SILICON-BASED DENDRIMERS

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ABSTRACT

The present review provides a comprehensive survey on the synthesis and modification of silicon-based dendrimers with different branching architecture (carbosilane, polysilane, alternating silicon-germanium, carbosilazane, siloxane and carbosiloxane).

INTRODUCTION

The chemistry of dendrimeric compounds has been developed for two last decades [1]. The term "dendrimer" (three-dimensional, treelike, starburst, branched, cascade molecule or arborols) describes the architecture of these compounds. The progress in this research field proceeded rapidly from the early 1990s and a variety of dendrimers with different cores (organic, inorganic, organometallic), branching units, and end groups have been prepared during this period. There are two fundamentally different concepts for constructing of dendrimeric compounds. The first one is the divergent method in which one branching unit after another is attached to the core molecule and by this route the dendrimer can be built up step by step. The convergent method takes the opposite course. The dendrimer is constructed stepwise starting from the end groups towards the inside and is finally treated with a core molecule to give the branched molecule. The application of dendrimers includes nanoscale catalysts, chemical sensors, high performance polymers and liquid crystals.

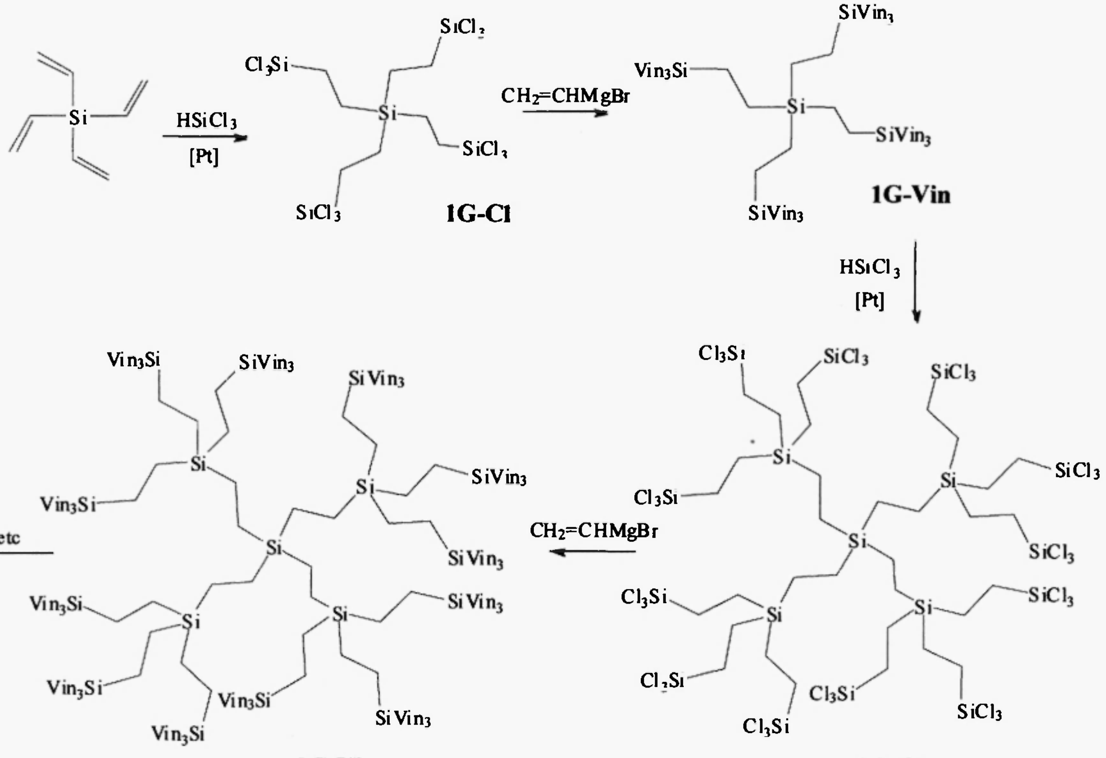
Data concerning the synthesis of the first dendrimeric organosiloxane were published in 1989 [2]. Condensation of methyltrichlorosilane with $(EtO)_2MeSiONa$ and subsequent substitution of ethoxy groups with $SOCl_2$ gave tris(dichloromethylsiloxy)methylsilane. By repetitive $(EtO)_2MeSiONa$ and $SOCl_2$ reaction steps dendrimer containing 48 silicon atoms was effected. Hyperbranched compounds with carbosilane, polysilane, alternating silicon-germanium, carbosilazane, and carbosiloxane cores have been synthesized later. Our review is an attempt to summarize data on the synthesis and transformations of these silicon-based materials.

1. CARBOSILANE DENDRIMERS

The carbosilane dendrimers have attracted wide attention as a base for dendrimeric compounds that are peripherally functionalized with transition metal fragments because the branches can easily be terminated with reactive groups, whereas their carbosilane skeleton is chemically inert to common organometallic reagents. These metallodendritic catalysts were successfully applied as homogeneous catalysts in organic synthesis [3].

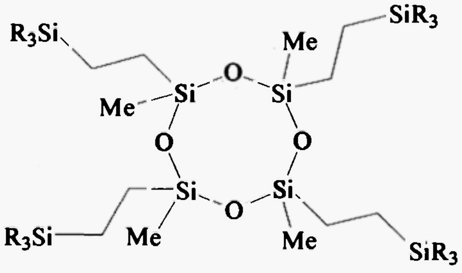
The common method for the construction of carbosilane dendrimers includes alternating hydrosilylation (by trichlorosilane or dichloromethylsilane) and Grignard reaction (with vinylmagnesium bromide or allylmagnesium bromide) starting from tetraallylsilane [4-8] or tetravinylsilane [9-11] as the initiator core. Both steps are very straightforward reactions and majority of products is formed in high to quantitative yields (Scheme 1). The most satisfactory results for Pt-catalyzed hydrosilylation of allyl or vinyl groups were obtained when the Karstedt catalyst (prepared from $[Me_2(CH_2{=}CH)Si]_2O$ and $H_2PtCl_6{\cdot}6H_2O$) was used instead of $H_2PtCl_6{\cdot}6H_2O$ in a reaction of an excess of Cl_3SiH or Cl_2MeSiH with dendrimers of different generations (**1G-Vin, 2G-Vin, 3G-Vin**). Attempts to prepare the fourth generation dendrimer (**4G-Cl**) by hydrosilylation of **3G-Vin** resulted in only partial reaction according to the ^1H NMR spectroscopy. Most likely, steric congestion in the periphery hindered complete reaction [10].

Dendrimeric carbosilanes based on 2-(*p*-bromophenyl)ethyltriallylsilane *p*-$BrC_6H_4CH_2CH_2Si(CH_2CH{=}CH_2)_3$ [12], 1,2-bis(triallylsilyl)ethane $[(CH_2{=}CHCH_2)_3SiCH_2]_2$ [13, 14], 2,4,6,8-tetramethyl-2,4,6,8-tetravinylcyclotetrasiloxane [15, 16] or polycarbosilanes containing allyl groups [17] as a core molecules have been prepared by repetitive hydrosilylation and alkenylation steps. Reaction of 1,2-bis(triallylsilyl)ethane with Cl_3SiH did not completely form a molecule containing 18 Si-Cl bonds, but the reaction with Cl_2MeSiH gave dendrimeric carbosilane $[(Cl_2MeSiCH_2CH_2)_3SiCH_2]_2$. Subsequent dendrimeric generation using Cl_2MeSiH and allylmagnesium bromide yielded dendrimer **3G** with 48 allylic end groups.



Scheme1

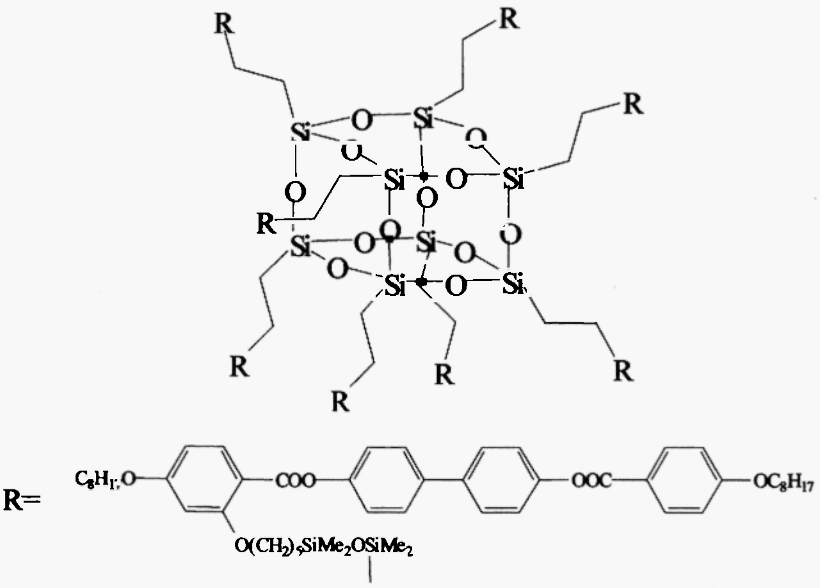
Hydrosilylation of 2,4,6,8-tetramethyl-2,4,6,8-tetravinylcyclotetrasiloxane [15, 16] with trichlorosilane in the presence of a platinum catalyst (10 % Pt/C) gave compound **1** (R_3Si = Cl_3Si) in quantitative yield. The reaction of this product with allylmagnesium bromide led to formation of compound **1** [R_3Si = $(CH_2{=}CHCH_2)_3Si$] containing 12 allylic end groups which readily added methylhalosilanes (Me_2ClSiH and $MeCl_2SiH$) and provided the products of second generation (2G) with terminal Me_2ClSi and $MeCl_2Si$ substituents. In contrast, the reaction with Cl_3SiH during 12 h in refluxing THF or in refluxing toluene during 2 days was not completed. Compounds of the second generation with Si-Cl bonds were terminated by phenylethynyl lithium, *p*-bromophenol and allylmagnesium bromide.



1

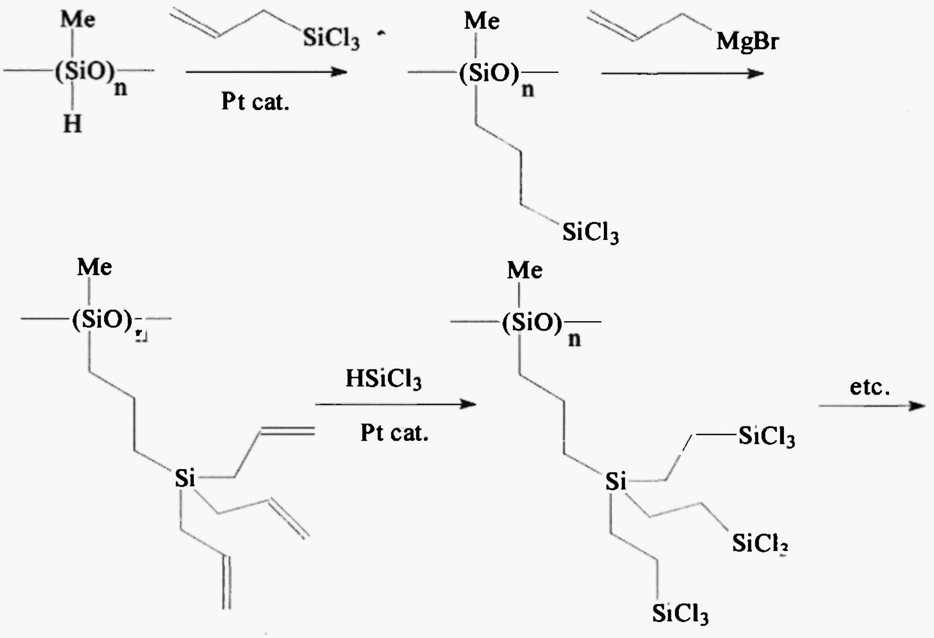
$R_3Si = Cl_3Si, (CH_2{=}CHCH_2)_3Si, (Me_2ClSiCH_2CH_2CH_2)_3Si, (MeCl_2SiCH_2CH_2CH_2)_3Si,$
$[(PhC{\equiv}C)Me_2SiCH_2CH_2CH_2)]_3Si,$
$[(p\text{-}BrC_6H_4O)Me_2SiCH_2CH_2CH_2)]_3Si, [(CH_2{=}CHCH_2)_2MeSiCH_2CH_2CH_2]_3Si$

Carbosiloxane dendrimer **2** was prepared starting from octavinylsilsesquioxane by attachment of 1-R,-1,1,3,3-tetramethyldisiloxane group using hydrosilylation reaction in the presence of Karstedt catalyst [18]..



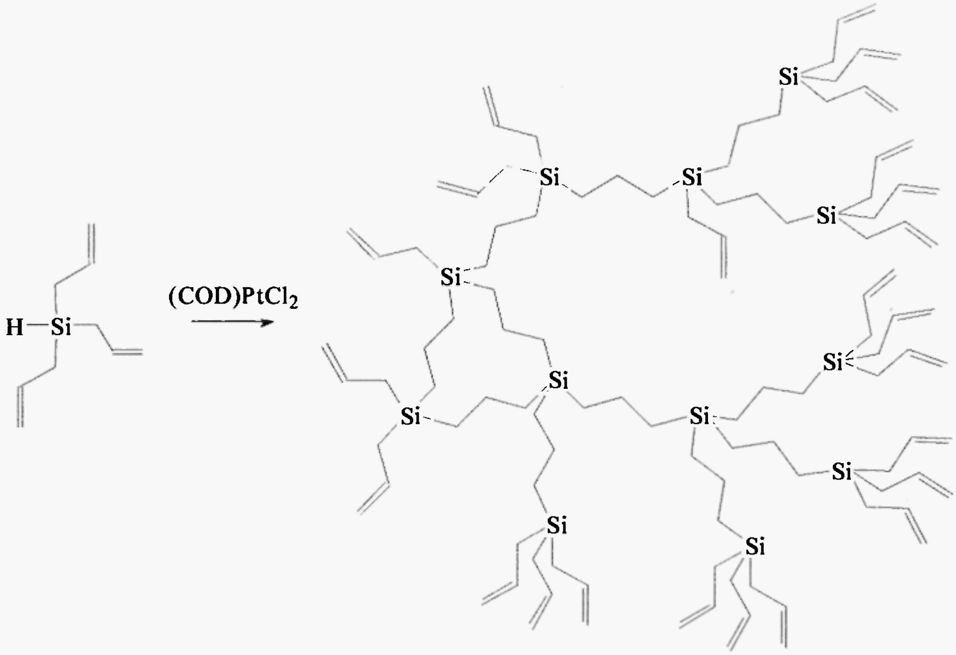
2

Wormlike dendrimers made of flexible and noninteracting segments were synthesized starting from polymethylhydrosiloxane and using short propylsilane branches, the synthesis did not go beyond the second generation due to steric congestion. The dendrimers were prepared as outlined in Scheme 2, using hydrosilylation and alkylation reactions [19].



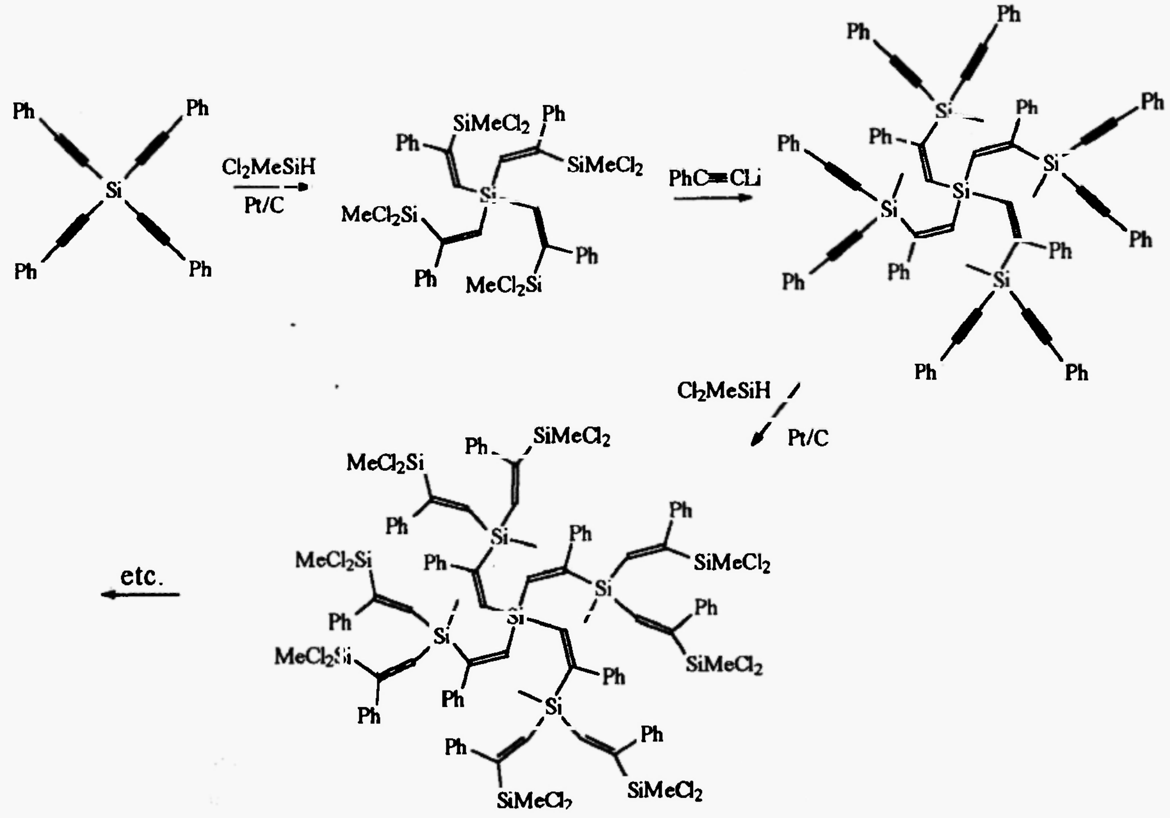
Scheme 2

To prepare hyperbranched carbosilane **3**, neat triallylsilane was polymerized with platinum catalyst $(COD)PtCl_2$. To keep the isomerization of the double bonds to a minimum, the reaction temperature was kept low (40°C). This, however, led to prolonged reaction times (4 days) [20] (Scheme 3).



3

Scheme 3



Scheme 4

Hyperbranched dendrimers, based on tetrakis(phenylethynyl)silane $(PhC{\equiv}C)_4Si$ as a core molecule with bis(phenylethynyl)methylsilyl end groups as a building blocks have been synthesized using hydrosilylation – alkylation sequences. The silylated generations were converted to the corresponding dendritic carbosilanes containing phenylethynyl groups by the treatment with phenylethynyl lithium in THF (Scheme 4). Carbosilane dendrimers with 8 (**1G**), 16(**2G**) and 32 (**3G**) alkynyl end substituents were obtained by using this synthetic approach. The subsequent generation with 64 Si-Cl groups did not make a unified form by the hydrosilylation step [21].

The availability of carbosilane dendrimers that have reactive peripheral groups such as Si-Cl, Si-H, $Si{-}CH{=}CH_2$, $Si{-}CH_2CH{=}CH_2$, $SiC{\equiv}C$, $Si{-}CH_2Cl$, $Si{-}CH_2PR_2$, Si-Ph offers the opportunity of introducing through appropriate chemistry many other interesting and potentially useful inorganic, organic and organometallic substituents.

A convenient divergent synthetic route to lipophilic dendrimeric polyols is based on quantitative hydroboration of carbosilane dendrimers with allyl end groups. The hydroboration reaction using 9-borabicyclo[3.3.1]nonane (9-BBN) with subsequent oxidation by H_2O_2/OH^- formally leads to anti-Markovnikov addition of water to double bonds (Scheme 5) [22, 23].

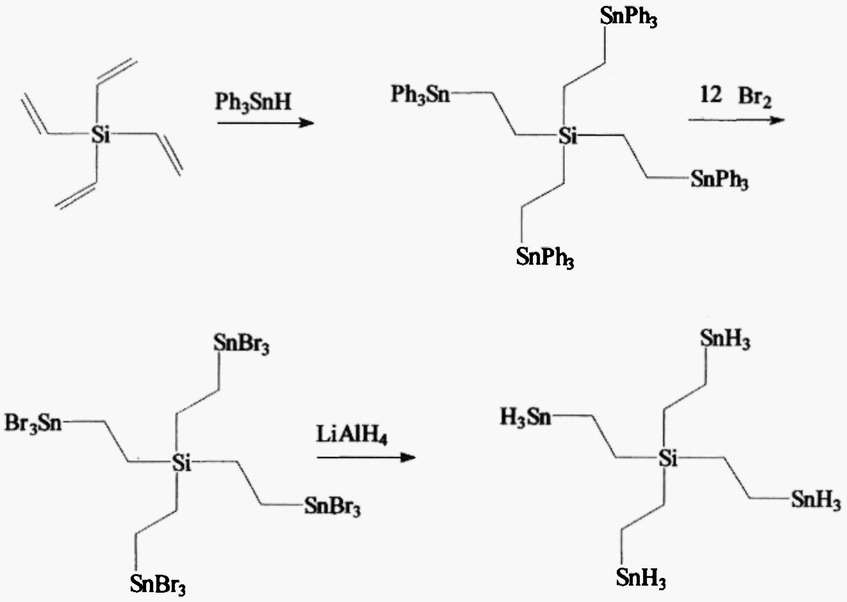
$$\{[(CH_2{=}CHCH_2)_3SiCH_2CH_2CH_2]_3CH_2CH_2CH_2\}_4Si$$

$$\text{1. 9-BBN}\ \Big\downarrow\ \text{2. } H_2O_2/NaOH$$

$$\{[(HOCH_2CH_2CH_2)_3SiCH_2CH_2CH_2]_3CH_2CH_2CH_2\}_4Si$$

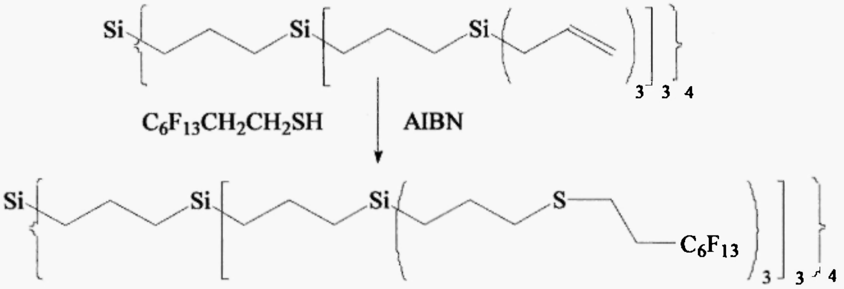
Scheme 5

Utilizing tetravinylsilane as a core molecule, the tin-containing dendrimer tetrakis[2-(triphenylstannyl)ethyl]silane was prepared in a high yield hydrostannylation reaction. Triphenylstannane, employed in excess, added cleanly to the vinyl groups in the presence of $H_2PtCl_6{\cdot}6H_2O$. The treatment of dendrimer with bromine in CCl_4 resulted in a selective and complete cleavage of the Sn – Ph bonds and tetrakis[2-(tribromostannyl)ethyl]silane formation. Reduction of the bromo derivative with $LiAlH_4$ at low temperature afforded tetrakis[2-(stannyl)ethyl]silane in high yield (Scheme 6). The molecular structure of Ph_3Sn and H_3Sn-substituted compounds was determined by X-ray diffraction [24].



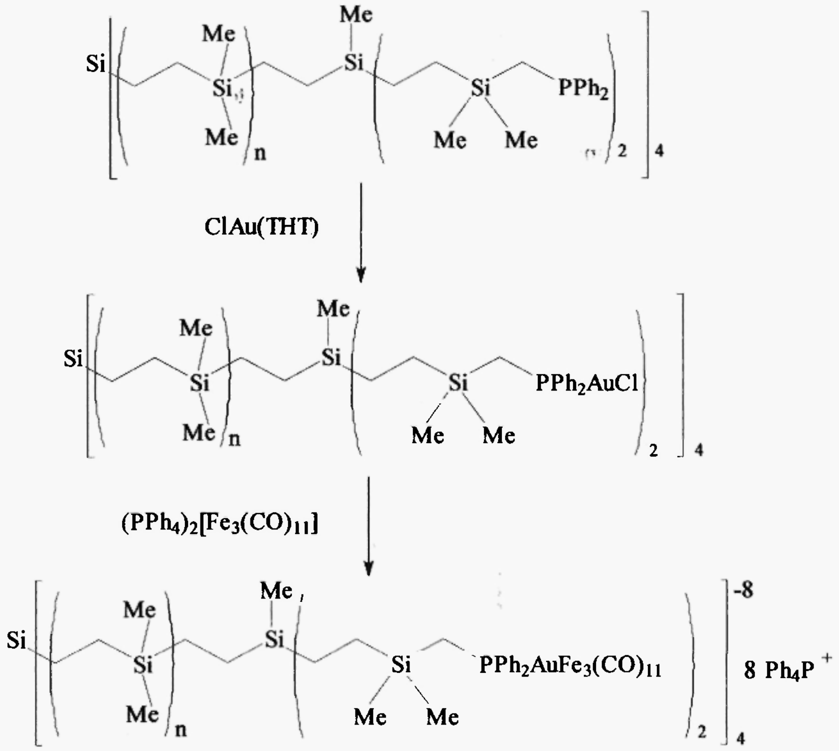
Scheme 6

Nucleophilic substitution of the chlorine atom in carbosilane dendrimers bearing (chloromethyl)silyl groups on their terminal branches by different mercapto derivatives [$HS(CH_2)_2NMe_2$, $HS(CH_2)_2OH$, $HS(CH_2)_2SO_3Na$] in the presence of NaOH occurred within several hours. Dendrimeric products having terminal sodium sulphonate groups were obtained as hygroscopic white solids, which were completely soluble in water and essentially insoluble in all organic solvents; on the other hand, alcohol and dimethylamino-terminated dendrimers were soluble in organic solvents and insoluble in water [25].



Scheme 7

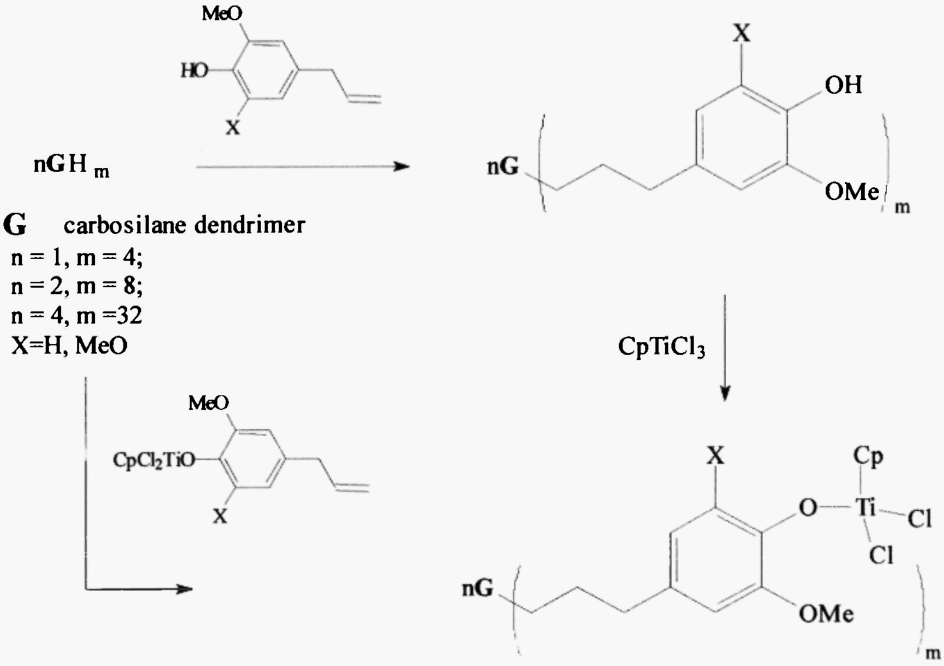
A series of carbosilane dendrimer generations (from **G0** to **G4**) with 4, 12, 36 and 108 end allylic groups, respectively, has been functionalized by perfluoroalkyl substituents. Attachment of the perfluorinated alkyl groups to the allyl fragments was performed via free radical addition of 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-*n*-octyl mercaptan $F(CF_2)_6CH_2CH_2SH$, which affords the corresponding thioether-functionalized end groups. In order to achieve complete reaction of all allylic groups, the fluorinated mercaptan was used in 20-60% excess. AIBN was used as a radical source. The synthesis of a perfluorinated dendrimer of the second generation is presented in Scheme 7 [26].



Scheme 8

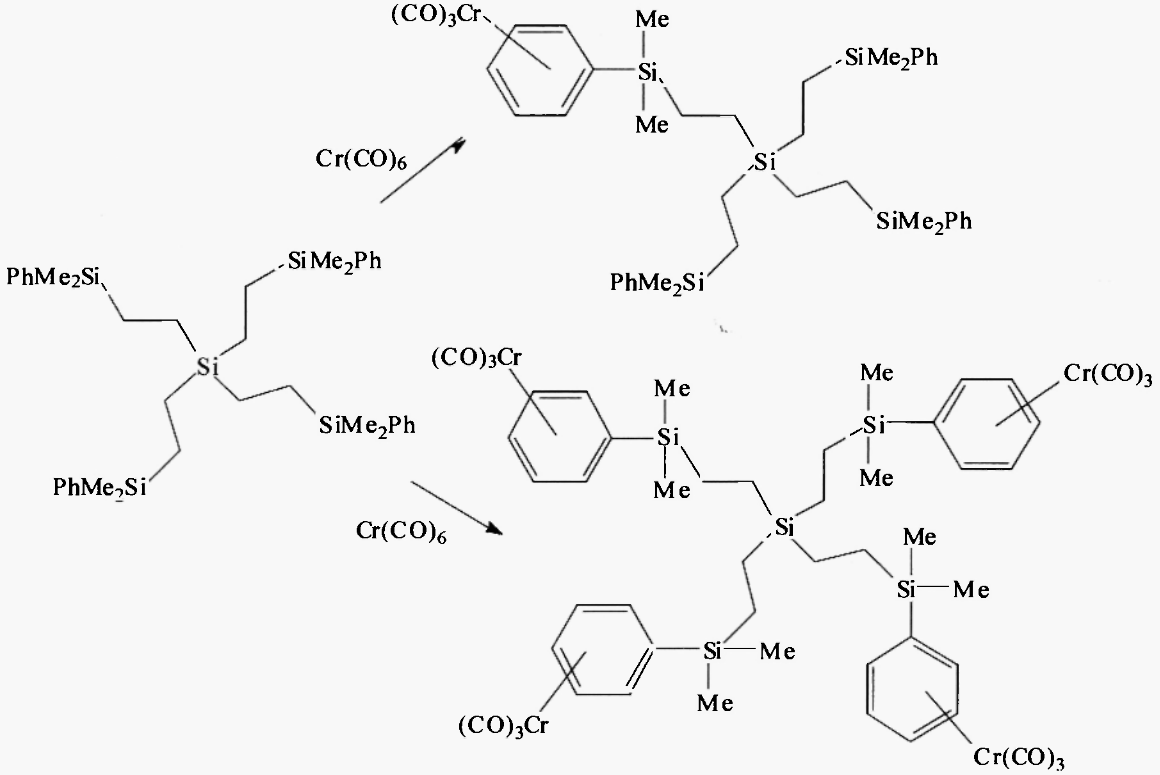
Introduction of alkyldiphenylphosphino groups to the branch ends by reaction with $LiCH_2PPh_2$ and attachment of AuCl units taking advantage of the lability of the tetrahydrothiophene (THT) ligand in ClAu(THT) and subsequent chloride displacement from gold by iron cluster anion represented a strategy to graft mixed transition metal fragments into dendrimeric structures (Scheme 8) [27].

The first-, second-, and fourth-generation dimethylsilyl-terminated dendrimers were the starting materials for the preparation of new dendrimers via hydrosilylation of 4-allyl-2-methoxyphenol or 4-allyl-2,6-dimethoxyphenol [8, 28]. The reaction of hydroxy groups of these dendrimers with $CpTiCl_3$ provides an effective route for the attachment of cyclopentadienyl titanium complexes to the dendrimeric periphery. The incorporation of titanium fragments in toluene at 80 °C proceeded quantitatively. In the case of the fourth-generation metallodendrimer, complete conversion was achieved by adding a drop of a base such as NEt_3 to the toluene solution. The alternative procedure consisting in the hydrosilylation of monomeric 4-allyl-2-methoxyphenol or 4-allyl-2,6-dimethoxyphenol titanium complexes by hydrosilyl-terminated dendrimers gave only low yields (Scheme 9).



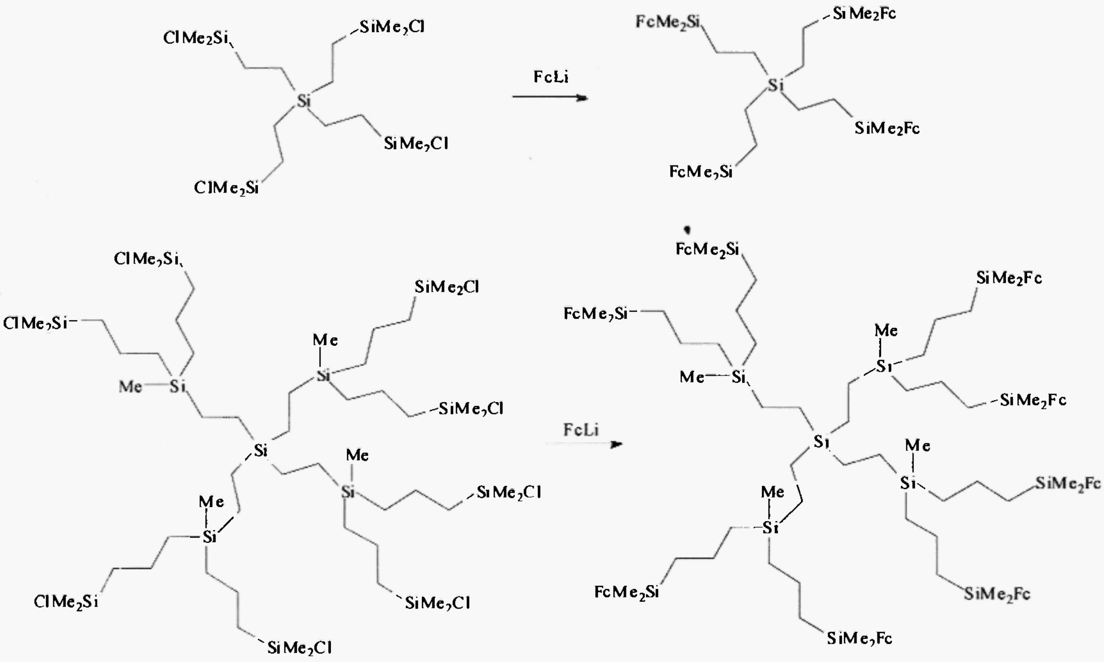
Scheme 9

The first synthetic approach for incorporation of $Cr(CO)_3$ moieties into organosilicon dendrimeric cores involved thermal replacement of CO ligands from chromium hexacarbonyl by the phenyl-terminated dendrimers. Thus, treatment of tetrakis[2-(phenyldimethylsilyl)ethyl]silane with an excess of $Cr(CO)_6$ in Bu_2O/THF at 140°C afforded the corresponding tetrachromium complex. Similarly, the reaction with one equivalent of $Cr(CO)_6$ gave a mononuclear molecule (Scheme 10). This synthetic procedure has also been attempted to obtain the complex of the next higer generation, but the functionalization of the eight phenyl-terminated dendrimer arms with $Cr(CO)_3$ units did not succeed [7].



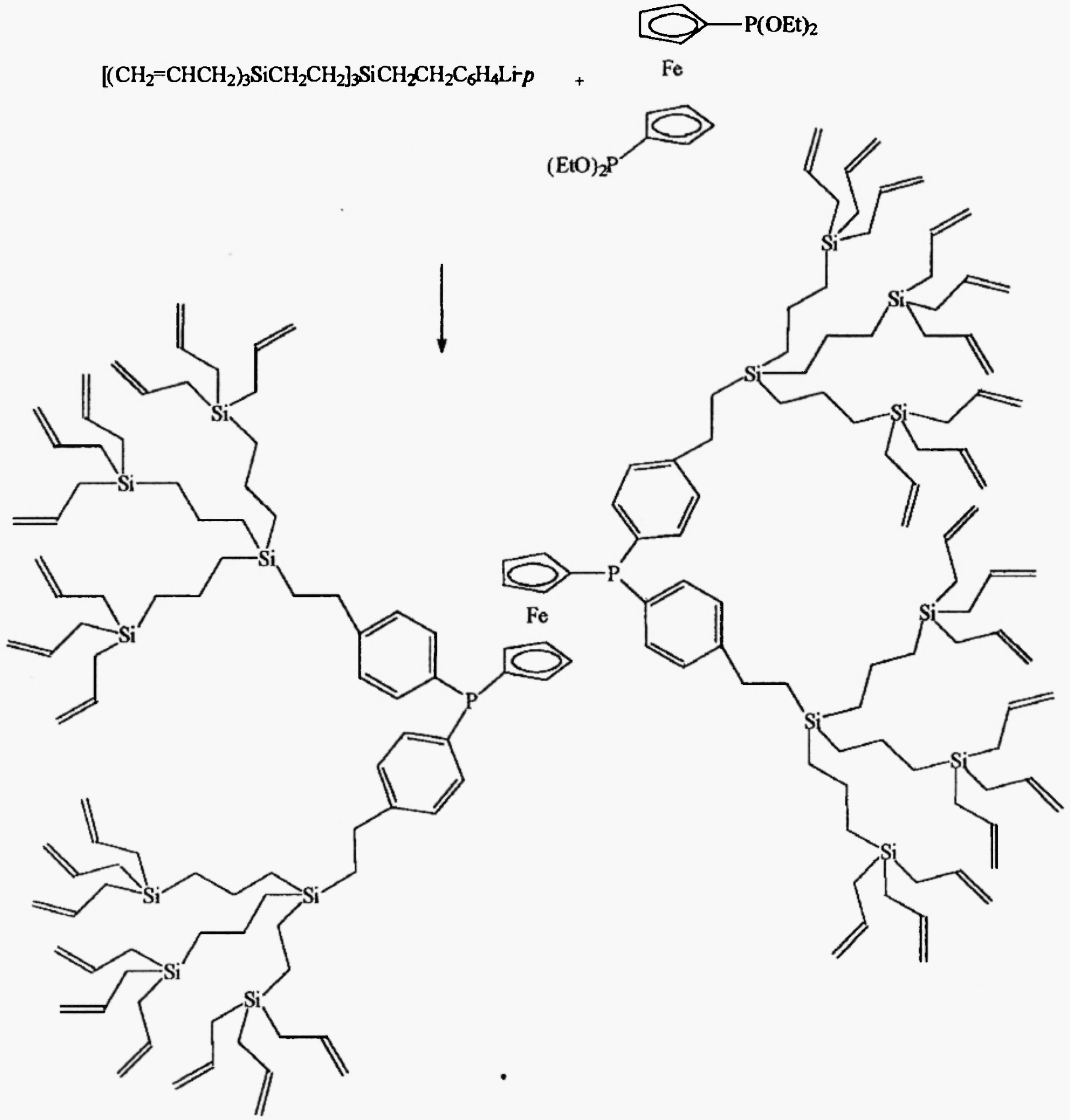
Scheme 10

Reactions of ferrocenyllithium with Si-Cl terminated carbosilanes were applied for incorporation of ferrocenyl-containing organometallic units into organosilicon cores (Scheme 11). This method afforded the branched macromolecules with four and eight ferrocenyl moieties [6].



Scheme 11

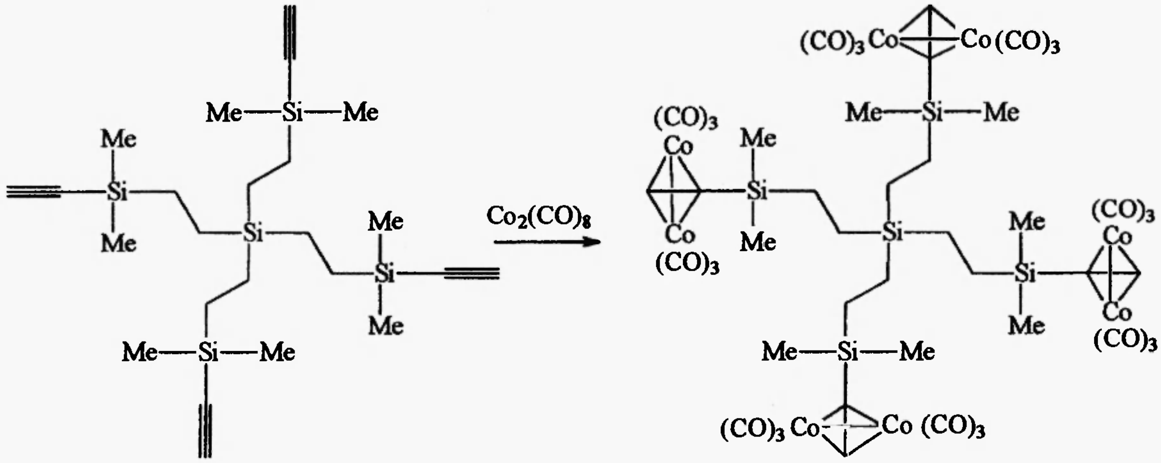
The introduction of organometallic fragments into terminal positions presents the example of the periphery strategy. Recently new core-functionalized dendrimers were prepared as examples of the other strategy [12]. Carbosilane dendrimers with 2-(*p*-bromophenyl)ethyl substituents at the central silicon atom have been used as starting compounds. The bromophenyl moiety can be utilized to synthesize a core-functionalized dendrimers in a convergent way. Lithiation of these compounds with BuLi and subsequent treatment by tetraethyl ferrocene-1,1'-diylbis(phosphonite) yielded the bidentate ferrocenyl complexes (Scheme 12). These complexes of different generations (**1G**, **2G** and **3G**) reacted with $Pd(MeCN)_2Cl_2$ in CH_2Cl_2 for 60 min. ^{31}P NMR spectroscopy confirmed complete complexation of the ligands in a bidentate *cis*-fashion.



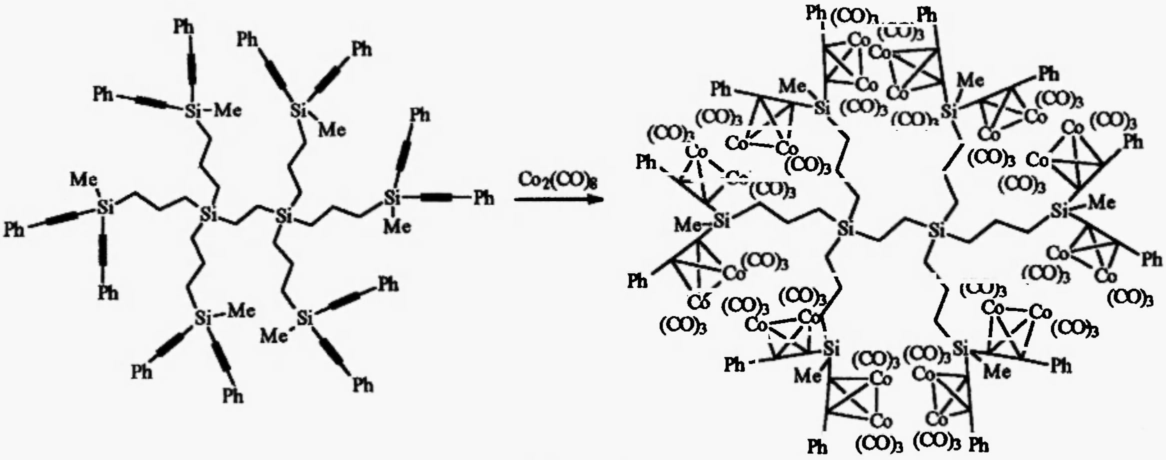
Scheme 12

In view of the high reactivity of the $HC\equiv C$ bond carbosilane dendrimers with ethynyl groups at the periphery were prepared and their reactions with $Co_2(CO)_8$ were investigated. Tetrakis[2-(ethynyldimethylsilyl)ethyl]silane reacted with 4 molar equivalents of $Co_2(CO)_8$ in petroleum ether during 24 h at room temperature to give dendrimer with four terminal acetylenedicobalt hexacarbonyl substituents as dark red crystals. X-ray diffraction of this complex clearly confirms such structure. The reaction of $Co_2(CO)_8$ (12 molar equivalents) with the acetylene dendrimer of the next generation proceeded similarly in 98% yield (Scheme 13) [11].

1,2-Bis(triallylsilyl)ethane and 2,4,6,8-tetramethyl-2,4,6,8-tetravinylcyclotetrasiloxane-based dendrimers containing terminal bis(phenylethynyl)methylsilyl $(PhC\equiv C)_2SiMe$ fragments [29] also reacted with $Co_2(CO)_8$ readily and completely (Scheme 14)

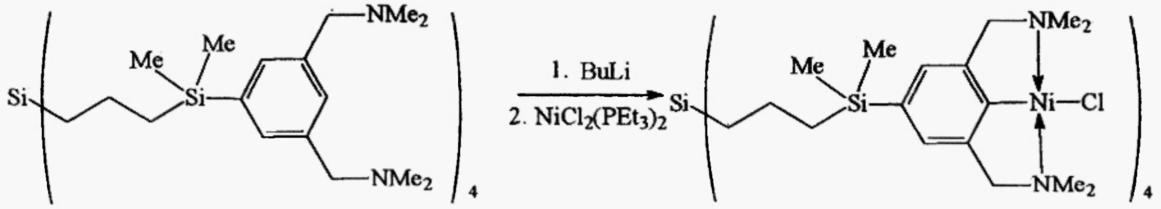


Scheme 13



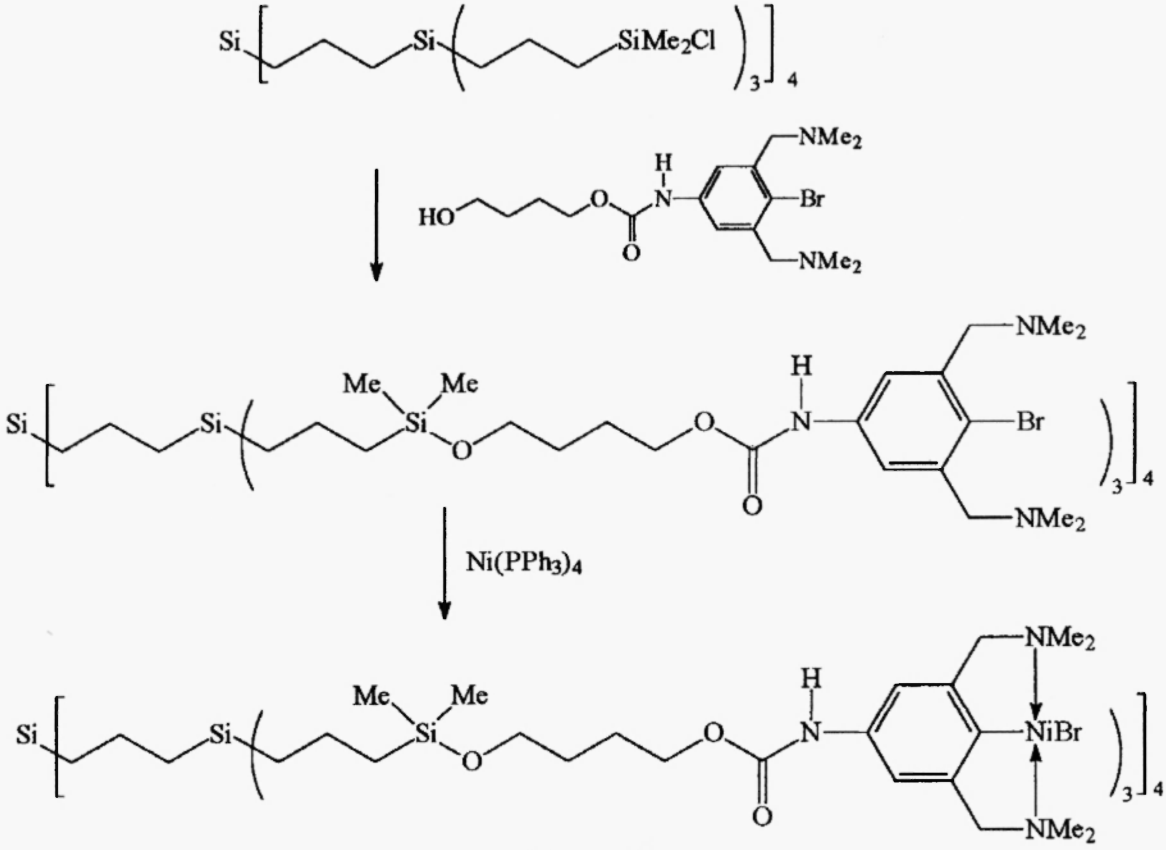
Scheme 14

Nickel-containing dendrimers were prepared by transmetallation of 3,5-bis(dimethylaminomethyl)-4-lithiophenyl derivatives with $NiCl_2(PEt_3)_2$ (Scheme 15) [30, 31]. A disadvantage of this procedure is that not all 3,5-bis(dimethylaminomethyl)phenyl groups become nickelated as a result of partial hydrolysis during workup of extremely moisture-sensitive lithium intermediates.



Scheme 15

Nickel complexes were also obtained by reaction of 3,5-bis(dimethylaminomethyl)-4-bromophenyl-terminated compounds with excess of nickel complex $N(PPh_3)_4$ in THF for 4 h at 60-70 °C (Scheme 16). These dendrimers showed regiospecific catalytic activity for the Kharasch addition of polyhaloalkanes to the carbon-carbon double bonds [32].

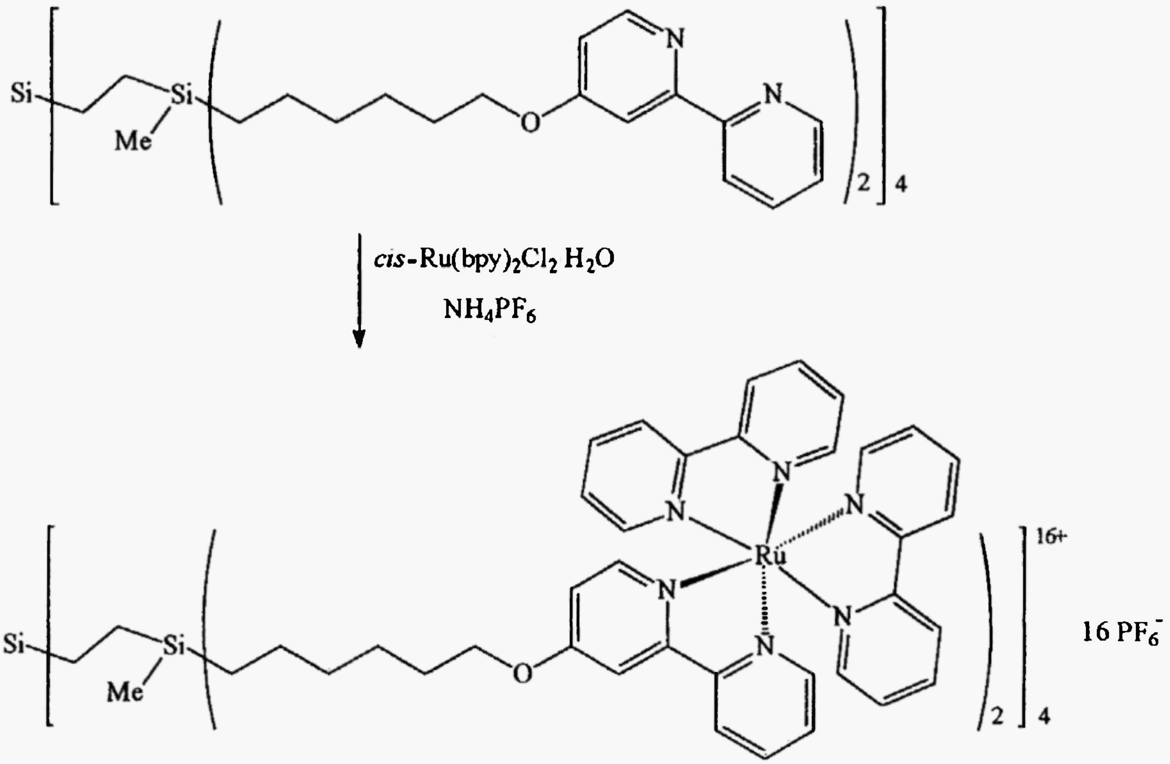


Scheme 16

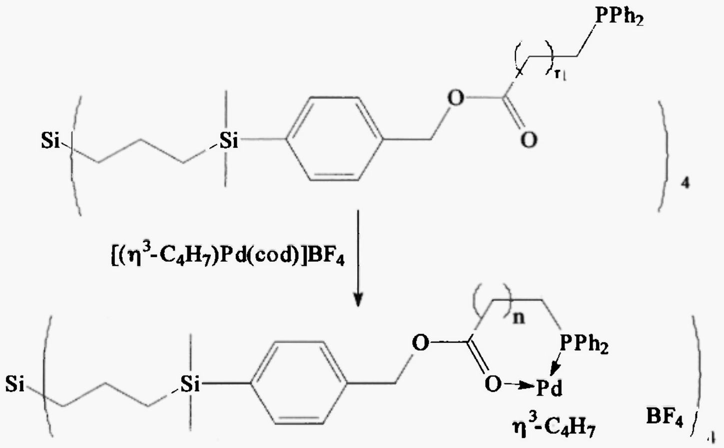
A supramolecular assembly with eight peripheral ruthenium tris(bipyridine) units covalently linked to a carbosilane dendrimer has been synthesized [33]. For this purpose dendrimer with 8 bipyridyloxy end groups was refluxed with excess of *cis*-$Ru(bpy)_2Cl_2 \cdot 2H_2O$ in ethanol during 3 days (yield 75%) (Scheme 17).

Carbosilane dendrimers with chelating monodentate ($SiCH_2PPh_2$) and bidentate phosphine [$Si(CH_2PPh_2)_2$] end ligands reacted with $[(\eta^3\text{-}C_3H_7)PdCl]_2$ to form allylpalladium complexes of these dendrimers. According to ^1H and $^{31}P\text{-}\{^1H\}$ NMR monodentate phosphine dendrimers gave rise to a mixture of products, while compounds with [$Si(CH_2PPh_2)_2$] terminal groups coordinated in a bidentate way resulting in well defined palladium complexes which were used as catalysts in the allylic alkylation reactions performed in a continuous flow membrane reactor [34].

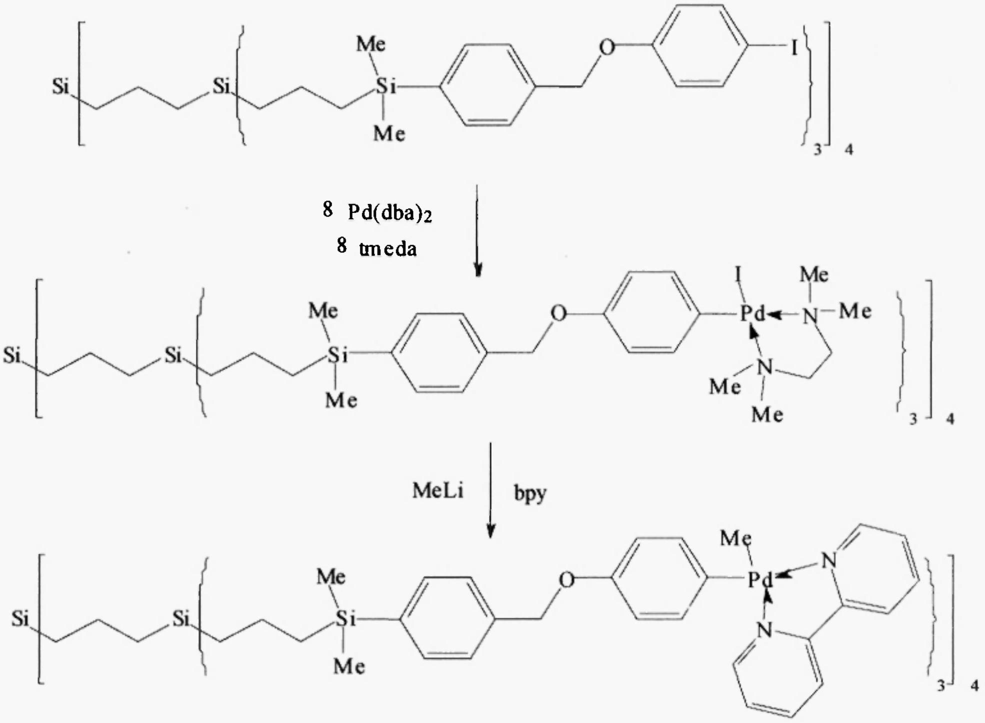
New Pd-catalysts were derived from carbosilane dendrimers with various ω-diphenylphosphinylcarboxylic acid ester end groups by reaction with equimolar amounts of $[(\eta\text{-}C_4H_7)Pd(COD)]BF_4$ (COD = 1,4-cyclooctadiene) in CH_2Cl_2 at 0°C during 1 h (Scheme 18) [35].



Scheme 17



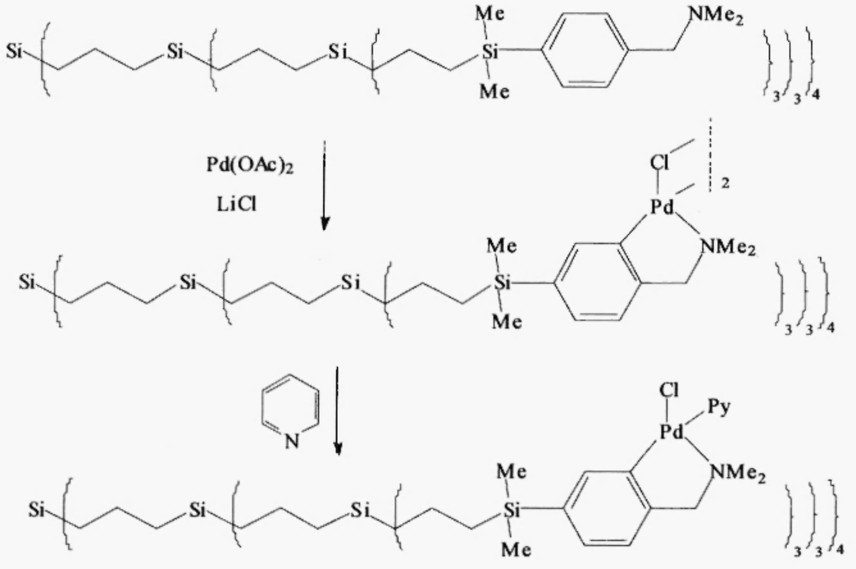
Scheme 18



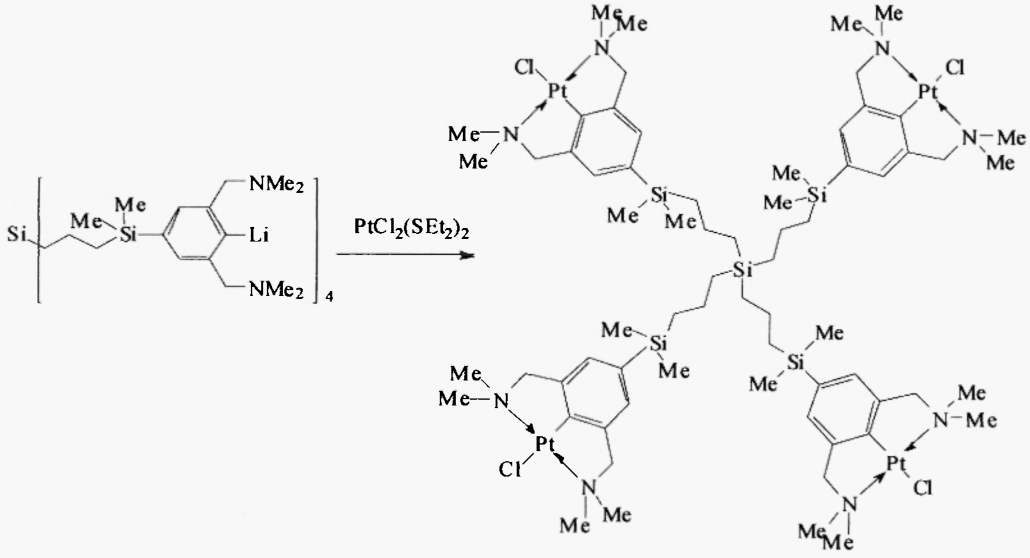
Scheme 19

The oxidative addition of substituted dendrimeric species with four (**G0**) or twelve (**G1**) peripheral iodoaryl groups to Pd(0) complex $Pd_2(dba)_2$·dba/tmeda (dba = dibenzylideneacetone, tmeda = N,N,N'.N'-tetramethylethylenediamine) proceeded in 88% and 33% overall yields, respectively. Reaction of tmeda-containing complexes with excess of MeLi gave diorganopalladium complexes without formation of metallic palladium. However, due to their thermal instability in the solid state, the ligand exchange reactions with 2,2'-bipyridine were performed as soon as possible. These complexes were synthesized in 63% and 51% yields, respectively (Scheme 19) [36, 37].

Cyclopalladation of 4-dimethylaminomethylphenyl-functionalized dendrimer via a multiple and selective C-H activation by $Pd(OAc)_2$ in methanol at ambient temperature yielded insoluble bispalladium chloride derivative after addition of LiCl. The insolubility of the presumed product could be explaned by a large increase in aggregation of this intermediate species. The obtained product was converted *in situ* into the correspondent pyridine adduct by reaction with an excess of pyridine (Scheme 20) [38].

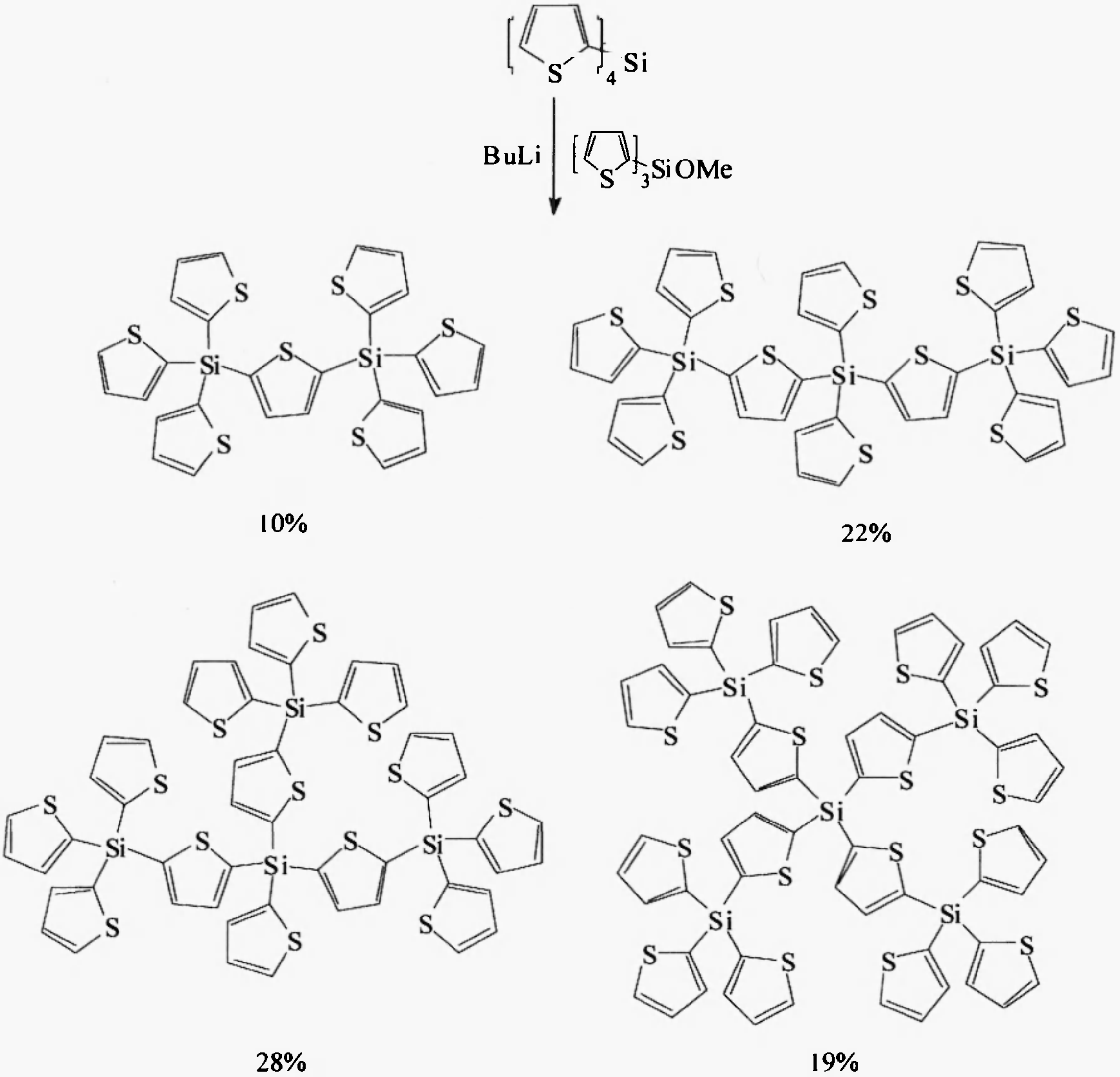


Scheme 20



Scheme 21

Incorporation of the platinum atom into dendrimeric carbosilane compounds was achieved by lithiation of tetrakis[bis(3,5-dimethylaminomethylphenyl)dimethylsilylethyl]silane with *t*-BuLi and subsequent treatment of freshly prepared lithium derivative with a slight excess of $PtCl_2(SEt_2)_2$ in THF solution (Scheme 21) [39].

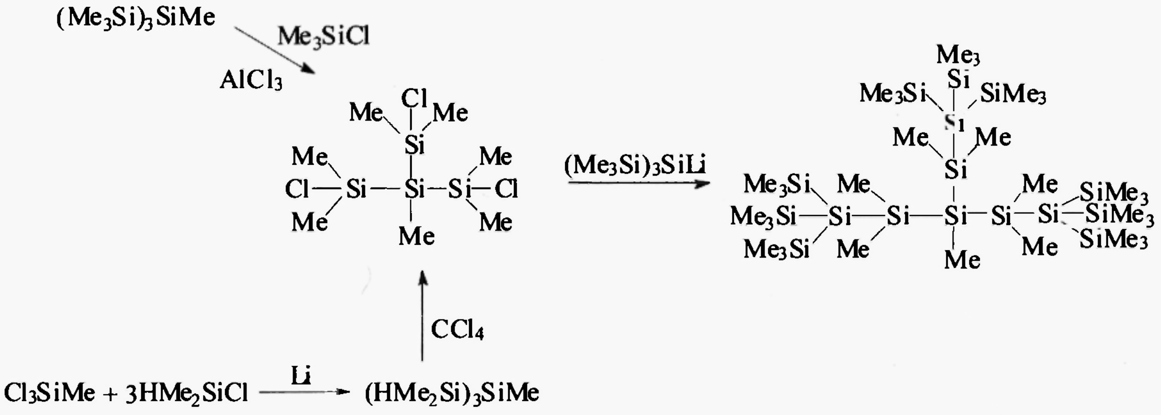


Scheme 22

Recently the first dendrimer containing both silicon atoms and thiophene rings has been prepared [40]. The zeroth generation dendrimer, tetra(2-thienyl)silane, was lithiated with 4 equimolar amounts of BuLi in ether and quenched with 4 molar amounts of methoxytri(2-thienyl)silane. The expected first generation dendrimer tetrakis{2-[5-tri(2-thienyl)silyl]thienyl}silane was separated in 19% yield along with products of mono- (10%), di- (22%) and trilithiation (28%) (Scheme 22).

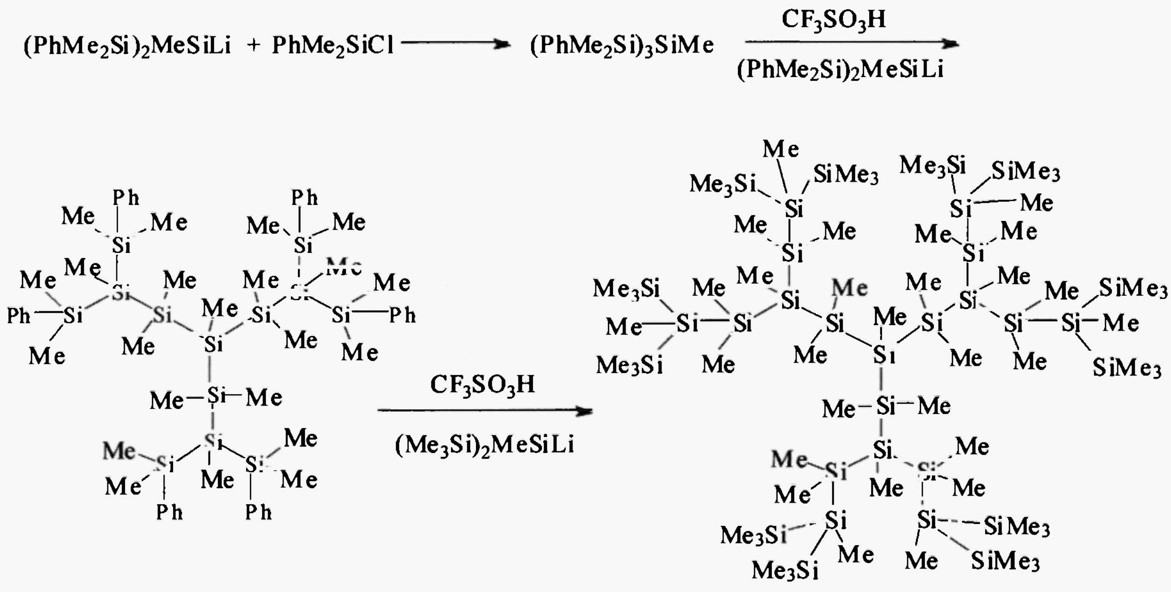
2. POLYSILANE DENDRIMERS

Polysilane dendrimers containing silicon atoms connected to three or four other silicon atoms are of interest for their structural, electronic, optical and chemical properties. Very few well-characterized branched polysilanes have been reported. The first example of a dendritic polysilane (methyl[tris(permethylneopentasilyl)silane) was published in 1995 [41]. This compound was prepared by two slightly different routes starting from methyltris(trimethylsilyl)silane [41, 42] or methyltrichlorosilane [43] (Scheme 23). The molecular structure of the product was confirmed by X-ray diffraction.

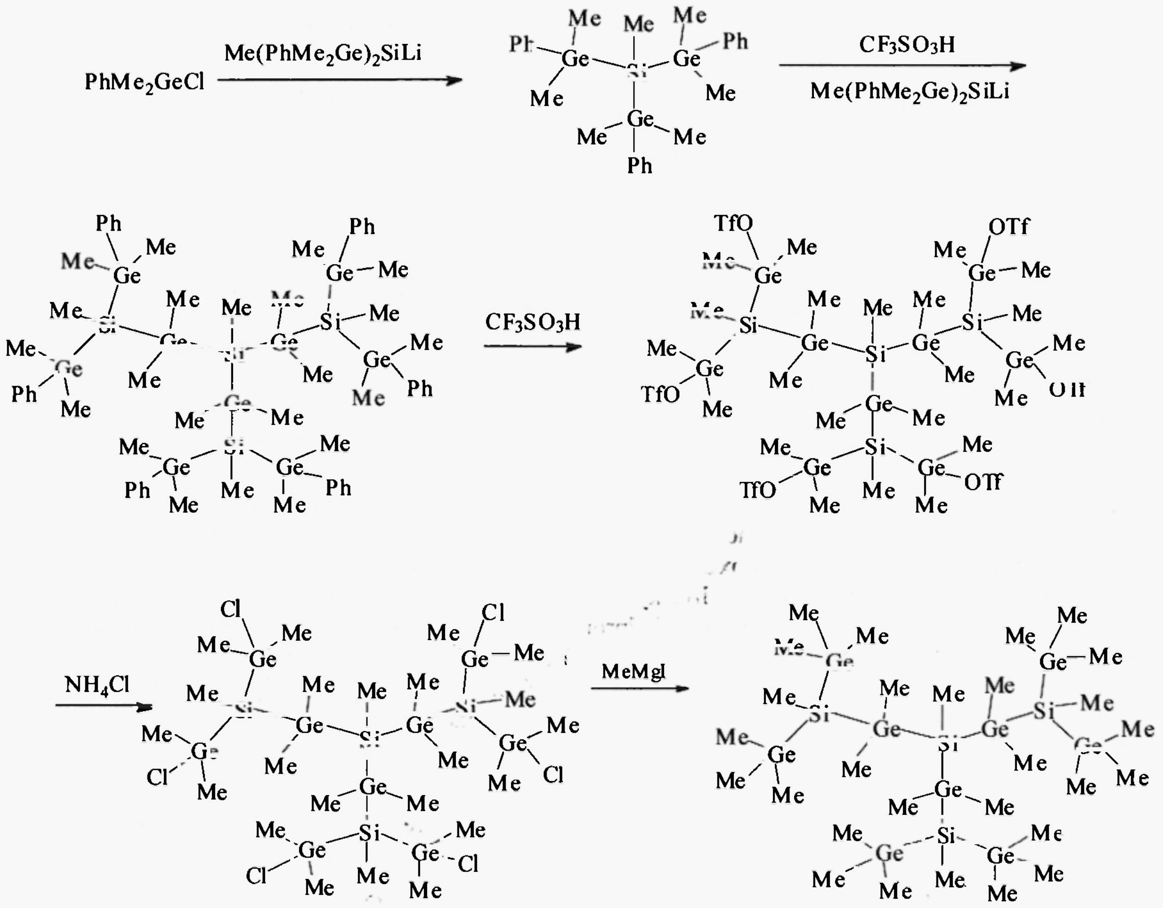


Scheme 23

The divergent method for the longest polysilane dendrimer synthesis is shown in Scheme 24. First, dimethylphenylchlorosilane $PhMe_2SiCl$ reacted with methylbis(dimethylphenylsilyl)silyllithium to give quantitatively methyltris(dimethylphenylsilyl)silane possessing a core and three branching points for a polysilane dendrimer. It was treated with 3 equivalents of trifluoromethanesulfonic acid in CH_2Cl_2 followed by the reaction with methylbis(dimethylphenylsilyl)silyllithium to yield the product of the first generation in 43% yield. The same procedure with 6 equivalents of trifluoromethanesulfonic acid and methylbis(trimethylsilyl)silyllithium resulted in the formation of the second generation polysilane characterized by X-ray analysis [44].



Scheme 24



Scheme 25

The divergent growth method was used to synthesize the first-generation permethylated dendrimer with alternating silicon and germanium atoms in the chain [45]. The reaction of chlorodimethylphenylgermane with bis(dimethylphenylgermyl)methylsilyllithium in ether gave the coupled product tris(dimethylphenylgermyl)methylsilane as the initiator core in quantitative yield. The initiator core of this compound possesses three branching points with phenyl protecting groups. These groups were readily substituted by treatment with 3 equivalents of trifluoromethanesulfonic acid in CH_2Cl_2 at 0 °C. The resulting deprotected product was subsequently treated with the branching reagent [bis(dimethylphenylgermyl)methylsilyllithium] to give the first-generation dendrimer with six terminal phenyl groups in 12 % yield. The hybrid permethyl-substituted dendrimer has been synthesized by subsequent reactions with CF_3SO_3H, NH_4Cl and MeMgI (Scheme 25).

The molecular structure of permethylated dendrimer was confirmed by X-ray diffraction. There are two independent molecules in the unit cell, the Si-Ge bond lengths (2.376 – 2.405 Å) are within the normal range, the inner Si-Ge distances being somewhat longer than the terminal ones.

3. CARBOSILAZANE DENDRIMERS

A novel family of air-stable dendrimers with SiN_3 centre has been prepared starting from trisilylamine $(CH_2=CHSiMe_2)_3N$ [46] by hydrosilylation with dimethylchlorosilane in the presence of Karstedt catalyst. A 1-to-2 branching of the product was achieved by reaction of three-directional core with $KN(SiMe_2CH=CH_2)_2$. By repeating the above two steps, the dendrimers of second, third and fourth generations were obtained (Scheme 26). The branching unit $KN(SiMe_2CH=CH_2)_2$ can be replaced by metallated disilazanes such as $LiN(SiMe_2Ph)_2$ or $LiN(SiMe_3)_2$ to give phenyl- or methyl-substituted generations.

$$\mathrm{N(SiMe_2CH{=}CH_2)_3 + 3\,ClSiMe_2H \longrightarrow N(SiMe_2CH_2CH_2SiMe_2Cl)_3}$$

$$\xrightarrow{\mathrm{KN(SiMe_2CH{=}CH_2)_2}} \mathrm{N[SiMe_2CH_2CH_2SiMe_2N(SiMe_2CH_2CH_2SiMe_2Cl)_2]_3}$$

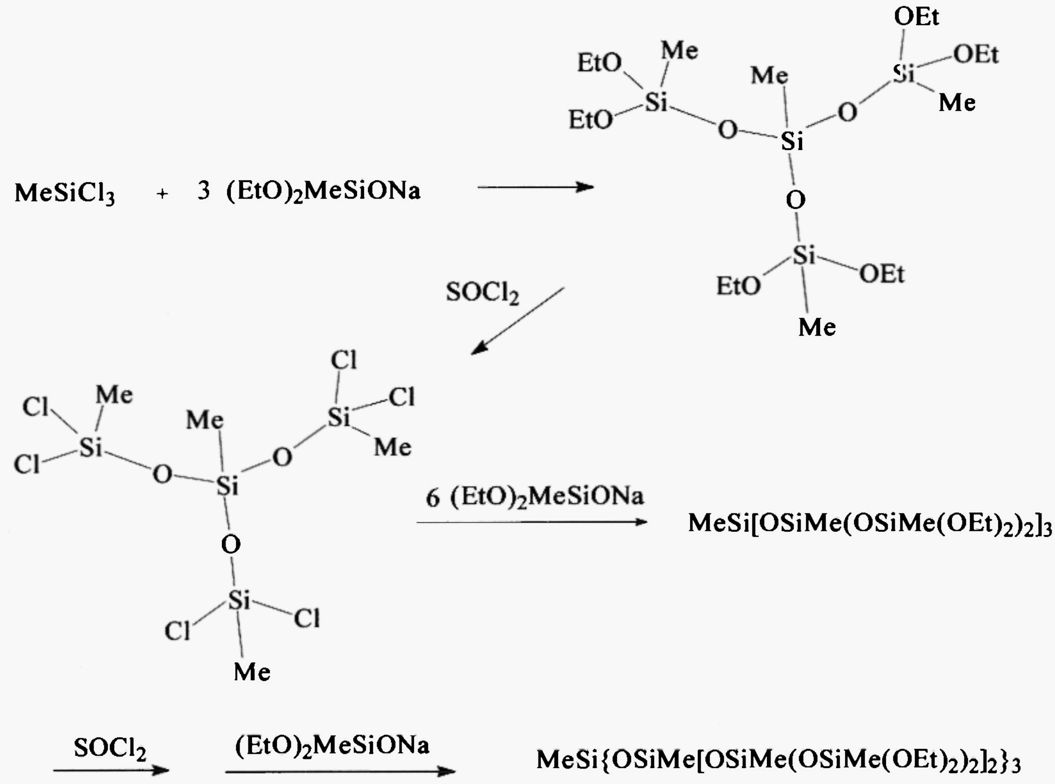
Scheme 26

4. SILOXANE AND CARBOSILOXANE DENDRIMERS

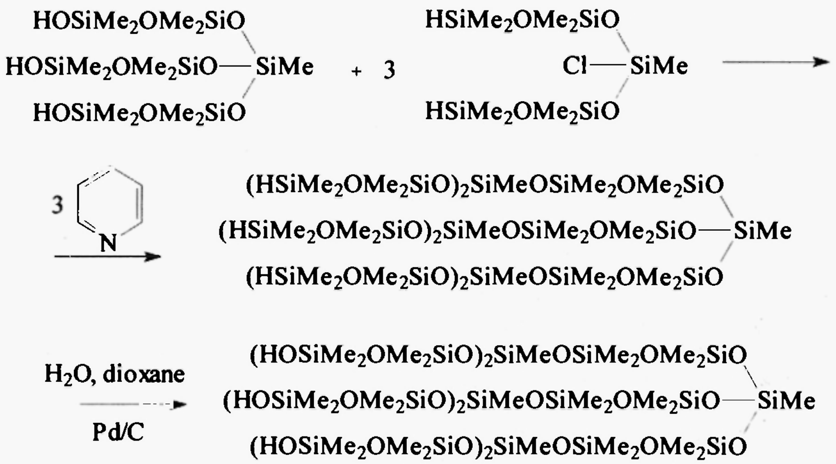
The construction of oligosiloxanes with defined structures is determined by the availability of various cores, elongation units and also by the reliable coupling methodology. As it was mentioned the first silicon-based dendrimer containing siloxane core was obtained by condensation of methyltrichlorosilane with $(EtO)_2MeSiONa$ and subsequent substitution of ethoxy groups with $SOCl_2$. By repetitive $(EtO)_2MeSiONa$ and $SOCl_2$ reaction steps dendrimer containing 48 silicon atoms was prepared (Scheme 27) [2, 47].

Coupling of $[Me_2(HO)SiOMe_2SiO]_3SiMe$ (core unit) and $(Me_2HSiOMe_2SiO)_2Si(Cl)Me$ (elongation unit) in the presence of pyridine proceeded smoothly to give the siloxane dendrimer of the first generation. Hydroxylation of this product (H_2O, dioxane, Pd/C) and repetition of the chain elongation led to dendrimers of the second and third generation without problem (Scheme 28) [48].

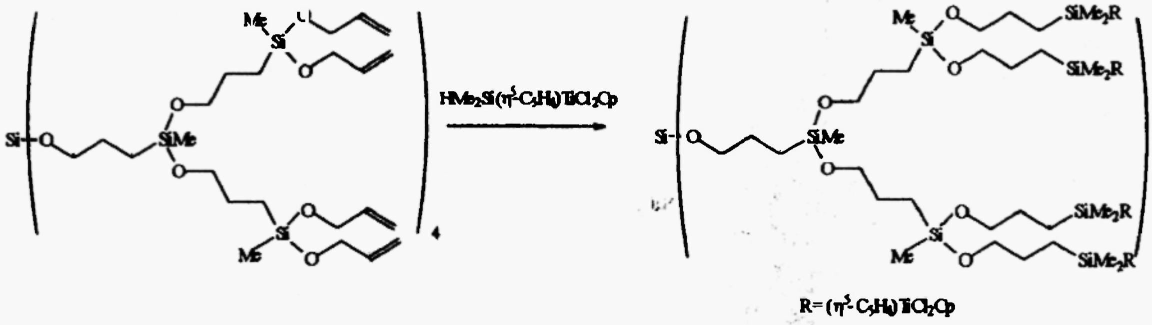
For the synthesis of carbosiloxane dendrimers repetitive hydrosilylation – alkoxylation cycles were applied [49-54]. Hydrosilylation of tetraallyloxysilane with $HSiMeCl_2$ in the presence of catalytic amounts of H_2PtCl_6 afforded tetrakis(3-dichloromethylsilylpropoxy)silane $(Cl_2MeSiCH_2CH_2CH_2O)_4Si$ in high yield. Treatment of this product with $CH_2{=}CHCH_2OH$ and Et_3N gave a dendrimer which was functionalized with titanocene fragment via hydrosilylation reactions (Scheme 29) [49]. 2,4,6,8-Tetramethyl-2,4,6,8-tetravinylcyclotetrasiloxane and 1,2-bis(triallyloxysilyl)ethane have been used as core molecules in similar procedures [53]



Scheme 27



Scheme 28



Scheme 29

Hyperbranched polycarbosiloxane was obtained by polymerization of tris(dimethylsiloxy)allylsilane $CH_2=CHCH_2Si(OSiMe_2H)$ in a 1:1 mixture of acetonitrile and ether under nitrogen using H_2PtCl_6 as catalyst [55].

AKNOWLEDGEMENT

We are grateful to the Latvian Council of Science (grant No. 187) for financial support.

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Received: November 28, 2001 - Accepted: January 10, 2002 - Accepted in publishable format: January 14, 2002