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Journal of Organometallic Chemistry 625 (2001) 160–172

Journal of Organometallic Chemistry

www.elsevier.nl/locate/jorganchem

Synthesis of silacycloalkenes and silaspirenes by Ru(II)-catalyzed ring-closing metathesis reactions

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Received 30 August 2000; received in revised form 7 October 2000; accepted 7 October 2000

Abstract

Cyclisation reactions of dienyl- and enynylsilanes by carbon–carbon bond formation under RCM conditions yield five-, six- and seven-membered silacycloalkenes. The relative ease of ring formation from dienes was in the order six- > seven- > five-membered rings. A conjugated vinylsilacyclopentene was formed from the corresponding enyne substrate. Silaspirenes have been prepared from silacarbacycles by the same methodology. Cyclisations effected under radical conditions gave complimentary silacycloheptane and silacycloheptene products. The ring closure proceeded by the *endo*-trig route.

Keywords: Synthesis; Silacycloalkenes; Ru(II)-ring-closing metathesis; Spiroannulation

1. Introduction

For some time we have been involved in transition metal effected carbocycle and heterocycle ring forming reactions using organometallic complexes of Pd, Ru, Rh and Co [1–4]. This report deals with carbon–carbon bond formation in the synthesis of silacarbacycles by Ru(II)-catalyzed ring-closing metathesis (RCM) and under free radical conditions. Silacycles are useful as reactants or intermediates in organic synthesis [5]. The methods available for the preparation of five- and six-membered silacarbacycles were recently classified by cycloadditions, ring enlargements of three- and four-membered cyclic silanes, ring closure of acyclic silanes by the formation of one Si–C bond or by the formation of two Si–C bonds, and by ring closure of acyclic silanes by C–C bond formation [6]. Vigorous reaction conditions with sodium or potassium vapour at 300°C in the presence of butadiene have been used to effect spiroannulation in low yields at the silicon atom in silacyclopentenes using 1,1-dichlorocyclocarbasilanes as substrates [7]. Silaspiro[4,4]nona-2,7-diene has also been prepared by five-membered ring spiroannulation in a one-pot synthesis from silyl tetrachloride and 1,3-butadiene with 'active' magnesium [8]. The magnesium metalacycle intermediate reacts further to form 1,1-dichlorosilacyclopent-2,7-dienes. Repetition of the reaction sequence results in spiroannulation. The dichlorosilane intermediate in this reaction is said to be a good substrate for spiroannulation [9]. In another modification, the silicon reagent was a dialkoxy–dichlorosilane which was reacted with substituted butadiene [10]. Lewis acid mediated cascade cyclisation of diallylsilanes has yielded silacycles [11], whereas vinylbenzylsilanes produced silatetralines [12].

RCM reactions have hitherto been little explored for the preparation of silacycles. Tungsten carbenoid complexes have been used in the cyclisation of diallyldimethylsilane and homologs [13]. Mainly silicon containing polymers together with a ten-membered silicon containing ring as byproduct were obtained with the Schrock MoF_6 catalyst [14]. When low chemoselectivity is acceptable, catalytically highly active carbenoid systems based on molybdenum complexes may be useful [15]. High substituent compatibility for ring-forming reactions with functionalized substrates is achieved using Grubbs RCM precatalyst bis(tricyclohexylphosphine)benzylidene–ruthenium dichloride [15–17]. We have used the Grubbs methodology extensively in the

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0022-328X/01/$ - see front matter
PII: S0022-328X(00)00818-4

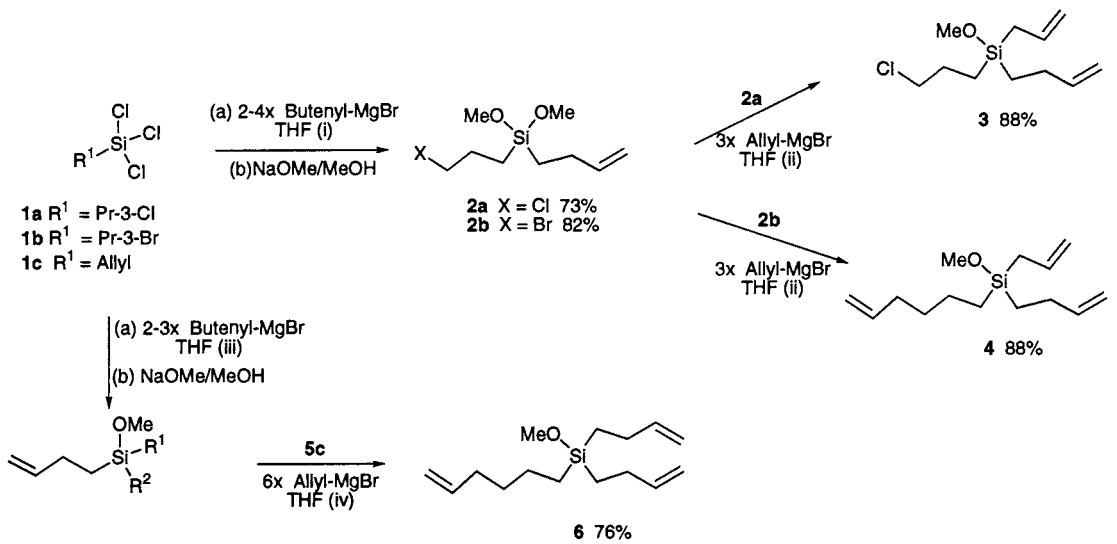
construction of heterospiranes as intermediates in amino acid syntheses [2]. The ring sizes available from the RCM reactions are in the main limited to five-, six- and seven-membered rings due to the reversible nature of metathesis reactions. Thermodynamic factors will largely control whether oligomerization or cyclization can occur. Because of the strain of three-, four-, and eight- to eleven-membered rings, these will be difficult to prepare by metathesis. On the other hand, the method is highly applicable for the preparation of larger ring structures [18]. To our knowledge the use of Ru(II)-catalyzed RCM reactions has not been described for the preparation of silacarbacycles. However, the method has been applied to the preparation of cyclic siloxanes and sildioxanes from appropriately functionalized alkoxysilanes [19].

2. Results and discussion

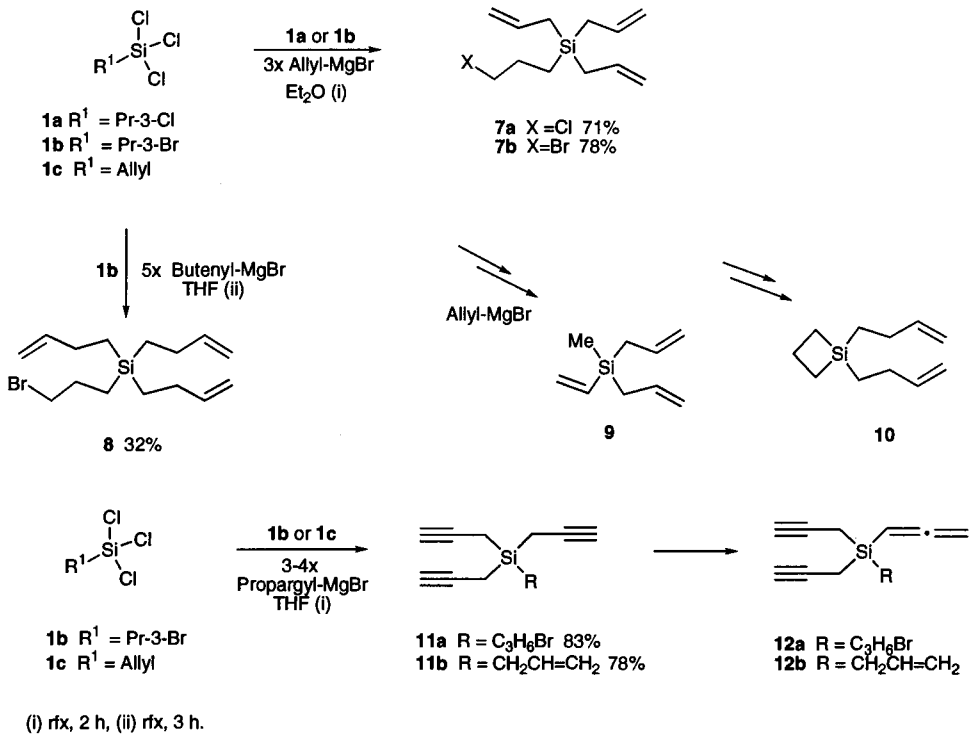
Preparations of diene- and diyne-silane substrates for RCM studies and for cyclizations under radical conditions are shown in Schemes 1 and 2. Alkenylations at the silicon atom in the alkyltrichlorosilanes (**1**) were effected under Grignard conditions. The silicon–halogen bond is highly reactive. The silicon–oxygen bond in the form of a Si–OR bond can also be cleaved, but less readily than cleavage of a corresponding silicon–halogen bond. In general, the ease of replacement at silicon decreases with increasing number of substituents. These differences in reactivities may be exploited for selective, stepwise substitution reactions at the silicon center.

The lengths of the unsaturated chains were varied to provide substrates for formation of different ring-sizes in the cyclisation reactions leading to silacycloalkenes.

Butenylation reactions at silicon were first studied. Excess of organometalic reagent was used to effect a high conversion of the silane substrate. In our first reaction, butenylation of the ω-chloropropylsilyl trichloride (**1a**) was effected at −30°C to provide a monoalkenylated dichlorosilane. In the subsequent reaction with the bromosubstrate (**1b**), the temperature was raised to 0°C in which case a small amount of dialkenylated product was also seen. This byproduct, however, was readily removed by flash chromatography after prior conversion to its dialkoxy derivative (**2b**). In general, the chlorine atoms remaining after the primary alkylation are easily exchanged with heteronucleophiles. Hydrolytic reactions therefore complicate the isolation and purification of the product. This problem was avoided by treatment of the crude product with methanolic sodium methoxide when the halogen substituents were replaced by methoxy groups. The methoxylated products can be purified by standard flash chromatography. Besides simplifying the isolation procedure, the methoxylated product can also be used as a substrate for further direct substitution reactions with organometallics under more vigorous conditions than for its halogen precursor. Alternatively, the methoxy group can be regarded as a protecting group which is to be cleaved by halogen acids. Silyl halides



Scheme 1.



Scheme 2.

are generated in this reaction and can be used in subsequent transformations.

The dimethoxy derivatives were further investigated as substrates for organometallic substitution reactions. Treatment of the ω-chloropropyl derivative (**2a**) with 3.5 mol equivalents of allylmagnesium bromide in THF at ambient temperature led to replacement of one of the methoxy groups to furnish the monoallylated silane (**3**) in high yield. Use of the same conditions in the reaction of the ω-bromopropyldimethoxysilane (**2b**), however, resulted in diallylation. One methoxy group had been replaced and coupling had occurred at the bromopropyl carbon thereby providing a hexenylsilane (**4**) where all carbosubstituents are different. The corresponding side-chain reaction was seen in the allylation of the ω-bromopropyl substrate (**5c**) which yielded the hexenyl derivative (**6**). Monobutenylation of the allylsilane (**1c**) was also effected at 0°C with isolation of the product as the dimethoxy derivative (**5a**). Slightly higher temperature was used for the dibutenylation of the substrates **1b** and **1c** which were isolated as their respective methoxy derivatives **5b** and **5c**.

Tetracarbosubstituted products were prepared from the same alkyl(trichloro)silane substrates (**1**) (Scheme 2). Triallylation to furnish the silanes (**7**) was effected by reactions between ω-halopropyl(trichloro)silane (**1a** or **1b**) and allylmagnesium bromide. The bromo derivative (**1b**) gave the tributenyl derivative (**8**) in 32% yield on heating with excess butenylmagnesium bromide. The other major product, when the reaction was stopped, was due to dibutenylation (15%). Diallylmethylvinylsilane (**9**) was prepared by a reaction between methylvinylsilyl dichloride and allylmagnesium bromide [20], and the silacyclobutane (**10**) from 1,1-dichlorosilacyclobutane and the butenylmagnesium reagent [21].

For the alkynylation reactions, propargylmagnesium bromide was prepared from propargyl bromide and magnesium with catalytic amounts of $HgCl_2$ present [22]. The conditions used, mixing of the reagents at -10°C and subsequent heating under reflux for 2 h, gave the trialkynylated products (**11**) in ca. 80% yield. A second product, which was isolated after flash chromatography in 5–7% yield, was identified by NMR as the alene derivatives **12a** and **12b**, respectively. The allenes arise from isomerization of a propargyl group under the strongly basic conditions of the reactions. No attempts were made to study this as a route towards allene target molecules [23].

Scheme 3 shows Ru(II)-catalyzed RCM reactions for the formation of five- and six-membered silacycles. Heating in benzene was necessarry to effect transformations into five-membered silacycles (**13**). Under these conditions the Ru(II)-catalyst system suffered gradual thermolytic decomposition. Therefore, when running relatively slow reactions at elevated temperature, additional catalyst had to be added at time intervals [24]. In the five-membered ring series, in all 7 mol% of catalyst was used.

With the diallylvinylsilane substrate (**9**) a five-membered or the less favourable four-membered ring forma-

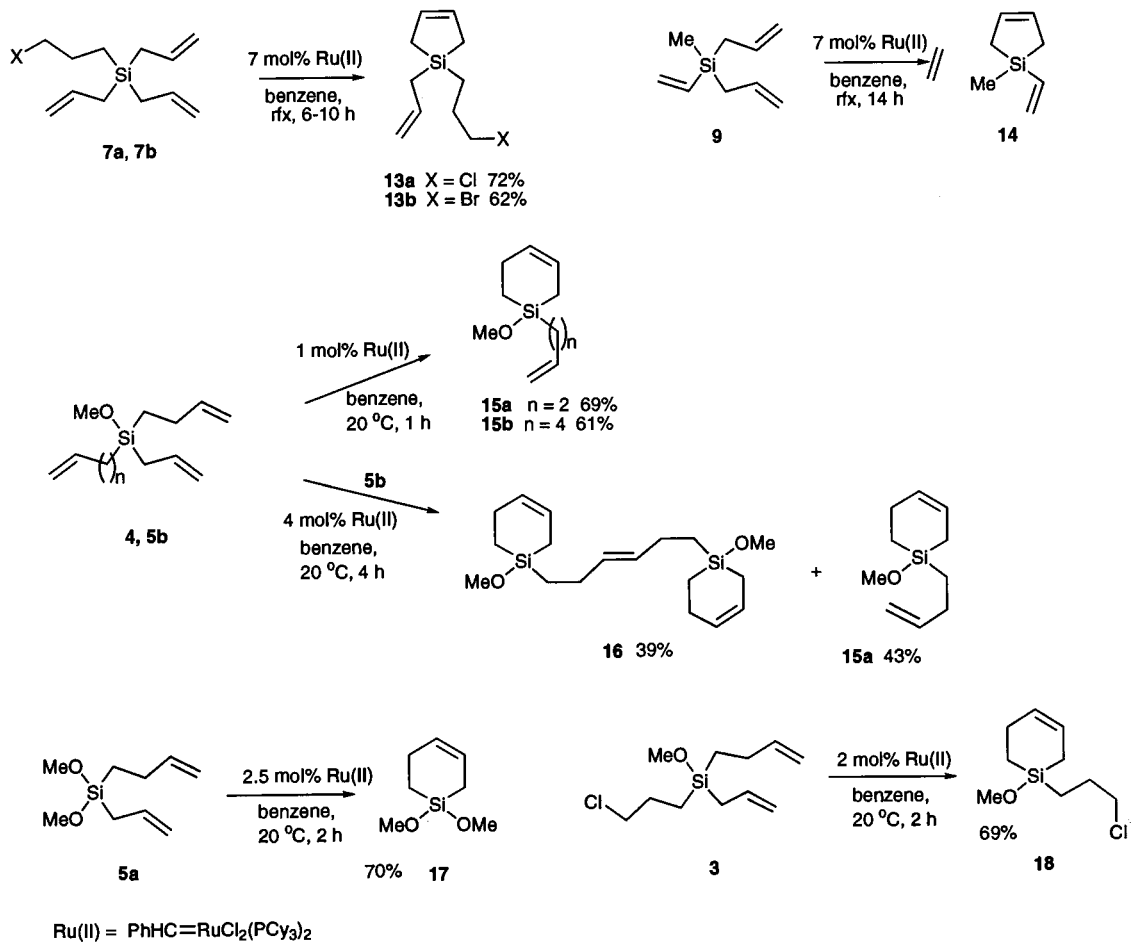
tion would in principle be possible by a metathesis reaction between the vinyl and an allyl group or between two allyl groups. Consumption of the substrate required up to 7 mol% catalyst in refluxing benzene. No silacycle was isolated from the reaction products. The vinylsilacyclopentene (**14**) has been prepared previously in 25% yield in a reaction between methylvinyl(dichloro)silane and the metallacycle from butadiene and magnesium [25].

For six-membered ring formation, the RCM reactions were run at ambient temperature using 1–2 mol% catalyst. Minor amounts of intermolecular RCM formed products could be detected. These products were removed during flash chromatography. Therefore, the initial intramolecular products can in principle be reacted further in intermolecular RCM reactions to furnish bis(silacycloalkenes). Thus in one case, when 4 mol% of the catalyst was used with a longer reaction time, the intramolecular silacyclohexene (**15a**) and the subsequent intermolecular bis(silacyclohexene) (**16**) were isolated in almost equimolar quantities. No attempts were made to optimize conditions for the conversion to the bis(silacycle) (**16**).

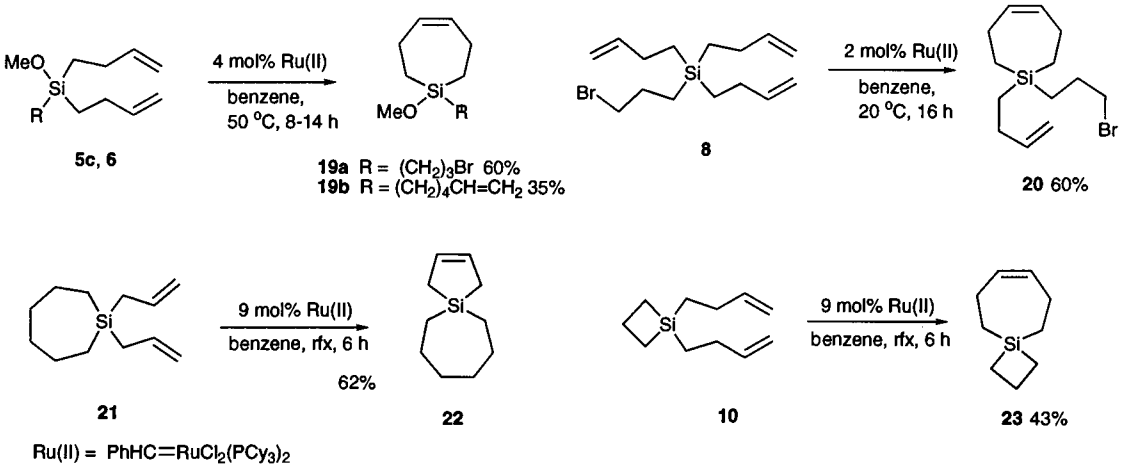
Scheme 4 shows that formation of the silacycloheptenes (**19** and **20**) required more vigorous reaction conditions than were used in the reactions leading to six-membered rings. Therefore, in a competitive set up for either six- or seven-membered ring formation, the smaller ring product would be favoured. This behaviour was demonstrated by the preferential or exclusive formation of the six-membered ring structure **15a** from the substrate **5b** in Scheme 3.

As can be seen (vide supra), the reaction conditions for silacyclopentene formation **13** (Scheme 3) are significantly more vigorous than the conditions for the formation of the silacyclohexenes (**15**, **17** and **18**). The reaction conditions used in the preparation of the silacycloheptenes (**19** and **20**) occupy an intermediate position. These findings are in general agreement with our previous experience with RCM reactions in the formation of heterospiranes [2].

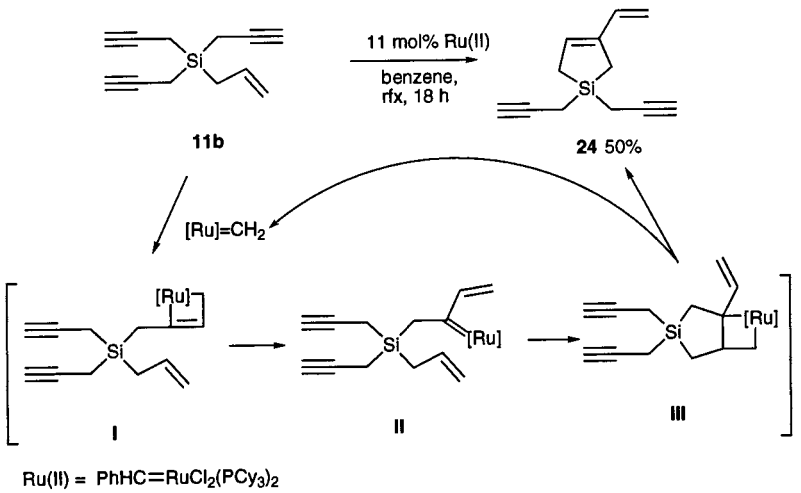
Silaspirane formation by RCM reactions is also shown in Scheme 4. The conditions used for spiroannulations reflect the conditions for five-membered ring formation in the case of the spirane (**22**) and for seven-membered ring formation in the case of the spi-



Scheme 3.



Scheme 4.



Scheme 5.

rane (**23**). 9 mol% of catalyst was used in either case with reflux in benzene for 6 h. It seems likely that more favourable ring-size silaspiranes would be available in a simple manner by this approach.

When allyltripropargylsilane (**11b**) was subjected to enyne RCM rearrangement conditions, a highly functionalized silacyclopentene (**24**) was formed. To effect the rearrangement, heating in benzene over an extended period of time was required, and the catalyst was added at intervals. When the reaction was stopped after 18 h, 11 mol% of the catalyst had been consumed. The product **24** was isolated in 50% yield.

For a comparison of this reaction with the reactions of dienes (vide supra) it is important to realize that enyne reactions differ from the diene RCM reactions. In the RCM reactions of dienes, the terminal methylenes are expelled as ethylenes during the ring closure. In the enyne reactions, on the other hand, the terminal alkylidene moiety of the alkene is transferred onto the alkyne carbon in the formation of the cyclic diene [26]. A rationalization of the process by the intermediate structures I–III is suggested in Scheme 5.

In an expansion of the scope of the cyclisation studies from the diene and diyne substrates some radical reaction procedures are shown in Scheme 6. In RCM reactions the carbons connected are joined by an olefinic bond whereas the carbons connected by a radical reaction are reduced. Initial adduct formation between a radical complex and the unsaturated bond followed by hydrogen abstraction converts a double bond to a saturated bond, and a triple bond to a double bond. In radical reactions designed for cyclisations, frequently competitive hydrogen abstraction by the radical centre is observed. The latter pathway is seen in the present case as dehalgenation of the initial substrate. The regiochemistry in radical cyclisation is expressed by addition to the unsaturated bond in an *endo*-trig or an *exo*-trig fashion [27]. In triallyl(3-bromopropyl)silane (**7b**), the radical generated at the propyl bromocarbon using tributylstannane and AIBN

adds in an *endo*-trig fashion to form the seven-membered ring structure **21** rather than the isomeric α-methylsilacyclohexane structure by the *exo*-trig fashion. With the bromo reactant **7b**, heating in benzene required 3 h before the substrate was consumed. With the chloro analog **7a**, when radical formation is more difficult to effect, the reaction time was increased to 62 h, but the total and relative yields in both cases were similar. With (ω-bromopropyl)tri(3-butenyl)silane (**8**) as substrate, none of the eight-membered ring structure **26** was seen. The dehalogenated acyclic silane (**27**) was the product isolated from the reaction.

Radical cyclisation over the triple bond in (ω-bromopropyl)tripropargylsilane was more difficult to effect than for the bromo substrates above. Heating in benzene for 32 h gave in low yields an almost equal amount of the highly functionalized silacycloheptene (**28**) by *endo*-trig addition to the triple bond and the acyclic silane (**29**).

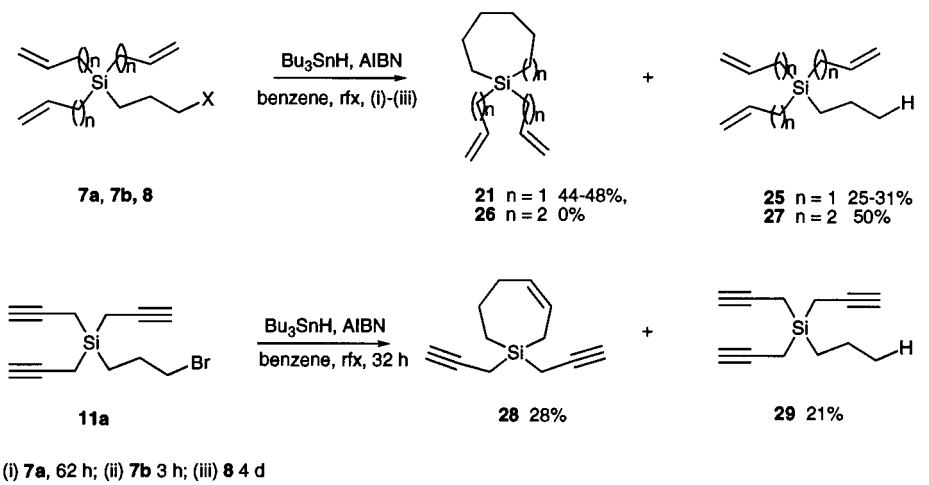
In conclusion, we have found carbon–carbon bond formation effected by Ru(II)-catalyzed RCM reactions to be a valuable method for the preparation of five-, six- and seven-membered silacycloalkenes. Cyclisation under radical conditions gave seven membered silacycles by the *endo*-trig route. Silaspirenes were formed from dienylcyclosilanes in RCM reactions and conjugated vinylsilacyclopentenes from enyne disubstituted silanes.

3. Experimental

All the glass equipment was dried in an oven at 120°C before use, and all the experiments were carried out under the gentle flow of argon gas. Diethyl ether and benzene were stored over sodium wire. Tetrahydrofuran and benzene were distilled from sodium benzophenone ketyl. All other solvents were freshly distilled before use. The products were purified either by vacuum distillation or by flash chromatography with silica MERCK Kiselgel 60 (F254). The ^{1}H-NMR spectra were recorded on a Bruker DPX 200 (200 MHz), Bruker DPX300 (300 MHz) spectrometers, respectively. The ^{13}C-NMR spectra were recorded on a Bruker DPX 200 (50 MHz) and Bruker DPX 300 (75 MHz) spectrometers, respectively. Mass spectra were recorded on a Fision ProSpec mass spectrometer. EI spectra were recorded at ionization potential 70 eV. CH_4 was used as ionization gas for CI spectra.

3.1. 1-(3-Butenyl)-1-(3-chloropropyl)-1,1-dimethoxylsilane (2a)

3-Chloropropyl(trichloro)silane (0.36 ml, 2.25 mmol) was added dropwise to a solution of 3-butenylmagnesium bromide (15 ml, 4.5 mmol) in THF (30 ml) at −30°C and the mixture stirred at −30°C for 2 h. Sodium methoxide (4.5 mmol) in methanol (10 ml) was added and the resultant mixture stirred at ambient temperature overnight. Saturated aqueous NH_4Cl (20 ml) was added, the phases separated and the aqueous phase extracted with diethyl ether (3 × 20 ml). The combined organic layers were washed with water (20 ml), saturated aqueous $NaHCO_3$ (20 ml) and brine (20 ml). The dried ($MgSO_4$) solution was evaporated at reduced pressure at 0°C and the residual oil subjected to flash chromatography using 5% EtOAc in hexane and the product isolated after flash chromatography; yield 366 mg (73%) of a colourless oil. HRMS: [M−butenyl] 167.0299. Calc. for $C_5H_{12}ClO_2Si$: 167.0295. ^{1}H-NMR ($CDCl_3$): δ 5.94–5.75 (1H, m, CH=), 5.04–4.86 (2H, m, =CH_2), 3.50 (6H, s, 2 × OCH_3), 3.49 (2H, t, *J* 6.7 Hz, CH_2Cl), 2.16–2.04 (2H, m, CH_2), 1.86–1.74 (2H, m, CH_2), 0.76–0.68 (4H, m, 2 × CH_2Si). ^{13}C-NMR ($CDCl_3$): δ 140.6 (CH), 113.2 (CH_2), 50.3 (CH_3),



Scheme 6.

47.5 (CH_2), 26.6 (CH_2), 26.3 (CH_2), 10.9 (CH_2), 9.6 (CH_2). MS (EI): 180 ([$M^+ - C_3H_6$], 1), 167 (19), 145 (22), 125 (100), 113 (37), 95 (16), 59 (18), 41 (3).

3.2. 1-(3-Bromopropyl)-1-(3-butenyl)-1,1-dimethoxysilane (**2b**)

Compound **2b** was prepared as above from 3-bromopropyl(trichloro)silane (0.18 ml, 1.12 mmol) and 3-butenylmagnesium bromide (2.25 mmol) in THF (10 ml). The reaction was run at 0°C for 2.5 h and the product was isolated after flash chromatography using CH_2Cl_2:hexane 1:1; yield 282 mg (82%) of a colourless oil. HRMS: [M−butenyl] 210.9789. Calc. for $C_5H_{12}BrO_2Si$: 210.9790. ^{1}H-NMR ($CDCl_3$): δ 5.88–5.74 (1H, m, CH=), 4.94–4.83 (2H, m, =CH_2), 3.46 (6H, s, 2 × OCH_3), 3.33 (2H, t, J 6.9 Hz, CH_2Br), 2.11–2.03 (2H, m, CH_2), 1.92–1.82 (2H, m, CH_2), 0.73–0.66 (4H, m, 2 × CH_2Si). ^{13}C-NMR ($CDCl_3$): δ 140.4 (CH), 113.1 (CH_2), 50.2 (CH_3), 36.5 (CH_2), 26.5 (CH_2), 26.4 (CH_2), 11.0 (CH_2), 10.9 (CH_2). MS (EI): 226 ([$M^+ - C_3H_4$], 1), 224 ([$M^+ - C_3H_4$] 1), 213 (28), 169 (100), 145 (45), 113 (67), 91 (16), 59 (36), 41 (6).

3.3. 1-Allyl-1-(3-butenyl)-1-(3-chloropropyl)-1-methoxysilane (**3**)

1-(3-Butenyl)-1-(3-chloropropyl)-1,1-dimethoxysilane (187 mg, 0.84 mmol) in anhydrous THF (2 ml) was added to a solution of allylmagnesium bromide (10 ml, 3.15 mmol of a 0.3 M solution in THF) over a period of 5 min and the resulting solution stirred at ambient temperature overnight. The reaction mixture was worked up as above and the product isolated after flash chromatography using 5% EtOAc in hexane; yield 172 mg (88%) of a colourless oil. HRMS: [M − allyl] 191.0650. Calc. for $C_8H_{16}ClOSi$: 191.0659. ^{1}H-NMR ($CDCl_3$): δ 5.86–5.73 (2H, m, 2 × CH=), 5.02–4.86 (4H, m, 2 × =CH_2), 3.49 (2H, t, J 6.8 Hz, CH_2Cl), 3.46 (3H, s, OCH_3), 2.12–2.08 (2H, m, CH_2), 1.84–1.79 (2H, m, CH_2), 1.68–1.65 (2H, m, CH_2), 0.78–0.72 (4H, m, 2 × CH_2). ^{13}C-NMR ($CDCl_3$): δ 140.8 (CH), 133.3 (CH), 114.3 (CH_2), 113.2 (CH_2), 50.9 (CH_3), 47.7 (CH_2), 26.9 (CH_2), 26.6 (CH_2), 21.2 (CH_2), 12.0 (CH_2), 10.6 (CH_2). MS (EI): 191 ([$M^+ - C_3H_5$], 7), 149 (59), 135 (11), 127 (5), 121 (33), 113 (100), 95 (23), 59 (36).

3.4. 1-Allyl-1-(3-butenyl)-1-(5-hexenyl)-1-methoxysilane (**4**)

Allylmagnesium bromide (15 ml, 2.25 mmol of a 0.15 M solution in THF) was added to a solution of 1-(3-bromopropyl)-1-(3-butenyl)-1,1-dimethoxysilane (181 mg, 0.68 mmol) in THF (3 ml) via a cannula over a period of 40 min and the mixture stirred at ambient temperature overnight. The reaction was worked up as above and the product isolated after flash chromatography using 2% EtOAc in hexane; yield 142 mg (88%) of a colourless oil. ^{1}H-NMR ($CDCl_3$): δ 5.90–5.74 (3H, m, 3 × CH=), 5.01–4.84 (6H, m, 3 × =CH_2), 3.44 (3H, s, OCH_3), 2.07–1.66 (4H, m, 2 × CH_2), 1.64 (2H, dt, J 1.8, 8.1 Hz, CH_2Si), 1.41–1.37 (4H, m, 2 × CH_2), 0.75–0.70 (2H, m, CH_2Si), 0.66–0.61 (2H, m, CH_2Si). ^{13}C-NMR ($CDCl_3$): δ 141.1 (CH), 138.8 (CH), 133.7 (CH), 114.2 (CH_2), 113.8 (CH_2), 112.9 (CH_2), 50.8 (CH_3), 33.3 (CH_2), 32.6 (CH_2), 26.9 (CH_2), 22.3 (CH_2), 21.3 (CH_2), 12.7 (CH_2), 11.9 (CH_2). MS (EI): 238 ([M^+], 2), 197 (16), 165 (8), 143 (88), 115 (100), 97 (7), 83 (19), 59 (63).

3.5. 1-Allyl-1-(3-butenyl)-1,1-dimethoxysilane (**5a**)

Compound **5a** was prepared as above from 3-butenylmagnesium bromide (3.22 mmol) in THF (15 ml) and allyl(trichloro)silane (0.23 ml, 1.61 mmol). The reaction mixture was stirred for 3 h at ambient temperature and worked up as above. The product was isolated after flash chromatography using 2% EtOAc in hexane; yield 274 mg (91%) of a colourless oil. HRMS: [M−allyl] 145.0675. Calc. for $C_6H_{13}O_2Si$: 145.0685. ^{1}H-NMR ($CDCl_3$): δ 5.89–5.70 (2H, m, 2 × CH=), 4.99–4.83 (4H, m, 2 × =CH_2), 3.48 (6H, s, 2 × OCH_3), 2.12–2.05 (2H, m, CH_2), 1.62 (2H, dt, J 1.2, 8.0 Hz, CH_2Si), 0.73–0.67 (2H, m, CH_2Si). ^{13}C-NMR ($CDCl_3$): δ 140.6 (CH), 132.7 (CH), 114.5 (CH_2), 113.0 (CH_2), 50.3 (CH_3), 26.5 (CH_2), 19.8 (CH_2), 10.7 (CH_2). MS (EI): 186 ([M^+], 1), 145 (45), 113 (50), 91 (13), 78 (100), 59 (19), 52 (11), 39 (7).

3.6. 1-Allyl-1,1-di(3-butenyl)-1-methoxysilane (**5b**)

Compound **5b** was prepared as above from 3-butenylmagnesium bromide (7.4 mmol) in THF (30 ml) and allyl(trichloro)silane (0.34 ml, 2.38 mmol). The mixture was stirred at ambient temperature overnight and worked up as above. The product was isolated after flash chromatography using 2% EtOAc in hexane; yield 205 mg (41%) of a colourless oil. HRMS: [M−allyl] 169.1047. Calc. for $C_9H_{17}OSi$: 169.1049. ^{1}H-NMR ($CDCl_3$): δ 5.92–5.72 (3H, m, 3 × CH=), 5.02–4.86 (6H, m, 3 × =CH_2), 3.46 (3H, s, OCH_3), 2.14–2.07 (4H, m, 2 × CH_2), 1.67 (2H, dt J 1.1, 8.1 Hz, CH_2Si), 0.78–0.72 (4H, m, 2 × CH_2Si). ^{13}C-NMR ($CDCl_3$): δ 140.9 (CH), 133.5 (CH), 114.0 (CH_2), 113.0 (CH_2), 50.8 (CH_3), 26.9 (CH_2), 21.3 (CH_2), 12.1 (CH_2). MS (EI): 169 ([$M^+ - C_3H_5$], 29), 141 (78), 127 (20), 115 (100), 95 (5), 83 (31), 75 (6), 59 (87).

3.7. 1-(3-Bromopropyl)-1,1-di(3-butenyl)-1-methoxysilane (**5c**)

Compound **5c** was prepared as above from 3-butenylmagnesium bromide (20 ml, 5.16 mmol of a 0.26

M solution in THF) and 3-bromopropyl-(trichloro)silane (0.27 ml, 1.72 mmol). The reaction mixture was stirred at ambient temperaure for 3 h and the product isolated after flash chromatography using 2% EtOAc in hexane; yield 274 mg (55%) of a colourless oil. HRMS: [M–C_4H_7] 235.0163 Calc. for $C_8H_{16}BrOSi$: 235.0154. ^{1}H-NMR ($CDCl_3$): δ 5.91–5.78 (2H, m, 2 × CH=), 5.02–4.86 (4H, m, 2 × =CH_2), 3.43 (3H, s, OCH_3), 3.37 (2H, t, J 6.9 Hz, CH_2Br), 2.11–2.04 (4H, m, 2 × CH_2), 1.90–1.81 (2H, m, CH_2), 0.75–0.68 (6H, m, 3 × CH_2Si). ^{13}C-NMR ($CDCl_3$): δ 140.8 (CH), 113.1 (CH_2), 50.7 (CH_3), 36.9 (CH_2), 26.9 (CH_2), 26.8 (CH_2), 12.4 (CH_2), 12.1 (CH_2). MS (EI): 237 ([$M^+ - C_4H_7$], 11), 235 ([$M^+ - C_4H_7$], 10), 195 (30), 163 (7), 141 (19), 113 (100), 83 (6), 59 (22).

3.8. 1,1-Di(3-butenyl)-1-(5-hexenyl)-1-methoxysilane (6)

Allylmagnesium bromide (2.82 mmol, 15 ml of a 0.2 M solution in THF) was added to a solution of 1-(3-bromopropyl)-1,1-di(3-butenyl)-1-methoxysilane (274 mg, 0.94 mmol) in THF (5 ml) over a period of 15 min via a cannula. The resulting solution was heated under reflux with stirring for 48 h. More allylmagnesium bromide (15 ml, 2.82 mmol of a 0.2 M solution in THF) was added and the solution was heated under reflux with stirring for another 48 h. Saturated aqueous NH_4Cl (20 ml) was added to the cold reaction mixture, the phases separated, the aqueous phase extracted with diethyl ether (3 × 20 ml) and the combined organic layers washed with water (20 ml), saturated aqueous $NaHCO_3$ (20 ml) and brine (20 ml). The dried ($MgSO_4$) solution was evaporated to dryness at reduced pressure and the residual material subjected to flash chromatography using 2% EtOAc in hexane; yield 180 mg (76%) of a colourless oil. Found: C, 71.52; H, 10.92. Calc. for $C_{15}H_{28}OSi$: C, 71.36; H, 11.18. ^{1}H-NMR ($CDCl_3$): δ 5.91–5.77 (3H, m, 3 × CH=), 5.02–4.87 (6H, m, 3 × =CH_2), 3.43 (3H, s, OCH_3), 2.14–2.07 (6H, m, 3 × CH_2), 1.39–1.37 (4H, m, 2 × CH_2), 0.74–0.65 (6H, m, 3 × CH_2Si). ^{13}C-NMR ($CDCl_3$): δ 141.2 (CH), 138.9 (CH), 114.2 (CH_2), 112.9 (CH_2), 50.7 (CH_3), 33.4 (CH_2), 32.7 (CH_2), 27.1 (CH_2), 22.5 (CH_2), 13.1 (CH_2), 12.4 (CH_2). MS (EI): 197 ([$M^+ - C_4H_7$], 18), 169 (17), 143 (61), 127 (6), 115 (100), 83 (17), 75 (5), 59 (35).

3.9. Triallyl(3-chloropropyl)silane (7a)

3-Chloropropyl(trichloro)silane (0.7 ml, 4.4 mmol in diethyl ether) was added to allylmagnesium bromide (21 ml, 14.5 mmol of a 0.73 M solution in diethyl ether) over 15 min and the mixture heated under reflux for 2 h. The reaction mixture was worked up as above and the product isolated after flash chromatography using hexane; yield 0.71 g (71%) of a colourless oil. Found: C, 63.00; H, 9.25. Calc. for $C_{12}H_{21}SiCl$: C, 62.98; H, 9.23. ^{1}H-NMR ($CDCl_3$): δ 5.83–5.69 (3H, m, 3 × CH=), 4.92–4.85 (6H, m, 3 × =CH_2), 3.46 (2H, t, J 6.9 Hz, CH_2Cl), 1.83–1.73 (2H, m, CH_2CH_2Cl), 1.55 (6H, d, J 8.0 Hz, 3 × CH_2Si), 0.76–0.66 (2H, m, CH_2Si). ^{13}C-NMR ($CDCl_3$): δ 133.9 (CH), 113.9 (CH_2), 47.7 (CH_2Cl), 27.2 (CH_2CH_2Cl), 19.4, 9.2 (CH_2Si).

3.10. Triallyl(3-bromopropyl)silane (7b)

3-Bromopropyl(trichloro)silane (0.86 ml, 5.5 mmol in diethyl ether) was added to allylmagnesium bromide (40 ml, 19.22 mmol of a 0.5 M solution in diethyl ether) over 15 min and the mixture heated under reflux for 2 h. The reaction mixture was worked up as above and the product isolated after flash chromatography using hexane; yield 1.17 g (78%) of a colourless oil. HRMS: [M–C_3H_5] 231.0204. Calc. for $C_9H_{16}SiBr$: 231.0205. ^{1}H-NMR ($CDCl_3$): δ 5.87–5.65 (3H, m, 3 × CH=), 4.94–4.82 (6H, m, 3 × =CH_2), 3.35 (2H, t, J 7.0 Hz, CH_2Br), 1.94–1.78 (2H, m, CH_2CH_2Br), 1.59 (6H, d, J 1.1, 8.1 Hz, 3 × CH_2Si), 0.74–0.65 (2H, m, CH_2Si). ^{13}C-NMR ($CDCl_3$): δ 133.9 (CH), 113.9 (CH_2), 36.8 (CH_2Br), 27.2 (CH_2CH_2Br), 19.4, 10.8 (CH_2Si). MS (EI): 233 ([$M^+ - C_3H_5$], 11), 231 ([$M^+ - C_3H_5$], 11), 205 (5), 191 (26), 175 (9), 163 (100), 161 (97), 149 (30) 1477 (26).

3.11. (3-Bromopropyl)tri(3-butenyl)silane (8)

3-Bromopropyl(trichloro)silane (0.5 ml, 3.2 mmol) was added dropwise over 15 min with stirring to a solution of 3-butenylmagnesium bromide, which was prepared from 4-bromo-1-butene (1.62 ml, 16 mmol), Mg (0.7 g, 32 mmol) and a catalytic amount of iodine in THF (40 ml), and the mixture heated under reflux for 3 h. The reaction was worked up as above and the product isolated after flash chromatography using 2% EtOAc in hexane; yield 324 mg (32%) of a colourless oil. HRMS: [M–C_4H_7] 259.0506. Calc. for $C_{11}H_{20}BrSi$: 259.0518. ^{1}H-NMR ($CDCl_3$): δ 5.92–5.76 (3H, m, 3 × CH=), 5.04–4.85 (6H, m, 3 × =CH_2), 3.36 (2H, t, J 7.0 Hz, CH_2Br), 2.10–1.98 (6H, m, 3 × CH_2), 1.87–1.78 (2H, m, CH_2), 0.70–0.62 (8H, m, 4 × CH_2Si). ^{13}C-NMR ($CDCl_3$): δ 141.2 (CH), 112.9 (CH_2), 37.0 (CH_2), 27.8 (2 × CH_2), 11.6 (CH_2), 11.4 (CH_2). MS (EI): 261 ([$M^+ - C_4H_7$], 29), 259 ([$M^+ - C_4H_7$], 28), 191 (75), 175 (15), 163 (100), 137 (28), 109 (40), 83 (59).

3.12. Diallylmethylvinylsilane (9)

Compound **9** was prepared from methylvinyl-(dichloro)silane and allylmagnesium bromide in 78% yield by a literature procedure [20].

3.13. 1,1-Di(but-3-enyl)silacyclobutane (**10**)

Compound **10** was prepared from 3-bromopropyl-(trichloro)silane and 3-butenylmagnesium bromide in the presence of magnesium metal as described [21].

3.14. (3-Bromopropyl)tripropargylsilane (**11a**)

A mixture of Mg powder (0.7 g, 28.5 mmol), $HgCl_2$ (40 mg, 0.15 mmol), propargyl bromide (0.6 ml, 3.75 mmol of a 80% solution in toluene) in THF (60 ml) was heated under reflux with stirring for 15 min. The mixture was then cooled to −10°C and additional propargyl bromide (1.9 ml, 16.9 mmol) in THF (10 ml) was added dropwise over 45 min. The light green coloured solution was stirred at ambient temperature for 3 h before 3-bromopropyl(trichloro)silane (0.6 ml, 3.75) in THF (10 ml) was added at −10°C over 15 min. The reaction mixture was stirred at ambient temperature for 2 h. Saturated aqueous NH_4Cl (30 ml) was added to the reaction mixture, the phases separated, the aqueous phase extracted with diethyl ether (3 × 20 ml), the combined organic solutions washed with water (20 ml), saturated aqueous $NaHCO_3$ (20 ml), brine (20 ml) and dried ($MgSO_4$) before evaporation at reduced pressure at 0°C. The product was isolated after flash chromatography using 9% CH_2Cl_2 in hexane; yield 830 mg (83%) of a colourless oil. Found: C, 54.06; H, 5.90. Calc. for $C_{12}H_{15}BrSi$: C, 53.94; H, 5.66. ^{1}H-NMR ($CDCl_3$): δ 3.40 (2H, t, J 6.8 Hz, CH_2Br), 2.04–1.98 (2H, m, CH_2), 1.86 (3H, t, J 3 Hz, 3 × CH), 1.76 (6H, d, J 3 Hz, 3 × CH_2Si), 1.04–0.99 (2H, m, CH_2Si). ^{13}C-NMR ($CDCl_3$): δ 79.8 (C), 68.5 (CH), 36.3 (CH_2), 26.9 (CH_2), 10.3 (CH_2), 1.6 (CH_2). MS (EI): 239 ([$M^+ - C_2H_5$], 0.3), 237 ([$M^+ - C_2H_5$], 0.2), 198 (5), 187 (100), 159 (18), 145 (16), 107 (32), 67 (38), 53 (17).

A second product was isolated in 5% yield after flash chromatography. The product has been identified as the following.

3.15. (3-Bromopropyl)-1-(propa-1,2-dienyl)-1,1-dipropargylsilane (**12a**)

HRMS: [M–C_3H_7] 222.9584. Calc. for C_9H_8BrSi: 222.9579. ^{1}H-NMR ($CDCl_3$): δ 4.98 (1H, t, J 7.2 Hz, CH), 4.46 (2H, d, J 7.2 Hz, CH_2), 3.39 (2H, t, J 6.9 Hz, CH_2Br), 1.99–1.91 (2H, m, CH_2), 1.84 (2H, t, J 2.9 Hz, 2 × CH), 1.74–1.72 (4H, m, 2 × CH_2Si), 1.02–0.93 (2H, m, CH_2Si). ^{13}C-NMR ($CDCl_3$): δ 214.3 (C), 80.1 (C), 74.9 (C), 68.6 (CH_2), 68.3 (CH), 36.3 (CH_2), 26.9 (CH_2), 10.9 (CH_2), 2.6 (CH_2). MS (EI): 225 ([$M^+ - C_3H_7$], 6), 223 ([$M^+ - C_3H_7$], 5), 187 (100), 185 (88), 145 (15), 109 (25), 107 (27), 67 (42).

3.16. Allyltripropargylsilane (**11b**)

Compound **11b** was prepared as above from propargyl bromide (2.1 ml, 18.6 mmol), Mg powder (0.97 g, 37.5 mmol), $HgCl_2$ (40 mg) and allyl(trichloro)silane (0.77 ml, 5.37 mmol) in THF (60 ml). The reaction mixture was stirred at ambient temperature for 1.5 h and heated under reflux with stirring for 2 h before being worked up as described above. The product was isolated after flash chromatography using 9% CH_2Cl_2 in hexane; yield 784 mg (78%) of a colourless oil. ^{1}H-NMR ($CDCl_3$): δ 5.90–5.68 (1H, m, CH=), 5.02–4.87 (2H, m, $=CH_2$), 1.88–1.86 (2H, m, CH_2Si), 1.84 (3H, t, J 3 Hz, 3 × CH), 1.72 (6H, d, J 3 Hz, 3 × CH_2Si). ^{13}C-NMR ($CDCl_3$): δ 132.0 (CH), 115.3 (CH_2), 79.8 (C), 68.3 (CH), 17.6 (CH_2), 0.9 (CH_2). MS (EI): 186 ([M^+], 0.3), 147 (29), 145 (59), 121 (22), 119 (35), 107 (40), 93 (20), 67 (100).

A second product was isolated after flash chromatography in 7% yield. The product has been identified as the following

3.17. 1-Allyl-1-(propa-1,2-dienyl)-1,1-dipropargylsilane (**12b**)

^{1}H-NMR ($CDCl_3$): δ 5.87–5.72 (1H, m, CH=), 5.00–4.89 (2H, m, $=CH_2$), 4.98 (1H, t, J 7.2 Hz, =CH), 4.45 (2H, d, J 7.2 Hz, $CH_2=$), 1.88–1.84 (2H, m, CH_2Si), 1.84 (2H, t, J 3 Hz, 2 × CH), 1.72 (4H, d, J 3.0 Hz, 2 × CH_2Si). ^{13}C-NMR ($CDCl_3$): δ 214.4 (C), 132.3 (CH), 115.2 (CH_2), 80.2 (C), 74.7 (C), 68.6 (CH_2), 68.2 (CH), 18.8 (CH_2), 2.1 (CH_2). MS (EI): 185 ([$M^+ - 1$], 4), 158 (19), 145 (76), 119 (43), 107 (42), 93 (22), 67 (100), 53 (37).

3.18. 1-Allyl-1-(3-chloropropyl)-1-silacyclopent-3-ene (**13a**)

Bis(tricyclohexylphosphine)benzylidene ruthenium dichloride (24 mg, 7 mmol%) and triallyl(3-chloropropyl)silane (114 mg, 0.5 mmol) were added to benzene (12 ml) and the mixture heated under reflux for 10 h. The reaction mixture was left to cool, the solvent distilled off at reduced pressure and the residual oil subjected to flash chromatography using hexane; yield 72 mg (72%) of a colourless oil. HRMS: [M–allyl] 159.0384. Calc. for $C_7H_{12}ClSi$: 159.0397. ^{1}H-NMR ($CDCl_3$): δ 5.85–5.72 (1H, m, CH=), 5.84 (2H, s, CH=CH), 4.92–4.82 (2H, m, $=CH_2$), 3.49 (2H, t, J 6.9 Hz, CH_2Cl), 1.84–1.74 (2H, m, CH_2), 1.68 (2H, dt, J 1.0, 8.0 Hz, CH_2Si), 1.35–1.20 (4H, m, 2 × CH_2Si), 0.83–0.77 (2H, m, CH_2Si). ^{13}C-NMR ($CDCl_3$): δ 134.1 (CH), 130.9 (CH), 113.6 (CH_2), 47.7 (CH_2), 27.6 (CH_2), 20.9 (CH_2), 14.4 (CH_2), 10.5 (CH_2). MS (EI): 159 ([$M^+ - C_3H_5$], 16), 131 (29), 117 (100), 105 (10), 81 (6), 63 (28), 55 (8), 43 (8).

3.19. 1-Allyl-1-(3-bromopropyl)-1-silacyclopent-3-ene (13b)

Compound **13b** was prepared from triallyl(3-bromopropyl)silane (112 mg, 0.41 mmol) and bis(tricyclohexylphosphine)benzylidene ruthenium dichloride (24 mg, 7 mmol%) which was added in portions. The benzene solution (12 ml) was heated under reflux for 6 h. The product was isolated after flash chromatography using hexane; yield 62 mg (62%) of a colourless oil. HRMS: [M–allyl] 202.9904. Calc. for $C_7H_{12}BrSi$: 202.9892. ^{1}H-NMR ($CDCl_3$): δ 5.86–5.69 (1H, m, CH=), 5.83 (2H, s, CH=CH), 4.92–4.82 (2H, m, =CH_2), 3.37 (2H, t, J 7.0 Hz, CH_2Br), 1.93–1.82 (2H, m, CH_2), 1.68 (2H, d, J 8.0, CH_2Si), 1.36–1.23 (4H, m, 2 × CH_2Si), 0.84–0.78 (2H, m, CH_2Si). ^{13}C-NMR ($CDCl_3$): δ 134.1 (CH), 130.9 (CH), 113.7 (CH_2), 36.7 (CH_2), 27.8 (CH_2), 20.9 (CH_2), 14.5 (CH_2), 12.1 (CH_2). MS (CI): 247 ([$M^+ + 1$], 2), 245 ([$M^+ + 1$], 2), 220 (40), 205 (100), 194 (38), 178 (33), 161 (45), 115 (45), 98 (94).

3.20. 1-(3-Butenyl)-1-methoxy-1-silacyclohex-3-ene (15a)

A solution of 1-allyl-1,1-di(3-butenyl)-1-methoxysilane (128 mg, 0.61 mmol) and bis(tricyclohexylphosphine)benzylidene ruthenium dichloride (5 mg, 1 mol%) in benzene (12 ml) was stirred at ambient temperature for 1 h. The solution was evaporated at reduced pressure and the residual oil subjected to flash chromatography using 5% EtOAc in hexane; yield 77 mg (69%) of a colourless oil. HRMS: M 182.1117. Calc. for $C_{10}H_{18}OSi$: 182.1127. ^{1}H-NMR ($CDCl_3$): δ 5.90–5.80 (1H, m, CH=), 5.75–5.65 (2H, m, CH=CH), 5.03–4.87 (2H, m, =CH_2), 3.45 (3H, s, OCH_3), 2.28–2.25 (2H, m, CH_2), 2.13–2.07 (2H, m, CH_2), 1.35–1.29 (2H, m, CH_2Si), 0.87–0.66 (4H, m, 4 × CH_2Si). ^{13}C-NMR ($CDCl_3$): δ 141.0 (CH), 130.5 (CH), 125.4 (CH), 113.0 (CH_2), 50.8 (CH_3), 27.0 (CH_2), 22.7 (CH_2), 12.9 (CH_2), 11.2 (CH_2), 8.1 (CH_2). MS (EI): 182 ([M^+], 4), 154 (8), 127 (66), 113 (26), 97 (17), 59 (100), 39 (5).

3.21. 1-(5-Hexenyl)-1-methoxy-1-silacyclohex-3-ene (15b)

A solution of 1-allyl-1-(3-butenyl)-1-(5-hexenyl)-1-methoxysilane (126 mg, 0.53 mmol) and bis(tricyclohexylphosphine)benzylidene ruthenium dichloride (5 mg, 1 mol%) in benzene (12 ml) was stirred at ambient temperature for 1 h. The mixture was evaporated to dryness at reduced pressure and the product isolated from the residual material after flash chromatography using 2% EtOAc in hexane; yield 68 mg (61%) of a colourless oil. ^{1}H-NMR ($CDCl_3$): δ 5.82–5.65 (3H, m, 3 × CH=), 4.99–4.88 (2H, m, =CH_2), 3.44 (3H, s, OCH_3), 2.29–2.23 (2H, m, CH_2), 2.07–1.99 (2H, m, CH_2), 1.41–1.27 (6H, m, 3 × CH_2), 0.85–0.62 (4H, m, 2 × CH_2Si). ^{13}C-NMR ($CDCl_3$): δ 138.9 (CH), 130.5 (CH), 125.5 (CH), 114.2 (CH_2), 50.7 (CH_3), 33.4 (CH_2), 32.5 (CH_2), 22.7 (CH_2), 22.5 (CH_2), 13.7 (CH_2), 11.2 (CH_2), 8.1 (CH_2). MS (EI): 210 ([M^+], 2), 182 (12), 143 (100), 127 (100), 115 (25), 97 (26), 75 (9), 59 (90).

3.22. 1,6-bis(1-Methoxysilacyclohex-3-en-1-yl)hex-3-ene (16)

A solution of 1-allyl-1,1-di(3-butenyl)-1-methoxysilane (128 mg, 0.61 mmol) and bis(tricyclohexylphosphine)benzylidene ruthenium dichloride (20 mg, 4 mol%) in benzene (12 ml) was stirred at ambient temperature for 4 h. The products were separated by flash chromatography using 5% EtOAc in hexane. The yield of compound **15a** was 43%. The yield of the title compound **16** was 39%. HRMS: M 336.1931. Calc. for $C_{18}H_{32}O_2Si_2$: 336.1941. ^{1}H-NMR ($CDCl_3$): δ 5.75–5.64 (6H, m, 3 × CH=CH), 3.44 (6H, s, 2 × OCH_3), 2.28–2.25 (4H, m, 2 × CH_2), 2.10–2.05 (4H, m, 2 × CH_2), 1.32–1.28 (4H, m, 2 × CH_2Si), 0.85–0.67 (8H, m, 4 × CH_2Si). ^{13}C-NMR ($CDCl_3$): δ 131.3 (CH), 130.5 (CH), 125.4 (CH), 50.8 (CH_3), 25.8 (CH_2), 22.7 (CH_2), 13.7 (CH_2), 11.2 (CH_2), 8.2 (CH_2). MS (EI): 336 ([M^+], 78), 282 (14), 269 (31), 250 (11), 241 (6), 178 (6), 127 (97), 97 (34), 59 (100).

3.23. 1,1-Dimethoxy-1-silacyclohex-3-ene (17) [28]

Compound **17** was prepared as above from 1-allyl-1-(3-butenyl)-1,1-dimethoxysilane (86 mg, 0.46 mmol) and bis(tricyclohexylphosphine)benzylidene ruthenium dichloride (10 mg, 2.5 mol%). The reaction time was 2 h at ambient temperature, and the product was isolated after flash chromatography using 2% EtOAc in hexane; yield 52 mg (70%) of a colourless oil.

3.24. 1-(3-Chloropropyl)-1-methoxy-1-silacyclohex-3-ene (18)

Allyl-1-(3-butenyl)-1-(3-chloropropyl)-1-methoxysilane (114 mg, 0.49 mmol) and bis(tricyclohexylphosphine)benzylidene ruthenium dichloride (8 mg, 2 mol%) in benzene (12 ml) was stirred at ambient temperature for 2 h. The reaction was worked up as above and the product isolated after flash chromatography using 5% EtOAc in hexane; yield: 69 mg (69%) of a colourless oil. HRMS: M 204.0721. Calc. for $C_9H_{17}ClOSi$: 204.0737. ^{1}H-NMR ($CDCl_3$): δ 5.75–5.63 (2H, m, CH=CH), 3.50 (2H, t, J 6.8 Hz, CH_2Cl), 3.45 (3H, s, OCH_3), 2.24 (2H, m, CH_2), 1.88–1.78 (2H, m, CH_2), 1.37–1.23 (2H, m, CH_2Si), 0.88–0.65 (4H, m, 2 × CH_2Si). ^{13}C-NMR ($CDCl_3$): δ 130.6 (CH), 125.2 (CH), 50.8 (CH_3), 47.7 (CH_2), 26.7 (CH_2), 22.7 (CH_2), 11.4 (CH_2), 11.0 (CH_2), 7.9 (CH_2). MS (EI): 204 ([M^+], 8), 162 (42), 134 (96), 126 (41), 121 (55), 108 (75), 95 (30), 59 (100).

3.25. 1-(3-Bromopropyl)-1-methoxy-1-silacyclohept-4-ene (**19a**)

Bis(tricyclohexylphosphine)benzylidene ruthenium dichloride (18 mg, 4 mol%) was added in three equal portions to a solution of 1-(3-bromopropyl)-1,1-di(3-butenyl)-1-methoxysilane (111 mg, 0.38 mmol) in benzene (10 ml) which was heated at 50°C with stirring for 8 h. The reaction mixture was worked up as above and the product isolated after flash chromatography using 2% EtOAc in hexane; yield 60 mg (60%) of a colourless oil. HRMS: M 262.0379. Calc. for $C_{10}H_{19}BrOSi$: 262.0388. ^{1}H-NMR ($CDCl_3$): δ 5.81–5.71 (2H, m, CH=CH), 3.41 (3H, s, OCH_3), 3.33 (2H, t, J 6.9 Hz, CH_2Br), 2.31–2.26 (2H, m, CH_2), 2.15–2.07 (2H, m, CH_2), 1.93–1.83 (2H, m, CH_2), 0.87–0.60 (6H, m, $3 \times CH_2Si$). ^{13}C-NMR ($CDCl_3$): δ 132.4 (CH), 50.3 (CH_3), 36.9 (CH_2), 26.8 (CH_2), 19.9 (CH_2), 13.4 (CH_2), 12.2 (CH_2). MS (EI): 264 ([M^+], 1), 262 ([M^+], 1), 222 (7), 194 (9), 154 (8), 141 (41), 113 (100), 83 (6), 59 (30).

3.26. 1-(5-Hexenyl)-1-methoxy-1-silacyclohept-4-ene (**19b**)

Compound **19b** was prepared as above from bis(tricyclohexylphosphine)benzylidene ruthenium dichloride (18 mg, 4 mol%) which was added in three equal portions to a solution of 1,1-di(3-butenyl)-1-(5-hexenyl)-1-methoxysilane (111 mg, 0.38 mmol) in benzene (10 ml) which was heated at 50°C with stirring for 14 h. The reaction mixture was worked up as above and the product isolated after flash chromatography using 2% EtOAc in hexane; yield 35 mg (35%) of a colourless oil. HRMS: M 224.1589. Calc. for $C_{13}H_{24}OSi$: 224.1596. ^{1}H-NMR ($CDCl_3$): δ 5.83–5.71 (3H, m, C*H*=CH, C*H*=C*H*), 5.00–4.88 (2H, m, =CH_2), 3.45 (3H, s, OCH_3), 2.31–2.26 (2H, m, CH_2), 2.12–2.01 (4H, m, $2 \times CH_2$), 1.42–1.25 (4H, m, $2 \times CH_2$), 0.85–0.56 (6H, m, $3 \times CH_2Si$). ^{13}C-NMR ($CDCl_3$): δ 138.9 (CH), 132.5 (CH), 114.2 (CH_2), 50.3 (CH_3), 33.4 (CH_2), 32.6 (CH_2), 22.3 (CH_2), 20.1 (CH_2), 14.2 (CH_2) 12.3 (CH_2). MS (EI): 224 ([M^+], 3), 196 (3), 183 (4), 141 (68), 113 (100), 83 (9), 59 (30).

3.27. 1-(3-Brompropyl)-1-(3-butenyl)-1-silacyclohept-4-ene (**20**)

Compound **20** was prepared as above from 3-bromopropyltri(3-butenyl)silane (110 mg, 0.35 mmol) and bis(tricyclohexylphosphine)benzylidene ruthenium dichloride (20 mg, 2.5 mol%). The reaction time was 16 h at ambient temperature and the product was isolated after flash chromatography using hexane; yield 60 mg (60%) of a colourless oil. HRMS: [M–C_4H_7] 231.0210. Calc. for $C_9H_{16}BrSi$: 231.0205. ^{1}H-NMR ($CDCl_3$): δ 5.92–5.79 (1H, CH=, m), 5.76–5.69 (2H, m, CH=CH), 5.02–4.86 (2H, m, CH_2=), 3.37 (2H, t, J 6.9 Hz, CH_2Br), 2.24–2.18 (4H, m, $2 \times CH_2$), 2.07–2.03 (2H, m, CH_2), 1.88–1.80 (2 H m, CH_2), 0.69–0.62 (8H, m, $4 \times CH_2Si$). ^{13}C-NMR ($CDCl_3$): δ 141.4 (CH), 132.4 (CH), 112.9 (CH_2), 37.1 (CH_2), 27.7 (CH_2), 27.6 (CH_2), 21.1 (CH_2), 12.5 (CH_2), 12.3 (CH_2), 10.9 (CH_2). MS (EI): 260 ([$M^+ - C_2H_4$], 0.5), 258 ([$M^+ - C_2H_4$], 0.5), 231 (26), 191 (34), 163 (100), 137 (62), 109 (37), 95 (12), 83 (51).

3.28. 5-Silaspiro[4,6]undec-2-ene (**22**)

A solution of 1,1-diallylsilacycloheptane (130 mg, 0.67 mmol) and bis(tricyclohexylphosphine)benzylidene ruthenium dichloride (50 mg, 9 mol%) in benzene (15 ml) was heated under reflux for 6 h. The solvent was removed at reduced pressure and the residual oily material subjected to flash chromatography using hexane; yield 69 mg (62%) of a colourless oil. HRMS: [M] 166.1164. Calc. for $C_{10}H_{18}Si$: 166.1178. ^{1}H-NMR ($CDCl_3$): δ 5.83 (2H, t, J 1.0 Hz, CH=CH), 1.67–1.49 (8H, m, $4 \times CH_2$), 1.27 (4H, d, J 1.0 Hz, $2 \times CH_2Si$), 0.87–0.78 (4H, m, $2 \times CH_2Si$). ^{13}C-NMR ($CDCl_3$): δ 131.0 (CH), 31.3 (CH_2), 24.2 (CH_2), 17.2 (CH_2), 14.1 (CH_2). MS (EI): 166 ([M], 100), 138 (22), 112 (74), 97 (19), 84 (95), 67 (9), 55 (27), 43 (16).

3.29. 4-Silaspiro[3,6]dec-7-ene (**23**)

A solution 1,1-di(3-butenyl)silacyclobutane (119 mg, 0.66 mmol) and bis(tricyclohexylphosphine)benzylidene ruthenium dichloride (25 mg, 9 mol%) in benzene (12 ml) was heated under reflux for 6 h. The catalyst was added in 3 portions at intervals during this time. The solvent was then removed at reduced pressure and the residual material subjected to flash chromatography using hexane; yield 43 mg (43%) of a colourless oil with spectroscopic data as previously described for the same product prepared by another route [21].

3.30. 1,1-Dipropargyl-3-vinylsilacyclopent-3-ene (**24**)

A solution of allyltripropargylsilane (101 mg, 0.54 mmol) and bis(tricyclohexylphosphine)benzylidene ruthenium dichloride (25 mg, 11 mol%) in benzene (12 ml) was heated under reflux for 18 h. The ruthenium catalyst was added at intervals in three portions. The solvent was then removed at reduced pressure and the residual material subjected to flash chromatography using hexane; yield 50 mg (50%) of a colourless oil. HRMS: [M] 185.0779. Calc. for $C_{12}H_{13}Si$: 185.0787. ^{1}H-NMR ($CDCl_3$): δ 6.53 (1H, dd, J 1.4, 17.1 Hz, CH=), 5.90 (1H, s, CH=), 5.10 (2H, dd, J 10.4, 17.1 Hz, =CH_2), 1.85–1.79 (6H, $2 \times CH_2Si$, m, $2 \times CH$), 1.61 (4H, d, J 18 Hz, $2 \times CH_2Si$). ^{13}C-NMR ($CDCl_3$): δ 142.1 (C), 137.5 (CH), 131.6 (CH), 113.7 (CH_2), 80.5

(C), 67.8 (CH), 15.2 (CH_2), 12.4 (CH_2), 2.9 (CH_2). MS (EI): 186 ([M^+], 5), 185 (7), 171 (11), 158 (42), 146 (78), 121 (37), 107 (44), 67 (100).

3.31. 1,1-Diallyl-1-silacycloheptane (**21**) and triallylpropylsilane (**25**)

3.31.1. From triallyl(3-chloropropyl)silane (**7a**)

A solution of triallyl(3-chloropropyl)silane (302 mg, 1.32 mmol), AIBN (41.7 mg, 0.264 mmol) and Bu_3SnH (0.53 ml, 1.98 mmol) in benzene (80 ml) was heated under reflux with stirring for 48 h. Since GLC showed that the reaction had not gone to completion, another portion of Bu_3SnH (0.27 ml, 1.02 mmol) and AIBN (20 mg, 0.132 mmol) was added and the mixture heated overnight. The solvent was distilled off at reduced pressure and the residual material subjected to flash chromatography using hexane to yield the silacycloheptane **21** in 48% yield (124 mg) and the acyclic product **25** in 31% yield (80 mg) as colourless oils.

3.31.2. From triallyl(3-bromopropyl)silane (**7b**)

A solution of triallyl(3-bromopropyl)silane (206 mg, 0.755 mmol), AIBN (12 mg, 75.5 mol) and Bu_3SnH (0.3 ml, 1.13 mmol) in benzene (80 ml) was heated under reflux and stirring for 3 h. The solvent was distilled off at reduced pressure and the residual material subjected to flash chromatography using hexane to yield the silacycloheptane **21** in 44% yield (64 mg) and the acyclic product **25** in 25% yield (36 mg) as colourless oils.

*3.31.2.1. 1,1-Diallyl-1-silacycloheptane (**21**).* HRMS: [M] 194.1489. Calc. for $C_{12}H_{22}Si$: 194.1491. ^{1}H-NMR ($CDCl_3$): δ 5.85-5.71 (2H, m, $2\times$ CH=), 4.87–4.79 (4 H m, $2\times$ =CH_2,), 1.60–1.47 (12H, m, $4\times CH_2$, $2\times$ CH_2Si), 0.71–0.66 (4H, m, $2\times CH_2Si$). ^{13}C-NMR ($CDCl_3$): δ 135.0 (CH), 112.9 (CH_2), 32.1 (CH_2), 23.8 (CH_2), 21.7 (CH_2), 12.3 (CH_2). MS (EI): 194 ([M^+], 0.3), 153 (84), 125 (100), 111 (34), 97 (50), 83 (40), 71 (22), 55 (13).

*3.31.2.2. Triallylpropylsilane (**25**).* HRMS: [M–allyl] 153.1107. Calc. for $C_9H_{17}Si$: 153.1099. ^{1}H-NMR ($CDCl_3$): δ 5.82–5.73 (3H, m, $3\times$ CH=), 4.90–4.82 (6H, m, $3\times$ =CH_2), 1.57 (6H, dt, J 1.1, 8.1 Hz, $3\times$ CH_2Si), 1.40–1.29 (2H, m, CH_2), 0.95 (3H, t, J 7.2 Hz, CH_3), 0.60–0.55 (2H, m, CH_2Si). ^{13}C-NMR ($CDCl_3$): δ 134.5 (CH), 113.5 (CH_2), 19.7 (CH_2), 18.4 (CH_2), 17.1 (CH_3), 14.1 (CH_2). MS (EI): 194 ([M^+], 0.3), 153 (46), 125 (24), 111 (76), 109 (9), 97 (12), 83 (100), 69 (78).

3.32. Tri(3-butenyl)propylsilane (**27**)

A solution of (3-bromopropyl)tri(3-butenyl)silane (206 mg, 0.755 mmol), AIBN (23 mg, 0.126 mmol) and u_3SnH (0.5 ml, 1.89 mmol) in benzene (50 ml) was heated under reflux with stirring for 48 h. GLC analysis showed that not all starting material had been consumed. Therefore more Bu_3SnH (0.27 ml, 1.02 mmol) and AIBN (18 mg) were added to the solution and the heating continued for 48 h. The solvent was distilled off and the residue subjected to flash chromatography using hexane; yield 150 mg (50%) of a colourless oil. HRMS: [$M-C_3H_7$] 193.1396. Calc. for $C_{12}H_{21}Si$: 193.1413. ^{1}H-NMR ($CDCl_3$): δ 5.93–5.79 (3H, m, $3\times$ CH=), 5.01–4.86 (6H, m, $3\times$ =CH_2), 2.72–1.99 (6H, m, $3\times CH_2$), 1.36–1.28 (2H, m, CH_2), 0.95 (3H, t, J 7.2 Hz, CH_3), 0.66–0.59 (6H, m, $3\times CH_2Si$), 0.57–0.51 (2H, m, CH_2Si). ^{13}C-NMR ($CDCl_3$): δ 141.7 (CH), 112.7 (CH_2), 27.9 (CH_2), 18.6 (CH_3), 17.3 (CH_2) 15.1 (CH_2), 11.6 (CH_2). MS (EI): 236 ([M^+], 2), 193 (20), 181 (60), 153 (40), 139 (84), 127 (63), 111 (88), 85 (100).

3.33. 1,1–Dipropargyl-1-silacyclohept-3-ene (**28**) and tripropargylpropylsilane (**29**)

A solution of (3-bromopropyl)tripropargylsilane (401 mg, 1.5 mmol), AIBN (25 mg, 0.15 mmol) and Bu_3SnH (0.6 ml, 2.25 mmol) in benzene (75 ml) was heated under reflux with stirring for 32 h. The solvent was distilled off at reduced pressure and the residual material subjected to flash chromatography using 5% CH_2Cl_2 in hexane to afford the silacycloheptene **28** in 28% yield (78 mg) and the acyclic silane **29** in 21% yield (59 mg) as colourless oils.

3.33.1. 1,1-Dipropargyl-1-silacyclohept-3-ene (**28**)

^{1}H-NMR ($CDCl_3$): δ 5.74–5.62 (2H, m, CH=CH), 2.11 (2H, q, J 6.2 Hz, CH_2), 1.82 (2H, t, J 2.9 Hz, $2\times$ CH), 1.76 (2H, d, J 6.1 Hz, CH_2), 1.64 (6H, d, J 2.9 Hz, $3\times CH_2Si$), 1.06 (2H, t, J 6.7 Hz, CH_2Si). ^{13}C-NMR ($CDCl_3$): δ 131.0 (CH), 125.8 (CH), 81.2 (C), 67.5 (CH), 28.5 (CH_2), 22.2 (CH_2), 14.2 (CH_2), 12.3 (CH_2), 2.3 (CH_2). MS (EI): 187 ([M^+-1], 1), 160 (45), 149 (50), 121 (100), 109 (21), 95 (36), 67 (56), 55 (15).

3.33.2. Tripropargylpropylsilane (**29**)

HRMS: [$M-C_3H_3$] 149.0797. Calc. for $C_9H_{13}Si$: 149.0787. ^{1}H-NMR ($CDCl_3$): δ 1.83 (3H, t, J 3 Hz, $3\times$ CH), 1.73 (6H, d, J 3 Hz, $3\times CH_2Si$), 1.54–1.41 (2H, m, CH_2), 0.98 (3H, t, J 7.3 Hz, CH_3), 0.90–0.85 (2H, m, CH_2Si). ^{13}C-NMR ($CDCl_3$): δ 80.3 (C), 68.0 (CH), 18.0 (CH_3), 16.7 (CH_2), 13.3 (CH_2), 1.6 (CH_2). MS (EI): 173 ([M^+-CH_3], 0.3), 150 (3), 145 (30), 131 (9), 121 (12), 107 (100), 81 (10), 67 (85).

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