79, 130.27, 130.05, 129.32, 127.56, 114.60, 19.83; MS: *m*/*z* (%): 258 (M^+, 2.54), 217 (100), 181 (13.60).

*3.4. General procedure for the synthesis of diallyl substituted silanes (**6a**–**c**)*

Allylsamarium bromide was prepared using the above procedure. Dichlorosilanes (2 mmol) were added dropwise, the purple color of the mixture disappeared slowly. The reaction mixture was stirred for 1–4 h and then was quenched with 0.1 M hydrochloric acid (10 mL). The resulting mixture was extracted with diethyl ether (3 × 10 mL), the diethyl ether solution was washed with saturated NaCl (2 × 5 mL) and dried over anhydrous $MgSO_4$. The solvent was removed by evaporation under reduced pressure. The crude product was purified by preparative TLC on silica gel (cyclohexane–ethyl acetate (5:1) as eluent).

*3.4.1. Diallylmethylphenylsilane (**6a**)*

IR: ν_{max} (liquid film) 3072.5, 2971.3, 2916.2, 1630.0, 1426.9, 1252.1, 1154.2, 1113.2 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.32–7.50 (5H, m, ArH), 5.73–5.79 (2H, m, $2\times CH$), 4.83–4.90 (4H, m, $2\times CH_2$=), 1.79–1.81 (4H, d, $2\times CH_2CH$=CH_2), 0.28 (3H, s, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.71, 134.05, 133.79, 129.06, 127.62, 113.73, 21.44, −5.98; MS: *m*/*z* (%): 202 (M^+, 2.1), 161 (100), 121 (30.5), 105 (11.9).

*3.4.2. Diallyldiphenylsilane (**6b**)*

IR: ν_{max} (liquid film) 3069.6, 2998.2, 1629.9, 1427.9, 1110.8, 907.9, 732.7 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.32–7.52 (10H, m, ArH), 5.78 (2H, m, $2\times CH$), 4.86–4.94 (4H, t, $2\times CH_2$=), 2.11–2.13 (4H, d, $2\times CH_2$-CH=CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.84, 134.12, 133.55, 129.32, 127.65, 114.59, 19.85; MS: *m*/*z* (%): 264 (M^+, 6.96), 223 (100), 183 (27.66), 145 (32.05).

*3.4.3. Diallylmethylvinylsilane (**6c**)*

IR: ν_{max} (liquid film) 3053.7, 2922.1, 2850.7, 1631.1, 1407.1, 1258.6, 1062.3, 892.6 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 5.99–6.12 (2H, m, $2\times CH$), 5.69–5.83 (3H, m, CH=CH_2), 4.85–4.90 (4H, m, $2\times CH_2$=), 1.62–1.64 (4H, d, $2\times CH_2CH$=CH_2), 0.08 (3H, s, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.28, 134.29, 132.99, 113.50, 21.34, −6.13; MS: *m*/*z* (%): 152 (M^+, 0.56), 111 (100), 83 (33.8).

3.5. The reaction of trichlorosilanes ($RSiCl_3$) with allylsamarium bromide

Allylsamarium bromide was added to a THF solution of trichlorosilanes ($RSiCl_3$), the respective amounts depending upon the desired allyl chlorosilanes. After the addition was completed the mixture was stirred for 1–2 h under room temperature. The inorganic precipitate was filtered off and washed repeatedly with dry ether. The filtrate was then freed from any solvents and the residual liquid fractionally distilled.

*3.5.1. Triallylphenylsilane (**7a**)*

IR: ν_{max} (liquid film) 3075.1, 2998.1, 2971.7, 2922.1, 2854.1, 1630.0, 1425.7, 1156.9, 1111.8, 1029.7 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.34–7.52 (5H, m, ArH), 5.73–5.84 (3H, m, $3\times CH$), 4.87–4.94 (6H, t, $3\times CH_2$=), 1.85–1.87 (6H, d, $3\times CH_2CH$=CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.22, 134.25, 133.87, 129.39, 127.79, 114.35, 19.55; MS: *m*/*z* (%): 228 (M^+, 5.64), 187 (67.37), 159 (100), 145 (73.68), 105 (58.00). Anal. Calc. $C_{15}H_{20}Si$: C, 78.88; H, 8.83; Si, 12.30. Found: C, 78.76; H, 8.76; Si, 12.25%.

*3.5.2. Diallylchlorophenylsilane (**8a**)*

IR: ν_{max} (liquid film) 3073.0, 3002.4, 2974.2, 2919.8, 1632.0, 1428.9, 1121.7 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.33–7.47 (5H, m, ArH), 5.74–5.82 (2H, m, $2\times CH$), 4.98–5.02 (4H, t, $2\times CH_2$=), 2.09–2.11 (4H, d, $2\times CH_2CH$=CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ 133.85, 131.38, 130.62, 128.09, 127.77, 116.34, 15.32; MS: *m*/*z* (%): 222 (M^+, 7.63), 183 (35.03), 181 (100), 145 (84,91), 142 (4.27). Anal. Calc. $C_{12}H_{15}ClSi$: C, 64.69; H, 6.79; Si, 12.61. Found: C, 64.76; H, 6.76; Si, 12.55%.

*3.5.3. Allyldichlorophenylsilane (**9a**)*

IR: ν_{max} (liquid film) 3070.6, 2969.1, 1630.0, 1427.9, 1112.5 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.28–7.72 (5H, m, ArH), 5.73–5.83 (1H, m, CH), 5.05–5.09 (2H, t, CH_2=), 2.30–2.32 (2H, d, CH_2CH=CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ 133.96, 131.77, 130.82, 130.53, 128.13, 115.66, 19.40; MS: *m*/*z* (%): 216 (M^+, 19.92), 175 (100), 77 (22.14).

*3.5.4. Triallylmethylsilane (**7b**)*

IR: ν_{max} (liquid film) 3078.0, 2971.8, 2919.9, 1630.5, 1254.3, 1159.2, 895.3 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 5.71–5.87 (3H, m, $3\times CH$), 4.84–4.94 (6H, m, $3\times CH_2$=), 1.55–1.66 (6H, m, $3\times CH_2CH$=CH_2), 0.40 (3H, s, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.34, 113.47, 20.80, −6.24; MS: *m*/*z* (%): 166 (M^+, 1.96), 125 (100).

3.6. The reaction of perchlorosilane ($SiCl_4$) with allylsamarium bromide

Allylsamarium bromide was added to a THF solution of perchlorosilanes ($SiCl_4$), the respective amounts depending upon the desired allyl chlorosilanes. After the addition was completed the mixture was stirred for 30 min under room temperature. The inorganic precipitate was filtered off and washed repeatedly with dry ether. The filtrate was then freed from any solvent and the residual liquid fractionally distilled.

*3.6.1. Tetraallylsilane (**10**)*

IR: ν_{max} (liquid film) 3077.6, 2972.8, 2919.3, 2882.9, 1630.8, 1163.2, 991.6, 930.2, 896.1 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 5.73–5.87 (4H, m, $4\times CH$), 4.87–4.97 (8H, m, $4\times CH_2$=), 1.60–1.68 (8H, m, $4\times CH_2CH$=CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): 133.12, 114.54, 21.99; MS: *m*/*z* (%): 192 (M^+, 3.26), 151 (81.93), 123 (100), 95 (93.68), 69 (35.87).

*3.6.2. Triallylchlorosilane (**11**)*

Colorless liquid; bp 96–97 °C (30 mmHg); ^1H NMR (400 MHz, $CDCl_3$): δ 5.76–5.90 (3H, m, $3\times CH$), 4.89–4.99 (6H, m, $3\times CH_2$=), 1.65–1.73 (6H, m, $3\times CH_2CH$=CH_2); MS: *m*/*z* (%): 186 (M^+, 2.21), 145 (79.83), 104 (100).

*3.6.3. Diallyldichlorosilane (**12**)*

Colorless liquid; bp 64–66 °C (26 mmHg); ^1H NMR (400 MHz, $CDCl_3$): δ 5.77–5.91 (2H, m, $2\times CH$), 4.88–4.98 (4H, m, $2\times CH_2$=), 1.66–1.74 (4H, m, $2\times$

$CH_2CH{=}CH_2$); MS: *m*/*z* (%): 180 (M^+, 1.31), 139 (80.83), 98 (100).

3.6.4. Allyltrichlorosilane (*13*)

Colorless liquid; bp 116–118 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 5.75–5.98 (1H, m, CH), 4.88–4.99 (2H, m, $CH_2{=}$), 1.68–1.77 (2H, m, $CH_2CH{=}CH_2$); MS: *m*/*z* (%): 174 (M^+, 2.24), 133 (100).

Acknowledgements

We are grateful to the Natural Science Foundation of Zhejiang Province (Project No. Y404380) for financial support.

References

[1] (a) B. Boutevin, F.G. Pietrasanta, A. Ratsimihety, in: R.G. Jones, W. Ando, J. Chojnowski (Eds.), Silicon-Containing Polymers, the Science and Technology of Their Synthesis and Applications, Kluwer Academic Publishers, Dordrecht, 2000, p. 79;
(b) B. Marciniec, M. Majchrzak, J. Organomet. Chem. 686 (2003) 228.

[2] (a) S.D. Rosenberg, J.J. Walburn, H.E. Ramsden, J. Org. Chem. 22 (1957) 1606;
(b) R.E. Scott, K.C. Frisch, J. Am. Chem. Soc. 73 (1951) 2599.

[3] (a) For reviews see E.W. Colvin, Silicon Reagents in Organic Synthesis;, Academic Press, London, 1988 (Chapter 3);
(b) L. Hevesi, in: A.R. Katritzky, R.J.K. Taylor (Eds.), Comprehensive Organic Functional Group Transformations I (COFGT-I), Elsevier, 1994 (Chapter 2.18);
(c) T.X. Luk, S.T. Lu, in: Z. Rappaport (Ed.), The Chemistry of Organosilicon Compounds, Wiley, Chichester, 1998 (Chapter 30);
(d) B. Marciniec, M. Zaidlewicz, C. Pietraszuk, I. Kownacki, in: A.R. Katritzky, R.J.K. Taylor (Eds.), Comprehensive Organic Functional Group Transformations II (COFGT-II), Elsevier, 2004 (Chapter 2.18);
(e) B. Marciniec, Coord. Chem. Rev. 249 (2005) 2374;
(f) E. Barnea, M.S. Eisen, Coord. Chem. Rev. 250 (2006) 855.

[4] (a) Y.S. Song, B.R. Yoo, G.-H. Lee, I.N. Jung, Organometallics 18 (1999) 3109;
(b) S.T. Phan, W.C. Lim, J.S. Joon Soo Han, N. Il Jung, B.R. Yoo, J. Organomet. Chem. 691 (2006) 604;
(c) J.Y. Zeng, M.-H. Hsieh, H.M. Lee, J. Organomet. Chem. 690 (2005) 5662;
(d) G.T.S. Andavan, E.B. Bauer, C.S. Letko, T.K. Keith Hollis, F.S. Tham, J. Organomet. Chem. 690 (2005) 5938;
(e) H. Sasabe, N. Kihara, K. Mizuno, A. Ogawa, T. Takata, Tetrahedron Lett. 46 (2005) 3851;
(f) S.V. Maifeld, M.N. Tran, D. Lee, Tetrahedron Lett. 46 (2005) 105;
(g) Y. Otomaru, T. Hayashi, Tetrahedron: Asymmetry 15 (2004) 2647.

[5] (a) For reviews see B. Marciniec, C. Pietraszuk, Curr. Org. Chem. 7 (2003) 691;
(b) B. Marciniec, C. Pietraszuk, in: R.H. Grubbs (Ed.), Handbook of Metathesis, Wiley/VCH, 2003 (Chapter 2.13);
(c) B. Marciniec, in: B. Cornils, W.A. Hermann (Eds.), Applied Homogeneous Catalysis with Organometallic Compounds, Weinheim, VCH, 2002 (Chapter 2.6);
(d) J.A. Reichl, D.H. Berry, Adv. Organomet. Chem. 43 (1998) 203;
(e) B. Marciniec, Appl. Organomet. Chem. 14 (2000) 527.

[6] (a) M. Jankowska, O. Shuvalova, N. Bespalova, M. Majchrzak, B. Marciniec, J. Organomet. Chem. 690 (2005) 4492;
(b) B. Marciniec, D. Chadyniak, S. Krompiec, J. Mol. Catal. A: Chem. 224 (2004) 111;
(c) M. Jankowska, B. Marciniec, C. Pietraszuk, J. Cytarska, M. Zaidlewicz, Tetrahedron Lett. 45 (2004) 6615;
(d) B. Marciniec, D. Chadyniak, S. Krompiec, Tetrahedron Lett. 45 (2004) 4065.

[7] (a) Z.F. Li, Y.M. Zhang, J. Chem. Res. (S) (2002) 297;
(b) Z.F. Li, Y.M. Zhang, Tetrahedron Lett. 42 (2001) 8507;
(c) Z.F. Li, Y.M. Zhang, Tetrahedron 58 (2002) 5301.

[8] S. Masaoka, T. Banno, M. Ishikawa, J. Organomet. Chem. 691 (2006) 182.

[9] (a) H. Gilman, R.N. Clark, J. Am. Chem. Soc. 69 (1947) 1499;
(b) A. Funatsu, T. Kubota, M. Endo, Jpn. Kokai Tokyo Koho, Jp 2001-039990.

[10] (a) C. Grogger, B. Loidl, H. Stueger, T. Kammel, B. Pachaly, J. Organomet. Chem. 691 (2006) 105;
(b) C. Jammegg, S. Graschy, E. Hengge, Organometallics 13 (1994) 2397;
(c) C. Grogger, H. Fallmann, G. Fürpaß, H. Sütger, J. Organomet. Chem. 665 (2003) 186;
(d) H. Fallmann, C. Grogger, in: N. Auner, J. Weis (Eds.), Organosilicon Chemistry IV. From Molecules to Materials, Weinheim, 2000, p. 229.

[11] T. Hanamoto, A. Sugino, T. Kikukawa, J. Inanaga, Bull. Soc. Chim. Fr. 134 (1997) 391.

[12] D.T. Hurd, G.F. Roedel, Ind. Eng. Chem. 40 (1948) 2078.

[13] D.T. Hurd, J. Am. Chem. Soc. 67 (1945) 1813.

[14] (a) L.H. Sommer, U.S. Patent 1950, 2, 512, 390, describe the reaction of alkyl- and arylmagnesium bromide with α-chlorovinyltrichlorosilane;
(b) R.E. Scott, K.C. Frisch, J. Am. Chem. Soc. 73 (1951) 2599.

[15] E.G. Rochow, An Introduction to the Chemistry of the Silicones, John Wiley and Sons Inc., New York, 1951, p. 35, for a brief discussion of this problem.