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Synthesis of 2-methylidene-1-silacyclohexanes from 2,6-dibromohex-1-ene and polyhalosilanes

Silvia Díez-González [1], Luis Blanco *

Laboratoire de Synthèse Organique et Méthodologie, Institut de Chimie Moléculaire et des Matériaux d'Orsay (Associé au CNRS), Bât. 420, Univ. Paris-Sud, 91405 Orsay, France

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Abstract

Various 2-methylidene-1-silacyclohexanes were prepared by straightforward syntheses from readily available polychloro- or polyfluorosilanes, magnesium and 2,6-dibromohex-1-ene using Barbier-type conditions or a previously synthesized Grignard reagent. Good yields were obtained considering the low stability of the products in the reaction conditions.

Keywords: Vinylsilane; Fluorosilane; Barbier-type conditions; Organodimetallic reagent; Cyclization

1. Introduction

The synthesis of silacycloalkanes has attracted much attention [1]. We were especially interested in the potential reactivity of *exo*-cyclic vinylsilanes and in particular in 2-methylidene-1-silacyclohexanes. To our surprise, in spite of the importance of vinylsilanes in organic synthesis [2], only a handful of examples of such organosilicon compounds are described in the literature. Most commonly, previously reported 2-methylidenesilacycloalkanes have a second heteroatom within the ring and sometimes have substituents on the olefinic carbon. Such compounds can be prepared from tethered alkynes by intramolecular silylformylation [3–5], hydrosilylation [6] or bis-silylation [7,8]. Other reactions such as radical cyclization [9], nickel-catalyzed photolysis of unsaturated organosilanes [10] or ruthenium-catalyzed silylation of ethylene [11], only lead to the formation of methylidenesilacycloalkanes derivatives as minor products.

2-Methylidene-1-silacyclohexanes with diverse substituents on the olefin or on the cycle have also been prepared by similar methods [12,13], beside ene reaction from isopropenylsilanes bearing a 3-oxopropyl chain [14] and ring expansion of a silacyclobutane in the presence of an allene [15,16]. To the best of our knowledge, the only reported 2-methylidene-1-silacyclohexane without any substituent on the carbon atoms was prepared by a Wittig reaction with a 2-silacyclohexan-1-one [17]. Such acylsilane can be prepared from a silacyclohexene by a sequence hydroboration/oxidative cleavage/oxidation [18] or by hydrolysis of the corresponding dithiane in the presence of mercury salts [19]. Both approaches are time-consuming and require the use of unstable or toxic reagents.

Reaction of a dihalogenated compound with a metal in the presence of a dihalosilane or reaction of a dihalosilane with an organodimetallic reagent would be more convergent approaches to a silacycloalkane. Yet very few alkylidenesilacycloalkanes were prepared by such methods [20–22]. Herein, we report the straightforward preparation of 2-methylidene-1-silacyclohexanes **7** from di- or trihalosilanes and 2,6-dibromohex-1-ene **4** using Barbier-type conditions or employing a preformed organodimetallic reagent (Scheme 1).

* Corresponding author. Tel.: +33 1 69 15 72 95; fax: +33 1 69 15 62 78.
E-mail address: lublanco@icmo.u-psud.fr (L. Blanco).
[1] Present address: Institute of Chemical Research of Catalonia (ICIQ), Av. Països Catalans, 16, 43007 Tarragona, Spain.

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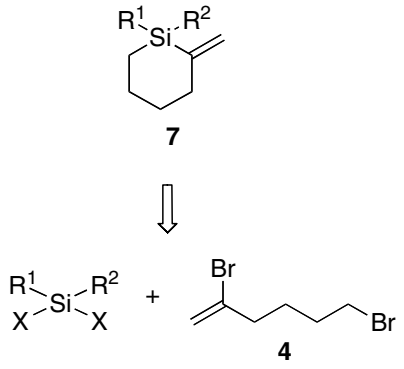
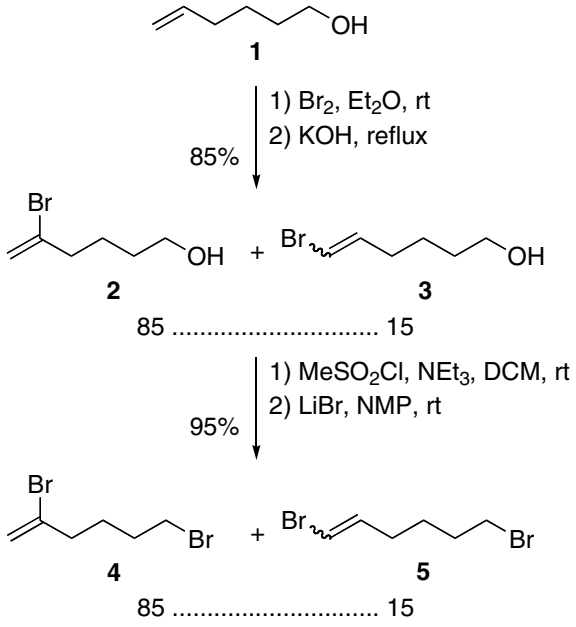


Scheme 1.

2. Results and discussion

2,6-Dibromohex-1-ene **4** was prepared from hex-5-en-1-ol **1** using a reported method [23] (Scheme 2). Addition of bromine to the alcohol **1** and treatment with potassium hydroxide of the resulting dibromide in ether gave a 85:15 mixture of 5-bromohex-5-en-1-ol **2** and the previously unnoticed 6-brominated isomer **3**. Various attempts with other bases have been made in order to increase the proportion of the desired isomer **2** but lower selectivities were obtained (with sodium hydroxide powder without solvent at 40–50 °C, **2**:**3** was 65:35; with a solution of tetrabutylammonium hydroxide in methanol at room temperature, **2**:**3** was 35:65; with an aqueous solution of lithium hydroxide in ether at reflux, **2**:**3** was 73:27). Substitution of the hydroxy group of the compounds **2** and **3** by a bromine atom was achieved by treatment of the corresponding methylsulfonates with LiBr in *N*-methylpyrrolidinone (NMP) at room temperature. A mixture of 2,6- and 1,6-dibromohex-1-ene **4** and **5** with the same ratio 85:15 was isolated by distillation and used in the next steps without separation of the isomers. No separation of the isomeric compounds **2** and **3** or **4** and **5** could be observed by liquid chromatography over silica gel. The overall yield of this two steps substitution (95%) was higher than the reported yield of the substitution using PBr_3 (56%) [23].

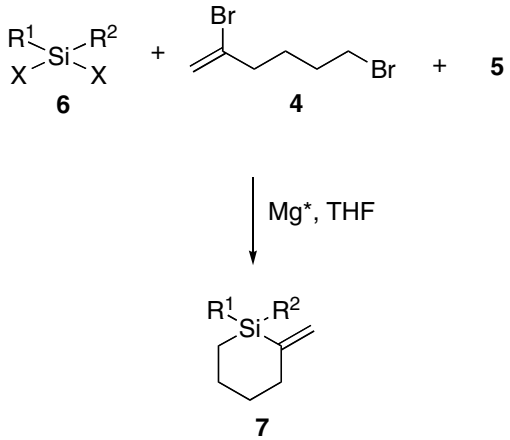


Scheme 2. Preparation of dibromohexenes **4** and **5**.

2.1. Reactions in the Barbier-type conditions

In a first approach we used the conditions reported for the preparation of a 2-methylidene-1-silacyclobutane [21]. Addition of a 0.85:0.15:1 mixture of 2,6-dibromohexene **4**, 1,6-dibromohexene **5** and trichloromethylsilane **6a** ($R^1 = Me$, $R^2 = X = Cl$) to an excess of magnesium (activated by reaction with 1,2-dibromoethane) in THF gave an exothermic reaction and after heating to reflux during 1 h, the chlorosilane **7a** was isolated in 9% yield by distillation (Scheme 3). A better yield (28%) was obtained after addition over 30 min of the same mixture of compounds **4**, **5** and **6a** to a stoichiometric amount of activated magnesium and subsequent heating of the reaction mixture at 60 °C for 2 h. Apart from the ratio (**4** + **5**):**6a**, all the others conditions tested (lower concentration of reactants, increased or decreased addition time, lower or higher temperature of the additional heating, activation of magnesium with zinc chloride, replacement of THF by DME, reaction in refluxing toluene in the presence of sodium) gave lower yields. A slightly better yield (31%) has been obtained using a ratio (**4** + **5**):**6a** = 1:2 but the purification of the chlorosilane **7a** was complicated by the presence of a larger amount of silanic oligomers. In order to obtain an easily workable crude product we preferred to run the reaction with the ratio (**4** + **5**):**6** = 1:1.

With the optimum conditions of the Barbier-type reaction described above various dihalo- and trichlorosilanes **6** [24] were used to prepare 2-methylidenesilacyclohexanes **7a**–**g**. Such as for the product **7a**, the chlorosilane **7b** and the hydrogenosilane **7f** were isolated by distillation.



Scheme 3. Preparation of 2-methylidenesilacyclohexanes **7** in the Barbier-type conditions.

All the others methylidenesilacyclohexanes have been purified by silica gel column chromatography. The results are reported Table 1.

With the dichloromethylsilanes **6c**, **6d**, **6e**, **6f** and **6g** bearing phenyl, allyl, vinyl, hydrogen or 3-chloropropyl substituent and with the trichorophenylsilane **6b** the yields were in the range 4–28%. The yield of the allylsilacyclohexane **7d** was higher from the difluorosilane **6d′** (27%) than from the corresponding dichlorosilane **6d** (22%). This trend was not general and the vinylsilacyclohexane **7e** was isolated in a slightly better yield from the dichlorosilane **6e** (5%) than from the difluorosilane **6e′** (2%). However, the high volatility of the latter could decrease the actual amount of the silane involved in the reaction. The low yield of the methylmethylidenesilacyclohexane **7f** can be explained in part by the difficulties to separate this compound (bp = 51 °C) from THF (bp = 66 °C). This silane is too instable to be purified by liquid chromatography over silica gel. The reaction with the chloropropylsilane **6g** gave the 3-chloropropylsilacyclohexane **7g** (20%) and the 1-methyl-2-methylidene-1-propyl-1-silacyclohexane **8** (9%) which should be formed by hydrolysis of the organomagnesium derivative of the chloropropylsilacyclohexane **7g**. Such a side-reaction was avoided using a preformed Grignard reagent (*vide infra*). We never observed, on the spectra of the crude reaction products, the presence of signals of a 1-silacyclohept-2-ene which could be issued from the 1,6-dibromohexene **5** although this dibromide was totally transformed under the reaction conditions.

2.2. Reactions with a Grignard reagent

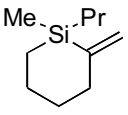
Reactions in THF of various dihalosilanes and trihalosilanes **6** [24] with 1 equiv of organodimagnesium reagent prepared from the mixture of dibromohexenes **4** and **5** (**4**:**5** = 85:15), between 20 and 30 °C or at 10 °C, followed by heating to reflux have generally allowed the preparation of 2-methylidene-1-silacyclohexanes **7** (Scheme 4). In these conditions, a 1-silacyclohept-2-ene was also never detected. Yields were calculated from the number of moles of organometallic reagents used in each reaction with the assumption that the ratio of the reagent derived from the dibromide **4** to that derived from the isomer **5** was also 85:15 (see Table 1).

When the preparation of the organodimetallic reagent was made between 20 and 30 °C, the yields of the methylidenesilacyclohexanes **7b–e** and **7g–i** were in the range 28–60%. The allylmethylsilacyclohexane **7d** was obtained in 6% yield starting from the dichlorosilane **6d** but the yield was increased to 24% using the corresponding difluorosilane **6d′**. However such improvement was not general: for the preparation of the 3-chloropropylsilane **7g** and the 3-bromopropylsilane **7h**, the yields starting with dichlorosilanes were higher than those obtained with the corresponding difluorosilanes. Using these conditions it was also possible to obtained chlorosilacyclohexanic compounds using trichlorosilanes but the yields were very low: the phenylated product **7b** was isolated in 7% yield and traces of the methylated product **7a** were observed.

Table 1
Preparation of 2-methylidene-1-silacyclohexanes **7** from polyhalosilanes **6** and 2,6-dibromohex-1-ene **4**

Polyhalosilanes				2-Methylidenesilacyclohexanes			
	X	R^1	R^2		Yield (%)		
					Barbier's conditions	Grignard's conditions	
						20–30 °C[a]	10 °C[a]
6a	Cl	Me	Cl	**7a**	28	Traces	39
6b	Cl	Ph	Cl	**7b**	28	7	53
6c	Cl	Me	Ph	**7c**	18	32	67
6d	Cl	Me	Allyl	**7d**	22	6	<13[b]
6d′	F	Me	Allyl	**7d**	27	24	<21[b]
6e	Cl	Me	Vinyl	**7e**	4	28	<17[b]
6e′	F	Me	Vinyl	**7e**	2		
6f	Cl	Me	H	**7f**	5	0	0
6g	Cl	Me	3-Chloropropyl	**7g**	20[c]	55	51
6g′	F	Me	3-Chloropropyl	**7g**		28	40
6h	Cl	Me	3-Bromopropyl	**7h**		60	35
6h′	F	Me	3-Bromopropyl	**7h**		35	42
6i	Cl	Ph	3-Chloropropyl	**7i**		33	36

[a] Temperature of preparation of the organodimetallic reagent.



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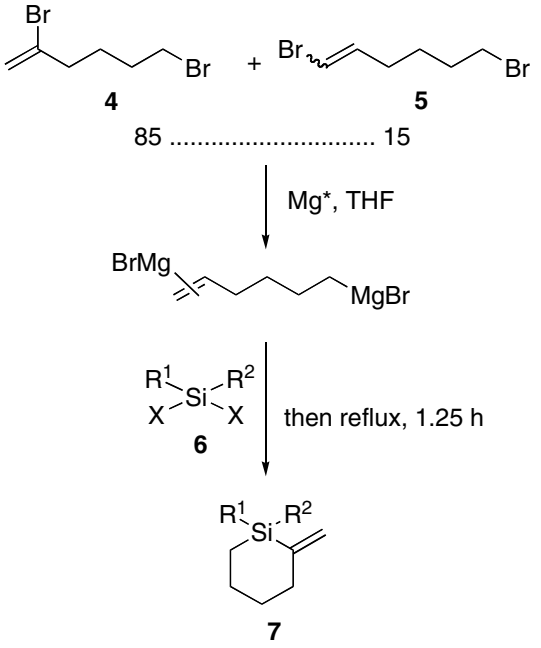
[b] Impure product has been isolated (see text).
[c] Compound **8** was also formed.



Scheme 4. Preparation of 2-methylidenesilacyclohexanes **7** *via* a Grignard reagent.

When the preparation of the organodimetallic reagent was run at 10 °C the yields of the methylidenesilacyclohexanes **7a–e** and **7g–i** were between 13% and 66%. By comparison to the reactions made with the organodimetallic reagent prepared between 20 and 30 °C, the general trend was an increase of the yields. The greatest improvements were observed for the preparation of the chlorosilanes **7a** (from traces to 39% yield) and **7b** (from 7% to 53% yield), however a decrease of the yield was noticed in some cases. Moreover after the synthesis of the allylated and the vinylated silacyclohexanes **7d** and **7e** with the organometallic reagent prepared at 10 °C, the purifications by silica gel chromatography were more tedious and only impure compounds were isolated (for the other cases and with the organometallic reagent prepared at 20–30 °C, the purities of the isolated products were higher than 95%). With this Grignard reagent, the methylidenesilane **7f** could not be prepared from dichloromethylsilane **6f**, regardless of the reaction temperature.

The stability of the organometallic reagent, prepared from **4** + **5** seems to decrease when raising the temperature. When this reagent was heated for 2 h at 50 °C before addition of the dichlorosilane **6c** and the subsequent heating, no signals corresponding to the silacyclohexane **7c** were observed in ^{1}H NMR spectrum of the crude product. Unfortunately, we did not succeed to prepare this reagent at 0 °C with the usual magnesium turnings. We postulate that the reagent formed from the dibromohexene **4** is an organodimetallic species, however, the formation of a 2-methylidene-1-magnesiacyclohexane cannot be ruled out.

Other modifications of the reaction conditions (decrease of the concentration of reactants, addition of CuCN) have been tested, in order to increase the yields of these reactions, without success. Reaction at −5 °C, followed by warming at 20 °C, of the dichlorosilane **6c** with the 2,6-dilithiated hex-1-ene prepared from lithium [25] and the mixture of dibromohexenes **4** and **5** (**4**:**5** = 85:15) gave also the expected methylphenylsilacyclohexane **7c** but the yield (19%) has been lower than those obtained with the Grignard derivative.

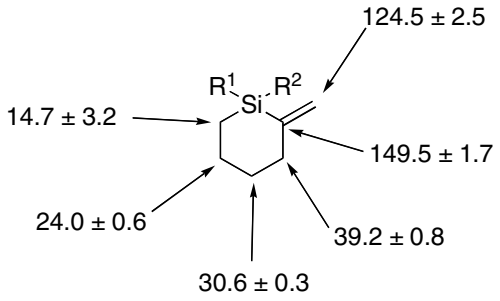


Fig. 1. ^{13}C Chemical shifts for 2-methylidenesilacyclohexanes **7**.

2.3. Comments

Comparison of the yields of the methylidenesilacyclohexanes **7** obtained with the preformed organodimetallic reagent or using the Barbier-type conditions shows that the latter conditions appear more interesting only for the synthesis of the compounds **7d** and **7f** bearing an allyl group or an hydrogen atom on the silicon atom. It should be underlined that the organodimetallic reagent was generally prepared in about 50% yield. Comparison of the yields of the silacyclohexanes **7** prepared using the Barbier type conditions with the overall yields of the syntheses using the Grignard conditions calculated from the utilized amounts of dibromide **4** shows that the latter conditions are generally more interesting, once again.

Another factor that partially explains the modest yields of the syntheses of 2-methylenesilacyclohexanes **7** is their instability in the reaction medium. For example, 82% of the methylidenesilacyclohexane **7c** was degradated after heating in THF at 68–70 °C for 16 h in the presence of equimolecular amounts of $MgBr_2$ and $MgCl_2$.

The ^{1}H NMR spectra of the 2-methylidenesilacyclohexanes **7** show two signals (one between 5.66 and 5.40 ppm, the other between 5.34 and 5.06 ppm) attributed to the methylenic protons. Their ^{13}C NMR spectra show that the chemical shifts of the carbon atoms of the core are slightly variable (Fig. 1).

3. Conclusion

Two related synthetic methods have been optimized to prepare 2-methylidenesilacyclohexanes **7** from magnesium, di- or trihalosilanes and 2,6-dibromohex-1-ene *via* a preformed organodimetallic reagent or using Barbier-type conditions. No general trend was observed regarding the

nature of the halogen (chlorine or fluorine) on the starting silane. Lowering the temperature of the Grignard reagent formation resulted in general improvement of the isolated yields. We should emphasized the simplicity of theses methods where two carbon-silicon bonds were formed in the same flask and the instability of the intermediate reagent and/or of the products in the reaction medium. In many cases, the yields were good enough to allow the use of these 2-methylidenesilacyclohexanes as synthetic intermediates. The chlorosilanes **7a** and **7b** are particularly interesting, they are useful synthons to prepare various methylidenesilacyclohexanes by nucleophilic substitution of the chlorine atom. Studies on the reactivity and the synthetic utility of this scarcely known family of vinylsilanes are ongoing in our laboratory and results will be published in due course.

4. Experimental

4.1. General informations

All reactions were performed under an argon atmosphere using oven-dried glassware. All the commercially available silanes **6a**–**f** were used without further purification. Sodium tetrafluoroborate and hexachloroplatinic acid were kept in a desiccator filled with P_2O_5. THF was distilled prior to use over the radical anion of benzophenone. Cyclohexane was filtered through basic alumina prior to use. Column chromatographies were performed on silica gel SDS (70–200 μm).

NMR spectra were recorded on Bruker AC 200, AC 250 or DRX 400 spectrometers at room temperature. Chemical shifts (δ) are reported in ppm with respect to tetramethylsilane, a signal of the solvent ($CDCl_3$) was used as internal reference ($CHCl_3$: 7.27 and $CDCl_3$: 77.0 ppm). The assignment of certain signals was done after COSY, HSQC, HMBC, DEPT or TOCSY experiments on the DRX 400 instrument. IR spectra were recorded on a Perkin–Elmer FT-IR Spectrum One instrument with neat samples, the band positions are given in cm^{-1}. Mass spectra were obtained by electron ionization method (70 eV) on a Nermag R10-10 instrument, coupled to an OKI DP125 chromatographer (Low Resolution) or on a Finnigan MAT 95 S instrument (High Resolution). Elemental analyses were made by the Microanalyse Service of the Institut de Chimie des Substances Naturelles at Gif-sur-Yvette (ICSN).

4.2. Preparation of dihalosilanes

Allyldifluororomethylsilane **6d′** [26], (3-bromopropyl)dichloromethylsilane **6h** [27] and dichloro(3-chloropropyl)phenylsilane **6i** [28] are known products and only complementary spectroscopic data to the literature are provided.

4.2.1. Allyldifluoromethylsilane (*6d′*)

Reaction of allyldichloromethylsilane **6d** (5 mL, 34.2 mmol) and sodium tetrafluoroborate (8.75 g, 79.7 mmol) in tetraglyme (14 mL), as described by Farooq and Tiers [26] (oil bath temperature = 70 °C), gave the difluorosilane **6d′**, isolated as a colorless oil (3.63 g, 87%) after purification by distillation under argon atmosphere: bp = 63 °C/760 Torr; ^{13}C NMR (62.9 MHz, $CDCl_3$) δ −5.1 (t, $J_{C-F} = 16$ Hz, Si–CH_3), 20.6 (t, $J_{C-F} = 16$ Hz, Si–CH_2), 116.9 (=CH_2), 129.2 (=CH); IR 3087 ($\nu_{=CH}$), 2980, 1636 ($\nu_{C=C}$), 1419 ($\delta_{=CH}$), 1271 (δ_{Si-CH_3}), 1180, 911 ($\delta_{=CH}$), 879, 812.

4.2.2. Difluoromethylvinylsilane (*6e′*)

Reaction of dichloromethylvinylsilane **6e** (5 mL, 38 mmol) and sodium tetrafluoroborate (13.84 g, 126.1 mmol) in tetraglyme (16 mL), as described by Farooq and Tiers [26] (oil bath temperature = 130 °C), gave the difluorosilane **6e′**, isolated as a colorless oil (1.24 g, 30%) after purification by distillation under argon atmosphere: bp = 28 °C/760 Torr; ^1H NMR (400 MHz, $CDCl_3$) δ 0.44 (t, $J_{H-F} = 6.1$ Hz, 3H, Si–CH_3), 6.00–6.11 (m, 1H, Si–CH), 6.21–6.34 (m, 2H, CH_2); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ −5.1 (t, $J_{C-F} = 17$ Hz, Si–CH_3), 129.1 (CH_2), 138.9 (t, $J_{C-F} = 14$ Hz, Si–CH); IR 2961, 2931, 2874, 2861, 1464, 1271 (δ_{Si-CH_3}), 1123, 1073, 798.

4.2.3. (3-Chloropropyl)difluoromethylsilane (*6g′*)

Reaction of (3-chloropropyl)dichloromethylsilane **6g** (2.73 g, 14.3 mmol) and sodium tetrafluoroborate (5.40 g, 49.2 mmol) in tetraglyme (6 mL) as described by Farooq and Tiers [26] (reaction temperature = 120 °C), gave the difluorosilane **6g′**, isolated as a colorless oil (1.85 g, 82%) after purification by distillation under reduced pressure: bp = 70 °C/5 Torr; ^1H NMR (250 MHz, $CDCl_3$) δ 0.40 (t, $J_{H-F} = 6.3$ Hz, 3H, Si–CH_3), 0.87–1.06 (m, 2H, Si–CH_2), 1.83–2.03 (m, 2H, Si–CH_2–CH_2), 3.57 (t, $J = 6.5$ Hz, 2H, CH_2–Cl); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ −4.7 (t, $J_{C-F} = 16$ Hz, Si–CH_3), 10.8 (t, $J_{C-F} = 16$ Hz, Si–CH_2), 24.8 (Si–CH_2–CH_2), 46.6 (CH_2–Cl); LR–MS *m/z* 145 (2, $M^+ - 15$), 143 (8, $M^+ - 15$), 131 (13), 119 (6), 107 (7), 82 (6), *81* (100), 80 (5), 69 (20), 47 (10), 43 (3); IR 2962, 2894, 1439, 1315, 1270 (δ_{Si-CH_3}), 1167, 1123, 997, 879, 807; HR–MS calculated for $C_4H_9ClF_2Si$ 158.0130, found 158.0131 (M^+).

4.2.4. (3-Bromopropyl)dichloromethylsilane (*6h*) [27]

To cyclohexane (30 mL) with Speier's catalyst (≈1 mg) was added at room temperature a mixture of dichloromethylsilane (4.7 mL, 45 mmol) and allyl bromide (5 mL, 57.4 mmol) and the reaction mixture was stirred and heated at reflux overnight. After evaporation of the solvent, distillation of the residue under reduced pressure gave **6h** as a colorless oil (1.6 g, 15%): bp = 82 °C/8 Torr; ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 5.2 (Si–CH_3), 20.5 (Si–CH_2), 26.0 (Si–CH_2–CH_2), 35.3 (CH_2–Br); LR–MS *m/z* 225 (2, $M^+ - 15$), 223 (13, $M^+ - 15$), 221 (28, $M^+ - 15$), 219 (16, $M^+ - 15$), 179 (28), 177 (17), 159 (8), 157 (6), 117 (13), 115 (82), 114 (8), *113* (100), 65 (5), 63 (15), 43 (82).

4.2.5. (3-Bromopropyl)difluoromethylsilane (**6h′**)

Reaction of dichlorosilane **6h** (0.94 g, 3.98 mmol) and sodium tetrafluoroborate (0.895 g, 8.15 mmol) in tetraglyme (1 mL), as described by Farooq and Tiers [26] (reaction temperature = 120 °C), gave the difluorosilane **6h′**, isolated as a colorless oil (0.65 g, 80%) after purification by distillation under reduced pressure: bp = 90 °C/6 Torr; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.40 (t, $J_{H-F} = 6.3$ Hz, 3H, Si–CH_3), 0.88–1.09 (m, 2H, Si–CH_2), 1.90–2.02 (m, 2H, Si–CH_2–CH_2), 3.42 (t, $J = 6.6$ Hz, 2H, CH_2–Br); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ −4.2 (t, $J_{C-F} = 16$ Hz, Si–CH_3), 12.6 (t, $J_{C-F} = 16$ Hz, Si–CH_2), 25.0 (Si–CH_2–CH_2), 35.6 (CH_2–Br); LR–MS *m/z* 189 (13, $M^+ - 15$), 187 (13, $M^+ - 15$), 147 (6), 145 (6), 143 (5), 123 (42), 109 (15), 107 (17), 83 (7), 82 (12), *81* (100), 80 (8), 69 (6), 47 (9), 43 (81); IR 2965, 2855, 1436, 1270 (δ_{Si-CH_3}), 1242, 1035, 874, 802; HR–MS calculated for $C_4H_9BrF_2Si$ 201.9625, found 201.9623 (M^+).

4.2.6. Dichloro(3-chloropropyl)phenylsilane (**6i**)

After reaction of dichlorophenylsilane (5 mL, 34.2 mmol), allyl chloride (3.7 mL, 44.5 mmol) and Speier's catalyst as described by Speier et al. [28], distillation under reduced pressure afforded a mixture of trichlorophenylsilane and dichlorophenylpropylsilane (3.80 g, bp = 84–92 °C/6 Torr) and the dichloro(3-chloropropyl)phenylsilane **6i** as a colorless oil (2.48 g, 29%): bp = 82 °C/0.1 Torr; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.43–1.58 (m, 2H, Si–CH_2), 1.91–2.15 (m, 2H, Si–CH_2–CH_2), 3.60 (t, $J = 6.6$ Hz, 2H, CH_2–Cl), 7.40–7.59 (m, 3H, H_{Ar}), 7.68–7.82 (m, 2H, H_{Ar}); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 12.2 (Si–CH_2), 25.9 (Si–CH_2–CH_2), 46.5 (CH_2–Cl), 128.4 (CH_{Ar}), 131.5 (CH_{Ar}), 131.8 (CH_{Ar}), 133.4 (C_{Ar}); LR–MS *m/z* 256 (2, M^+), 254 (4, M^+), 252 (5, M^+), 214 (11), 212 (32), 210 (31), 179 (12), 177 (68), 176 (12), *175* (100), 174 (33), 78 (14), 77 (16); IR 3031 ($\nu_{=CH}$), 2957, 1591 ($\nu_{C=C}$), 1431 (ν_{Si-Ar}), 1312 ($\delta_{=C-H}$), 1268, 1162 (δ_{Si-Ar}), 1118, 997, 909, 740 ($\delta_{=CH}$), 696; HR–MS calculated for $C_9H_{11}Cl_3Si$ 251.9700, found 251.9710 (M^+).

4.3. Preparation of 2-methylidene-1-silacyclohexanes

4.3.1. General procedure A to synthesize 2-methylidene-1-silacyclohexanes under Barbier type conditions

To a mixture of magnesium turnings (0.535 g, 22 mmol) activated by 1,2-dibromoethane (0.17 mL, 2 mmol) in THF (5 mL) was added slowly (exothermic reaction) a solution of a polyhalosilane (10 mmol) and a 85:15 mixture of dibromohexenes **4** and **5** (2.42 g, 10 mmol) in THF (5 mL). Then, the reaction mixture was stirred at 60 °C for 2 h. When the resulting product was a chlorosilane, the reaction mixture was concentrated under reduced pressure and dry pentane was added. The organic phase was separated by filtration through a filtrating canula equipped with paper and recovered under argon. The solid part was washed four times with dry pentane, the organic phase being removed each time through the filtrating canula. The combined organic phases were concentrated under reduced pressure and the chloromethylidenesilacyclohexane was isolated by distillation. When the resulting product was not a chlorosilane, a saturated NH_4Cl aqueous solution and diethyl ether were added. After separation, the aqueous phase was extracted two times with diethyl ether. The combined organic phases were washed with water, dried over Na_2SO_4, concentrated under reduced pressure and the methylidenesilacyclohexane was purified by silica gel column chromatography or distillation.

4.3.2. General procedure B to synthesize 2-methylidene-1-silacyclohexanes via a Grignard reagent

To a mixture of magnesium turnings (0.60 g, 24.7 mmol) activated by 1,2-dibromoethane (70 μL, 0.81 mmol) in THF (0.5 mL) was added over 1 h a solution of a 85:15 mixture of dibromohexenes **4** and **5** (2.42 g, 10 mmol) and 1,2-dibromoethane (0.3 mL, 3.48 mmol) in THF (20 mL). During the addition, temperature is maintained under 30 °C then the reaction mixture was stirred 3 h at 20 °C and the resulting solution of Grignard reagent was titrated. Generally a closed to 0.54 N solution was obtained. On the assumption that organodimetallic compounds are the sole products, the concentration of the prepared Grignard reagents should be closed to 0.27 M. The requisite volume of this Grignard reagent solution (1 equiv) was added to a solution of a polyhalosilane in THF (the volume of THF was calculated in order to obtain a 0.1 M solution of the reactants). The mixture was heated to reflux for 1.4 h. Further treatment of the mixture was made as previously described for the Barbier type conditions.

4.3.3. General procedure B′ to synthesize 2-methylidene-1-silacyclohexanes via a Grignard reagent

Same conditions than in procedure B apart from the temperature of the reaction during the addition of the mixture dibromohexenes **4** and **5** to the activated magnesium. This time, the reaction temperature was maintained to 10 °C.

4.3.4. 1-Chloro-1-methyl-2-methylidene-1-silacyclohexane (**7a**)

The compound **7a** was prepared from trichloromethylsilane **6a** and isolated, as a colorless oil, by distillation under reduced pressure. (a) From trichlorosilane **6a** (1.2 mL, 10 mmol) and using procedure A was isolated **7a** (0.42 g, 28%). (b) From trichlorosilane **6a** (0.14 mL, 1.17 mmol) and using procedure B′ was isolated **7a** (65 mg, 39%). Bp = 52 °C/5 Torr; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.54 (s, 3H, CH_3), 0.80 (ddd, $J = 5.4$, 9.9, 15.5 Hz, 1H, H6), 1.00–1.17 (m ,1H, H6′), 1.23–1.44 (m, 1H, H4), 1.63–2.01 (m, 3H, H4′ + H5 + H5′), 2.28–2.57 (m, 2H, H3 + H3′), 5.34 (broad s, 1H, C2=CH_2), 5.58 (broad s, 1H, C2=CH_2); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ −1.2 (CH_3), 17.8 (C6), 23.5 (C5), 30.3 (C4), 38.4 (C3), 124.1 (C2=CH_2), 148.9 (C2); LR–MS *m/z* 162 (22, M^+), 160

(61, M^+), 145 (16), 132 (45), 119 (57), 117 (67), 96 (52), 93 (26), 92 (34), *81* (100), 80 (61), 79 (97), 78 (52), 67 (69), 66 (40), 65 (59), 63 (98), 53 (24), 43 (27); IR 3075 ($\nu_{=CH}$), 3039 ($\nu_{=CH}$), 2922, 2856, 1642 ($\nu_{C=C}$), 1439, 1260 (δ_{Si-CH_3}), 925, 894 ($\delta_{=CH}$), 802; HR–MS calculated for $C_7H_{13}{}^{35}ClSi$, 160.0470, found 160.0461 (M^+).

4.3.5. 1-Chloro-2-methylidene-1-phenyl-1-silacyclohexane (7b)

The compound **7b** was prepared from trichlorophenylsilane **6b** and isolated, as a colorless oil, by distillation under reduced pressure. (a) From trichlorosilane **6b** (1.6 mL, 10 mmol) and using procedure A was isolated **7b** (0.49 g, 28%). (b) From trichlorosilane **6b** (1.6 mL, 10 mmol) and using procedure B was isolated **7b** (0.12 g, 7%). (c) From trichlorosilane **6b** (0.195 mL, 1.22 mmol) and using procedure B′ was isolated **7b** (0.122 g, 53%). Bp = 70 °C/0.08 Torr; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.14–1.41 (m, 2H, H6 + H6′), 1.46–1.64 (m, 1H, H4), 1.69–1.85 (m, 1H, H4′), 1.85–2.04 (m, 2H, H5 + H5′), 2.39–2.69 (m, 2H, H3 + H3′), 5.30 (d, $J = 2.9$ Hz, 1H, C2=CH_2), 5.65 (d, $J = 2.9$ Hz, 1H, C2=CH_2), 7.30–7.58 (m, 3H, *m*- and *p*-H_{Ar}), 7.58–7.81 (m, 2H, *o*-H_{Ar}); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 17.0 (C6), 24.2 (C5), 30.7 (C4), 39.3 (C3), 127.0 (C2=CH_2), 128.5 (*m*-CH_{Ar}), 131.1 (*p*-CH_{Ar}), 132.7 (C_{Ar}), 134.6 (*o*-CH_{Ar}), 147.7 (C2); LR–MS *m/z* 224 (14, M^+), 222 (38, M^+), 167 (10), 166 (10), 154 (12), 146 (12), 145 (11), 144 (36), 143 (21), 142 (16), 141 (49), 140 (29), 131 (29), 129 (13), 118 (13), 117 (10), 116 (34), 105 (11), 91 (25), 81 (14), 80 (23), 79 (18), 67 (10), 65 (44), *63* (100), 53 (16), 51 (12); IR 3071 ($\nu_{=CH}$), 3051 ($\nu_{=CH}$), 2924, 2856, 1590 ($\nu_{C=C}$), 1429 (ν_{Si-Ar}), 1114 (δ_{Si-Ar}), 936, 891 ($\delta_{=CH}$), 736, 672; HR–MS calculated for $C_{12}H_{15}{}^{35}ClSi$, 222.0626, found 222.0625 (M^+).

4.3.6. 1-Methyl-2-methylidene-1-phenyl-1-silacyclohexane (7c)

The compound **7c** was prepared from dichloromethylphenylsilane **6a** and isolated, as a colorless oil, after chromatography (pentane). (a) From dichlorosilane **6c** (1.63 mL, 10 mmol) and using procedure A was isolated **7c** (0.31 g, 18%). (b) From dichlorosilane **6c** (0.33 mL, 2.01 mmol) and using procedure B was isolated **7c** (0.11 g, 32%). (c) From dichlorosilane **6c** (0.44 mL, 2.7 mmol) and using procedure B′ was isolated **7c** (0.31 g, 66%). R_f (pentane) = 0.47; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.35 (s, 3H, CH_3), 0.79 (ddd, $J = 3.9$, 10.5, 14.7 Hz, 1H, H6), 1.16 (ddd, $J = 3.9$, 7.8, 14.7 Hz, 1H, H6′), 1.39–1.55 (m, 1H, H4), 1.60–1.80 (m, 2H, H4′ + H5), 1.80–2.20 (m, 1H, H5′), 2.22–2.58 (m, 2H, H3 + H3′), 5.20 (d, $J = 3.4$ Hz, 1H, C2=CH_2), 5.60 (d, $J = 3.4$ Hz, 1H, C2=CH_2), 7.30–7.45 (m, 3H, *m*- and *p*-H_{Ar}), 7.48–7.59 (m, 2H, *o*-H_{Ar}); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ −4.4 (CH_3), 13.6 (C6), 24.4 (C5), 30.9 (C4), 39.8 (C3), 123.4 (C2=CH_2), 127.8 (*m*-CH_{Ar}), 129.0 (*p*-CH_{Ar}), 134.2 (*o*-CH_{Ar}), 136.8 (C_{Ar}), 150.5 (C2); LR–MS *m/z* 202 (41, M^+), 187 (19), 159 (31), 145 (15), 134 (30), 131 (12), 124 (50), 122 (13), *121* (100), 119 (15), 109 (23), 105 (54), 96 (11), 80 (15), 53 (10), 43 (18); IR 3068 ($\nu_{=CH}$), 3045 ($\nu_{=CH}$), 2916, 2852, 1618 ($\nu_{C=C}$), 1428 (ν_{Si-Ar}), 1250 (δ_{Si-CH_3}), 1111 (δ_{Si-Ar}), 1000, 923, 795 ($\delta_{=CH}$), 728; HR–MS calculated for $C_{13}H_{18}Si$ 202.1178, found 202.1177 (M^+).

4.3.7. 1-Allyl-1-methyl-2-methylidene-1-silacyclohexane (7d)

The compound **7d** was prepared from allyldichloromethylsilane **6b** or the corresponding difluorosilane **6d′** and isolated, as a colorless oil, after chromatography (pentane). (a) From dichlorosilane **6d** (2.6 mL, 10 mmol) and using procedure A was isolated **7d** (0.31 g, 22%). (b) From dichlorosilane **6d** (0.65 mL, 2.52 mmol) and using procedure B was isolated **7d** (21 mg, 6%). (c) From difluorosilane **6d′** (1.52 mL, 12.5 mmol) and using procedure A was isolated **7d** (0.47 g, 27%). (d) From difluorosilane **6d′** (0.27 mL, 2.22 mmol) and using procedure B was isolated **7d** (75 mg, 24%). R_f (pentane) = 0.64; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.10 (s, 3H, CH_3), 0.58 (ddd, $J = 4.9$, 9.8, 14.6 Hz, 1H, H6), 0.80 (ddd, $J = 4.9$, 7.2, 14.6 Hz, 1H, H6′), 1.33–1.51 (m, 1H, H4), 1.57–1.89 (m, H4′ + H5 + H5′) and 1.67 (d, $J = 7.0$ Hz, CH_2–CH=CH_2) (5 H), 2.28–2.41 (m, 2H, H3 + H3′), 4.84 (d, $J = 9.8$ Hz, 1H, CH=CH_2 *cis*), 4.88 (d, $J = 18.4$ Hz, 1H, CH=CH_2 *trans*), 5.15 (d, $J = 3.4$ Hz, 1H, C2=CH_2), 5.51 (d, $J = 3.4$ Hz, 1H, C2=CH_2), 5.80 (ddt, $J = 9.8$, 18.4, 7 Hz, 1H, C*H*=CH_2); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ −5.9 (CH_3), 13.1 (C6), 20.9 (Si–CH_{2Allyl}), 24.3 (C5), 30.8 (C4), 39.8 (C3), 113.0 (CH=CH_2), 122.0 (C2=CH_2), 134.7 (CH=CH_2), 151.2 (C2); LR–MS *m/z* 166 (6, M^+), 151 (2), 126 (25), *125* (100), 124 (18), 123 (11), 109 (11), 99 (21), 98 (12), 97 (94), 95 (20), 85 (14), 83 (14), 71 (24), 69 (16), 67 (11), 59 (65), 55 (22), 53 (13), 45 (42), 43 (79), 41 (14), 39 (16); IR 3077 ($\nu_{=CH}$), 3041 ($\nu_{=CH}$), 2917, 2852, 1630 ($\nu_{C=C}$), 1438, 1419 ($\delta_{=CH_2}$), 1251 (δ_{Si-CH_3}), 1152, 990 ($\delta_{=CH}$), 921, 894 ($\delta_{=CH}$), 820; HR–MS calculated for $C_{10}H_{18}Si$ 166.1178, found 166.1178 (M^+).

4.3.8. 1-Methyl-2-methylidene-1-vinyl-1-silacyclohexane (7e)

The compound **7e** was prepared from dichloromethylvinylsilane **6e** or the corresponding difluorosilane **6e′** and isolated, as a colorless oil, after chromatography (pentane). (a) From dichlorosilane **6e** (2 mL, 15.3 mmol) and using procedure A was isolated **7e** (73.2 mg, 4%). (b) From dichlorosilane **6e** (2.26 mL, 2.22 mmol) and using procedure B was isolated **7e** (0.58 g, 28%). (c) From difluorosilane **6e′** (0.96 g, 8.85 mmol) and using procedure A was isolated **7e** (18 mg, 2%). R_f (pentane) = 0.63; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.19 (s, 3H, CH_3), 0.67 (ddd, $J = 5.1$, 9.2, 14.4 Hz, 1H, H6), 0.87 (ddd, $J = 5.1$, 7.7, 14.4 Hz, 1H, H6′), 1.36–1.50 (m, 1H, H4), 1.50–1.66 (m, 1H, H4′), 1.66–1.83 (m, 2H, H5 + H5′), 2.23–2.50 (m, 2H, H3 + H3′), 5.16 (d, $J = 3.6$ Hz, 1H, C2=CH_2), 5.51 (d, $J = 3.6$ Hz, 1H, C2=CH_2), 5.77 (dd, $J = 4.6$, 19.6 Hz, 1H, CH=CH_2 *trans*), 6.04 (dd, $J = 4.6$, 14.6 Hz, 1H,

CH=CH_2 *cis*), 6.18 (dd, $J = 14.6$, 19.6 Hz, 1H, CH=CH$_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ −5.6 (CH_3), 13.7 (C6), 24.4 (C5), 30.9 (C4), 39.8 (C3), 122.4 (C2=CH_2), 133.1 (CH=CH_2), 136.5 (CH=CH$_2$), 150.9 (C2); LR–MS *m/z* 152 (1, M^+), 137 (17), 124 (30), 123 (16), 111 (61), *110* (100), 109 (84), 97 (28), 96 (25), 95 (23), 84 (15), 83 (21), 80 (12), 79 (11), 71 (44), 70 (30), 69 (17), 67 (11), 59 (22), 58 (17), 57 (12), 55 (39), 54 (22), 53 (19), 45 (40), 44 (23), 43 (48); IR 3046 ($\nu_{=CH}$), 2923, 2853, 1641 ($\nu_{C=C}$), 1447, 1403 (δ_{Si-CH_3}), 1008, 952, 922, 893 ($\delta_{=CH}$), 866, 796 ($\delta_{=CH}$), 749; HR–MS calculated for $C_9H_{16}Si$ 152.1021, found 152.1016 (M^+).

4.3.9. 1-Methyl-2-methylidene-1-silacyclohexane (7f)

From dichlorosilane **6f** (1.55 mL, 15 mmol) and using procedure A was isolated, after purification by distillation under argon atmosphere, the compound **7f** as a colorless oil (77.5 mg, 5%). Bp = 51 °C/760 Torr; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.22 (d, $J = 3.6$ Hz, 3H, CH_3), 0.60 (ddd, $J = 4.9$, 10.0, 19.4 Hz, 1H, H6), 0.86–1.02 (m, 1H, H6′), 1.30–1.51 (m, 1H, H4), 1.51–1.75 (m, 3H, H4′ + H5 + H5′), 2.23–2.49 (m, 2H, H3 + H3′), 3.99–4.09 (m, 1H, H1), 5.21 (d, $J = 3.4$ Hz, 1H, C2=CH$_2$), 5.52 (d, $J = 3.4$ Hz, 1H, C2=CH$_2$); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ −6.9 (CH_3), 12.6 (C6), 24.6 (C5), 30.8 (C4), 40.0 (C3), 122.4 (C2=CH_2), 150.0 (C2) [29].

4.3.10. 1-(3-Chloropropyl)-1-methyl-2-methylidene-1-silacyclohexane (7g)

The compound **7g** was prepared from dichloro(chloropropyl)methylsilane **6g** or the corresponding difluorosilane **6g′** and isolated, as a colorless oil, after chromatography (pentane). (a) From dichlorosilane **6g** (1.08 g, 5,6 mmol) and using procedure A were isolated 1-methyl-2-methylidene-1-propyl-1-silacyclohexane **8** (79 mg) and **7g** (194 mg, 20%). (b) From dichlorosilane **6g** (0.59 g, 3.08 mmol) and using procedure B was isolated **7g** (0.28 g, 55%). (c) From dichlorosilane **6g** (0.23 g, 1.2 mmol) and using procedure B′ was isolated **7g** (0.10 g, 51%). (d) From difluorosilane **6g′** (0.55 g, 3.47 mmol) and using procedure B was isolated **7g** (0.17 g, 28%). (e) From difluorosilane **6g′** (0.19 g, 1.17 mmol) and using the general procedure B′ was isolated **7g** (82 mg, 40%). R_f (pentane) = 0.45; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.14 (s, 3H, CH_3), 0.60 (ddd, $J = 4.8$, 9.8, 14.5 Hz, 1H, H6), 0.69–0.85 (m, CH_2–CH$_2$–CH$_2$Cl) and 0.70–0.83 (m, H6′) (3H), 1.38–1.53 (m, 1H, H4), 1.53–1.77 (m, 2H, H4′ + H5), 1.76–1.89 (m, CH_2–CH$_2$Cl) and 1.77–1.92 (m, H5′) (3 H), 2.27–2.45 (m, 2H, H3 + H3′), 3.53 (t, $J = 6.9$ Hz, 2H, CH$_2$Cl), 5.13 (d, $J = 2.9$ Hz, 1H, C2=CH$_2$), 5.50 (d, $J = 2.9$ Hz, 1H, C2=CH$_2$); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ −5.6 (CH_3), 10.5 (CH_2–CH$_2$–CH$_2$Cl), 13.4 (C6), 24.4 (C5), 27.5 (CH_2–CH$_2$Cl), 30.8 (C4), 39.8 (C3), 47.9 (CH$_2$Cl), 121.9 (C2=CH_2), 151.1 (C2); LR–MS *m/z* 189 (1, $M^+ - 15$), 187 (2, $M^+ - 15$), 162 (14), 161 (15), 160 (36), 159 (35), 147 (15), 145 (43), 134 (12), 132 (31), 126 (11), 125 (86), 123 (10), 123 (15), 121 (45), 120 (11), 119 (33), 109 (29), 99 (16), 98 (11), *97* (100), 96 (18), 93 (44), 92 (49), 81 (39), 80 (57), 79 (33), 62 (17), 59 (30), 43 (18); IR 3040 ($\nu_{=CH}$), 2916, 2852, 1606 ($\nu_{C=C}$), 1437, 1252 (δ_{Si-CH_3}), 1119, 1003, 921, 893 ($\delta_{=CH_2}$), 794. Anal. Calc. for $C_{10}H_{19}ClSi$: C, 59.23; H, 9.44. Found: C, 59.22; H, 9.49%.

4.3.11. 1-(3-Bromopropyl)-1-methyl-2-methylidene-1-silacyclohexane (7h)

The compound **7h** was prepared from (bromopropyl)dichloromethylsilane **6h** or the corresponding difluorosilane **6h′** and isolated, as a colorless oil, after chromatography (pentane). (a) From dichlorosilane **6h** (0.64 g, 2.71 mmol) and using procedure B was isolated **7h** (0.34 g, 60%). (b) From dichlorosilane **6h** (0.30 g, 1.26 mmol) and using procedure B′ was isolated **7h** (90 mg, 35%). (c) From difluorosilane **6h′** (0.61 g, 3.01 mmol) and using procedure B was isolated **7h** (0.225 g, 35%). (d) From difluorosilane **6h′** (0.27 g, 1.26 mmol) and using procedure B′ was isolated **7h** (0.11 g, 42%). R_f (pentane) = 0.47; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.13 (s, 3H, CH_3), 0.62 (ddd, $J = 4.5$, 10.1, 14.5 Hz, 1H, H6), 0.73–0.82 (m, CH_2–CH$_2$–CH$_2$Br) and 0.77 (ddd, $J = 4.5$, 7.4, 14.5 Hz, H6′) (3 H), 1.37–1.50 (m, 1H, H4), 1.55–1.61 (m, 1H, H4′), 1.61–1.77 (m, 1H, H5), 1.78–1.88 (m, H5′) and 1.78 (quintuplet, $J = 7$ Hz, CH_2–CH$_2$Br) (3 H), 2.26–2.43 (m, 2H, H3 + H3′), 3.42 (t, $J = 7$ Hz, 2H, CH$_2$Br), 5.13 (d, $J = 3.7$ Hz, 1H, C2=CH$_2$), 5.50 (d, $J = 3.7$ Hz, 1H, C2=CH$_2$); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ −5.6 (CH_3), 12.0 (CH_2–CH$_2$–CH$_2$Br), 13.4 (C6), 24.4 (C5), 27.8 (CH_2–CH$_2$Br), 30.8 (C4), 36.9 (CH$_2$Br), 39.7 (C3), 122.0 (C2=CH_2), 151.1 (C2); LR–MS *m/z* 233 (2, $M^+ - 15$), 231 (2, $M^+ - 15$), 204 (31), 191 (25), 189 (25), 167 (46), 165 (48), 164 (14), 163 (27), 161 (17), 139 (21), 138 (44), 137 (23), 136 (45), 125 (84), 123 (26), 109 (35), *97* (100), 96 (25), 81 (35), 80 (61), 71 (16), 59 (27), 43 (21); IR 3040 ($\nu_{=CH}$), 2915, 2851, 1641 ($\nu_{C=C}$), 1436, 1251 (δ_{Si-CH_3}), 1231, 921, 893 ($\delta_{=CH_2}$), 793. Anal. Calc. for $C_{10}H_{19}BrSi$: C, 48.58; H, 7.75. Found: C, 48.77; H, 7.85%.

4.3.12. 1-(3-Chloropropyl)-2-methylidene-1-phenyl-1-silacyclohexane (7i)

The compound **7i** was prepared from dichloro(chloropropyl)phenylsilane **6i** and isolated, as a colorless oil, after chromatography (pentane). (a) From dichlorosilane **6i** (2.27 g, 8.96 mmol) and using procedure B was isolated **7i** (0.67 g, 33%). (b) From dichlorosilane **6i** (198 mg, 0.78 mmol) and using procedure B′ was isolated **7i** (64 mg, 36%). R_f (pentane) = 0.32; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.78 (ddd, $J = 4.2$, 10.9, 14,.9 Hz, 1H, H6), 0.89–0.98 (m, 2H, CH_2–CH$_2$–CH$_2$Cl), 1.10 (ddd, $J = 4.2$, 7.3, 14.9 Hz, 1H, H6′), 1.42–1.57 (m, 1H, H4), 1.61–1.76 (m, 2H, H4′ + H5), 1.76–1.93 (m, 3H, H5′ + CH_2–CH$_2$Cl), 2.28–2.39 (m, 1H, H3), 2.39–2.50 (m, 1H, H3′), 3.43 (t, $J = 7.0$ Hz, 2H, CH$_2$Cl), 5.19 (d, $J = 4.0$ Hz, 1H, C2=CH$_2$), 5.59 (d, $J = 4.0$ Hz, 1H, C2=CH$_2$), 7.24–7.40

(m, 3H, *m*- and *p*-H_{Ar}), 7.42–7.54 (m, 2H, *o*-H_{Ar}); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 10.0 (CH_2–CH_2–CH_2Cl), 11.5 (C6), 24.2 (C5), 27.4 (CH_2–CH_2Cl), 30.7 (C4), 39.9 (C3), 47.9 (CH_2Cl), 124.1(C2=CH_2), 128.0 (*m*-CH_{Ar}), 129.3 (*p*-CH_{Ar}), 134.5 (*o*-CH_{Ar}), 135.1 (C_{Ar}), 148.9 (C2); LR–MS *m*/*z* 264 (0,2, M^+), 223 (11), 222 (20), 221 (20), 188 (17), *187* (100), 185 (13), 183 (40), 159 (67), 156 (13), 155 (10), 154 (38), 145 (21), 144 (23), 143 (16), 141 (41), 140 (12), 131 (15), 109 (26), 107 (26), 105 (38), 91 (23), 80 (19), 63 (16); IR 3068 ($\nu_{=CH}$), 3046 ($\nu_{=CH}$), 2917, 2853, 1590 ($\delta_{C=C}$), 1428 (ν_{Si-Ar}), 1309, 1264, 1110 (δ_{Si-Ar}), 1013, 996 ($\delta_{=CH}$), 924, 891 ($\delta_{=CH}$), 735; HR–MS calculated for $C_{15}H_{21}{}^{35}ClSi$ 264.1100, found 264.1096.

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