Dendrimers are a wide group of chemical compounds that are still being studied extensively. New dendrimer cores are sought to improve their physicochemical properties. We present the syntheses of silsesquioxane dendrimers with different cores, from mono-T8, octa-T8 silsesquioxane to di- and tetrafunctional double-decker silsesquioxanes. These compounds were obtained by a sequence of hydrosilylation and reduction reactions in a one-pot protocol. As part of the research, the location of reactive Si–H and Si–Vi bonds on the selectivity of the hydrosilylation process was verified, as well as two reducing agents LiAlH4 and Red-Al®, on the reduction process. In addition, the reactivity of the obtained new hydrogen derivatives of these SQs was tested in the process of hydrosilylation with selected olefins and in a repetitive one-pot route to increase the generation of these dendritic systems.

Introduction

Dendrimers are specific macromolecular compounds of precisely defined, often spherical three-dimensional structure, built of a multifunctional core with respectively attached branching units (arms). Their important aspect is the architecture which is constituted of three parts: the core – placed in its interior, repeating units forming tree-like branched structure and external surface functional groups. Various types of connections are used in the chemistry of dendrimers, e.g. the polyamidoamines, polyamides, poly(1-lysine), organophosphorus or organosilicon compounds, i.e. silanes, carbosilanes, siloxanes, carbosiloxanes.1–3 Systems bearing phosphorus or silicon branching points have recently emerged within this family of dendrimers.4

With regards to carbosilane dendrimers, two synthetic paths to their formation can be distinguished. The first method applies hydrosilylation reactions, e.g. tetravinylsilane hydrosilylated with dichloromethylsilane to obtain Si–Cl bonds. The Grignard reaction follows, which usually forms a compound possessing unsaturated carbon–carbon – silicon bonds, e.g. Si–vinyl, Si–allyl.5–7 The second protocol is based on the reduction of the Si–Cl bond to introduce Si–H.10 The compounds resulting from both these methods contain reactive Si–Vi or Si–H, susceptible to further transformation, increasing dendrimer’s generation with more branching units. For carbosilanes, the procedure employing Grignard reagents is more popular.

The properties that determine dendrimers’ subsequent application depend on, i.e. their size and type of surface/end groups. There are reports on the investigation of pure carbosilane dendrimer series (G3–G8 generations) vs. their hybrid carbosilane–siloxane analogues (G4, G6, G7 generations).11,12 Interestingly, there is a correlation between the Tg and the type of functional groups in the surface layer but not in terms of dendrimer generation. On the contrary, the high molecular weight of dendrimers is responsive to specific interactions between molecules with the increasing generation and it is manifested by increases in melt viscosity and an effective liquid–solid transition. As for the surface groups, in addition to standard silane groups, the hydroxyl, imidazole, sulfonate, and carboxylate phosphonium groups enabling anchoring metal atoms are interesting.13–17 Considering organosilicon-based dendrimers, carbosilanes are one of particularly important systems due to their properties that influence further application. They have been used in diverse areas of chemistry or medicine, e.g. in catalysis, anticancer therapy, immunotherapy and drug/gene delivery.18–22 The cores of such systems can
be constructed of silanes, cyclosiloxanes, 1,3,5-trisilacyclohexane, as well as more extensive structures, such as silsesquioxanes.3,23,24

The latter, *i.e.* silsesquioxanes (SQs), are hybrid compounds characterized by the presence of a rigid, inorganic Si–O–Si core and organic substituents attached to silicon atoms of this core. Their general formula, *i.e.* (RSiO1.5)n, where R stands for organic functional group and n reflects the number of repetitions of this unit from 6 to 18,25 does not give insight into the spatial architecture of these systems. They may constitute random resins or more defined ladder, open- or closed cage, and recently also double-decker silsesquioxanes (DDSQ).26–28

In the literature, there is limited information on the use of T8-type SQ dendrimer cores with a particular emphasis on octa-functionalized SQs due to their spherical architecture.24 The advantage of the surface area of octa-T8 SQs with diverse organic functionalities is the possibility of increasing their compatibility with organic materials. The use of this system makes it possible to obtain a large number of functional groups with a small number of synthetic steps.29,30 It should also be mentioned that SQs are present in dendrimers not only cores but also as repeat units (known as hyperbranched oligomers) and recently also double-decker silsesquioxanes (DDSQ).26–28

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Results and discussion

Synthesis of the first generation of carbosilane dendrimers with silsesquioxane cores

Hydrosilylation of C–C multiple bonds is still one of the major catalytic routes for functionalization of organosilicon compounds and is also common in industry. This process is characterized by its atom-efficiency, broad substrate scope, and widespread application.45,46 However, the reaction may not proceed with complete selectivity control and two main products may be obtained, *i.e.* α or β due to the Markovnikov rule. Moreover, the possibility for other side processes, *i.e.* dehydrogenative silylation, isomerization or hydrogenation may also be observed.47

In general, for olefin hydrosilylation β-regioselectivity is preferred especially in terms of dendrimer formation. It is favoured, *e.g.* due to steric hindrance of the surface groups and their further availability. The reaction selectivity may be influenced by various factors, *e.g.* a suitable catalyst, and reaction temperature, but also by the location of Si–H and olefin (Si–Vi) reactive bonds in reactants. Therefore, it was decided to verify the location of the Si–H moiety, whether in the silsesquioxane structure or in the olefin, *i.e.* unsaturated chloroorganosilicon component, susceptible to further modification.

A model reaction was selected with the hydrogen derivative iBu-T8-OSiH, (synthesized according to the literature data)48 and dichloromethylvinylsilane ([Cl2MeSiVi]) to be tested in Pt-mediated hydrosilylation (Scheme 2, PATH A). In this way, the reaction could be monitored easily by FT-IR via analysis of changes in the area of the bands at ca. ν = 2100 and 900 cm⁻¹ corresponding to the stretching vibrations of Si–H bond, located in the SQs reagent. The reaction was carried out in the presence of Karstedt’s catalyst ([Pt2(dvds)3]) for 24 h at 95 °C.49 After reaction completion, which was manifested by complete disappearance of the Si–H band in the FT-IR spectrum, the solvent and unreacted chlorosilane were evaporated. The crude product containing two Si–Cl moieties was subjected to consecutive reduction to form Si–H groups testing lithium alu-
minium hydride (LiAlH₄) as a convenient reducing agent (Scheme 2).

However, after the isolation of the product resulting from PATH A, the ²⁹Si NMR analysis showed the presence of doubled peaks in the area of all types of silicon atoms present in the postulated compound containing two Si–H moieties. These resonance lines, e.g. 11.69, 11.44 (M-unit Si), −29.08, −30.21 (Si–H), −66.89, −67.03, −67.07, −67.10, −67.74, −67.87, −67.90 (T-unit Si), and −109.64 and −109.93 (Q-unit Si) ppm indicated the presence of a mixture of two products, i.e. β and α obtained in a 80 : 20 ratio, abbreviated as G1-1iBuOSi-2H-β and G1-1iBuOSi-2H-α, respectively (Fig. 1a).¹³C NMR spectra revealed the presence of resonance lines at 2.37 and 11.80 ppm corresponding to −CH₂ moieties of the β isomer (G1-1iBuOSi-2H-β) and 4.53 and 9.83 ppm correlating to −CH₃ units in α isomer (G1-1iBuOSi-2H-α). Also verified by DEPT-135 (see ESI, Fig. S50†).

As the hydrosilylation reaction resulted in formation β and α addition products some literature discusses the impact of the location of Si–H moiety (at the SQs core or olefin) on reaction.
tion selectivity, we decided to verify this.\textsuperscript{50,51} For this reason, an analogous hydrosilylation and reduction protocols were designed (PATH B) but varying in the structure of reagents, i.e. iBu-T\textsubscript{4}-OSiVi and dichloromethylsilane (Cl\textsubscript{3}MeSiH) were used as substrates. Interestingly, preservation of almost all reaction conditions, with the sole change in the location of the Si–H group, from silsesquioxane to chlorosilane, enabled the regioselective formation of G\textsubscript{1}-1iBuOSi-2H-\textsubscript{β} system, confirmed by NMR analyses. It may be seen, especially in the \textsuperscript{29}Si NMR spectrum the presence of peaks corresponding to respective silicon atoms, e.g. 11.44 (M-unit Si), –29.08 (Si–H), –67.07, –67.10, –67.87, –67.90 (T-unit Si), and –109.64 (Q-unit Si) ppm (Fig. 1b). The selectivity of this reaction may be a derivative of two factors, i.e. steric bulkiness of SQs core but also the electronic effect of substituents (i.e. Cl vs. O) in reactive Si–H and Si–HC=CH\textsubscript{2} groups. It affects the type of olefin insertion into the Pt–H bond of active catalyst occurring as either 1,2- or 2,1-insertion that results in the formation of β or α isomer respectively. Also, it was reported that the presence of electron-withdrawing atom(s) increases the reactivity of Si–H moiety.\textsuperscript{51} This is in accordance with the Chalk–Harrod’s mechanism.\textsuperscript{47,63}

The obtained results facilitated the selection of the optimal location of the Si–H and Si–Vi bonds in applied reactants. This also helped to develop an efficient protocol for the synthesis of dendritic systems using different types of silsesquioxane cores, i.e. di- and tetra-DDSQ as well as octa-T\textsubscript{8}. As the usage of silsesquioxanes possessing reactive Si–Vi moieties affects the final regioselectivity of the β-addition product, it was decided to apply two compounds directly linked to the vinyl group to T\textsubscript{8} core, without the –Osi(Me\textsubscript{2})– unit between them. For this purpose, we omitted the β symbol in the abbreviations of products (unless needed) in further parts of the manuscript. Additionally, the iBu-T\textsubscript{4}-Vi is obtained in fewer steps of the synthetic path.\textsuperscript{52} For the proper exploration of the sequence of hydrosilylation (1.) and reduction reactions (2.), the iBu-T\textsubscript{4}-Vi was used as a model reagent to react with dichloromethylsilane (Cl\textsubscript{3}MeSiH) in order to optimize reaction conditions and enable the formation of G\textsubscript{1}-1Bu-2H. The first of the reaction sequence was hydrosilylation, which was carried out using Karstedt’s catalyst ([Pt\textsubscript{2}(dvds)\textsubscript{2}]) at 95 °C for 24 h with stoichiometry [iBu-T\textsubscript{4}-Vi] : [Cl\textsubscript{3}MeSiH] : ([Pt\textsubscript{2}(dvds)\textsubscript{2}]) = 1 : 2 : 1 \times 10^{-4}. Two-fold excess of Cl\textsubscript{3}MeSiH enabled >99% conversion of iBu-T\textsubscript{4}-Vi. After completion of the reaction, the solvent and unreacted chlorosilane were evaporated under reduced pressure and crude dichloro product as an intermediate product (G\textsubscript{1}-1Bu-2Cl) was dried and the subsequent step of the PATH B was maintained. The reduction was performed in toluene, and 1.2 equiv. of reducing agent per one reactive Si–Cl group was added and the reaction was conducted at room temperature for 20 h. In this case, LiAlH\textsubscript{4} was used. When the reaction was finished, the by-products, such as lithium chloride and aluminium chloride, were removed by a syringe filter (0.2 μm). The product (G\textsubscript{1}-1Bu-2H) was obtained in 89% isolate yield. An analogue synthetic approach was applied for other monosubstituted T\textsubscript{8} derivatives with iBu groups (G\textsubscript{0}-1Bu-1H, G\textsubscript{2}-2Bu-4H). The comparison of FT-IR spectra of iBu-T\textsubscript{4}-Vi and G\textsubscript{1}-1Bu-2H showed apparent proof of the differences in their structure. The disappearance of stretching vibration bands deriving from =C–H and C–C bonds at ca. ν\textsubscript{ν} = 3050 and ν\textsubscript{ν} = 1600 cm\textsuperscript{−1}, was noted respectively, with the simultaneous presence of Si–H stretching vibration bands in the range of ca. ν\textsubscript{ν} = 2100 and 900 cm\textsuperscript{−1} (Fig. S53 in ESI\textsuperscript{†}).

The double-decker silsesquioxane is specific construction of cage silsesquioxanes. It is characterized by two decks of cyclosiloxane rings that are stacked one above the another and connected by two oxygen bridges with phenyl groups at Si core atoms. They may occur in the form of di- and tetrafuctional analogues.\textsuperscript{53,54} As octafuctional T\textsubscript{8} SQs are applied as cores for dendrimers and the reports on DDSQ-based systems resembling dumbbell-shaped dendrimers are very rare in the literature.\textsuperscript{15}

For this, we applied the developed sequence of hydrosilylation reaction (1.) with subsequent reduction (2.) using LiAlH\textsubscript{4} that was verified in terms of di- and tetrafuctional DDSQ, e.g. to obtain G\textsubscript{0}-2D-2H. The \textsuperscript{1}H NMR spectrum of crude product pointed to the disappearance of resonance lines from vinyl groups at ca. 5.90–6.20 ppm. However, as there was no resonance line deriving from Si–H bond which supposed to be present at ca. 3.50–3.70 ppm, there was no evidence on the successful completion of Si–Cl to Si–H reduction. The solution for this was to replace the reducing agent from LiAlH\textsubscript{4} to sodium bis(2-methoxyethoxy) aluminium hydride (Red-Al\textsuperscript{8}). Red-Al\textsuperscript{8} possesses two active reactive hydrogen atoms in its structure and is considered a milder reducing agent.\textsuperscript{55} In the procedure elaborated to yield G\textsubscript{0}-2D-2H the step Si–Cl to Si–H reduction (2.) was performed using 0.6 fold excess of Red-Al\textsuperscript{8} per one reactive Si–Cl group in the DDSQ.

Despite the fact that reduction of Si–Cl to Si–H is a well-known reaction, it has never been verified in situ, so we decided to study this process using real-time FT-IR spectroscopy. The conducted experiment using G\textsubscript{1}-4D-8Cl\textsubscript{1} (to gain G\textsubscript{1}-4D-8H\textsubscript{1}), revealed that the consumption of Si–Cl with simultaneous formation of Si–H bonds proceeded extremely fast (Scheme 3). Specifically, it occurred immediately after the addition of Red-Al\textsuperscript{8} which was evident from the appearance of a new band in the range of 880–970 cm\textsuperscript{−1} (Fig. 2a). We also observed a notable increase in the process temperature, from approximately 23 °C to 26 °C (Fig. 2b). However, the reaction was performed on a small scale, indicating that, for larger-scale synthesis, the addition of the reducing agent to the reaction mixture along with reaction time should be carefully controlled due to the exothermic nature of the process and possible diffusion issues.

Scheme 3. Synthetic path to obtain G\textsubscript{1}-4D-8H via hydrosilylation followed by reduction.
Another problem to be solved was the isolation of the pure \( \text{G0-2D-2H} \) product with good yield. In general, the purification of SQ-based compounds can be performed using various techniques such as column chromatography, precipitation, extraction or their combination. Herein, at first, the crude \( \text{G0-2D-2H} \) product was precipitated in acetonitrile (MeCN). This is a good solvent in which Red-Al\(^\circledR\) is soluble, so could be easily decanted. \( \text{G0-2D-2H} \) was properly separated from the impurities by washing with DCM to dissolve the \( \text{G0-2D-2H} \). After decantation and evaporation of DCM, pure \( \text{G0-2D-2H} \) product was obtained in 64% yield. This isolation procedure was described as Method I and is depicted in Fig. 3 and in Table 1.

Interestingly, we found that using a higher excess of reducing agent (\( i.e. \) 1.5 equiv. of Red-Al\(^\circledR\)) did not improve the product yield, despite being tested for its impact.

The procedure developed for the effective formation of \( \text{G0-2D-2H} \) was transferred to other DDSQ compounds, \( e.g. \) to obtain \( \text{G1-2D-4H} \) (0.6 equiv. Red-Al\(^\circledR\) on the reactive group). Unfortunately, the isolation yield was unsatisfactory, \( i.e. \) only 23%. In this case, a different method of isolation was developed which includes a combination of different techniques.

One of the procedures was a dropwise addition of the reaction mixture to cold isopropanol (iPrOH) to decompose Red-Al\(^\circledR\) followed by solvent evaporation. The crude product was filtered on a chromatography column with DCM as eluent. Another method was based also on iPrOH used for Red-Al\(^\circledR\) decomposition and washing of resulting precipitate with DCM to extract \( \text{G1-2D-4H} \). However, none of the presented protocols provided a positive result in the increase of \( \text{G1-2D-4H} \) yield. Finally, as the crucial aspect is decomposition of Red-Al\(^\circledR\) and the fact that DDSQ compounds are not soluble in water, the extraction was performed using toluene and 10% acetic acid water solution. Surprisingly, this procedure enabled the isolation of \( \text{G1-2D-4H} \) in 85% yield and was described as Method II, shown in Fig. 4. All DDSQ-based dendrimers were isolated using both methods to compare their impact on the isolation yield, which was presented in Table 1. As a result, Method II based on the extraction using toluene and 10% acetic acid water solution.
significantly affected the isolation yields of verified compounds when compared to Method I.

After optimizing the conditions for various SQ derivatives, we decided to apply the developed methodology for the functionalization of more challenging structures, namely spherolitocages bearing a significantly greater number of reactive Si–H species. The Pt-catalyzed hydrosilylation of trichlorovinylsilane with octakis(dimethyl-siloxy)silsesquioxane (octaT₈-OSiH) followed by subsequent reduction of the Si–Cl intermediate in the presence of Red-Al® gave a mixture of isomers (β:α = 64:36). This phenomenon was expected and also observed in synthesis of advanced SQs. However, the opposite approach based on the application of octakis(dimethyl-vinylsiloxy)silsesquioxane (octaT₈-OSiVi) and trichlorosilane resulted in the regioselective formation of β isomer. The same behaviour was observed when the dichloromethylsilane and octaT₈-OSiVi were used, which was corroborated by ¹H, ¹³C and ²⁵Si NMR analyses (Fig. S35–S37). The outcomes of these experiments clearly indicated that the application of the chlorohydrosilanes and vinyl-SQ derivatives always leads to the anti-Markovnikov addition products (β isomer), regardless of the type of SQ structure and the number of reactive groups bonded to the SQ cage. Surprisingly, this observation has not been reported so far. The isolation procedure for octa-T₈ derivatives relied on the decomposition of Red-Al® in 2-propanol followed by evaporation of the volatiles and subsequent product extraction by n-hexane. This simple methodology allowed us to isolate products with satisfactory yields i.e. >80%.

The synthesized novel derivative [G1-8T-16H], due to the easily accessible hydrosilyl units, opens possibilities for the synthesis of functionalized dendritic SQ-derivatives bearing sixteen organic groups around the cage, as well as the formation of a higher generation through the above-described one-pot protocol.

While searching for the most effective purification methodology enabling efficient product isolation, two methods were developed (Fig. 3 and 4) depending on the type of the SQ core. Method 1 involves the use of MeCN, a good precipitating solvent for silesquioxanes. During the isolation of respective SQ derivatives, some crystal material of the following systems were obtained: G₀-₄D-₄H and G₁-₂D-₄H, which were amenable to XRD analysis. These two systems were found to be more susceptible to crystallization in MeCN when compared to other compounds. Perspective views of the molecules G₀-₄D-₄H and G₁-₂D-₄H are shown in Fig. 5a and b. The molecule G₁-₂D-₄H is C₁-symmetrical, lying across the inversion center in the space group Pbcₐ. As observed in similar structures, the geometry around Si atom is quite stable, as shown by the mean values and their esd’s (Table 2). On the other hand, the range of Si–O–Si angles is quite extensive. In principle, the overall geometries and shapes of both open and closed structures are similar to those shown by us earlier.⁵⁶,⁵⁷

In the elaboration of the synthetic protocol for the DDSQ-based dendrimers based on Red-Al® instead of LiAlH₄, some tests were performed to obtain mono-T₈ systems with Ph inert groups, which exhibited some failures in the formation. It was decided to verify the methods using LiAlH₄ and Red-Al® for these derivatives. In the beginning, a similar procedure to gain G₀-₁Ph-₁H was conducted using LiAlH₄ by analogy to the G₀-₁Bu-₁H system. Unfortunately, similar lack of Si–H bond was observed on ¹H NMR spectra. Analogous reduction protocol based on Red-Al® was applied and the desired products (G₀-₁Ph-₁H and G₁-₁Ph-₂H) were obtained with good yields. Both methods were validated to obtain G₁-1Ph-2H. Interestingly, for this system, the use of LiAlH₄ and Red-Al® made it possible to obtain a product with a yield of 45% and 60%, respectively, showing improvement for Red-Al®. The G₁-1Ph-2H is again a good example of the fact that silesquioxanes, due to their differences in architectures and presence of diverse inert groups should be approached individually. This concerns the synthetic protocol conditions for their formation as well as their isolation and purification.⁵⁵,⁵⁸

The reactivity of Si–H modified SQ-based dendrimers

Silsesquioxane dendrimers of G₀ and G₁ generation possessing Si–H bond can be modified to increase their generation by a sequence of hydrosilylation and reduction as well as hydrosilylation reaction with functional alkenes.⁴⁹,⁵⁹ To verify the reactivity of the Si–H bond of selected compounds, the G₁-₄D-₄H was reacted with allyl glycidyl ether via hydrosilylation reaction with elaborated reaction conditions, i.e. the following...
The second generation of carboxilane dendrimers with silsesquioxane cores

The essence of dendritic systems is the possibility to create compounds with the highest generation. Consequently, the next step of our research were attempts at obtaining the G2 generation of the studied systems. Isobutyl derivative (G1-1Bu-2H) was used as a model reagent. The same hydrosilylation/reduction sequence protocol was applied with LiAlH₄ as a reducing reagent to the synthesized G1 dendritic system. Hydrosilylation conditions: [G1-1Bu-2H] : [Cl₃MeSiv] : [Pt₃(dvds)] = 1 : 4 : 4 × 10⁻³; reduction conditions: LiAlH₄ 1.2 equiv. per one –Si–Cl group. The ¹H NMR analysis of the reaction mixture revealed the presence of two multiplets deriving from Si–H bond in a range of 3.70–3.80 ppm (G2-1Bu-4H). These resonance lines were slightly low-field-shifted when compared to the placement of protons of Si–H in G1-1Bu-2H (3.69–3.73 ppm). Moreover, the ²⁹Si NMR analysis of G2-1Bu-4H displayed the presence of three peaks at ca. −2.60, −3.30 and −4.30 ppm, deriving from the created −Si(CH₃)–C– moiety. Additionally, there were four peaks derived from Si–H groups, i.e. at −29.19, −29.27, −29.63 and −29.66 ppm. These results may suggest that a mixture of β- and α-addition products was obtained. These are isomers of statistical substitution and three possible products may be obtained, because of different addition of each Si–H double bond of olefin. The ¹³C NMR supported by the DEPT-135 NMR technique enabled analysis of the reaction mixture and selection and assignment of peaks to respective β- and α-addition products, as there are three possible placement of substituents (Scheme 4, Fig. S11 and S13 in ESI†).

Although the product of double β-addition is the preferred substitution position in the synthesis of dendrimers during the hydrosilylation reaction, all of the products in this mixture have the G2 generation. For the β, β-product, a longer flexible, ethylene bridge reduces steric hindrance in subsequent generations. On the other hand, for the α, β- or α, α – systems, the reactive groups are available for further modification, though the steric hindrance may be an obstacle to further modification which may not proceed easily. Moreover, the same result was obtained when G1-8T-16H was used as a starting material in the synthesis of the SQ-based second dendrimer generation (G2-16T-32H) which was depicted in Scheme 5. This in turn confirms the previously emphasized conclusion describing the crucial role of the Si–H and Si–Vi location in reagents on the reaction regioselectivity. Nevertheless, the presence of α-regioisomers does not exclude their susceptibility to further functionalization through catalytic reactions.⁴⁷,⁶³,⁶⁴

The GPC analysis may enable the determination of the dispersity of dendritic systems. The obtained chromatograms confirmed the monodispersity of all the obtained systems. It should be also emphasized that no increase in the value of the polydispersity index (PDI) was observed in any of the example. Its value is in the range of 1.08–1.24, which proves the high selectivity of the process without the formation of any duplex systems (see ESI†). Such relationships were observed for silsesquioxane-based dendritic systems.⁶⁵–⁶⁸
Conclusions

To conclude, an effective one-pot synthesis of dendrimers with a different type of silsesquioxane core, from mono-T₈, octa-T₈ SQ to di- and tetrafunctional DDSQ, was presented. The synthetic protocol was based on the reaction sequence, i.e. hydro-
silylation followed by the reduction. To obtain the β-product, the placement of Si–H and Si–Vi reactive groups was verified in regards to respective products. Within the scope of our studies, two reducing agents were tested: LiAlH₄ and Red-Al®. The systems with a mono-functional SQ core, LiAlH₄ revealed to be good reducing agents, however, for dendrimers with a DDSQ and octa-T₈ core, the Red-Al® was preferable. These studies are another example that macromolecular systems, despite similar structures, should be approached individually, which was also observed when purifying the obtained compounds. In addition, the structures of the compounds G₀-4D-4H and G₁-2D-4H were confirmed by XRD analysis. Hydrogen derivatives of the G₀ and G₁ generations are characterized by the presence of a reactive Si–H bond, which was confirmed in the hydroisilylation reaction with 1-octene and allyl glycidyl ether. Additionally, reactive G₁ generation systems were developed to obtain higher generation dendrimers. Despite the non-selectivity of the hydroisilylation, reactive G₂ generation dendritic systems with mixed α and β substitution were obtained. All synthesized compounds can be modified in catalytic processes, such as hydroisilylation.

Author contributions

B.D. and R.J. conceived the experiment and designed the study; A.M., R.J., J.D. participated in the planning of the study; M.D performed GPC analysis; M.K. carried out the X-ray analysis and description; all authors discussed the results and contributed to the interpretation of data. B.D, A.M, and R.J. co-wrote the manuscript. All authors read and agreed to the published version of the manuscript.

Conflicts of interest

There are no conflicts to declare.

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References

15. M. Müllerová, S. Šabata, J. Matoušek, M. Kormunda, J. Holubová, R. Báliková, R. Petričkovič, M. Koštejn,
Bifunctional carbosilane dendrons for the immobilization of antiviral drugs as antiviral agents, Cañadilla, R. Gómez-Ramírez, J. L. Jiménez and J. Kup, 2023, 11, 2098–2118.


38. N. R. Vautravers and D. J. Cole-Hamilton, Diphenylphosphine containing macromolecules in the methoxycarbonylation of ethene: The effect of macromol-


