EurJIC
European Journal of Inorganic Chemistry

A Journal of ChemPubSoc Europe

Accepted Article

Title: Vinyl functionalized silsesquioxanes and germasilsesquioxanes

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To be cited as: *Eur. J. Inorg. Chem.* 10.1002/ejic.201700465

Link to VoR: http://dx.doi.org/10.1002/ejic.201700465

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Vinyl functionalized silsesquioxanes and germasilsesquioxanes

Magdalena Grzelak,[a] Dawid Frąckowiak,[b] and Bogdan Marciniec*[a,b]

Abstract: We report herein an efficient procedure for the synthesis of new POSS derivatives, as a multifunctional reagents. This study concerns the incompletely condensed silsesquioxanes and germasilsesqiuoxanes with vinylsubstituted silyl and germyl functional groups which allow to further modification. Furthermore, our experiments have been extended to synthesis new subclass of completely condensed vinylgermasilsesquioxanes. These hybrid building blocks were obtained selectively within a few hours and were isolated with excellent yields.

Introduction

Polyhedral oligomeric silsesquioxanes (POSS) make a large class of structurally well-defined inorganic-organic materials. Thanks to their nanometric size and unusual three-dimensional structure of the silicon-oxygen core they are suitable for the introduction to the hybrid systems. A considerable number of reactions has been proposed that allow straightforward functionalization of POSS endowing them with well-defined physical, chemical and biological properties.[1] Furthermore, silsesquioxanes are also used in composite materials,[2] as hanging groups[3] or dendrimeric cores[4] for the synthesis of hybrid integrated POSS-chromophores which can be used in organic light emitting diodes (OLEDs).[5]

Currently, the most widely described group of POSS are completely condensed silsesquioxanes (Figure 1 A, B)[6] with various organic substituents.[7] Over the past few years, research on incompletely condensed silsesquioxanes have been also extended (Figure 1 C, D, E).[8]

The number of reports regarding the modified incompletely condensed silsesquioxanes is scarce.[9] However, these compounds exhibit distinct physicochemical properties and different reactivity.[10] Only a few examples have been reported in literature on modification of POSS silanols in reactions with chlorosilanes that lead to the formation of incompletely condensed silsesquioxane derivatives. Lorenz et al. have provided only one example of complete substitution of the trisilanolcyclohexyl POSS -OH groups with chlorodimethylvinylsilane.[11] Other examples are based on the substitution of one or two groups in trisilanol POSS,[10,12] and then the formation of complexes, e.g. with tetrahedrally coordinated tin atom.[13] There are also reports on trimethylsilyl (TMS)-capped compounds, e.g. trimethylsilylated heptaphenylsilsesquioxane.[14]

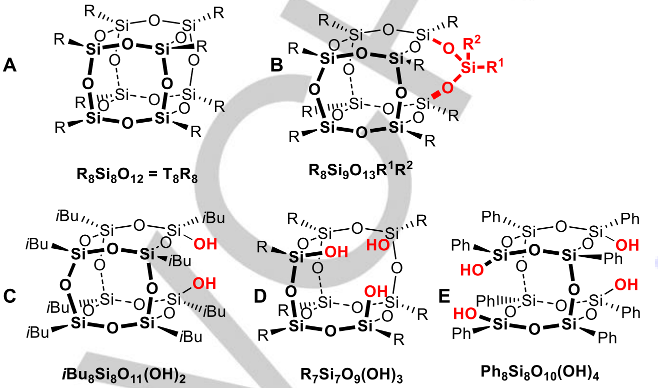

Figure 1. General structures of completely condensed silsesquioxanes (A,B), and POSS silanols (C,D,E).

Recently, studies on the POSS chemistry have been extended to include heterosilsesquioxanes, e.g. germasilsesquioxanes. These compounds containing Ge-O-Si moiety in their structure combine the features of the known silsesquioxanes and germasiloxanes, with improved parameters, e.g. higher refractive index.[15] First germasilsesquioxane has been synthesized by Feher et al.[16] while Roesky and co-workers have described the synthesis of a cubic germasilsesquioxane containing four germanium atoms.[17] Other studies have concerned theoretical calculations.[18] Our group has synthesized the fully condensed vinylgermasilsesquioxanes and dimethylvinylgermoxysilsesquioxanes,[19] as well as double-decker germasilsesquioxane and examined their reactivity in olefin cross-metathesis.[20] So far, there has been no reports on the synthesis of incompletely condensed POSS with germanium atoms.

This study was undertaken to design vinylsubstituted silsesquioxane and germasilsesquioxane derivatives and to provide an efficient procedure for their synthesis. The condensation reactions of chloroalkylvinyl- and chloroarylvinylsilanes and germanes with POSS silanols allowed us to obtain various types of incompletely condensed POSS with vinylsubstituted Si and Ge atoms. Introduction of vinylmetalloid moieties make them a good multifunctional templates for further modifications e.g. as polydentate ligands for the metal complexes and cross linking agents for composite materials. Furthermore, our experiments have been extended to synthesis of a new subclass of completely condensed vinylgermasilsesquioxanes.

Results and Discussion

The first stage of our studies was to develop efficient synthetic methods for the preparation of chlorovinylgermanes which in contrast to silicon analogues are not commercially available.

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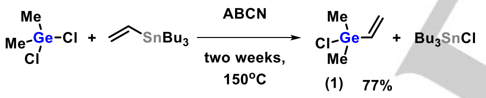
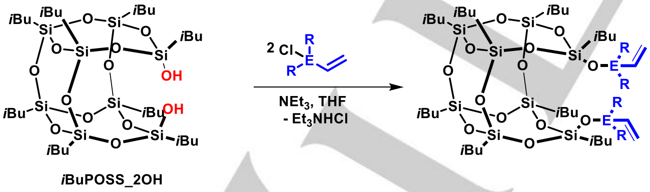
Chloroarylvinyl- and chloroalkylvinylgermanes can be synthesized by transmetalation of chlorogermanes with organotin reagents in the presence of radical initiator.[19-21] These reactions were carried out under inert gas atmosphere (Ar), using a vacuum-gas line and a standard Schlenk techniques due to the sensitivity of the reagents. The next step was condensation of POSS silanols and the respective chlorovinylometalloids. Our introductory experiments showed that it was necessary to use dilute THF solutions of reagents to avoid side reactions. At the initial stage of the process the reaction mixture was cooled in an ice bath. Then, chlorometalloid was added, and the cooling bath was left to warm up to room temperature. The progress of the condensation reaction (disappearance of the signals from stretching vibrations of the -OH in POSS silanols) was analyzed by FT-IR. At the end the crude product was isolated from the reaction mixture and purified.

Synthesis of incompletely condensed silsesquioxanes and germasilsesquioxanes

We converted the commercially available dichlorodimethylgermane to chlorodimethylvinylgermane via ABCN-mediated transmetallation with tributylvinylstannane (Scheme 1). Chlorodimethylvinylgermane **(1)** was isolated by trap-to trap distillation of the reaction mixture in 77% yield (purity ca. 98%). The next step of the synthesis of the open caged POSS was a typical condensation reaction of commercially available POSS di- and trisilanols with chloroarylvinyl- and chloroalkylvinylmetalloids in the presence of triethylamine as a base (Scheme 2).



Scheme 1. Synthesis of chlorodimethylvinygermane.

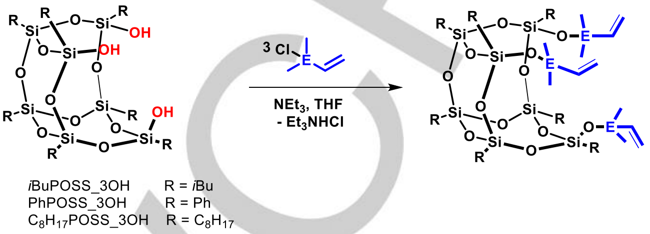


R = Me, E = Si **(2)** R = Me, E = Ge **(3)** R = Ph, E = Si **(4)**

Scheme 2. Synthesis of divinylyfunctional silsesquioxane and germasilesquioxane derivatives.

For the synthesis of divinylfunctional POSS we used disilanolisobutyl POSS (*i*BuPOSS_2OH) and chlorodimethylvinylsilane, chlorodiphenylvinylsilane and chlorodimethylvinylgermane respectively to obtain the final products **2-4** (Scheme 2).

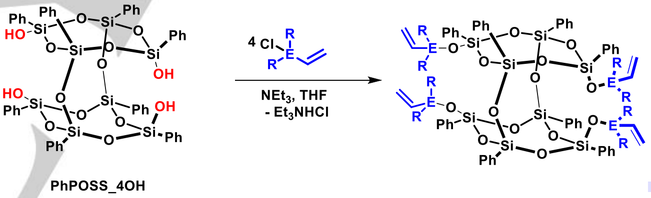
Following the procedure adopted before, we used the same reaction conditions for condensation and we obtained trivinylfunctional silsesquioxanes and germasilsesquioxanes **(5-9)** from trisilanol(isobutyl/phenyl/isooctyl) POSS (*i*Bu/Ph/C_8H_{17}_3OH POSS) and the same vinylmetalloids (Scheme 3).



R = *i*Bu, E = Si **(5)**, R = *i*Bu, E = Ge **(6)**, R = Ph, E = Si **(7)**, R = Ph, E = Ge **(8)**, R = C_8H_{17}, E = Si **(9)**,

Scheme 3. Synthesis of trivinylyfunctional silsesquioxane and germasilesquioxane derivatives.

Taking into consideration the positive results of the previous syntheses, we decided to expand the range of obtained compounds to the derivatives containing four vinyl groups. The tetravinylfunctional derivatives **(10-11)** were prepared in the same way as trifunctional POSS (Scheme 4).



R = Me, E = Ge **(10)**, R = Ph, E= Si **(11)**

Scheme 4. Synthesis of tetravinylyfunctional silsesquioxane and germasilesquioxane derivatives.

In each case the product was isolated and purified in an analogous manner (by evaporation of the solvent from the reaction mixture and then extraction from water-toluene mixture) Then, toluene extracts were dried over magnesium sulfate, filtered off and evaporated to dryness. Results of our experiments are collected in Table 1.

Table 1. Condensation of POSS silanols with monochlorovinylmetalloids

POSS silanol	$R_2E(Cl)CH=CH_2$	Product	Reaction time [h][a]	Isolated yield [%]
*i*BuPOSS_2OH	$Me_2Si(Cl)CH=CH_2$	2	2	92
*i*BuPOSS_2OH	$Me_2Ge(Cl)CH=CH_2$	3	2.5	91
*i*BuPOSS_2OH	$Ph_2Si(Cl)CH=CH_2$	4	4	91

*i*BuPOSS_3OH	$Me_2Si(Cl)CH=CH_2$	5	2.5	90
*i*BuPOSS_3OH	$Me_2Ge(Cl)CH=CH_2$	6	3	91
PhPOSS_3OH	$Me_2Si(Cl)CH=CH_2$	7	3	93
PhPOSS_3OH	$Me_2Ge(Cl)CH=CH_2$	8	3	90
C_8H_{17}POSS_3OH	$Me_2Si(Cl)CH=CH_2$	9	2.5	92
PhPOSS_4OH	$Me_2Ge(Cl)CH=CH_2$	10	4	90
PhPOSS_4OH	$Ph_2Si(Cl)CH=CH_2$	11	4	91

[POSS silanol] : [chlorometalloid] = 1 : 2 (products 2, 3, 4), 1 : 3 (products 5-9), 1 : 4 (products 10, 11), THF, 0-25°C, 2-4 h, reactions carried out in an open system [a] progress of the reaction was followed by IR spectroscopy

The HRMS and NMR spectral analysis of the compounds showed their high purity. The ^{1}H and ^{29}Si NMR spectra of **(5)** showed us a pretty clean example of trifunctionalvinylsilsesquioxane (Figure 2).

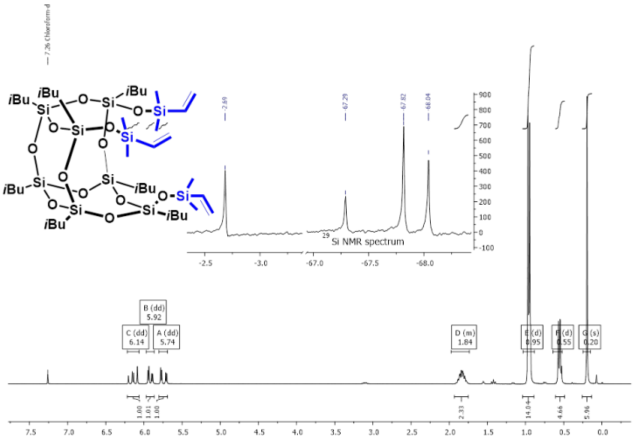
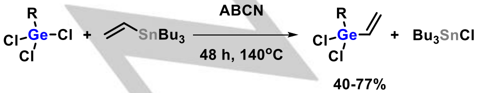


Figure 2. Example of the ^{1}H NMR and ^{29}Si NMR spectrum of 5 (after isolation) in $CDCl_3$ at 25 °C.

Synthesis of completely condensed germasilsesquioxanes

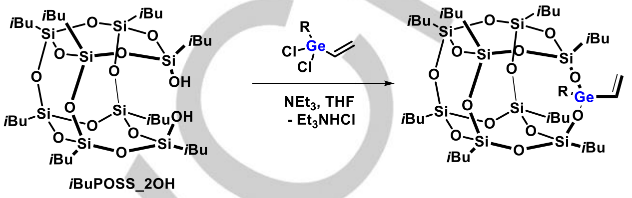
The outcome of our earlier studies enabled us to work out effective syntheses of di-, tri- and tetrafunctional derivatives and encouraged us to extend the range of our studies. The absence of literature reports on capping reaction of disilanolisobutyl POSS with dichlorogermanes prompted us to synthesise a new subclass of germasilsesquioxanes. Firstly, we successfully synthesized selected dichloro(alkyl/aryl)vinylgermanes from the commercially available trichlorogermanes (Scheme 5).



R = Me **(12)**, Et **(13)**, Ph **(14)**

Scheme 5. Synthesis of dichloro(alkyl/aryl)lvinylgermanes.

Equimolar reaction of disilanolisobutyl POSS (*i*BuPOSS_2OH) and dichloromethylvinylgermane **(12)**, dichloroethylvinylgermane **(13)** or dichlorophenylvinylgermane **(14)** led to formation of completely condensed germasilsesquioxanes **(15-17)** with front-ended germyl moiety in silicon-oxygen core.



R = Me **(15)**, Et **(16)**, **Ph (17)**

Scheme 6. Synthesis of completely condensed *g*ermasilsesquioxanes.

Products **15-17** were purified in a similar fashion as the incompletely condensed sil- and germasilsesquioxanes and were obtained in high yields (91-95%) (Table 2).

Table 2. Condensation of *i*BuPOSS_2OH silanol with dichlorovinylgermanes

POSS silanol	$R_2E(Cl)CH=CH_2$	Product	Reaction time [h][a]	Isolated yield [%]
*i*BuPOSS_2OH	$Me_2Ge(Cl)CH=CH_2$	15	6	95
*i*BuPOSS_2OH	$Et_2Ge(Cl)CH=CH_2$	16	6	92
*i*BuPOSS_2OH	$Ph_2Ge(Cl)CH=CH_2$	17	8	91

[POSS silanol] : [dichlorometalloid] = 1 : 1 (products 15, 16, 17), THF, 0-25°C, 6-8 h, reactions carried out in an open system [a] progress of the reaction was followed by IR spectroscopy

As mentioned above, the reaction progress was followed by FT-IR spectroscopy by sampling of the reaction mixture. We observed disappearance of the characteristic band of -OH in POSS silanol 3000cm^{-1} during the course of reaction. The reaction was run over for 2-4 h **(2-11)** and for 6-8 h **(15, 16, 17)**. We discovered that after such a short time the conversion of substrates was complete in 100%. The IR spectra of reaction mixtures of **15–17** after complete conversion of POSS silanols and disilanolisobutyl POSS are shown in Figure 3. The reason for longer condensation time of silanol POSS with chlorogermanes is the poorer reactivity of the former in substitution reactions.

All POSS derivatives (**2-11** and **15-17**) were obtained in excellent yields and were fully characterized by ^{1}H, ^{13}C and ^{29}Si NMR as well as HRMS mass spectrometry. These compounds are air-stable white powders and gels, which are easy to handle and can be prepared on a multigram scale. Furthermore, the solubility of obtained compounds in common organic solvents was good.

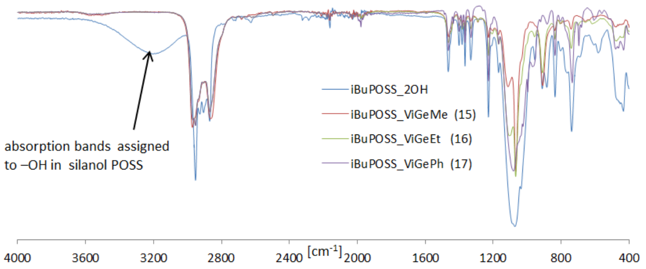


Figure 3. Example of the IR spectra of a reaction mixtures of 15 and 16 (after 6 h) and 17 (after 8 h) compared to disilanolisobutyl POSS.

Conclusions

We prepared novel incompletely condensed silsesquioxanes and germasilsesquioxanes and completely condensed germasilsesquioxanes with vinylsubstituted metalloid groups that could be used for further functionalization. We reveal simple and efficient way of their synthesis and isolation with high purity. The study presented is an important element in the search for new materials and efficient methods of their syntheses. Physicochemical properties of incompletely condensed silsesquioxanes that result from their open framework make them attractive potential ligand systems and unique cross linking agents.

Experimental Section

Methods and Materials: The chemicals were obtained from the following sources: toluene, tetrahydrofuran, magnesium sulfate ($MgSO_4$) from Chempur and P.O.Ch. Gliwice, triethylamine, chloro(dimethyl)vinylsilane, chloroform-d ($CDCl_3$), tributylchlorostannane, vinylmagnesium bromide, ABCN (1,1'-Azobis(cyclohexanecarbonitrile) from Sigma Aldrich, chloro(diphenyl)vinylsilane, trichloromethylgermane from ABCR, dichlorodimethylgermane, trichloroethylgermane, trichlorophenylgermane form Gelest, disilanolisobutyl POSS, trisilanolisobutyl POSS, trisilanolphenyl POSS, trisilanolisooctyl POSS, tetrasilanolphenyl POSS from Hybrid Plastics. Tributylvinylstannane was prepared according to the procedure given in literature. [22]
Liquid substrates were purified by 'bulb-to-bulb' distillation and degassed. All the syntheses of chloro(alkyl/aryl)vinylgermananes were carried out under an inert argon atmosphere. Tetrahydrofuran was dried over sodium benzophenone ketyl and freshly distilled prior to use.
Nuclear magnetic resonance (NMR) spectroscopy: ^{1}H NMR (300, 400 MHz), ^{13}C NMR (75, 101 MHz) and ^{29}Si NMR (79 MHz) spectra were recorded on a Varian XL 300 MHz spectrometer, Varian VNMR-S 400 MHz spectrometer in $CDCl_3$ solution. Chemical shifts are reported in δ (ppm) with reference to the residue solvent (^{1}H NMR δ_H = 7.26 ppm, ^{13}C NMR δ_C = 77.36 ppm for $CDCl_3$). The mass spectra of the chlorovinylgermanes were obtained by GC-MS analysis (Varian Saturn 2100T, equipped with a CP-SLI 6CB capillary column (30 m × 0.25 mm) and an ion trap detector). Mass spectrometry analyses were performed using a Synapt G2-S HDMS (Waters) and UltrafleXtreme (Bruker) mass spectrometer equipped with the electrospray ion source and quadrupole-time-of-flight mass analyzer.

Synthesis of vinylchlorogermanes

Chlorodimethylvinylgermane **(1)**[19] and dichloroethylvinylgermane **(13)** [20] were prepared according to the procedures given in literature.

Dichloromethylvinylgermane (12): A glass Schlenk reactor equipped with Rotaflo® stopcock and filled with argon was charged with tributylvinylstannane (7.5 mL, 25.7 mmol), trichloromethylgermane (2.93 mL, 25.7 mmol) and ABCN (0.3 g, 1.2 mmol). The whole mixture was frozen in liquid nitrogen bath and subjected to freeze-pump-thaw cycling. After the mixture warmed up to room temperature, it was heated on an oil bath for the 48 h, at 130°C. Then the reaction mixture was cooled down to room temperature and transferred to 25 mL round bottom flask. Careful trap-to-trap distillation gave 3.28 g (70% yield) of dichloromethylvinylgermane. ^{1}H NMR ($CDCl_3$, δ, ppm): 6.43 (dd, 1H), 6.25 (dd, 1H), 6.09 (dd, 1H), 1.25 (s, 3H). ^{13}C NMR ($CDCl_3$, δ, ppm): 135.43, 134.64, 8.94; MS: m/z (rel. intensity): 186 (17), 171 (100), 167 (39), 159 (31)

Dichlorophenylvinylgermane (14): A 25 mL high-pressure Rotaflo Schlenk vessel connected to gas and vacuum line was filled with ABCN (0.152 g, 0.62 mmol), tributylvinylstannane (4.56 mL, 15.62 mmol) and trichlorophenylgermane (2.51 mL, 4 g, 15.62 mmol). The whole mixture was frozen in liquid nitrogen bath and subjected to freeze-pump-thaw cycling. After the mixture warmed up to room temperature, it was heated on an oil bath for the 24 h at 140°C. The reaction mixture was cooled down to room temperature and transferred to 25 mL round bottom flask. Fractional distillation gave 1.55 g (40% yield) of dichlorophenylvinylgermane (contaminated with ca. 5% of Bu_3SnCl).
^{1}H NMR ($CDCl_3$, δ, ppm): 7.79 – 7.32 (m, 7H), 6.53 (dd, 1H), 6.36 (dd, 1H), 6.18 (dd, 1H). ^{13}C NMR ($CDCl_3$, δ, ppm): 136.94, 134.52, 133.24, 132.58, 132.55, 131.96, 131.55, 129.62, 129.16, 128.89; MS: m/z (rel. intensity): 248 (7), 221 (14), 186 (16), 109 (28), 104 (100), 77 (35), 51 (42)

Synthesis of POSS compounds

Difunctional compounds

***i*$Bu_8Si_8O_{11}[OSiMe_2(CH{=}CH_2)]_2$ (2):** A two-necked, 250 mL flask equipped with a magnetic stirring bar, reflux condenser and connected to gas and vacuum line was charged under argon with disilanolisobutyl POSS (2 g, 2.24 mmol), tetrahydrofuran (80 mL), and triethylamine (1.25 mL, 8.96 mmol). The reaction mixture was cooled in an ice bath and then chloro(dimethyl)vinylsilane (0.62 mL, 4.49 mmol) was added dropwise and the cooling bath left to warm up to room temperature. The molar ratio of the reactants was as follows: [silanol POSS] : [chlorovinylmetalloid] = 1 : 2. Progress of the reaction was followed by IR spectroscopy. After that, tetrahydrofuran was evaporated from the filtrate on rotary evaporator. Crude product was purified by extraction in toluene-water system, dried over anhydrous $MgSO_4$, filtered off. The excess of solvent was evaporated under vacuum. The product was thoroughly dried giving waxy solid (2.19 g, 92%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.23 – 6.08 (m, 2H), 5.93 (dd, 2H), 5.74 (dd, 2H), 1.92 – 1.77 (m, 8H), 0.96 (m, 48H), 0.57 (m, 16H), 0.23 (s, 4H), 0.19 (s, 8H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.37, 131.91, 26.13, 26.06, 26.01, 25.94, 25.87, 25.79, 25.06, 24.06, 23.73, 23.18, 22.65, 0.44, -0.03. ^{29}Si NMR (79 MHz, $CDCl_3$) δ -2.33, -65.94, -65.99, -68.03. HRMS (m/z) calcd for $C_{40}H_{90}O_{13}Si_{10}Na$: 1081.39, found 1081.39.
***i*$Bu_8Si_8O_{11}[OGeMe_2(CH{=}CH_2)]_2$ (3):** Product (3) was prepared using the same procedure and the following reagents: disilanolisobutyl POSS (1 g, 1.12 mmol), tetrahydrofuran (40 mL), triethylamine (0.63 mL, 4.49 mmol) and chloro(dimethyl)vinylgermane (0.29 mL, 2.35 mmol). Finally, a waxy solid was obtained (1.2 g, 91%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.24 – 6.07 (m, 2H), 5.92 (dd, 2H), 5.74 (dd, 2H), 2.0 – 1.71 (m, 8H), 0.96 (m, 48H), 0.58 (m, 16H), 0.19 (s, 12H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.55, 131.74, 25.95, 25.81, 24.08, 23.26, 23.20, 22.64, 22.59, 0.65. ^{29}Si NMR (79 MHz, $CDCl_3$) δ -57.90, -66.65, -68.39. HRMS (m/z) calcd for $C_{40}H_{90}Ge_2O_{13}Si_8$: 1150.30, found 1149.31.
***i*$Bu_8Si_8O_{11}[OSiPh_2(CH{=}CH_2)]_2$ (4)** Product (4) was prepared using the same procedure and the following reagents: disilanolisobutyl POSS (1 g, 1.12 mmol), tetrahydrofuran (40 mL), triethylamine (0.63 mL, 4.49 mmol) and chloro(diphenyl)vinylsilane (0.5 mL, 2.24 mmol). Finally, a waxy solid was obtained (1.34 g, 91%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 –7.07 (m, 20H), 6.53 – 6.33 (m, 2H), 6.24 – 6.02 (m, 2H), 5.92 – 5.62 (m, 2H), 1.87 – 1.57 (m, 8H), 0.95 – 0.68 (m, 48H), 0.58 – 0.34 (m, 16H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.69, 135.08, 134.97, 134.74, 130.25, 129.92, 129.56, 128.08, 127.78, 127.59, 26.10, 25.95, 24.00. ^{29}Si NMR (79 MHz, $CDCl_3$)

δ -6.29, -67.62, -67.79, -68.29. HRMS (m/z) calcd for $C_{60}H_{98}O_{13}Si_{10}Na$: 1329.46, found 1330.45.

Trifunctional compounds: These compounds were prepared using an analogous procedure and the following molar ratio of the reactants: [silanol POSS] : [chlorovinylmetalloid] = 1 : 3

$iBu_7Si_7O_9[OSiMe_2(CH=CH_2)]_3$ (5): Product (5) was prepared using the same procedure and the following reagents: trisilanolisobutyl POSS (2 g, 2.52 mmol), tetrahydrofuran (80 mL), triethylamine (2.11 mL, 15.16 mmol) and chloro(dimethyl)vinylsilane (1.05 mL, 7.58 mmol). Finally, a waxy solid was obtained (2.38 g, 90%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.14 (dd, 3H), 5.92 (dd, 3H), 5.74 (dd, 3H), 1.97 – 1.74 (m, 7H), 0.95 (d, 42H), 0.55 (d, 14H), 0.20 (s, 18H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.31, 131.91, 26.17, 26.01, 25.78, 25.12, 24.21, 24.10, 23.88, 0.50. ^{29}Si NMR (79 MHz, $CDCl_3$) δ -2.69, -67.29, -67.82, -68.04. HRMS (m/z) calcd for $C_{40}H_{90}O_{12}Si_{10}Na$: 1065.40, found 1065.40.

$iBu_7Si_7O_9[OGeMe_2(CH=CH_2)]_3$ (6): Product (6) was prepared using the same procedure and the following reagents: trisilanolisobutyl POSS (2 g, 2.52 mmol), tetrahydrofuran (80 mL), triethylamine (2.11 mL, 15.16 mmol) and chloro(dimethyl)vinylgermane (0.93 mL, 7.58 mmol). Finally, a waxy solid was obtained (2.72 g, 91%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.42 – 6.27 (m, 3H), 5.97 (dd, 3H), 5.73 (dd, 3H), 1.92 – 1.80 (m, 7H), 0.95 (d, 42H), 0.55 (m, 14H), 0.49 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.57, 139.11, 131.45, 131.01, 26.28, 26.14, 25.85, 25.77, 24.34, 24.06, 1.36, 1.00. ^{29}Si NMR (79 MHz, $CDCl_3$) δ -58.00, -63.76, -64.83, -66.65, -67.44, -67.53, -68.28, -68.55. HRMS (m/z) calcd for $C_{40}H_{90}Ge_3O_{12}Si_7Na$: 1203.24, found 1201.24.

$Ph_7Si_7O_9[OSiMe_2(CH=CH_2)]_3$ (7): Product (7) was prepared using the same procedure and the following reagents: trisilanolphenyl POSS (2 g, 2.14 mmol), tetrahydrofuran (120 mL), triethylamine (1.8 mL, 12.88 mmol) and chloro(dimethyl)vinylsilane (0.89 mL, 6.44 mmol). Finally, a white solid was obtained (2.38 g, 93%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 – 7.02 (m, 35H), 6.22 (dd, 3H), 5.98 (dd, 3H), 5.83 (dd, 3H), 0.31 (s, 15H), 0.15 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 134.17, 132.88, 132.55, 131.27, 130.22, 127.60, 0.54. ^{29}Si NMR (79 MHz, $CDCl_3$) δ -0.15, -77.39, -77.78, -78.14. HRMS (m/z) calcd for $C_{54}H_{62}O_{12}Si_{10}Na$: 1205.18, found 1205.18.

$Ph_7Si_7O_9[OGeMe_2(CH=CH_2)]_3$ (8): Product (8) was prepared using the same procedure and the following reagents: trisilanolphenyl POSS (2.5 g, 2.68 mmol), tetrahydrofuran (140 mL), triethylamine (2.24 mL, 16.1 mmol) and chloro(dimethyl)vinylgermane (0.99 mL, 8.05 mmol). Finally, a waxy solid was obtained (3.19 g, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92– 7.04 (m, 35H(-Ph)), 6.41 – 5.22 (m, 9H(-CH=CH$_2$)), 0.72 – 0.07 (m, 18H(-CH$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.93, 138.81, 138.60, 134.66, 134.47, 134.37, 134.29, 131.52, 131.38, 131.27, 130.21, 130.11, 129.79, 129.70, 127.91, 127.70, 127.53, 127.43, 1.41, 1.18, 0.76. ^{29}Si NMR (79 MHz, $CDCl_3$) δ -72.71, -72.86, -75.96, -76.10, -79.83, -79.94. HRMS (m/z) calcd for $C_{54}H_{62}Ge_3O_{12}Si_7Na$: 1343.02, found 1341.02.

$(C_8H_{17})_7Si_7O_9[OSiMe_2(CH=CH_2)]_3$ (9): Product (9) was prepared using the same procedure and the following reagents: trisilanolisooctyl POSS (1 g, 0.84 mmol), tetrahydrofuran (40 mL), triethylamine (0.71 mL, 5.1 mmol) and chloro(dimethyl)vinylsilane (0.35 mL, 2.53 mmol). Finally, a viscous oil was obtained (1.12 g, 92%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.24 – 6.05 (m, 3H), 5.91 (dd, 3H), 5.74 (dd, 3H), 1.36 – 0.44 (m, 119H), 0.17 (s, 18H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.35, 131.94, 55.16, 54.75, 31.33, 30.42, 26.45, 25.81, 25.44, 25.36, 0.60. ^{29}Si NMR (79 MHz, $CDCl_3$) δ -2.85, -67.51, -67.86, -68.24. HRMS (m/z) calcd for $C_{68}H_{146}O_{12}Si_{10}N$: 1457.84, found 1458.84.

Tetrafunctional compounds

These compounds were prepared using analogous procedure and the following molar ratio of the reactants: [silanol POSS] : [chlorovinylmetalloid] = 1 : 4

$Ph_8Si_8O_{10}[OGeMe_2(CH=CH_2)]_4$ (10): Product (10) was prepared using the same procedure and the following reagents: tetrasilanolphenyl POSS (2 g, 1.87 mmol), tetrahydrofuran (120 mL), triethylamine (2.08 mL, 14.96 mmol) and chloro(dimethyl)vinylgermane (0.92 mL, 7.48 mmol). Finally, a white precipitate was obtained (2.68 g, 90%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63 – 7.13 (m, 40H), 6.48 – 6.32 (m, 4H), 5.99 (dd, 4H), 5.78 (dd, 4H), 0.59 (s, 24H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.83, 134.29, 131.34, 130.29, 127.86, 127.58, 1.32. ^{29}Si NMR (79 MHz, $CDCl_3$) δ -72.96, -76.53, -78.57. HRMS (m/z) calcd for $C_{64}H_{76}Ge_4O_{14}Si_8Na$: 1611.01, found 1607.01.

$Ph_8Si_8O_{10}[OSiPh_2(CH=CH_2)]_4$ (11): Product (11) was prepared using the same procedure and the following reagents: tetrasilanolphenyl POSS (1 g, 0.935 mmol), tetrahydrofuran (60 mL), triethylamine (1.04 mL, 7.48 mmol) and chloro(diphenyl)vinylsilane (0.83 mL, 3.74 mmol). Finally, a white precipitate was obtained (1.62 g, 91%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57 – 7.28 (m, 17H), 7.24 – 6.67 (m, 28H), 6.47 – 6.31 (m, 4H), 6.16 (dd, 4H), 5.83 (dd, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.00, 136.65, 135.02, 134.73, 130.22, 129.18, 128.37, 128.06, 127.77, 125.44. ^{29}Si NMR (79 MHz, $CDCl_3$) δ -14.59, -18.17, -68.28, -68.47, -73.43, -73.65, -77.67, -77.93, -78.16, -78.81. HRMS (m/z) calcd for $C_{104}H_{92}O_{14}Si_{12}Na$: 1923.36, found 1925.38.

Monofunctional vinylgermasilsesquioxanes

These compounds were prepared using analogous procedure and the following molar ratio of the reactants: [silanol POSS] : [chlorovinylmetalloid] = 1 : 1

$iBu_8Si_8O_{13}[GeMe(CH=CH_2)]$ (15): Product (15) was prepared using the same procedure and the following reagents: disilanolisobutyl POSS (2 g, 2.24 mmol), tetrahydrofuran (100 mL), triethylamine (1.25 mL, 8.97 mmol) and dichloromethylvinylgermane (0.31 mL, 2.3 mmol). Finally, a waxy solid was obtained (2.14 g, 95%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.32 – 6.21 (m, 1H), 6.08 (dd, 1H), 5.88 (dd, 1H), 1.92 – 1.78 (m, 8H), 0.96 (m, 48H), 0.66 (s, 3H), 0.61 – 0.55 (m, 16H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.54, 133.47, 26.06, 26.00, 25.86, 24.58, 24.37, 24.14, 23.41 22.72, 0.69. ^{29}Si NMR (79 MHz, $CDCl_3$) δ -65.82, -67.19, -69.21. HRMS (m/z) calcd for $C_{35}H_{78}GeO_{13}Si_8Na$: 1027.27, found 1027.27.

$iBu_8Si_8O_{13}[GeEt(CH=CH_2)]$ (16): Product (16) was prepared using the same procedure and the following reagents: disilanolisobutyl POSS (2 g, 2.24 mmol l), tetrahydrofuran (100 mL), triethylamine (1.25 mL, 8.97 mmol) and dichloroethylvinylgermane (0.27 mL, 2.29 mmol). Finally, a waxy solid was obtained (2.12 g, 92%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.27 – 6.13 (m, 1H), 6.08 (dd, 1H), 5.89 (dd, 1H), 1.95 – 1.72 (m, 8H), 1.23 – 1.08 (m, 5H), 0.97 – 0.93 (m, 48H), 0.56 (m, 16H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 134.15, 133.91, 25.96, 25.84, 24.58, 24.40, 24.09, 23.37, 22.70, 10.86, 7.05. ^{29}Si NMR (79 MHz, $CDCl_3$) δ -66.00, -67.20, -69.20, -69.24. HRMS (m/z) calcd for $C_{36}H_{80}GeO_{13}Si_8$: 1018.30, found 1019.32.

$iBu_8Si_8O_{13}[GePh(CH=CH_2)]$ (17): Product (17) was prepared using the same procedure and the following reagents: disilanolisobutyl POSS (2 g, 2.24 mmol), tetrahydrofuran (100 mL), triethylamine (1.25 mL, 8.97 mmol) and dichlorophenylvinylgermane (0.42 mL, 2.35 mmol). Finally, a waxy solid was obtained (2.19 g, 91%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63 (d, 2H), 7.43 (t, 3H), 6.36 (dd, 1H), 6.15 (dd, 1H), 5.91 (dd, 1H), 1.93 – 1.74 (m, 8H), 0.93 (m, 48H), 0.63 – 0.51 (m, 16H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.54, 133.47, 26.06, 26.00, 25.86, 24.58, 24.37, 24.14, 23.41, 22.72, 0.69. ^{29}Si NMR (79 MHz, $CDCl_3$) δ -65.49, -67.18, -69.00, -69.09. HRMS (m/z) calcd for $C_{40}H_{80}GeO_{13}Si_8Na$: 1089.29, found 1089.30

Acknowledgements

We gratefully acknowledge financial support from the National Science Centre (Poland) (Project UMO-2011/02/A/ST5/00472).

Keywords: silsesquioxane • germasilsesquioxane • POSS • incompletely condensed silsesquioxane • heterosilsesquioxane

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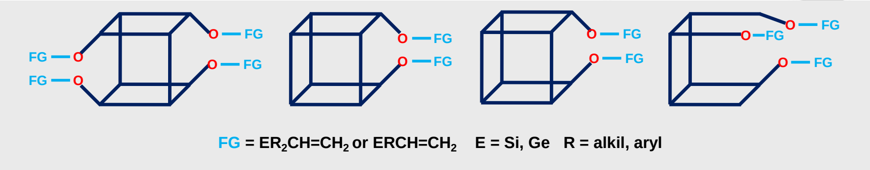

A new group of incompletely condensed silsesquioxanes and germasilsesqiuoxanes and completely condensed germasilsesquioxanes with vinylsubstituted metalloid functional groups were synthesized.

Silsesquioxanes, germasilsesquioxanes*

Magdalena Grzelak, Dawid Frąckowiak, Bogdan Marciniec

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Synthesis of incompletely condensed silsesquioxanes and germasilsesquioxanes

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