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Synthesis of a new class of silsesquioxanes with alkynyl and germyl functionality†

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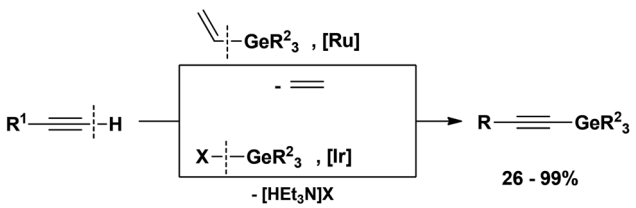
Although there are a variety of functional compounds in the vast family of silsesquioxanes (POSS), the number of protocols describing specific monosubstituted silsesquioxanes is limited. There are even fewer reports on alkynyl and/or germyl functionalities appearing together with the POSS compounds. Here, a series of novel kinds of cubic monosubstituted POSS bearing alkynyl and germyl functionality in one molecule are reported. These compounds were synthesized by effective germylative coupling of terminal alkynes with vinylgermanes in the presence of a Ru–H complex. The structures of the products were determined. Moreover, stoichiometric reactions of a complex possessing Ru–Ge were also performed to propose the general mechanistic scheme of this reaction.

Introduction

Silsesquioxanes (POSS) are a wide class of compounds with rigid Si–O–Si cores and organic coronae of various architectures of the general formula $(RSiO_{3/2})_n$. One of this category involves cubic systems with one reactive functional group, *i.e.* T_8R_7R'.[1] The most attractive, due to their possible applications and further modifications, are systems with unsaturated functionalities and/or possessing the Si–H group. They are susceptible to several types of stoichiometric and catalytic reactions, *e.g. trans*-metallation and cross-metathesis, but the reports are less numerous than in the case of T_8R_8 analogues.[2] As a result, silsesquioxanes are used in many branches of chemistry, ranging from catalysis (*e.g.* as ligands), medicine (*e.g.* drug deliveries) and electronics to materials chemistry.[3]

The alkynyl-substituted silsesquioxanes have been hitherto scarcely covered in literature reports. There is information about the silsesquioxane-pyridine ligand Si–C≡C– spacer, used as ligand for palladium in the catalytic oxidation of benzyl alcohol to benzaldehyde.[4] Analogously, Laine *et al.* presented a procedure for the synthesis of octaalkynylsilsesquiuoxanes *via* palladium catalyzed Sonogashira reaction of brominated octaphenylsilsesquioxanes with silylacetylene.[5,6] Combination of POSS and germanium derivatives is even less present in the literature. These systems may be so-called heterosilsesquioxanes owing to the presence of heteroatoms incorporated into the POSS cage (*e.g.* Ge, Al, P, TM, *etc.*) and are studied for their potential application. The first example of a germasilsesquioxane containing germanium atom (substituted with a methyl group) in one of the corners was described by Feher and co-workers in 1989.[7] Last year, our group published procedures for the synthesis of vinylgermanium derivatives of silsesquioxanes, *i.e.* with germanium as a part of the cubic structure, in a corner, and with the dimethylvinylgermoxy group connected with one of the silicon atoms of the T_8 core.[8]

The introduction of the germanium moiety into the –CC– bond *via* germylative coupling (GC) of terminal alkynes with vinylgermanes was developed by Marciniec *et al.* and described in 2007.[9] Another catalytic route using terminal alkynes and halogermanes proceeding in the presence of an iridium catalytic system was reported in 2014 and this year.[10] These processes are some of the few known catalytic methods leading to alkynyl-substituted organogermanes (Scheme 1).



R^1 = alkyl, aryl, silyl, germyl
R^2_3 = alkyl, aryl
X = I, Cl (+LiI)
[Ru] = $[RuHCl(CO)(PR^3_3)_{3-n}]$, R^3 = Ph, iPr, Cy (n=0, 1)
[Ir]= $[\{Ir(\mu\text{-}Cl)(CO)_2\}_2]$, Et_3N or $(iPr)Et_2N$

Scheme 1 Germylative coupling reactions leading to functionalized alkynylgemanes.

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In these reactions, in the presence of ruthenium(II) or iridium(I) complexes, the terminal C_{sp}–H bond in alkyne is activated by vinylgermanes or halogermanes, which enables obtaining the desired alkynylgermanes.

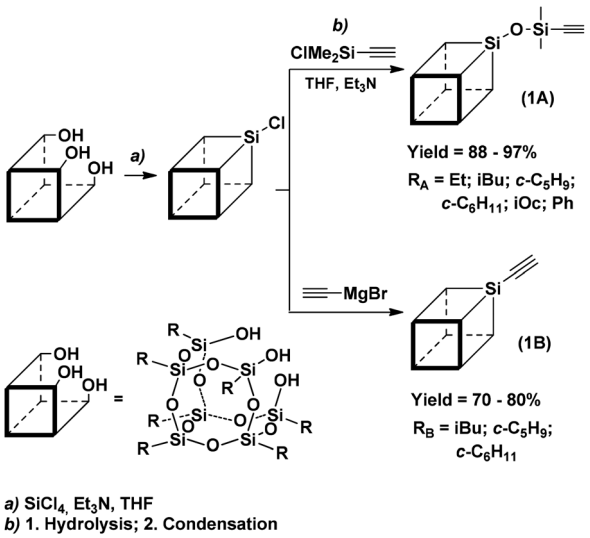
In this paper, we focus on demonstrating an efficient and selective route for the synthesis of a new class of silsesquioxanes with alkynyl and germyl functionality in one molecule, using ruthenium(II) germylative coupling reaction. This is the first paper to report on this kind of silsesquioxane derivatives, synthesized by an elegant and effective route.

Results and discussion

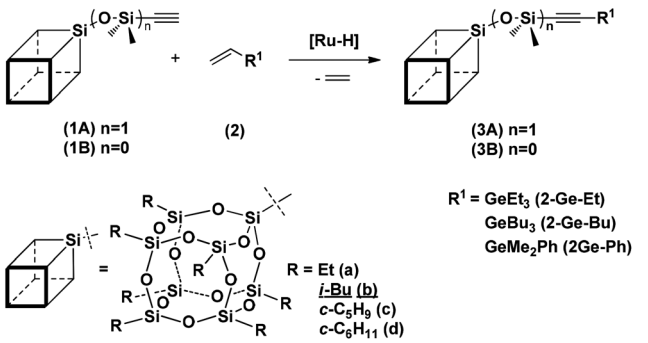
The optimization of the reaction conditions of germylative coupling of a variety of alkynes performed and presented in our previous paper[9] enabled efficient synthesis of a series of new functionalized alkynylgermanes. This prompted us to extend this procedure to new alkynes, *i.e.* ethynyl(siloxy)silsesquioxanes (**1A**) an efficient synthesis of which has been elaborated by our group.[11] It was also revealed that an ethynyl moiety may also be attached in the close proximity of the POSS core (**1B**) and we present here an adequate synthetic path for its formation (Scheme 2).

Selected ethynyl(siloxy)silsesquioxanes (**1A**) and ethynylsilsesquioxanes (**1B**) were tested as substrates in a germylative coupling reaction to verify their potential in the formation of a new class of germa(alkynyl)-derivatives of POSS. The overview of this process is presented in Scheme 3.

The reaction conditions were optimized in terms of ruthenium-hydride catalyst type, its amount, temperature, time and reagent stoichiometry, based on the results of the synthesis of alkynylgermane compounds, in our previous paper.[9] For this purpose, ethynyl(dimethylsiloxy)hepta(isobutyl)octasilsesquioxane (**1A-b**) and $H_2C{=}CHGeEt_3$ (**2Ge-Et**)



Scheme 2 Synthetic path for monoethynyl-derivatives of POSS (**1A** and **1B**).



Scheme 3 General procedure for the synthesis of monogermaalkynylsilsesquioxanes (**3A** and **3B**).

were selected as reagents for a model reaction. The reason for this was the ease of post reaction mixture analysis *i.e.* by ^{1}H and ^{13}C NMR spectroscopy. The results of optimization tests are presented in Table 1.

The optimal reaction conditions for achieving the highest alkyne conversion are: $[Ru(Cl)(H)(CO)(PCy_3)_2]$ (**II**) as active catalyst, 0.5 equiv. excess of $H_2C{=}CHGeEt_3$ (**2Ge-Et**) – to avoid known ruthenium mediated alkyne dimerization,[12] 120 °C and 48 hours. Shorter reaction time causes incomplete **1A-b** conversion.

The product (**3B-2-Ge-Et**) and the reaction were monitored *via* ^{1}H, ^{13}C, and ^{29}Si NMR by a comparison of its spectra with those of POSS substrate, **1A** (Fig. 1–3).

Fig. 1 presents correlation between ^{1}H NMR spectra of **1A-b** and (model) product with **2Ge-Et** (**3B-2-Ge-Et**) in the range of 0.2–2.8 ppm. The absence of a chemical shift derived from **1A-b** (2.38 ppm) was the crucial aspect to achieve, as because of **1A** or **1B** and its germyl product chemical similarity, their separation from the reaction mixture was almost impossible. The protons of the i-BuPOSS core remained at the same resonance lines. The ^{1}H NMR data of the **3B-2-Ge-Et** product confirm the appearance of new resonance lines, *i.e.* a triplet at

Table 1 Germylative coupling of $H_2C{=}CHGeEt_3$ (**2Ge-Et**) with ethynyl (dimethylsiloxy) silsesquioxane (**1A-b**) – optimization of the reaction conditions[a]

Entry	Reaction temp. [°C]	Stoichiometry [**1A-b**] : [**2Ge-Et**] : [Ru–H]	Conversion of **1A-b** [%]
1	100	1 : 1 : 0.01[b]	40
2	100	1 : 1 : 0.02[b]	65
3	100	1 : 1 : 0.01[c]	60
4	100	1 : 1 : 0.02[c]	80
5	120	1 : 1 : 0.02[c]	85
6	120	1 : 1.5 : 0.02[c]	99
7	120	1 : 1.25 : 0.02[c]	88
8	120	1 : 2 : 0.02[c]	99[d]
9	120 (24 h)	1 : 1.5 : 0.02[c]	77

[a] Reaction conditions: a closed system, argon, toluene (0.25 M), t = 48 h. [b] Catalyst: $[Ru(Cl)(H)(CO)(PPh_3)_3]$ (**I**). [c] Catalyst: $[Ru(Cl)(H)(CO)(PCy_3)_2]$ (**II**). [d] Accompanied by traces of vinylgermane homocoupling product. Conversion of POSS was detected based on ^{1}H NMR.

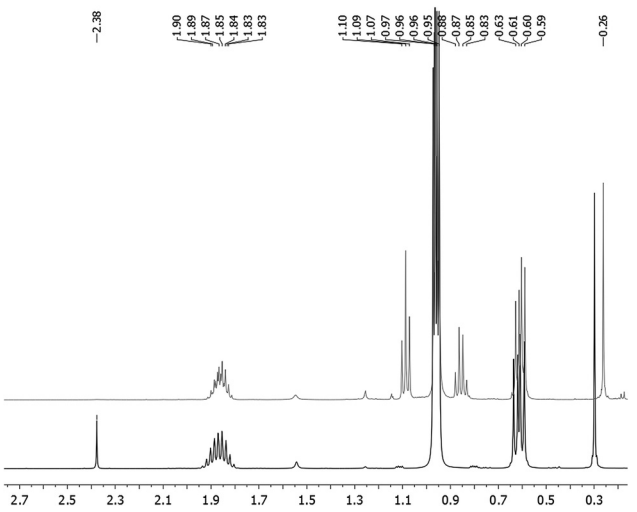


Fig. 1 ^{1}H NMR stacked spectra of **3B-2-Ge-Et** (grey – top) and **1A** (black – bottom).

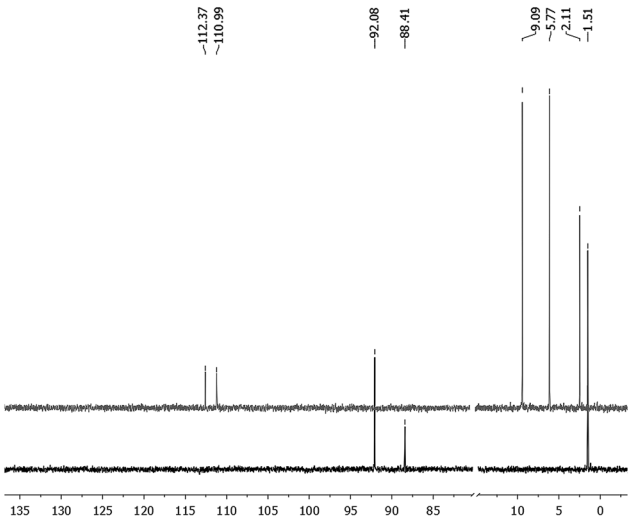


Fig. 2 ^{13}C NMR stacked spectra of **3B-2-Ge-Et** (grey – top) and **1A** (black – bottom).

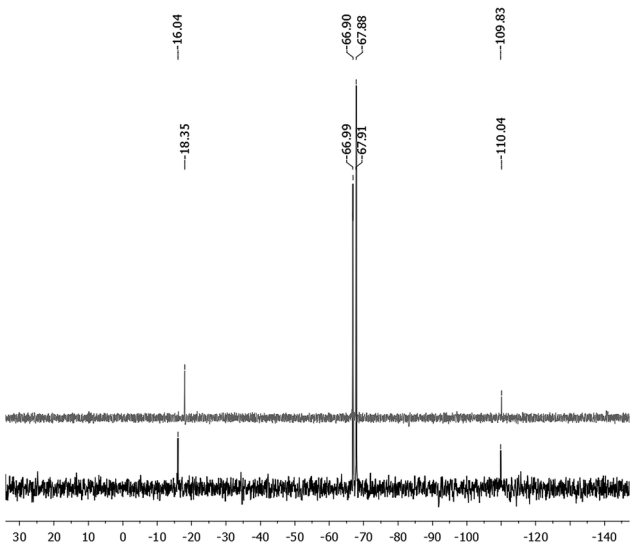


Fig. 3 ^{29}Si NMR stacked spectra of **3B-2-Ge-Et** (grey – top) and **1A** (black – bottom).

1.09 ppm (t, J = 7.9 Hz, 9H) and a quartet present at 0.86 ppm (q, J = 7.8 Hz, 6H), and they can be assigned to ethyl groups of germyl moieties. The germa(alkynyl) fragment affects the chemical shift of the methyl group at the silicon of the siloxy group (0.26 ppm) when compared with the substrate **1A-b** (0.30 ppm).

Fig. 2 shows a comparison of ^{13}C NMR spectra of ethynyl (dimethylsiloxy)hepta(isobutyl)-octasilsesquioxane (**1A-b**) and the product **3B-2-Ge-Et**. It can be noted that no resonance lines of free vinyl carbon moieties of **2-Ge-Et** (130.94 and 137.49 ppm), as well as terminal C≡CH bonds (88.59 and 92.26 ppm), are present in the spectrum of **3B-2-Ge-Et**. New signals for the substituted acetylene C≡C bonds appeared (110.99 and 112.37 ppm). The signals of carbon atoms derived from the i-Bu groups on ^{13}C NMR spectrum remain unaffected by the presence of a substituted germa(alkynyl) group and only a slight change in the chemical shift of methyl groups attached to the silicon of a spacer unit is visible (from 1.69 to 2.11 ppm) as well as arise of two resonance lines from ethyl moieties from germyl substituent (5.77 and 9.09 ppm).

With regard to the ^{29}Si NMR spectra, there is little difference in chemical shifts of silicon in the siloxy fragment in **1A** (−16.04 ppm) and **3B-2-Ge-Et** (−18.35 ppm). It is even less visible in the resonance line shift change for the Si (Q^4) core in substrate and product. The presented procedure ensures the efficiency of GC reaction and also allows the undesirable enynes to be avoided without the need for any inhibitor addition.

After the reaction condition optimization, a series of germaalkynyl POSS derivatives were obtained (Table 2). Products (**3A** and **3B**) were thoroughly analysed and their structures were confirmed *via* spectroscopic methods. The absence of a dimethylsiloxy linker between the POSS core and ethynyl moiety did not affect the POSS conversion.

As a result, we obtained 16 new germa(alkynyl)-substituted silsesquioxanes with excellent or good yields. All of them were isolated and characterized using spectroscopic techniques.

Stoichiometric reaction of $[Ru(Cl)(GeEt_3)(CO)(PPh_3)_2]$ (III) with 1-ethynyl(dimethylsiloxy)hepta(isobutyl)octasilsesquioxane (1A-b)

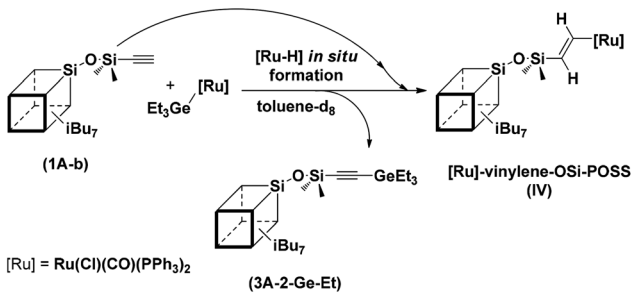
As was previously demonstrated for the germylative coupling mechanism of vinylgermanium compounds and terminal alkynes, $[Ru(Cl)(GeEt_3)(CO)(PPh_3)_2]$ (**III**) can be treated as an intermediate in the catalytic cycle. In order to understand better the mechanism of this reaction, an equimolar reaction between the ruthenium–germyl complex and **1A-b** was performed (Scheme 4).

The tests were performed under an argon atmosphere at different temperatures, starting from −20 to +60 °C, with a gra-

Table 2 Ruthenium-catalyzed germylation of ethynylsilsesquioxane derivatives[a]

Entry	**1A** and **1B**	**2**	Isolated yield [%] (**3A** and **3B**)
1	**1B-b**	-$GeEt_3$	94
2		-Ge(*n*-Bu)$_3$	75
3		-$GeMe_2Ph$	70
4	**1B-c**	-$GeEt_3$	69
5		-Ge(*n*-Bu)$_3$	96
6	**1B-d**	-$GeEt_3$	83
7		-Ge(*n*-Bu)$_3$	97
8	**1A-b**	-$GeEt_3$	87
9		-Ge(*n*-Bu)$_3$	89
10	**1A-a**	-$GeEt_3$	90
11		-Ge(*n*-Bu)$_3$	92
12		-$GeMe_2Ph$	68
13	**1A-c**	-$GeEt_3$	84
14		-Ge(*n*-Bu)$_3$	96
15	**1A-d**	-$GeEt_3$	82
16		-Ge(*n*-Bu)$_3$	97

[a] Reaction conditions: [**II**] : [**1A** or **1B**] : [**2**] = 2 × 10^{-2} : 1 : 1.5, 48 h, a closed system, argon, toluene (0.25 M).



Scheme 4 Stoichiometric reaction of [Ru(Cl)($GeEt_3$)(CO)(PPh_3)$_2$] (**III**) with **1A-b**.

dation step of 10 °C and monitored by ^{1}H, ^{31}P and ^{13}C NMR spectroscopy. The characteristic features of respective spectra are analogous to those presented in our first communication.[9] The formation of a [Ru–H] active species was detected at low temperature (product of alkyne insertion into Ru–Ge (**III**) complex, followed by elimination of **3A-2-Ge-Et**), confirmed by the presence of doublets of triplets at −6.46 ppm (J_{H-P} = 103.7 Hz, J_{H-P} = 24.5 Hz). With the rise of temperature, these resonance lines decrease as the ruthenium hydride complex reacts with the **1A-b** molecule, forming a [Ru]-vinylene-OSi-POSS (**IV**) complex – appearing as vinylene signals in the ^{1}H NMR spectrum at 8.98 (J_{H-H} = 13.7 Hz) and 5.69 ppm (J_{H-H} = 13.7 Hz) (Fig. 4).

The respective ^{31}P spectra of stoichiometric reactions also enable monitoring them with the starting Ru–Ge (**III**) complex with the 34.70 ppm (s, 2*P*Ph) resonance line. The signal of phosphines of the [Ru–H] complex which is formed *in-situ* is visible at 40.48 ppm (d, J_{H-P} = 15.6 Hz, 2*P*Ph) (with a slight shift in its resonance line) and almost invisible signal from the axial phosphine as well as the temperature gradation

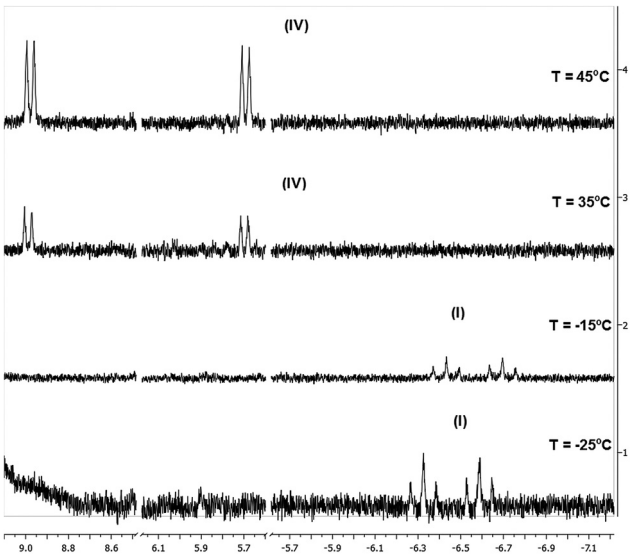


Fig. 4 ^{1}H NMR stacked spectra of temperature dependent stoichiometric reaction [Ru(Cl)($GeEt_3$)(CO)(PPh_3)$_2$] (**III**) with **1A-b**.

reveal the presence of arising signals at 31.74 ppm (s, 2*P*Ph), derived from appearing **IV** complex (Fig. 5) (analogous to its Ru-vinylene-SiR_3 derivatives[13]).

The elimination of a reaction product, *i.e.* **3A-2-Ge-Et**, may be confirmed from ^{13}C NMR spectra (presence of a substituted –CC– bond revealed by resonance lines at 110.19 and 112.28 ppm) of the post reaction mixture. These stoichiometric reactions could be performed due to the lower activity of the ruthenium PPh_3 (**I**) complex compared to (**II**) bearing PCy_3 ligands.

The results of stoichiometric experiments as well as the catalytic reaction data allow us to propose the mechanism for the coupling of vinylgermanes with ethynyl-substituted silsesquioxanes that follows a similar reaction mechanism

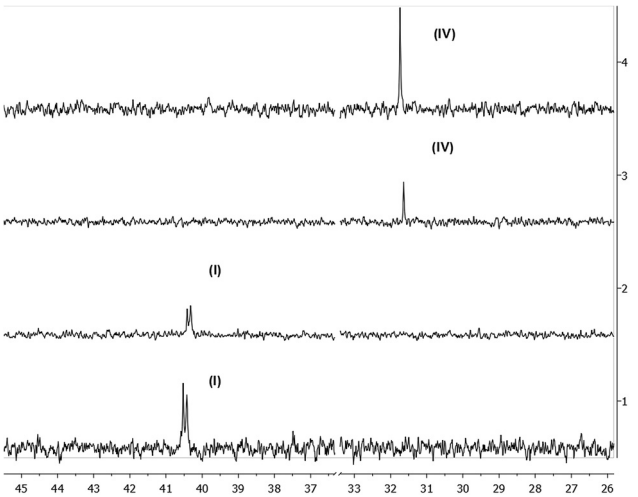
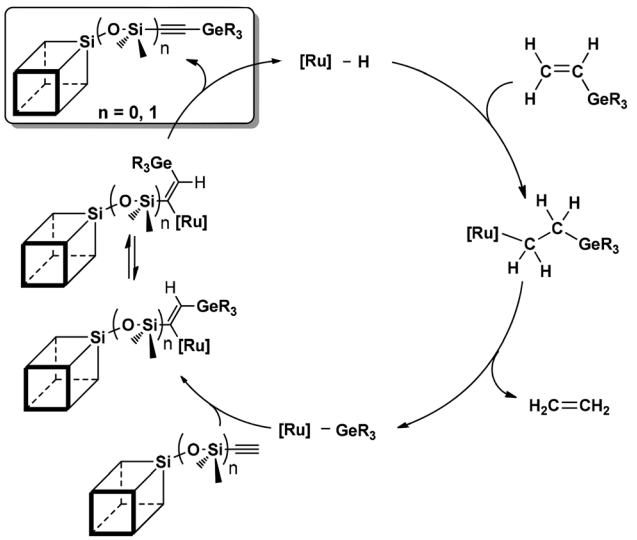


Fig. 5 ^{31}P NMR stacked spectra (they are presented in selected regions) of temperature dependent stoichiometric reaction [Ru(Cl)($GeEt_3$)(CO)(PPh_3)$_2$] (**III**) with **1A-b**.



Scheme 5 General mechanistic path for the germylative coupling of ethynyl(siloxy)silsesquioxanes with vinylgermanes.

pattern, *i.e.* a well-recognized insertion–elimination mechanism (Scheme 5).[9] In the first step, a vinylgermane insertion into the Ru–H bond occurs to give a β-germylethyl complex that decomposes *via* β-germyl group migration onto the ruthenium centre and ethylene evolution to form a [Ru]–GeR_3 complex. The next step involves migratory insertion of terminal alkyne into the Ru–Ge bond followed by isomerization of the intermediate ruthenium–alkenylsilsesquioxyl complex and subsequent β-H elimination of the product and ruthenium hydride coordination compound recovery. Since the POSS moiety attached to the ethynyl group (either by a dimethylsiloxy linker between the POSS core) is not involved in the first part of the catalytic cycle, the presence of the abovementioned –SiO– spacer does not affect the catalytic reactivity of either **1A** or **1B**. This test could not have been performed if the vinylgermane contained the POSS core, as has been reported lately.[8]

Experimental

Materials and methods

All syntheses and manipulations were carried out under an argon atmosphere using standard Schlenk-line and vacuum techniques. ^{1}H, ^{13}C, and ^{29}Si NMR spectra were recorded in $CDCl_3$ or [D_8]toluene (for stoichiometric reactions) using Varian XL 300 MHz and Bruker Avance 400 MHz spectrometers and referenced to the residual protonated solvent peaks (^{1}H δ_H = 7.26 ppm, ^{13}C δ_C = 77.0 ppm for $CDCl_3$ and ^{1}H δ_H = 2.09; 6.98–7.1 ppm, ^{13}C δ_C = 20.4; 125.49–137.86 ppm for [D_8] toluene) or external $Si(CH_3)_4$ (^{29}Si δ_{Si} = 0.00 ppm). Coupling constants are expressed in Hz. Mass spectrometry analyses were performed using a Synapt G2-S mass spectrometer (Waters) equipped with an electrospray ion source and a quadrupole-time-of-flight mass analyzer. Methanol was used as a solvent. The measurements were performed in positive ion mode with the desolvation gas flow of 600 L h^{-1} and the capillary voltage set to 4500 V with the flow rate of 100 μl min^{-1}. Fourier Transform-Infrared (FT-IR) spectra were recorded on a Bruker Tensor 27 Fourier transform spectrophotometer equipped with a SPECAC Golden Gate and a Diamond ATR unit at a resolution of 2 cm^{-1}. Elemental analyses were performed using a Vario EL III instrument. Stuart SMP30 apparatus was used for melting point determination.

The trisilanol precursors of POSS were obtained from Hybrid Plastics; other chemicals were purchased from Aldrich, ABCR and Gelest. $[Ru(Cl)(H)(CO)(PPh_3)_3]$,[14] $[Ru(Cl)(H)(CO)(PCy_3)_2]$,[15] $[Ru(Cl)(GeEt_3)(CO)(PPh_3)_2]$[16] and ethynyl(dimethylsiloxy)siloxy-silsesquioxanes (**1A**)[11] were prepared according to literature procedures. Thin layer chromatography (TLC) was performed on plates coated with 250 mm thick silica gel and column chromatography was performed on silica gel 60 (70–230 mesh) using *n*-hexane. All solvents and liquid reagents were dried and distilled under an argon atmosphere prior to being used.

Synthetic procedures

General procedure for the synthesis of ethynyl-substituted silsesquioxanes (1B). A mixture consisting of 1,3,5,7,9,11,14-heptaisobutyltricyclo[7.3.3.$1^{5,11}$]heptasiloxane-*endo*-3,7,14-riol (7.5 g, 9.5 mmol) (dried under vacuum for 30 min prior to use), triethylamine (4.63 mL, 33 mmol) and 150 mL of THF was placed under an Ar atmosphere in a Schlenk bomb flask fitted with a plug valve. The flask was placed in an ice bath and the respective amount of $SiCl_4$ (1.11 mL, 9.7 mmol) was added to the mixture dropwise. The suspension was stirred for 24 h at room temperature, and then chloro(heptaisobutyl)silsesquioxane was separated *via* cannula from ammonium salt and the filtrate was evaporated. In the next step, POSS-Cl was added dropwise to the respective amount of ethynylmagnesium bromide (0.5 M in THF) placed in a two-necked, 150 mL flask equipped with a reflux condenser and connected to a gas and vacuum line. The reaction mixture was maintained at 45 °C for 24 h. After the reaction completion, unreacted ethynylmagnesium bromide was decomposed with 4 mL of i-PrOH and water, and the product was extracted with $CHCl_3$. The organic phase was collected and dried with $MgSO_4$. The crude product was isolated by purification using column chromatography (SiO_2) with hexane as eluent, and then crystallized in methanol or acetonitrile as a white solid.

1-Ethynyl-3,5,7,9,11,13,15-hepta(isobutyl)-pentacyclo[9.5.1.$1^{3,9}$.$1^{5,15}$.$1^{7,13}$]-octasiloxane (1B-b). Yield: 4.62 g (58%); white solid; m.p. 215–219 °C; R_f = 0.49 (*n*-hexane; I_2). Anal. calcd for $C_{30}H_{64}O_{12}Si_8$ (%): C, 42.82; H, 7.67; found: C, 42.83; H, 7.67. **IR** (ATR) (cm^{-1}): 3298 (C_{sp}–H), 2954, 2927, 2871, 2058 (–CC–), 1464, 1383, 1366, 1332, 1229, 1090, 954, 838, 739, 685, 555, 473; **^{1}H NMR** (500 MHz, $CDCl_3$, 25 °C) δ 2.24 (s, 1H), 1.91–1.85 (m, 7H), 0.99–0.96 (m, 42H), 0.67–0.61 (m, 14H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 25 °C) δ 89.8 (CC), 82.2 (CC), 25.7, 25.6, 23.9, 23.8, 22.4, 22.2 ppm; **^{29}Si NMR** (99 MHz, $CDCl_3$, 25 °C) δ −66.70, −67.27, −67.83, −99.44 (HCC*Si*) ppm;

HRMS (FD). Calcd for $C_{30}H_{64}O_{12}Si_8$ + Na^+: *m*/*z* 863.2444 [M + Na^+]. Found: *m*/*z* 863.2411.

1-Ethynyl-3,5,7,9,11,13,15-hepta(cyclopentyl)-pentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]-octasiloxane (1B-c). Yield: 4.28 g (54%); white solid; m.p. >350 °C; R_f = 0.37 (*n*-hexane; I_2). Anal. calcd for $C_{37}H_{64}O_{12}Si_8$ (%): C, 48.01; H, 6.97; found: C, 48.09; H, 6.99. **IR** (ATR) (cm^{-1}): 3292 (C_{sp}–H), 2947, 2864, 2056 (–CC–), 1450, 1247, 1083, 948, 913, 827, 729, 685, 495; **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C) δ 2.24 (s, 1H), 1.77–1.72 (m, 14H), 1.59–1.50 (m, 42H), 1.09–0.95 (m, 7H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$, 25 °C) δ 89.6 (CC), 82.4 (CC), 27.3, 27.0, 22.2, 22.0 ppm; **^{29}Si NMR** (79 MHz, $CDCl_3$, 25 °C) δ −65.70, −66.20, −66.51, −98.33 (HCC*Si*) ppm.

1-Ethynyl-3,5,7,9,11,13,15-hepta(cyclohexyl)-pentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]-octasiloxane (1B-d). Yield: 4.10 g (52%); white solid; m.p. >350 °C; R_f = 0.43 (*n*-hexane; I_2). Anal. calcd for $C_{44}H_{78}O_{12}Si_8$ (%): C, 51.62; H, 7.68; found: C, 51.77; H, 7.71. **IR** (ATR) (cm^{-1}): 3292 (C_{sp}–H), 2921, 2848, 2057 (–CC–), 1447, 1264, 1196, 1095, 998, 894, 826, 738, 509; **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C) δ 2.25 (s, 1H), 1.73 (m, 28H), 1.25–1.23 (m, 42H), 0.86–0.79 (m, 7H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$, 25 °C) δ 89.7 (CC), 82.3 (CC), 27.5, 26.6, 26.5, 23.1, 22.8 ppm; **^{29}Si NMR** (99 MHz, $CDCl_3$, 25 °C) δ −67.97, −68.32, −68.55, −97.99 (HCC*Si*) ppm.

General procedure for germylative coupling of vinylgermane (2) with ethynyl(siloxy)silsesquioxanes (1A and 1B). The glass Schlenk reactor equipped with a magnetic stirring bar was evacuated and flushed with argon and a given amount of the ruthenium complex [RuH(CO)Cl(PCy_3)$_2$] (respective amount) was added, and then distilled and degassed toluene (2.3 mL), **1A** or **1B** (0.2 g) and **2** (respective amount) were added. The reaction was conducted in a closed system for 48 h. After the reaction was completed, a solvent and any excess of other volatile reagents were removed under reduced pressure. The crude product was isolated by purification using column chromatography (SiO_2) with hexane as an eluent and then crystallized in methanol or acetonitrile as a white/pale yellow solid.

The reaction of equimolar amounts of [Ru(GeEt$_3$)Cl(CO)(PPh_3)$_2$] with 1-ethynyldimethylsiloxy-3,5,7,9,11,13,15-hepta(isobutyl)pentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane (1A-b). In an equimolar test, the ruthenium catalyst [Ru(Cl)(GeEt$_3$)(CO)(PPh_3)$_2$] was placed in an NMR ampoule under an argon atmosphere along with a toluene-d8. The ampoule was cooled in a mixture of acetone/dry ice to −30 °C and **1A-b** (at the molar ratio of [Ru] : [triethylethynylgermane] = 1 : 1.2) was added subsequently. The following ^{1}H, ^{31}P and ^{13}C analyses were performed using a Bruker Avance 400 MHz spectrometer and recorded at different temperatures starting from −20 to +60 °C, with a gradation step of 10 °C.

Analytical data for obtained products

1-((Triethylgermyl)ethynyl)-3,5,7,9,11,13,15-hepta(isobutyl)-pentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane (1). (223 mg, 94% yield). White solid. R_f = 0.45 (*n*-hexane; I_2). Anal. calcd for $C_{36}H_{78}GeO_{12}Si_8$ (%): C, 43.22; H, 7.86; found: C, 43.38; H, 7.91. **IR** (ATR) (cm^{-1}): 2952–2871, 2160 (–CC–), 1464, 1366, 1332, 1228, 1089, 954, 837–701, 572, 475; **^{1}H NMR** (300 MHz, $CDCl_3$, 25 °C) δ 1.92–1.81 (m, 7H), 1.09 (t, *J* = 7.9 Hz, 9H), 0.99–0.96 (m, 42H), 0.86 (q, *J* = 7.8 Hz, 6H), 0.62 (d, *J* = 7.0 Hz, 6H), 0.60 (d, *J* = 7.0 Hz, 8H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$, 25 °C) δ 110.0 (CC), 105.2 (CC), 25.7, 23.8, 23.8, 22.5, 22.2, 8.8, 5.5 ppm; **^{29}Si NMR** (80 MHz, $CDCl_3$, 25 °C) δ −67.43, −67.89, −100.98 ppm; HRMS (FD). Calcd for $C_{36}H_{78}GeO_{12}Si_8$ + Na^+: *m*/*z* 1023.2751 [M + Na^+]. Found: *m*/*z* 1023.2740.

1-((Tri(*n*-butyl)germyl)ethynyl)-3,5,7,9,11,13,15-hepta(isobutyl)pentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane (2). (193 mg, 75% yield). White solid. R_f = 0.51 (*n*-hexane; I_2). Anal. calcd for $C_{42}H_{90}GeO_{12}Si_8$ (%): C, 46.52; H, 8.36; found: C, 46.62; H, 8.38. **IR** (ATR) (cm^{-1}): 2953–2862, 2161 (–CC–), 1452, 1261, 1090, 911, 792–701, 496; **^{1}H NMR** (300 MHz, $CDCl_3$, 25 °C) δ 1.92–1.81 (m, 7H), 1.46–1.32 (m, 18H), 0.99–0.95 (m, 42H), 0.93–0.89 (m, 9H), 0.65 (d, *J* = 6.9 Hz, 6H), 0.60 (d, *J* = 6.8 Hz, 8H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$, 25 °C) δ 110.8 (CC), 104.9 (CC), 27.5, 27.2, 26.5, 26.1, 23.8, 22.2, 13.7, 12.7 ppm; **^{29}Si NMR** (80 MHz, $CDCl_3$, 25 °C) δ −67.39, −67.46, −67.89, −100.95 ppm.

1-((Dimethylphenylgermyl)ethynyl)-3,5,7,9,11,13,15-hepta(isobutyl)-pentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane (3). (170 mg, 70% yield). White solid. R_f = 0.28 (*n*-hexane; I_2). Anal. calcd for $C_{38}H_{74}GeO_{12}Si_8$ (%): C, 44.73; H, 7.31; found: C, 44.81; H, 7.32. **IR** (ATR) (cm^{-1}): 2955–2870, 2162 (–CC–), 1451–1330, 1232, 1089, 953, 910, 790–684, 562, 483; **^{1}H NMR** (300 MHz, $CDCl_3$, 25 °C) δ 7.57 (s, 2H), 7.38 (s, 3H), 1.93–1.82 (m, 7H), 1.00–0.96 (m, 42H), 0.67 (d, *J* = 6,9 Hz, 6H), 0,61 (d, *J* = 7.45 Hz, 8H), 0.51 (s, 6H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$, 25 °C) δ 137.9, 133.1, 129.1, 128.8, 109.6 (CC), 105.2 (CC), 25.7, 25.7, 23.9, 23.8, 22.5, 22.2, −1.3 ppm; **^{29}Si NMR** (80 MHz, $CDCl_3$, 25 °C) δ −67.34, −67.86, −67.89, −100.88 ppm.

1-((Triethylgermyl)ethynyl)-3,5,7,9,11,13,15-hepta(cyclopentyl)pentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane (4). (162 mg, 69% yield). White solid. R_f = 0.35 (*n*-hexane; I_2). Anal. calcd for $C_{43}H_{78}GeO_{12}Si_8$ (%): C, 47.63; H, 7.25; found: C, 47.68; H, 7.27. **IR** (ATR) (cm^{-1}): 2949, 2865, 2161 (–CC–), 1450, 1253, 1091, 954, 912, 835–704, 495; **^{1}H NMR** (300 MHz, $CDCl_3$, 25 °C) δ 1.75–1.50 (m, 63H), 1.11 (t, *J* = 7.83 Hz, 9H), 0.92–0.84 (q, *J* = 7.7 Hz, 6H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$, 25 °C) δ 109.7 (CC), 105.5 (CC), 27.3, 27.0, 22.2, 22.0, 8.8, 5.5 ppm; **^{29}Si NMR** (80 MHz, $CDCl_3$, 25 °C) δ −65.56, −66.32, −66.56, −99.78 ppm.

1-((Tri(*n*-butyl)germyl)ethynyl)-3,5,7,9,11,13,15-hepta(cyclopentyl)pentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane (5). (242 mg, 96% yield). White solid. R_f = 0.52 (*n*-hexane; I_2). Anal. calcd for $C_{49}H_{90}GeO_{12}Si_8$ (%): C, 50.36; H, 7.67; found: C, 50.51; H, 7.70. **IR** (ATR) (cm^{-1}): 2950, 2865, 2160 (–CC–), 1450, 1264, 1090, 948, 913, 788–705, 497; **^{1}H NMR** (300 MHz, $CDCl_3$, 25 °C) δ 1.75–1.34 (m, 74H), 1.02–0.96 (m, 7H), 0.93–0.71 (m, 9H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$, 25 °C) δ 110.5 (CC), 105.3 (CC), 27.3, 27.0, 26.9, 26.1, 22.2, 22.1, 13.9, 13.7 ppm; **^{29}Si NMR** (80 MHz, $CDCl_3$, 25 °C) δ −65.56, −66.36, −66.56, −100.01 ppm; HRMS (FD). Calcd for $C_{49}H_{90}GeO_{12}Si_8$ + Na^+: *m*/*z* 1191.3690 [M + Na^+]. Found: *m*/*z* 1191.3701.

1-((Triethylgermyl)ethynyl)-3,5,7,9,11,13,15-hepta(cyclohexyl)pentacyklo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane (6). (192 mg, 83%

yield). White solid. R_f = 0.32 (*n*-hexane; I_2). Anal. calcd for $C_{50}H_{92}GeO_{12}Si_8$ (%): C, 50.78; H, 7.84; found: C, 50.92; H, 7.86. **IR** (ATR) (cm^{-1}): 2951, 2864, 2160 (–CC–), 1450, 1262, 1082, 953, 913, 825–705, 497; **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C) δ 1.73 (m, 28H), 1.26–1.23 (m, 42H), 1.11 (t, J = 7.5 Hz, 9H), 0.93–0.72 (q, J = 8.1 Hz, 6H), 0.79–0.72 (m, 7H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$, 25 °C) δ 109.9 (CC), 105.5 (CC), 27.5, 27.4, 26.6, 26.5, 23.1, 22.9, 8.9, 4.2 ppm; **^{29}Si NMR** (80 MHz, $CDCl_3$, 25 °C) δ −67.84, −67.95, −68.66, −99.43 ppm.

1-((Tri(*n*-butyl)germyl)ethynyl)-3,5,7,9,11,13,15-hepta(cyclohexyl)pentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane (7). (240 mg, 97% yield). White solid. R_f = 0.53 (*n*-hexane; I_2). Anal. calcd for $C_{56}H_{104}GeO_{12}Si_8$ (%): C, 53.10; H, 8.28; found: C, 53.26; H, 8.30. **IR** (ATR) (cm^{-1}): 2952, 2861, 2161 (–CC–), 1452, 1258, 1084, 914, 786–704, 496; **^{1}H NMR** (300 MHz, $CDCl_3$, 25 °C) δ 1.73–1.25 (m, 88H), 0.91 (t, J = 6.5 Hz, 9H), 0.86–0.76 (m, 7H) ppm; **^{13}C NMR** (75.48 MHz, $CDCl_3$, 25 °C) δ 110.7 (CC), 105.2 (CC), 27,5, 27.3, 26.6, 26.5, 26.0, 23.1, 22.9, 22.7, 13.9, 13.7 ppm; **^{29}Si NMR** (80 MHz, $CDCl_3$, 25 °C) δ −67.84, −68.45, −68.67, −99.83 ppm.

1-((Triethylgermylethynyl)dimethylsiloxy)-3,5,7,9,11,13,15-hepta(isobutyl)pentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane (8). (220 mg, 87% yield). White solid. R_f = 0.35 (*n*-hexane; I_2). Anal. calcd for $C_{38}H_{84}GeO_{13}Si_9$ (%): C, 42.48; H, 7.88; found: C, 42.55; H, 7.90. **IR** (ATR) (cm^{-1}): 2953–2872, 2161 (–CC–), 1464, 1366, 1229, 1075, 1009, 955, 836–705, 473; **^{1}H NMR** (300 MHz, $CDCl_3$, 25 °C) δ 1.90–1.84 (m, 7H), 1.10 (t, J = 7.6 Hz, 9H), 0.98–0.96 (m, 42H), 0.89–0.84 (q, J = 7.7 Hz, 6H), 0.64–0.60 (m, 14H), 0.27 (s, 6H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$, 25 °C) δ 112.2 (CC), 110.8 (CC), 25.7, 23.9, 23.8, 22.5, 22.3, 8.9, 5.6, 2.0 ppm; **^{29}Si NMR** (80 MHz, $CDCl_3$, 25 °C) δ −18.33, −66.98, −67.91, −110.03 ppm; HRMS (FD). Calcd for $C_{38}H_{84}GeO_{13}Si_9$ + Na^+: m/z 1097.2939 [M + Na^+]. Found: m/z 1097.2948.

1-((Tri(*n*-butyl)germylethynyl)dimethylsiloxy)-3,5,7,9,11,13,15-hepta(isobutyl)pentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane (9). (225 mg, 89% yield). White solid. R_f = 0.55 (*n*-hexane; I_2). Anal. calcd for $C_{44}H_{96}GeO_{13}Si_9$ (%): C, 45.61; H, 8.35; found: C, 45.69; H, 8.37. **IR** (ATR) (cm^{-1}): 2953–2870, 2160 (–CC–), 1461–1332, 1253, 1073, 1010, 955, 836–684, 539; **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C) δ 1.90–1.84 (m, 7H), 1.45–1.33 (m, 18H), 0.98–0.96 (m, 42H), 0.93–0.85 (m, 9H), 0.64–0.60 (m, 14H), 0.27 (s, 6H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 25 °C) δ 112.0 (CC), 111.9 (CC), 27.3, 26.0, 25.7, 25.7, 23.9, 23.8, 22.5, 22.3, 14.0, 13.7, 2.0 ppm; **^{29}Si NMR** (100 MHz, $CDCl_3$, 25 °C) δ −18.35, −66.98, −67.89, −110.09 ppm.

1-((Triethylgermylethynyl)dimethylsiloxy)-3,5,7,9,11,13,15-hepta(ethyl)pentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane (10). (219 mg, 90% yield). White solid. R_f = 0.31 (*n*-hexane; I_2). Anal. calcd for $C_{24}H_{56}GeO_{13}Si_9$ (%): C, 32.83; H, 6.43; found: C, 32.91; H, 6.44. **IR** (ATR) (cm^{-1}): 2960–2880, 2160 (–CC–), 1461, 1414, 1253, 1073, 1011, 966, 836–694, 528, 463; **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C) δ 1.09 (t, J = 7.8 Hz, 9H), 1.03–0.9 (m, 21H), 0.89–0.83 (q, J = 7.8 Hz, 6H), 0.65–0.58 (m, 14H), 0.30 (s, 6H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$, 25 °C) δ 112.2 (CC), 111.0 (CC), 8.9, 6.4, 5.6, 4.0, 1.9 ppm; **^{29}Si NMR** (80 MHz, $CDCl_3$, 25 °C) δ −17.93, −65.08, −65.75, −109.06 ppm; **HRMS** (FD). Calcd for $C_{24}H_{56}GeO_{13}Si_9$ + Na^+: m/z 901.0748 [M + Na^+]. Found: m/z 901.0743.

1-((Tri(*n*-butyl)germylethynyl)dimethylsiloxy)-3,5,7,9,11,13,15-hepta(ethyl)pentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane (11). (246 mg, 92% yield). White solid. R_f = 0.53 (*n*-hexane; I_2). Anal. calcd for $C_{30}H_{68}GeO_{13}Si_9$ (%): C, 37.45; H, 7.12; found: C, 37.57; H, 7.14. **IR** (ATR) (cm^{-1}): 2945, 2850, 2161 (–CC–), 1448, 1267, 1074, 1010, 960, 835–785, 485. **^{1}H NMR** (300 MHz, $CDCl_3$, 25 °C) δ 1.45–1.27 (m, 18H), 1.03–0.97 (m, 21H), 0.93–0.87 (m, 9H), 0.66–0.58 (m, 14H), 0.29 (s, 6H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 25 °C) δ 112.1 (CC), 111.9 (CC), 27.2, 26.0, 13.8, 13.7, 6.4, 3.9, 1.9 ppm; **^{29}Si NMR** (80 MHz, $CDCl_3$, 25 °C) δ −17.94, −65.07, −65.74, −109.09 ppm.

1-((Dimethylphenylgermylethynyl)dimetylsiloxy)-3,5,7,9,11,13,15-hepta(ethyl)pentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane (12). (170 mg, 68% yield). White solid. R_f = 0.29 (*n*-hexane; I_2). Anal. calcd for $C_{26}H_{52}GeO_{13}Si_9$ (%): C, 34.77; H, 5.84; found: C, 34.83; H, 5.85. **IR** (ATR) (cm^{-1}): 2953–2870, 2161 (–CC–), 1464–1332, 1228, 1072, 1009, 953, 837–684, 562, 473; **^{1}H NMR** (300 MHz, $CDCl_3$, 25 °C) δ 7.60–7.57 (m, 2H), 7.39–7.37 (m, 3H), 1.00 (t, J = 7.7 Hz, 21H), 0.65–0.59 (m, 14H), 0.33 (s, 6H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$, 25 °C) δ 138.4, 133.1, 128.9, 128.2, 111.9 (CC), 110.7 (CC), 6.5, 4.0, 1.8, −1.1 ppm; **^{29}Si NMR** (80 MHz, $CDCl_3$, 25 °C) δ −17.41, −65.03, −65.73, −108.95 ppm.

1-((Ethylgermylethynyl)dimethylsiloxy)-3,5,7,9,11,13,15-hepta(cyclopentyl)pentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane (13). (195 mg, 84% yield). White solid. R_f = 0.33 (*n*-hexane; I_2). Anal. calcd for $C_{45}H_{84}GeO_{13}Si_9$ (%): C, 46.65; H, 7.31; found: C, 46.76; H, 7.32. **IR** (ATR) (cm^{-1}): 2943–2848, 2162 (–CC–), 1461–1253, 1092, 1010, 965, 789–684, 539; 497; **^{1}H NMR** (500 MHz, $CDCl_3$, 25 °C) δ 1.77–1.72 (m, 28H), 1.59–1.50 (m, 42H), 1.09 (t, J = 7.9 Hz, 9H), 1.04–0.96 (m, 7H), 0.88–0.84 (q, J = 7.8 Hz, 6H), 0.29 (s, 6H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 25 °C) δ 112.3 (CC), 110.8 (CC), 27.3, 27.0, 22.2, 22.1, 8.9, 5.6, 2.0 ppm; **^{29}Si NMR** (99 MHz, $CDCl_3$, 25 °C) δ −18.24, −65.95, −66.55, −108.77 ppm; **HRMS** (FD). Calcd for $C_{45}H_{84}GeO_{13}Si_9$ + Na^+: m/z 1181.2939 [M + Na^+]. Found: m/z 1181.2935.

1-((Tri(*n*-butyl)germylethynyl)dimethylsiloxy)-3,5,7,9,11,13,15-hepta(cyclopentyl)pentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane (14). (238 mg, 96% yield). White solid. R_f = 0.58 (*n*-hexane; I_2). Anal. calcd for $C_{51}H_{96}GeO_{13}Si_9$ (%): C, 49.29; H, 7.79; found: C, 49.41; H, 7.81. **IR** (ATR) (cm^{-1}): 2925, 2850, 2160 (–CC–), 1447, 1268, 1091, 1017, 963, 896, 835, 475; **^{1}H NMR** (500 MHz, $CDCl_3$, 25 °C) δ 1.77–1.72 (m, 28H), 1.59–1.33 (m, 60H), 1.04–0.96 (m, 7H), 0.92–0.84 (m, 9H), 0.29 (s, 6H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 25 °C) δ 112.1 (CC), 111.9 (CC), 27.3, 27.3, 27.0, 26.0, 22.2, 22.1, 13.9, 13.7, 1.99 ppm; **^{29}Si NMR** (99 MHz, $CDCl_3$, 25 °C) δ −18.19, −65.95, −66.54, −108.76 ppm.

1-((Triethylgermylethynyl)dimethylsiloxy)-3,5,7,9,11,13,15-hepta(cyclohexyl)pentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane (15). (188 mg, 82% yield). White solid. R_f = 0.34 (*n*-hexane; I_2). Anal. calcd for $C_{52}H_{98}GeO_{13}Si_9$ (%): C, 49.70; H, 7.86;

found: C, 49.90; H, 7.88. **IR** (ATR) (cm^{-1}): 2962–2878, 2160 (–CC–), 1463, 1412, 1253, 1087, 1009, 956, 836–694, 528, 467; **^{1}H NMR** (500 MHz, $CDCl_3$, 25 °C) δ 1.75–1.73 (m, 28H), 1.26–1.23 (m, 42H), 1.10 (t, J = 7.9 Hz, 9H), 0.89–0.84 (q, J = 7.9 Hz, 6H), 0.80–0.72 (m, 7H), 0.30 (s, 6H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 25 °C) δ 112.3 (CC), 110.9 (CC), 27.5, 26.6, 26.5, 23.1, 23.0, 8.9, 5.6, 2.1 ppm; **^{29}Si NMR** (99 MHz, $CDCl_3$, 25 °C) δ −18.39, −68.05, −68.68, −108.78 ppm.

1-((Tri(*n*-butyl)germylethynyl)dimethylosiloxy)-3,5,7,9,11,13,15-hepta(cyclohexyl)pentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane (16). (236 mg, 97% yield). White solid. R_f = 0.57 (*n*-hexane; I_2). Anal. calcd for $C_{58}H_{110}GeO_{13}Si_9$ (%): C, 51.95; H, 8.27; found: C, 52.01; H, 8.28. **IR** (ATR) (cm^{-1}): 2921, 2848, 2161 (–CC–), 1447, 1268, 1089, 955, 895, 836, 514, 473; **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C) δ 1.75 (m, 28H), 1.46–1.31 (m, 18H), 1.27–1.23 (m, 42H), 0.93–0.85 (m, 9H), 0.78–0.76 (m, 7H), 0.30 (s, 6H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$, 25 °C) δ 112.05 (CC), 112.04 (CC), 27.5, 27.3, 26.6, 26.5, 26.0, 23.1, 23.0, 13.9, 13.7, 2.1 ppm; **^{29}Si NMR** (99 MHz, $CDCl_3$, 25 °C) δ −18.32, −68.04, −68.67, −108.71 ppm.

Conclusions

This work has shown that ethynyl-substituted silsesquioxanes with or without a –SiO– linker between the POSS core an ethynyl moiety, may be used as reagents in effective germylative coupling with vinylgermane. This is the first paper to report on silsesquioxane derivatives with alkynyl and germyl functionality. A series of the obtained products of these reactions possess alkynyl and germyl functionality at one POSS unit and their structures were confirmed by spectroscopic methods. The results of catalytic studies as well as stoichiometric reactions of the Ru–Ge (**III**) complex with ethynyl(siloxy) silsesquioxane enabled us to confirm and propose the general mechanistic scheme of this process.

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