

New dendritic systems based on sterically hindered carbosilane units – synthesis and application

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Dedicated to Professor Edmunds Lukevics on his 70th birthday

Abstract

Carbosilane dendrimers of a novel architecture were prepared by setting up building blocks, incorporating sterically hindered tris(trimethylsilyl)methyl ligand. This method gives a possibility to synthesize abundantly functionalized low generation dendrimers. Such molecules, functionalized with vinyl groups in their outer sphere, were used for preparation of new Pt(0) complexes.

Keywords: Trisyl, dendrimers, platinum, catalyst

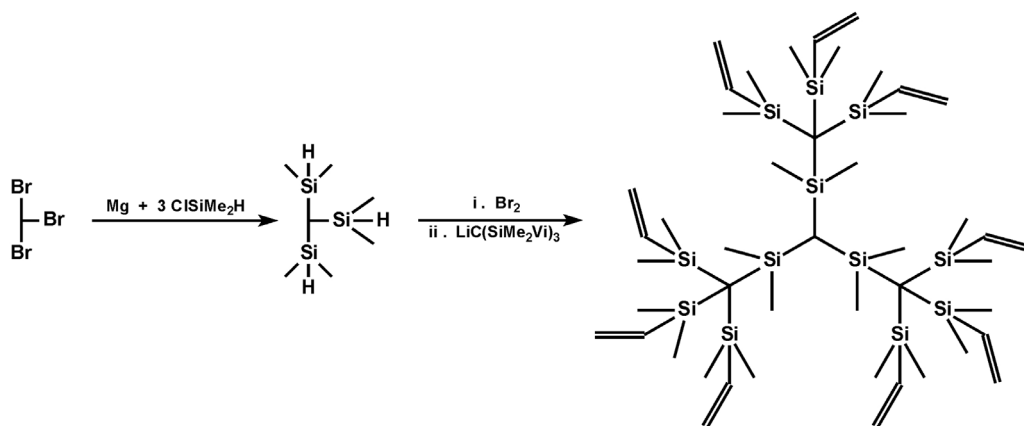
Introduction

Dendritic polymers of carbosilane type structure, because of their kinetic and thermodynamic stability,¹ have been widely used as anchoring support for catalytic moieties. These systems draw considerable attention, since their well-defined architecture allows for construction of a precisely controlled catalyst structure. Molecules, functionalized in their core, focal point and outer sphere are widely used in the synthesis of catalytic systems.² The number of catalytic sites, anchored to the support as well as their distribution, can be tailored, which is of importance for the catalytic system performance (activity, selectivity, stability, and recycling). Various platinum dendritic catalysts have been already made by Pt coordination to ligands bearing such functional groups as amino, phosphanyl, and related sites.^{3,4} However, the existing, classic platinum(0) complexes are those involving multiple carbon-carbon bonds.⁵ Such Pt-complexes are frequently used as catalysts for hydrosilylation of olefins and alkynes. The most common active Pt-containing system is Karstedt catalyst – a zerovalent, planar and three-coordinate platinum complex $\{\text{Pt}_2(\text{CH}_2=\text{CHSiMe}_2)_2\text{O}\}_3$. Whereas there are not many reports on carbosilane dendrimers with vinyl-Pt(0) complexes on their periphery, similar Pt(0) catalysts supported on branched vinyl

functionalized polysiloxanes grafted on silica were also reported.⁶ This work presents a new way for preparation of carbosilane dendrimers and their transformation into platinum(0) scaffolds.

Results and Discussion

A group of sterically hindered “trisyl”(Tsi)-type carbosilane species, named after their “parent” compound tris(trimethylsilyl)methane, have been studied for some years now for their unique properties and chemistry.⁷ More recently, they were utilized in polymer science, for example as side functional groups⁸ or catalysts in cationic polymerization.⁹ In this report $\text{HC}(\text{SiMe}_2\text{R})_3$ ($\text{R} = \text{H}, \text{Br}, \text{CH}=\text{CH}_2$) were used as building blocks for the synthesis of dendritic carbosilane species. In the synthesis of dendritic molecules, two general strategies can be applied.¹⁰ The divergent one is based on dendrimer construction outwards from the core, whereas the opposite convergent approach is a stepwise dendrimer construction from the periphery to the focal point. A mixed convergent-divergent modification of the two is also possible. The Tsi-based carbosilane dendrimers were prepared applying this method. The central core (HCBR_3) is coupled with chlorosilane in the first step and then, the independently prepared, multifunctional segments are attached to form next generations (Scheme 1). The reaction between halogenated silyl groups and lithiated segments allows the preparation of a regular network with alternating Si-C bonds.



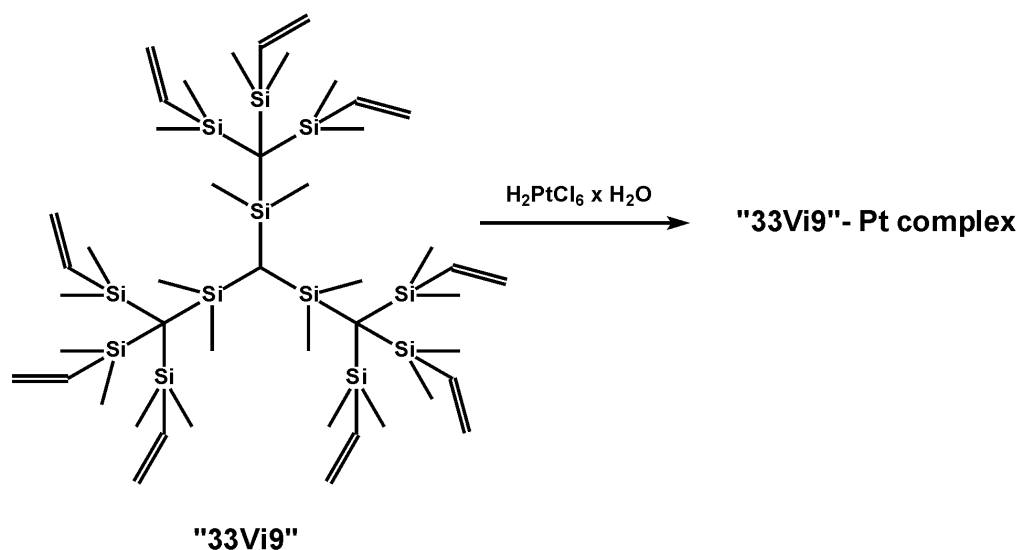
Scheme 1. Preparation of Tsi-type carbosilane dendrimers.

Tsi-carbosilane dendrimers functionalized with various groups in their outer sphere can be utilized¹¹ as crosslinker as well as core molecules in star shape polymers, etc. The presence of reactive groups on the surface of dendrimers make them an attractive support for coordination of metals from platinum group. Platinum was coordinated to vinyl-carbosilane 33Vi9 (Scheme 2) based on the procedure of Lappert et al.^{5b} The polymer is a waxy solid and thus it had to be dissolved in toluene, prior to modification. After the reaction, all volatiles were removed in

vacuo to give a dark brown viscous solid, soluble in common solvents (CH_2Cl_2 , toluene, acetone etc.).

NMR techniques can afford interesting information about structure of Pt-complexes.^{5c,12} Typically, ^1H and ^{13}C NMR show broad resonances characteristic of Pt(0)-vinyl at 2-4 ppm and 54-59 ppm¹³, respectively. A similar shift of vinyl protons for $^{33}\text{Vi}9$ -Pt complex was observed. The reagents ($^{33}\text{Vi}9$ and H_2PtCl_6) were mixed to give 3-fold molar excess of vinyl groups to platinum. The ^1H NMR spectrum of ^{33}Vi -Pt contains only resonances of vinyl groups coordinated to platinum. It points to coordination of three vinyl groups to each platinum atom, similarly to Karstedt catalyst. It was also noticed that shortening of the reaction time leads to the formation of a material with vinyl groups partly coordinated to platinum atoms (50 % yield after 2.25 h at 50 °C). In both cases, the NMR resonances are recorded as broad sets of peaks rather than isolated signals, which suggest the presence of a mixture of compounds of related structure.

^{195}Pt NMR distinguishes Pt(0) and Pt(II) regions (upfield of -4000 ppm, and -2500 to -4500 ppm, respectively). In the NMR spectrum of a commercial solution of Karstedt catalyst in xylenes (ABCR) gave ^{195}Pt NMR signal at -6339.8 ppm. Complex $^{33}\text{Vi}9$ -Pt shows that the ^{195}Pt NMR peak shifts upfield to -7369.2, presumably due to different electron density for outer sphere vinyl groups of ^{33}Vi -9, compared to those in $\text{ViMe}_2\text{SiOSiMe}_2\text{Vi}$.



Scheme 2. Platinum functionalization of carbosilane dendrimer $^{33}\text{Vi}9$.

FT-IR spectra of $^{33}\text{Vi}9$ material, registered before and after reaction with $\text{H}_2\text{PtCl}_6/\text{H}_2\text{O}$, are shown on figure 1. The comparison of spectra does indicate changes in carbosilane structure. Broadening of bands due to Pt-Vi interactions occurred, but the ones characteristic to $\text{Si}-\text{CH}=\text{CH}_2$ group (1400, 1010 and 980 cm^{-1}) can be clearly seen.

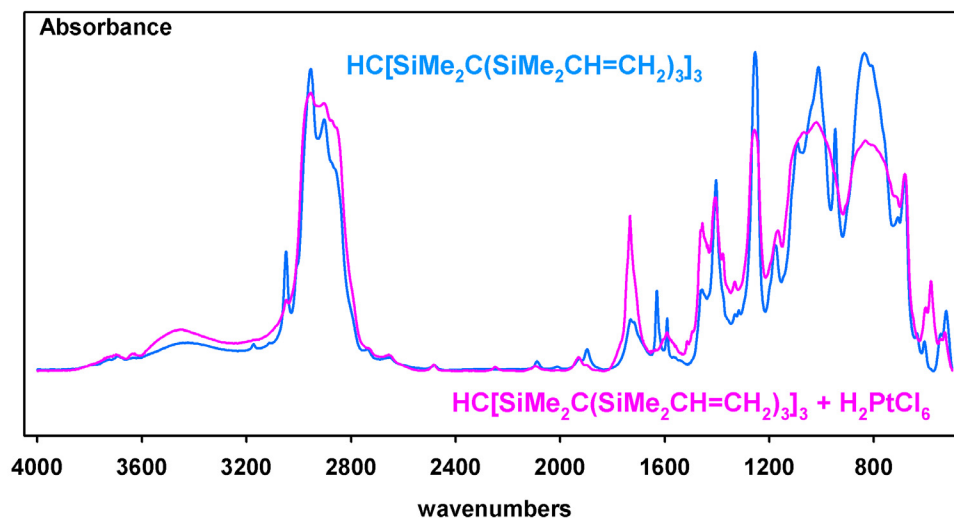


Figure 1. FT-IR spectra of 33Vi9 and its platinum complex.

Experimental Section

General Procedures. Dendrimer 33Vi-9 was prepared under an inert atmosphere using standard Schlenk line techniques. $\text{HC}(\text{SiMe}_2\text{R})_3$ ($\text{R} = \text{H}$ or $\text{CH}=\text{CH}_2$) were prepared from HCBBr_3 and the respective chlorosilanes by standard procedures.¹⁴ $\text{HC}(\text{SiMe}_2\text{Br})_3$ was prepared as described previously.^{14a} Tetrahydrofuran was dried and distilled from LiAlH_4 prior to use. HCBBr_3 , MeLi (1.6 M solution in diethyl ether), CBr_4 and chlorosilanes (Aldrich) were used, as supplied.

^1H , ^{13}C , ^{29}Si and ^{195}Pt NMR spectra were recorded in deuterated chloroform used as a solvent, on a Bruker spectrometer operating at 500 MHz. CDCl_3 was used as an internal reference standard for ^1H , ^{13}C and ^{29}Si NMR. ^{195}Pt -NMR data were collected with K_2PtCl_6 as reference standard. IR spectra were recorded using a FT-IR ATI Mattson spectrometer. Elemental analyses were performed by Microanalysis Services at Center of Molecular and Macromolecular Studies in Lodz.

Dendrimer 33Vi-9 (1). $\text{LiC}(\text{SiMe}_2\text{CH}=\text{CH}_2)_3\text{-THF}$ complex was prepared, following a typical procedure,¹⁵ from 1.54 g (5.7 mmol) of $\text{HC}(\text{SiMe}_2\text{CH}=\text{CH}_2)_3$ and 5.9 mmol of MeLi (3.7 ml, 1.6 M solution in Et_2O) in 50 ml of THF. After the lithiation of $\text{HC}(\text{SiMe}_2\text{CH}=\text{CH}_2)_3$ was complete, a solution of $\text{HC}(\text{SiMe}_2\text{Br})_3$ (803 mg, 1.88 mmol) in 50 ml of THF was transferred drop-wise via a canula at 60 °C to the Schlenk flask containing the orange solution of $\text{LiC}(\text{SiMe}_2\text{CH}=\text{CH}_2)_3\text{-THF}$ complex. The solution turned yellow upon the addition of $\text{HC}(\text{SiMe}_2\text{Br})_3$. The reaction mixture was stirred for 16 h at 60 °C and then THF was removed under vacuum, Et_2O (50 ml) was added and the solution was washed with cold water until $\text{pH} = 7$ and dried over MgSO_4 . After concentration, the resulting dendrimer was precipitated with MeOH and dried in vacuo (1.42 g, 76% yield). FT-IR: $\nu_{\text{max}}/\text{cm}^{-1}$ 3047, 2953, 2902, 1732, 1630, 1590, 1403, 1254, 1176, 1092, 1077, 1011, 947, 836, 708, 681. ^1H -NMR (CDCl_3): δ -0.55 (singlet, 1H, HCSi), 0.18

(singlet, 18H, CSiMe_2C), 0.20 (singlet, 54H, $\text{SiMe}_2\text{CH}=\text{CH}_2$), 5.7 (multiplet, 18H, $\text{SiMe}_2\text{CH}=\text{CH}_2$) 6.3 (multiplet, 9H, $\text{SiMe}_2\text{CH}=\text{CH}_2$). ^{13}C -NMR (CDCl_3): δ 0.59 ($\text{SiMe}_2\text{CH}=\text{CH}_2$), 1.24 (HCSiMe_2), 5.80 [$\text{SiC}(\text{SiMe}_2\text{CH}=\text{CH}_2)_3$], 30.6 (HCSiMe_2), 130.63 ($\text{SiMe}_2\text{CH}=\text{CH}_2$), 141.65 ($\text{SiMe}_2\text{CH}=\text{CH}_2$). ^{29}Si -NMR (CDCl_3): δ 13.8 (HCSiMe_2), -4.74 ($\text{SiMe}_2\text{CH}=\text{CH}_2$). Anal. Calcd for $\text{C}_{46}\text{H}_{100}\text{Si}_{12}$: C, 55.79; H, 10.18. Found C, 54.42; H, 10.01.

Platinum complex of 33Vi-9 (2). 33Vi-9 (161 mg, 0.162 mmol) was placed in a 3-necked flask equipped with a condenser and neutral gas inlet, and dissolved in toluene (2 ml). H_2PtCl_6 (253 mg, 0.489 mmol) and H_2O (30 mg, 1.7 mmol) were added to form a bi-phase system with 33Vi-9 solution. The mixture was stirred and heated at 50 °C for 4.5 h. The toluene layer turned brown and was separated after cooling to 25 °C. Volatiles were removed under vacuum to give 250 mg (97 % yield) of a dark brown liquid material. ^1H -NMR (CDCl_3): δ -0.83 (singlet, 1H, HCSiMe_2C), (-0.1)-0.4 {set of peaks, 72H, $\text{HC}[\text{SiMe}_2\text{C}(\text{SiMe}_2\text{CH}=\text{CH}_2)_3]_3$ }, 3.6 (multiplet, 18H, $\text{SiMe}_2\text{CH}=\text{CH}_2$), 4.15 (multiplet, 9H, $\text{SiMe}_2\text{CH}=\text{CH}_2$). ^{13}C -NMR (CDCl_3): δ (-0.1)-6.5 set of peaks $\text{HC}[\text{SiMe}_2\text{C}(\text{SiMe}_2\text{CH}=\text{CH}_2)_3]_3$, 31.6 (HCSiMe_2), 62-65 ($\text{SiMe}_2\text{CH}=\text{CH}_2$). ^{195}Pt -NMR (CDCl_3): δ -7369.2. Anal. Calcd for $\text{C}_{46}\text{H}_{100}\text{Si}_{12}\text{Pt}_3$: C, 35.07; H, 6.40. Found C, 33.92; H, 6.09.

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