

# Synthesis of Carbosilane Dendrimers Containing Peripheral (Cyclopentadienyl)(aryloxy)titanium(IV) Units

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Treatment of  $[\text{Ti}(\text{C}_5\text{H}_5)\text{Cl}_3]$  with 4-allyl-2,6-dimethoxyphenol (**II**) gave the corresponding aryloxy complex  $[\text{Ti}(\text{C}_5\text{H}_5)\{\text{OC}_6\text{H}_2(\text{OMe})_2(\text{C}_3\text{H}_5)\}\text{Cl}_2]$  (**2**), while hydrosilylation reactions of the allyl group of 4-allyl-2-methoxyphenol (eugenol; **I**) or 4-allyl-2,6-dimethoxyphenol (**II**) with  $\text{HSiEt}_3$  and subsequent reaction with  $[\text{Ti}(\text{C}_5\text{H}_5)\text{Cl}_3]$  led to the mononuclear compounds  $[\text{Ti}(\text{C}_5\text{H}_5)\{\text{OC}_6\text{H}_{4-n}(\text{OMe})_n(\text{C}_3\text{H}_6\text{SiEt}_3)\}\text{Cl}_2]$  ( $n = 1$  (**3**), 2 (**4**)) in high yield. This synthetic procedure has been used as a model for the preparation of new peripheral carbosilane metallodendrimers. Series of carbosilane dendrimer generations G1, G2, and G4, with 4, 8, and 32 end groups, respectively, have been functionalized with these phenol groups on the surface. The divergent synthesis was accomplished via hydrosilylation of the olefinic group of the phenols with the corresponding silicon hydride terminated dendrimers, giving 4G- $[(\text{CH}_2)_3\{\text{C}_6\text{H}_3(\text{OMe})\}\text{OH}]_{32}$  (**9**), 1G- $[(\text{CH}_2)_3\{\text{C}_6\text{H}_2(\text{OMe})_2\}\text{OH}]_4$  (**10**), 2G- $[(\text{CH}_2)_3\{\text{C}_6\text{H}_2(\text{OMe})_2\}\text{OH}]_8$  (**11**), and 4G- $[(\text{CH}_2)_3\{\text{C}_6\text{H}_2(\text{OMe})_2\}\text{OH}]_{32}$  (**12**) as oils in high yield. Reaction of **9–12** with  $[\text{Ti}(\text{C}_5\text{H}_5)\text{Cl}_3]$  afforded corresponding metallodendrimers containing (cyclopentadienyl)-(aryloxy)titanium units at their periphery 4G- $[(\text{CH}_2)_3\{\text{C}_6\text{H}_3(\text{OMe})\}\text{O}]\text{Ti}(\text{C}_5\text{H}_5)\text{Cl}_2]_{32}$  (**15**), 1G- $[(\text{CH}_2)_3\{\text{C}_6\text{H}_2(\text{OMe})_2\}\text{O}]\text{Ti}(\text{C}_5\text{H}_5)\text{Cl}_2]_4$  (**16**), 2G- $[(\text{CH}_2)_3\{\text{C}_6\text{H}_2(\text{OMe})_2\}\text{O}]\text{Ti}(\text{C}_5\text{H}_5)\text{Cl}_2]_8$  (**17**), and 4G- $[(\text{CH}_2)_3\{\text{C}_6\text{H}_2(\text{OMe})_2\}\text{O}]\text{Ti}(\text{C}_5\text{H}_5)\text{Cl}_2]_{32}$  (**18**). The compounds have been characterized by  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{29}\text{Si}$  NMR spectroscopy and elemental analysis and, up to the second generation of phenol-terminated dendrimers, by MALDI-TOF mass spectrometry. Gel permeation chromatography was used for all phenolic dendrimers, showing good linear relationships between calculated molecular weight and retention time.

## Introduction

The immobilization of well-defined, homogeneous olefin polymerization catalysts on solid supports combines the advantages of both heterogeneous and homogeneous processes, such as the morphological control of the resulting polymer and the presence of single active sites.<sup>1</sup> Group 4 metallocenes are examples that must be heterogenized for some industrial applications.<sup>2</sup> Several approaches have been used for this purpose, such as the use of organic support materials such as cross-linked polystyrene,<sup>3</sup> inorganic materials widely used for Ziegler–Natta and Phillips catalysts (silica, alumina, magnesium chloride, etc.),<sup>4</sup> or the self-

immobilization of metallocene catalysts.<sup>2c,5</sup> All these procedures of heterogenization have proven to be very successful for the commercial-scale production of polyolefins. However, transition-metal complexes anchored to these supports are difficult to study at the molecular level for several reasons, which include an inaccurate control of the number and location of the active sites.

In search of models that could elucidate a structure–activity relationship of the active sites, several authors have studied different strategies such as the synthesis of group 4 metal silsesquioxane precursors,<sup>6</sup> as mimics for silica-grafted catalysts. Another approach to this might consist of the use of dendrimers,<sup>7</sup> which are highly branched monodisperse, polyfunctionalized macromolecules. Two general strategies for the construction of dendritic molecules containing transition metals have

(1) Hungenberg, K. D.; Kerth, J.; Langhauser, F.; Marczinke, B.; Schlund, R. In *Ziegler Catalysts*; Fink, G., Mühlaupt, R., Brintzinger, H. H., Eds.; Springer-Verlag: New York, 1995; pp 363–386.

(2) (a) Abbenhuis, H. C. L. *Angew. Chem., Int. Ed.* **1999**, *38*, 1058 and references therein. (b) Alt, H. G.; Schertl, P.; Köppl, A. *J. Organomet. Chem.* **1998**, *568*, 263. (c) Alt, H. G. *J. Chem. Soc., Dalton Trans.* **1999**, 1703. (d) Hlatky, G. G. *Coord. Chem. Rev.* **1999**, *181*, 243.

(3) For example see: (a) Grubbs, R. H.; Gibbons, C.; Kroll, L. C.; Bonds, W. D., Jr.; Brubaker, C. H., Jr. *J. Am. Chem. Soc.* **1973**, *95*, 2373. (b) Sun, L.; Hsu, C. C.; Bacon, D. W. *J. Polym. Sci., Part A* **1994**, *32*, 2127. (c) Roscoe, S. B.; Fréchet, J. M.; Walzer, J. F.; Dias, A. J. *Science* **1998**, *280*, 270.

(4) For example see: (a) Kaminsky, W. *Macromol. Chem. Phys.* **1996**, *197*, 3907. (b) Soga, K.; Kaminaga, M. *Makromol. Chem. Phys.* **1994**, *195*, 1369. (c) Tudor, J.; O'Hare, *Chem. Commun.* **1997**, 603.

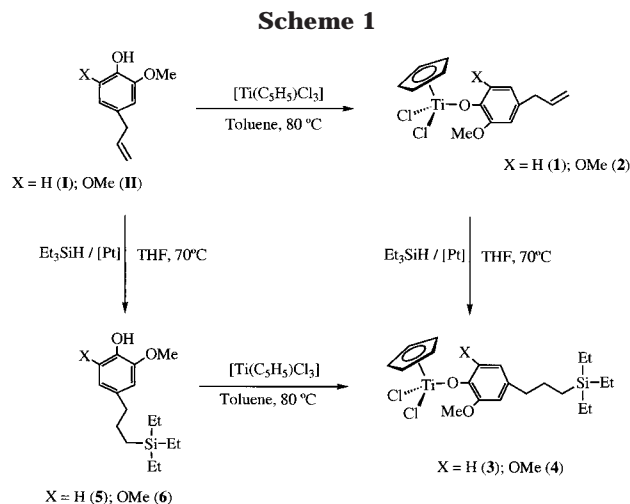
(5) Peifer, B.; Milius, W.; Alt, H. G. *J. Organomet. Chem.* **1998**, *553*, 205.

(6) (a) Crocker, M.; Herold, R. H. M.; Orpen, A. G.; Overgaag, M. T. *A. J. Chem. Soc., Dalton Trans.* **1999**, 3791 and references therein. (b) Duchateau, R.; Abbenhuis, H. C. L.; van Santen, R. A.; Thiele, S. K. H.; van Tol, M. F. H. *Organometallics* **1998**, *17*, 5222. (c) Duchateau, R.; van Santen, R. A.; Yap, G. P. A. *Organometallics* **2000**, *19*, 809.

(7) (a) Issberner, J.; Moors, R.; Vögtle, F. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2413. (b) Lothian-Tomalia, M. K.; Hedstrand, D. M.; Tomalia, D. A.; Padias, A. B.; Hall, H. K., Jr. *Tetrahedron* **1997**, *53*, 15495. (c) Fischer, M.; Vögtle, F. *Angew. Chem., Int. Ed.* **1999**, *38*, 884. (d) Majoral, J. P.; Caminade, A. M. *Chem. Rev.* **1999**, *99*, 845. (e) Hearshaw, M. A.; Moss, J. R. *Chem. Commun.* **1999**, 1.

been applied. The first one entails the formation of one or more catalytic sites in the core of the dendrimer,<sup>8</sup> while the second one involves the attachment of multiple sites at the periphery of the dendritic macromolecules.<sup>9,10</sup> Both types of metallodendrimers represent nanoscopic materials with physical characteristics such as size, solubility, and dispersity of catalytic sites, very precisely defined. All this could afford advantageous properties for physical separation and catalyst recycling while all the characteristics found in the analogous mononuclear model are retained. With respect to the second strategy, although an increasing number of reports have been published about peripheral late-transition-metal dendrimers,<sup>9</sup> titanium and other early transition metals have been scarcely represented.<sup>10</sup>

We are interested in the development of peripheral group 4 metallodendrimers based on a chemically inert carbosilane framework.<sup>11</sup> Furthermore, as a part of our current research, we are involved in the synthesis of mono(cyclopentadienyl)(aryloxy)titanium complexes which are very attractive for polymerization processes.<sup>12</sup> We have previously reported that the reaction of 4-allyl-2-methoxyphenol (**I**; commonly called eugenol) with  $[\text{Ti}(\text{C}_5\text{H}_5)\text{Cl}_3]$  cleanly produced the mononuclear com-



pound  $[\text{Ti}(\text{C}_5\text{H}_5)\{\text{OC}_6\text{H}_3(\text{OMe})(\text{C}_3\text{H}_5)\text{Cl}_2\}]$  (**1**).<sup>13</sup> Eugenol, complex **1** itself, or other related derivatives containing pendant allyl groups are suitable systems for their introduction on the surface of organosilicon dendrimers containing Si–H bonds<sup>11d</sup> via hydrosilylation reactions. We report here the synthesis and characterization of carbosilane dendrimers with peripheral phenolic functionalities and their reaction with  $[\text{Ti}(\text{C}_5\text{H}_5)\text{Cl}_3]$ . A preliminary account of part of this work has been published.<sup>10e</sup>

## Results and Discussion

**Synthesis of Mononuclear Models.** In a synthetic method similar to that previously reported for the aryloxy complex  $[\text{Ti}(\text{C}_5\text{H}_5)\{\text{OC}_6\text{H}_3(\text{OMe})(\text{C}_3\text{H}_5)\text{Cl}_2\}]$  (**1**),<sup>13</sup> the reaction of  $[\text{Ti}(\text{C}_5\text{H}_5)\text{Cl}_3]$  with 1 equiv of 4-allyl-2,6-dimethoxyphenol (**II**) in toluene at 80 °C gave the analogous compound  $[\text{Ti}(\text{C}_5\text{H}_5)\{\text{OC}_6\text{H}_2(\text{OMe})_2(\text{C}_3\text{H}_5)\text{Cl}_2\}]$  (**2**) as red microcrystals in 85% yield (Scheme 1). Hydrosilylation of compounds **1** and **2** with triethylsilane ( $\text{HSiEt}_3$ ) were studied using the Karstedt catalyst (platinum divinyltetramethyldisiloxane).<sup>14</sup> The reactions proceeded in toluene at 60–70 °C, affording  $[\text{Ti}(\text{C}_5\text{H}_5)\{\text{OC}_6\text{H}_4-n(\text{OMe})_n(\text{C}_3\text{H}_6\text{SiEt}_3)\text{Cl}_2\}]$  ( $n = 1$  (**3**), 2 (**4**)) as the main products, resulting from anti-Markovnikov addition ( $\beta$ -isomer) of  $\text{HSiEt}_3$ . The complexes obtained by this method were always contaminated with compounds resulting from the isomerization of the allyl group to propenyl  $[\text{Ti}(\text{C}_5\text{H}_5)\{\text{OC}_6\text{H}_4-n(\text{OMe})_n(\text{CH}=\text{CHCH}_3)\text{Cl}_2\}]$  ( $n = 1, 2$ ) as indicated by their <sup>1</sup>H NMR spectra.<sup>15</sup> Attempts to separate these derivatives failed. However, the Markovnikov  $\alpha$ -isomer units  $-\text{CH}_2\text{CH}(\text{SiEt}_3)\text{CH}_3$  were not observed in any cases.

A more suitable procedure for the synthesis of **3** and **4** involved the prior hydrosilylation of the organic precursors and the subsequent reaction with  $[\text{Ti}(\text{C}_5\text{H}_5)\text{Cl}_3]$ . Hence, treatment of 4-allyl-2-methoxyphenol (**I**) or 4-allyl-2,6-dimethoxyphenol (**II**) with an excess of  $\text{HSiEt}_3$  (using Karstedt catalyst) in neat silane or THF, respectively, at 70 °C, produced the  $\beta$ -addition deriva-

(8) (a) Oosterom, G. E.; van Hareen, R. J.; Reek, J. N. H.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *Chem. Commun.* **1999**, 1119 and references therein. (b) Maraval, V.; Laurent, R.; Caminade, A. M.; Majoral, J. P. *Organometallics* **2000**, *19*, 4025.

(9) (a) Newkome, G. R.; He, E.; Moorefield, C. N. *Chem. Rev.* **1999**, *99*, 1689 and references therein. Selected references on the synthesis of periphery-metalated carbosilane dendrimers are: (b) Knapen, J. W. J.; van der Made, A. W.; de Wilde, J. C.; van Leeuwen, P. W. N. M.; Wijkens, P.; Grove, D. M.; van Koten, G. *Nature* **1994**, *372*, 659. (c) Hoare, J. L.; Lorentz, K.; Hovestad, N. J.; Smeets, W. J. J. H.; Spek, A. L.; Canty, A. J.; Frey, H.; van Koten, G. *Organometallics* **1997**, *16*, 4167. (d) Kleijj, A. W.; Kleijj, H.; Jastrzebski, J. T. B. H.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *Organometallics* **1999**, *18*, 268. (e) Hovestad, N. J.; Hoare, J. L.; Jastrzebski, J. T. B. H.; Canty, A. J.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *Organometallics* **1999**, *18*, 2970. (f) Alonso, B.; Cuadrado, I.; Morán, M.; Losada, J. *J. Chem. Soc., Chem. Commun.* **1994**, 2575. (g) Lobete, F.; Cuadrado, I.; Casado, C. M.; Alonso, B.; Morán, M.; Losada, J. *J. Organomet. Chem.* **1996**, *509*, 109. (h) Casado, C. M.; Cuadrado, I.; Alonso, B.; Morán, M.; Losada, J. *J. Electroanal. Chem.* **1999**, *463*, 87. (i) Seyferth, D.; Kugita, T.; Rheingold, A. L.; Yap, G. P. A. *Organometallics* **1995**, *14*, 5362. (j) Benito, M.; Rossell, O.; Seco, M.; Segalés, G. *Organometallics* **1999**, *18*, 5191. (k) Kim, C.; Jung, I. *J. Organomet. Chem.* **1999**, *588*, 9. (l) de Groot, D.; Eggeling, E. B.; de Wilde, J. C.; Kooijmann, H.; van Haaren, R. J.; van der Made, A. W.; Spek, A. L.; Vogt, D.; Reek, J. N. H.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *Chem. Commun.* **1999**, 1623.

(10) (a) Cadierno, V.; Igau, A.; Donnadiou, B.; Caminade, A. M.; Majoral, J. P. *Organometallics* **1999**, *18*, 1580. (b) Brüning, K.; Lang, H. *J. Organomet. Chem.* **1999**, *575*, 153. (c) Sellner, H.; Seebach, D. *Angew. Chem., Int. Ed.* **1999**, *38*, 1918. (d) Rheiner, P. B.; Seebach, D. *Chem. Eur. J.* **1999**, *5*, 3221. (e) Arevalo, S.; Benito, J. M.; de Jesús, E.; de la Mata, F. J.; Flores, M.; Losada, J. *J. Organomet. Chem.* **2000**, *602*, 208. (f) Seyferth, D.; Wryrwa, R.; Franz, U. W.; Becke, S. *PCT Int. Appl. WO 97/32908*, 1997; *Chem. Abstr.* **1997**, *127*, 263179p. (g) Reetz, M. T.; Giebel, D. *Angew. Chem., Int. Ed.* **2000**, *39*, 2498.

(11) (a) van der Made, A. W.; van Leeuwen, P. W. N. M. *J. Chem. Soc., Chem. Commun.* **1992**, 1400. (b) van der Made, A. W.; van Leeuwen, P. W. N. M.; de Wilde, J. C.; Brandes, R. A. C. *Adv. Mater.* **1993**, *5*, 466. (c) Zhou, L. L.; Roovers, J. *Macromolecules* **1993**, *26*, 963. (d) Seyferth, D.; Son, D. Y.; Rheingold, A. L.; Ostrander, R. L. *Organometallics* **1994**, *13*, 2682. (e) Cuadrado, I.; Morán, M.; Losada, J.; Casado, C. M.; Pascual, C.; Alonso, B.; Lobete, F. In *Advances in Dendritic Macromolecules*; Newkome, G. R., Ed.; Jai Press: Greenwich, CT, 1996; Vol. 3, pp 151–191. (f) Kim, C.; Son, S. *J. Organomet. Chem.* **2000**, *599*, 123 and references therein.

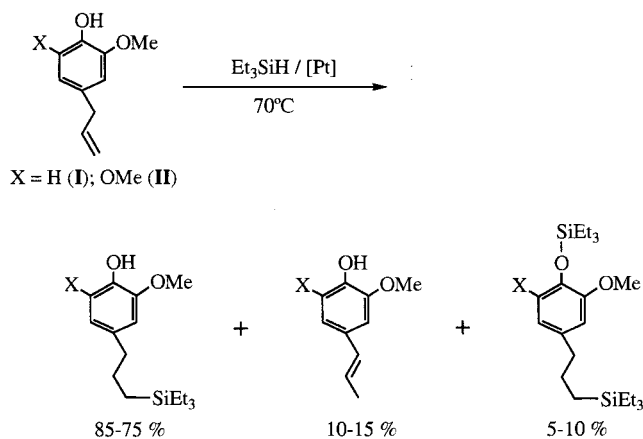
(12) (a) Skupinski, W.; Wasilewski, A. *J. Organomet. Chem.* **1981**, *220*, 39. (b) Skupinski, W.; Wasilewski, A. *J. Organomet. Chem.* **1985**, *282*, 69. (c) Nomura, K.; Naga, N.; Miki, M.; Yanagi, K.; Imai, A. *Organometallics* **1998**, *17*, 2152. (d) Vilardo, J. S.; Thorn, M. G.; Fanwick, P. E.; Rothwell, I. P. *Chem. Commun.* **1998**, 2425. (e) Doherty, S.; Errington, R. J.; Jarvis, A. P.; Collins, S.; Clegg, W.; Elsegood, M. R. *J. Organometallics* **1998**, *17*, 3408. (f) Nomura, K.; Naga, N.; Miki, M.; Yanagi, K. *Macromolecules* **1998**, *31*, 7588.

(13) Arevalo, S.; Benito, J. M.; de Jesús, E.; de la Mata, F. J.; Flores, J. C.; Gómez, R. *J. Organomet. Chem.* **1999**, *592*, 265.

(14) Karstedt, B. D. U.S. Patent 3,775,452, 1973.

(15) Selected <sup>1</sup>H NMR data in CDCl<sub>3</sub> for  $[\text{Ti}(\text{C}_5\text{H}_5)\{\text{OC}_6\text{H}_4-n(\text{OMe})_n(\text{CH}=\text{CHCH}_3)\text{Cl}_2\}]$  ( $n = 1, 2$ ):  $\delta$  6.70 (s, 5H, C<sub>5</sub>H<sub>5</sub>), 6.25 (m, 1H, CH=CHCH<sub>3</sub>), 6.18 (m, 1H, CH=CHCH<sub>3</sub>), 3.85 (s, 3H or 6H, OMe), 1.88 (m, 3H, CH=CHCH<sub>3</sub>).

Scheme 2



tives  $\{\text{HOC}_6\text{H}_{4-n}(\text{OMe})_n(\text{C}_3\text{H}_6\text{SiEt}_3)\}$  ( $n = 1$  (**5**), **2** (**6**)) in 85–75% yield, along with certain amounts (less than 10–15%) of the propenyl isomers of **I** (*trans*-2-methoxy-4-propenylphenol) or **II** (*trans*-2,6-dimethoxy-4-propenylphenol), respectively,<sup>16</sup> and other products (5–10%) resulting from O-silylation (Scheme 2). The latter impurities were the result of competitive reaction of the Si–H groups with the phenolic hydroxy group.<sup>17</sup> The formation of siloxy derivatives  $\text{Et}_3\text{Si–O–Ph}$  was detected by  $^1\text{H}$  NMR spectroscopy, as the *m*-methoxy substituent of the phenyl ring is sensitive to the presence of a hydroxy ( $\delta$  3.86) or siloxy group ( $\delta$  3.76).<sup>18</sup> For the former side products and under these reaction conditions, the hydro-silylation was found to compete with the isomerization of the allyl to propenyl groups induced by the platinum catalyst used. To improve the chemoselectivity for hydro-silylation vs isomerization, and the C-silylation vs O-silylation, higher concentrations of catalyst were used. Interestingly, hydro-silylation of the commercially available 2,6-dimethoxy-4-propenylphenol (isoeugenol) under analogous conditions led very slowly to the formation of **6** in low yield as the sole reaction product, showing that no hydro-silylation occurred at the internal double bond. Derivatives **5** and **6** could be purified from the unwanted materials by chromatography, giving spectroscopically pure oils in 40% overall yield.

Treatment of **5** and **6** with 1 molar equiv of  $[\text{Ti}(\text{C}_5\text{H}_5)_2\text{Cl}_2]$  in toluene at 80 °C gave **3** and **4**, respectively, which were obtained as red oils in high yields. No reaction was observed when the mixture was stirred overnight at room temperature. Derivatives **2–6** were soluble in all common organic solvents, and the organometallic complexes **2–4** are thermally stable but moisture sensitive. The structures proposed for **2–6** are shown in Scheme 1, and their spectroscopic and analytical data are collected in the Experimental Section.

(16) Selected  $^1\text{H}$  NMR data in  $\text{CDCl}_3$  for *trans*-2-methoxy-4-propenylphenol or *trans*-2,6-dimethoxy-4-propenylphenol:  $\delta$  6.31 (dc, 1H), 6.06 (dc, 1H), 3.87 (s, OMe), 1.84 (dd,  $\text{CH}_3$ ).

(17) Zhang, C.; Laine, R. M. *J. Am. Chem. Soc.* **2000**, *122*, 6979 and references therein.

(18) Protection of eugenol (**I**) or 4-allyl-2,6-dimethoxyphenol (**II**) with  $\text{SiMe}_3\text{Cl}$  afforded  $[\text{Me}_3\text{SiOC}_6\text{H}_{4-n}(\text{OMe})_n(\text{CH}_2\text{CH}=\text{CH}_2)]$  ( $n = 1, 2$ ). Selected  $^1\text{H}$  NMR data in  $\text{CDCl}_3$ :  $\delta$  5.96 (m, 1H,  $\text{CH}=\text{CHCH}_3$ ), 5.10 (m, 1H,  $\text{CH}=\text{CHCH}_3$ ), 3.76 (s, 3H or 6H, OMe), 3.30 (m, 3H,  $\text{CH}=\text{CHCH}_3$ ), 0.19 (s, 9H,  $\text{SiMe}_3$ ). When the (aryloxy)trimethylsilane was used in the hydro-silylation instead of the phenol, the reaction proceeded exclusively via C-silylation and formation of small amounts of the isomers  $[\text{Me}_3\text{SiOC}_6\text{H}_{4-n}(\text{OMe})_n(\text{CH}=\text{CHCH}_3)]$  ( $n = 1, 2$ ).

The  $^1\text{H}$  NMR spectrum of complex **2** shows one singlet for the cyclopentadienyl ligand at  $\delta$  6.71 and one resonance located at  $\delta$  121.1 for the corresponding carbon atoms in the  $^{13}\text{C}$  NMR spectrum, both in the same position as those found in the NMR spectra of compound **1**.<sup>13</sup> For compounds **3** and **4**, the cyclopentadienyl ligand affords chemical shifts identical with those shown for complexes **1** and **2**. Thus, it can be assumed that hydro-silylation of the allyl fragment does not produce significant changes on the electron density of the metal center. In the case of derivatives **3–6**, the  $^1\text{H}$  NMR data show the presence of the  $-\text{CH}_2\text{CH}_2\text{CH}_2\text{SiEt}_3$  grouping as the result of an anti-Markovnikov addition. For the  $\alpha$ -addition grouping  $-\text{CH}_2\text{CH}(\text{SiEt}_3)\text{CH}_3$ , the expected doublets are not observed and, therefore,  $\beta$ -addition products occur exclusively.

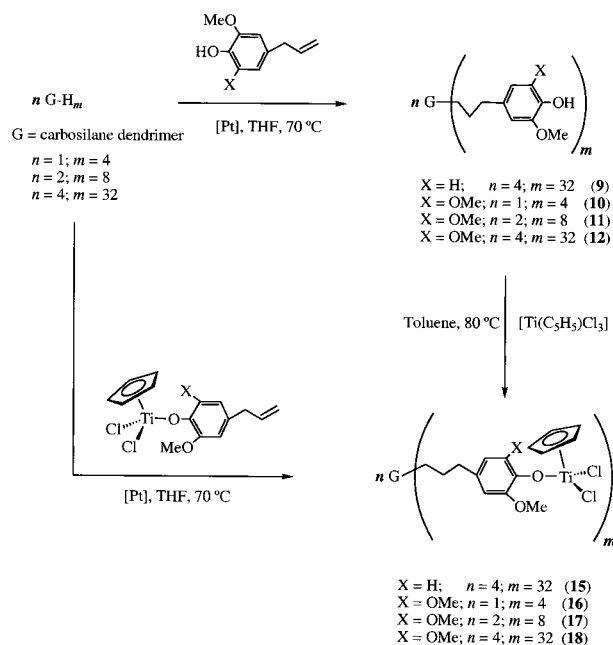
The synthetic procedures described for these mononuclear compounds along with their spectroscopic characterization provided a useful basis for the synthesis of their peripheral carbosilane dendrimer analogues.

**Synthesis of Dendrimers and Metallo-dendrimers.** The syntheses of dendrimers containing phenols or titanium metal centers at their periphery have been studied. For this purpose, allylsilane-terminated dendrimers of first, second, and fourth generation were synthesized according to previously reported methods.<sup>11</sup> Typically, we used tetraallylsilane as the initiator core, dichloromethylsilane in the hydro-silylation step, and allylmagnesium bromide in the allylation step. The first-, second-, and fourth-generation chlorodimethylsilyl-terminated dendrimers were obtained by a hydro-silylation reaction, adding  $\text{HSiMe}_2\text{Cl}$  to allyl-terminated dendrimers in the presence of a platinum catalyst (Karstedt catalyst). Finally, these dendrimers containing peripheral Si–Cl bonds were converted into the well-known Si–H analogues 1G-H<sub>4</sub>, 2G-H<sub>8</sub>, and 4G-H<sub>32</sub> by reduction with  $\text{LiAlH}_4$ .<sup>11d</sup> The H–Si-terminated dendrimers were the starting materials for the preparation of new dendrimers via hydro-silylation reactions of the organic monomers **I** and **II**.

The synthesis of the new dendrimers was carried out by the same routes as those described for model compounds **5** and **6**. Furthermore, we have recently published<sup>10e</sup> that reaction of **I** with 1G-H<sub>4</sub> or 2G-H<sub>8</sub> afforded the corresponding dendrimers 1G- $[(\text{CH}_2)_3\text{C}_6\text{H}_3(\text{OMe})\text{OH}]_4$  (**7**) and 2G- $[(\text{CH}_2)_3\text{C}_6\text{H}_3(\text{OMe})\text{OH}]_8$  (**8**) in high yields. To increase the number of generations and to modify the environment around the metal center for catalytic purposes, a fourth generation has been synthesized and first, second, and fourth generations, using the more encumbered end group 4-allyl-2,6-dimethoxyphenol (**II**), were prepared as well. Then, hydro-silylation reactions of eugenol (**I**) with 4G-H<sub>32</sub> or the phenol ligand **II** with 1G-H<sub>4</sub>, 2G-H<sub>8</sub>, or 4G-H<sub>32</sub> performed in THF at 70 °C and using the Karstedt catalyst afforded the corresponding dendrimers 4G- $[(\text{CH}_2)_3\text{C}_6\text{H}_3(\text{OMe})\text{OH}]_{32}$  (**9**), 1G- $[(\text{CH}_2)_3\text{C}_6\text{H}_2(\text{OMe})_2\text{OH}]_4$  (**10**), 2G- $[(\text{CH}_2)_3\text{C}_6\text{H}_2(\text{OMe})_2\text{OH}]_8$  (**11**), and 4G- $[(\text{CH}_2)_3\text{C}_6\text{H}_2(\text{OMe})_2\text{OH}]_{32}$  (**12**) containing terminal phenol groups (Scheme 3).  $^1\text{H}$  NMR spectroscopy was used for following the progress of the reactions by monitoring the loss of the Si–H resonance.

As in the preparation of compounds **3–6**, only  $\beta$ -addition derivatives were formed. Again, certain amounts

Scheme 3



of O-silylated byproducts (between 5 and 10%)<sup>18</sup> and the internal olefinic isomers of **I** or **II** (between 10 and 15%)<sup>16</sup> were detected in the <sup>1</sup>H NMR spectra of the crude products. The competitive reaction of the dendrimeric terminal Si-H groups with the phenolic hydroxy group, resulting in O-silylation, should form species of higher molecular weight. In this case, the allyl phenols serve as bifunctional units that are able to cross-link different dendrimeric molecules.<sup>17</sup> The unwanted materials were readily removed by washing the crude products with hexane (olefinic isomers of **I** or **II**) and then by chromatographing the residue (mainly higher molecular weight components), giving in 70–75% yield spectroscopically and analytically pure oils of increasing viscosity on going from the first to the fourth generation. All these dendrimers are soluble in THF, diethyl ether, and chlorinated and aromatic solvents but insoluble in aliphatic hydrocarbons and water. Dendritic carbosilanes containing aliphatic hydroxy groups on their periphery have been reported recently.<sup>19</sup> Derivatives **7–12** are amphiphilic carbosilane dendrimers, and to our knowledge, they represent the first examples containing phenolic ligands as amphiphilic groups attached to the terminal branches of hydrophobic carbosilane backbones. Slow aggregation processes have been detected in such amphiphilic materials, but they can be stopped by storing them in THF or CH<sub>2</sub>Cl<sub>2</sub> solutions.<sup>19</sup>

Attempts to prepare macromolecules containing more than one peripheral phenol group on the outer silicon atoms, i.e., 1G-[(CH<sub>2</sub>)<sub>3</sub>{C<sub>6</sub>H<sub>2</sub>(OMe)<sub>2</sub>}OH]<sub>8</sub> from dihydride terminated carbosilane dendrimer 1G-H<sub>8</sub><sup>11</sup> under the same conditions as those described above, were unsuccessful, resulting in incomplete reactions accord-

ing to the <sup>1</sup>H NMR spectra. Most likely, steric congestion on the silicon atom hindered the completion of the reactions.

The incorporation of titanium centers on the carbosilane dendrimer surface containing phenol end groups was carried out by reaction with a Ti-Cl bond of [Ti(C<sub>5</sub>H<sub>5</sub>)Cl<sub>3</sub>] using a procedure similar to that described for the monomeric models **3** and **4** and used recently in the treatment with **7** or **8** to give 1G-[(CH<sub>2</sub>)<sub>3</sub>{C<sub>6</sub>H<sub>3</sub>(OMe)}O]Ti(C<sub>5</sub>H<sub>5</sub>)Cl<sub>2</sub><sub>4</sub> (**13**) or 2G-[(CH<sub>2</sub>)<sub>3</sub>{C<sub>6</sub>H<sub>3</sub>(OMe)}O]Ti(C<sub>5</sub>H<sub>5</sub>)Cl<sub>2</sub><sub>8</sub> (**14**),<sup>10e</sup> respectively. Reaction of dendrimers **9–12** with the appropriate amounts of [Ti(C<sub>5</sub>H<sub>5</sub>)Cl<sub>3</sub>] in toluene at 80 °C led quantitatively to the formation of organotitanium dendrimers 4G-[(CH<sub>2</sub>)<sub>3</sub>{C<sub>6</sub>H<sub>3</sub>(OMe)}O]Ti(C<sub>5</sub>H<sub>5</sub>)Cl<sub>2</sub><sub>32</sub> (**15**), 1G-[(CH<sub>2</sub>)<sub>3</sub>{C<sub>6</sub>H<sub>2</sub>(OMe)<sub>2</sub>}O]Ti(C<sub>5</sub>H<sub>5</sub>)Cl<sub>2</sub><sub>4</sub> (**16**), 2G-[(CH<sub>2</sub>)<sub>3</sub>{C<sub>6</sub>H<sub>2</sub>(OMe)<sub>2</sub>}O]Ti(C<sub>5</sub>H<sub>5</sub>)Cl<sub>2</sub><sub>8</sub> (**17**), and 4G-[(CH<sub>2</sub>)<sub>3</sub>{C<sub>6</sub>H<sub>2</sub>(OMe)<sub>2</sub>}O]Ti(C<sub>5</sub>H<sub>5</sub>)Cl<sub>2</sub><sub>32</sub> (**18**) with concomitant evolution of HCl (Schemes 3 and 4). In the case of the fourth-generation metallodendrimers **15** and **18**, complete conversion was achieved by adding a drop of a Lewis base such as NEt<sub>3</sub> to the toluene solution before isolation. The alternative procedure consisting of the hydrosilylation of complexes **1** and **2** with hydride-terminated dendrimers to prepare the organometallic dendrimers gave only low yields.

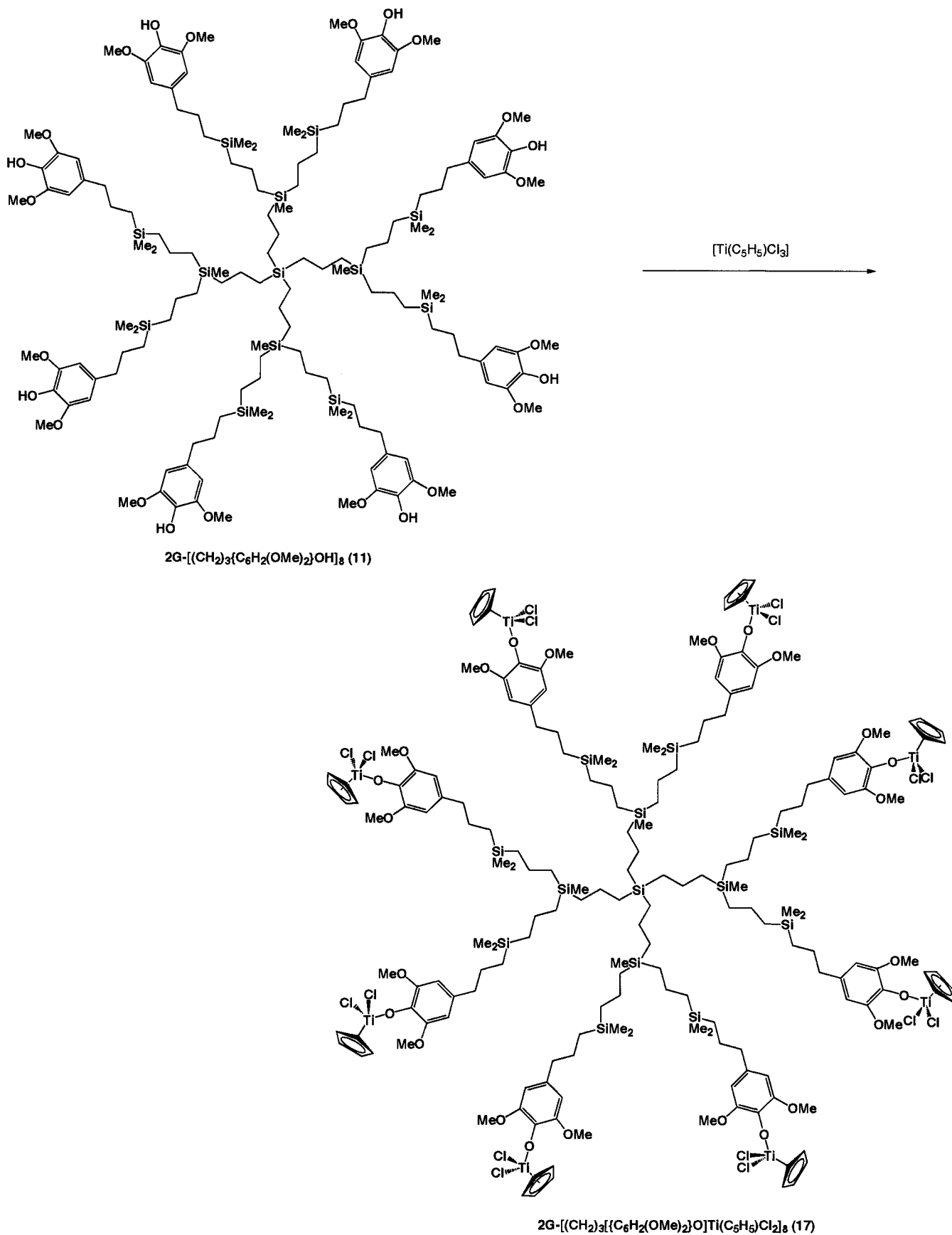
The dendritic organometallic systems are red oils, thermally stable but moisture sensitive. In the presence of water they afforded the starting phenol-terminated dendrimers and oxotitanium derivatives.<sup>20</sup> Therefore, the addition of an excess of water to diethyl ether solutions of the dendritic organotitanium derivatives **13–18** allows recovering the phenolic dendrimers almost quantitatively.

The NMR spectroscopic and analytical data of complexes **7–18** are consistent with their proposed structures shown in Schemes 3 and 4 and Figure 1. The <sup>1</sup>H NMR spectra of the carbosilane framework for dendrimers **7–12** have almost identical chemical shifts for analogous nuclei in different generations, although broader and unstructured resonances are present for the fourth generations. These features have been ascribed to both a polymer-like structure with slightly different chemical environments for nuclei in different generations and restricted mobility of the respective protons in the outer shells.<sup>19a</sup> Four sets of signals attributed to the methylene groups have been observed with the expected integration ratio. Those for the SiCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-Ph fragments appear at the same position as those detected for the monomers **3–6**. For the branches SiCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si, the middle methylenes are located at δ 1.28, while the methylene groups bonded directly to silicon atoms are centered at δ 0.53 and overlap the analogous groups in the SiCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Ph branches. The <sup>13</sup>C NMR spectra of these groups show three resonances located at δ 39.7, 26.4, and 15.3 for the outer branches SiCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si, and for the inner branches SiCH<sub>2</sub>-CH<sub>2</sub>CH<sub>2</sub>Si signals in the range δ 20.0–17.5 are observed. For the methyl groups, the corresponding signals for the <sup>1</sup>H and <sup>13</sup>C NMR spectra are detected, although only in the first and second generations can

(19) (a) Lorenz, K.; Mülhaupt, R.; Frey, H.; Rapp, U.; Mayer-Posner, F. J. *Macromolecules* **1995**, *28*, 6657. (b) Sheiko, S. S.; Muzafarov, A. M.; Winkler, R. G.; Getmanova, E. V.; Eckert, G.; Reineker, P. *Langmuir* **1997**, *13*, 4172. (c) Krska, S. W.; Seyferth, D. J. *Am. Chem. Soc.* **1998**, *120*, 3604. (d) Kim, C.; Son, S.; Kim, B. *J. Organomet. Chem.* **1999**, *588*, 1.

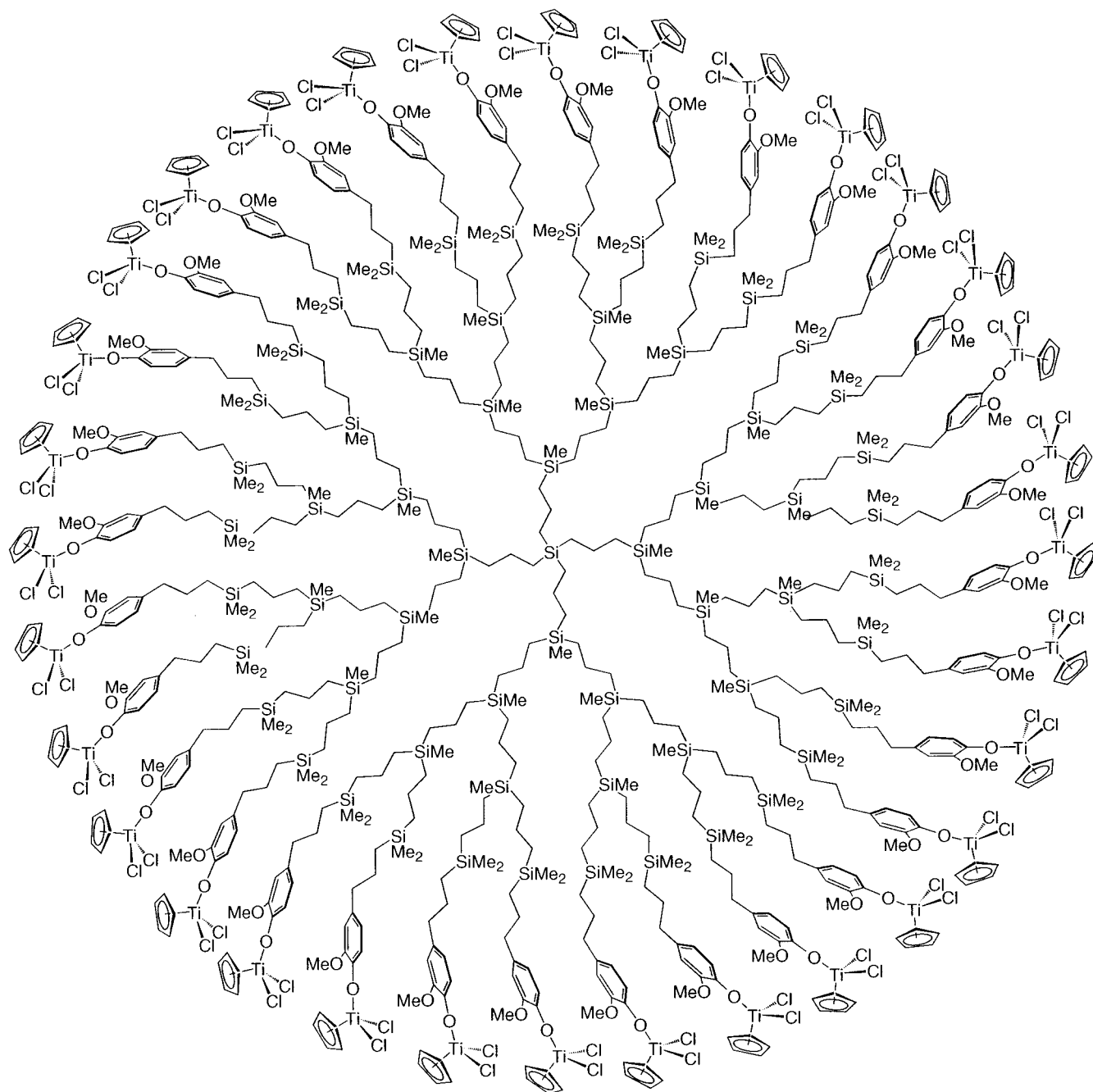
(20) (a) Thewalt, U.; Schomburg, D. *J. Organomet. Chem.* **1977**, *127*, 169. (b) Gowik, P.; Klapötke, T.; Pickardt, J. *J. Organomet. Chem.* **1990**, *393*, 343.

Scheme 4



–SiMe<sub>2</sub>– and –SiMe– fragments be distinguished. In the cases of the higher generations overlapping occurs due to the broadening mentioned above. The <sup>1</sup>H and <sup>13</sup>C NMR spectra also show an unchanged resonance for the

methoxy groups of 7–12 along with the corresponding signals of the aromatic rings in the expected regions. The hydroxy groups appear at δ 5.46 for the eugenol derivatives and δ 5.36 for the 2,6-dimethoxyphenol



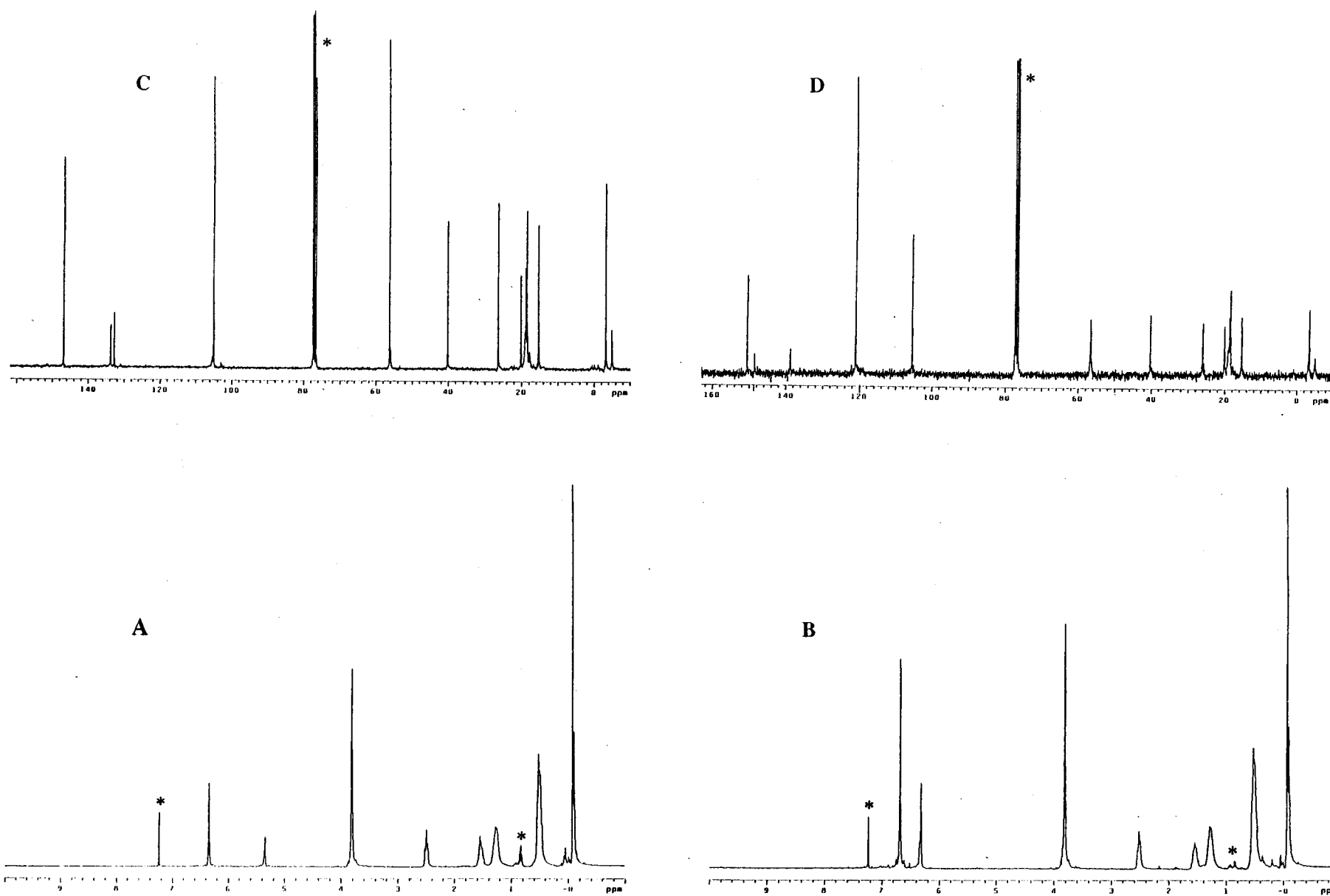
**Figure 1.** Molecular representation of the fourth-generation organotitanium dendrimer  $4G-[(CH_2)_3\{C_6H_3(OMe)\}O]-Ti(C_5H_5)Cl_2]_{32}$  (**15**).

compounds, typically shifted upfield again, as a consequence of the presence of a second *m*-methoxy substituent (see Figure 2 for  $^1H$  and  $^{13}C$  NMR of **12**). The  $^{29}Si$  NMR spectra of the first generations show two singlets at  $\delta$  1.02 and 1.98, whereas for the second and fourth generations only the two outer silicon atoms could be detected.

In addition, the air-stable titanium-free dendrimers have been studied by MALDI-TOF MS using 1,8,9-trihydroxyanthracene (dithranol) as a suitable matrix. In all compounds of the first and second generations  $MNa^+$ ,  $MK^+$ , and  $MH^+$  give the most intense peaks. However, the molecular peaks were not observed for the fourth generations, as described for many of the high-molecular-weight dendrimers.<sup>9k,11e,21</sup> Mass spectral studies are also useful for the identification of branching

defects. This information is important not only as a proof of purity but also as an indicator of building-up reactions that tend to be incomplete if they are not handled carefully. Defects are only found in a small fraction of molecules which contain no more than one error, as expected for a statistical distribution. The most frequent defects are those related to hydrosilylations, which could be minimized if they are monitored by NMR in order to ensure their completion. Complexes **7–12** have also been studied by gel permeation chromatography (GPC). As expected, the elution time of the six compounds increases from fourth to first generations.

(21) (a) Veith, M.; Elsässer, R.; Krüger, R. P. *Organometallics* **1999**, *18*, 656. (b) Kim, C.; Jung, I. J. *Organomet. Chem.* **2000**, *599*, 208.



**Figure 2.** <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) (A and B) and, <sup>13</sup>C{<sup>1</sup>H} NMR (75.43 MHz, CDCl<sub>3</sub>) (C and D) spectra of 4G-X<sub>32</sub> species **12** (A and C) and **18** (B and D). Solvent peaks are indicated by asterisks.

A good linear relationship is shown between theoretical molecular weight and elution time on GPC traces.<sup>21a, 22</sup>

The <sup>1</sup>H and <sup>13</sup>C NMR spectra of the new metallo-dendrimers **15–18** (see Figure 2 for <sup>1</sup>H and <sup>13</sup>C NMR of **18**) exhibit resonances identical with those observed in their counterparts **7–12** for the carbosilane framework and phenoxide group. In addition, the proton and carbon atoms of the cyclopentadienyl ring of the derivatives **15–18** appear at the same positions ( $\delta$  6.73 and 121.0, respectively) and compare well with the previously reported metallodendrimers **13** and **14**<sup>10e</sup> and the mononuclear complexes **1**<sup>13</sup> and **2**. All these spectroscopic data suggest that the differences in size and length of the dendritic species, as well as substitution of the eugenolate moiety for the 2,6-dimethoxyphenoxide fragment, are not extended to the metal microenvironment. Attempts to carry out MALDI-TOF MS of all the titanium-containing dendrimers failed, probably due to the use of unsuitable matrices, usually organic acids or alcohols. Analogous results have been reported for other metallodendrimers.<sup>9j,k, 23</sup>

In summary, a synthetic strategy has been developed for the preparation of new peripheral carbosilane dendrimers containing phenols or titanium metal centers. It consists of the hydrosilylation of phenols having pendant allyl groups with well-known hydride terminated dendrimers and the subsequent alcoholysis reaction of [Ti(C<sub>5</sub>H<sub>5</sub>)Cl<sub>3</sub>]. This procedure has been shown to be suitable for the growing of high generations. In addition, the hydrosilylation step using the Karstedt catalyst proceeds with both C-silylation and O-silylation in the ratio 9:1. An additional isomerization reaction of the allyl phenols was also observed. Investigations of the catalytic activity of the metallodendrimers prepared in this work for olefin polymerization are in progress.

## Experimental Section

**General Procedures.** All manipulations of oxygen- or water-sensitive compounds were carried out under an atmosphere of argon by using standard Schlenk techniques or an argon-filled glovebox equipped with a  $-40$  °C freezer. <sup>1</sup>H, <sup>13</sup>C, and <sup>29</sup>Si NMR spectra were recorded on a Variant Unity VXR-300 or Variant 500 Plus instruments. Chemical shifts ( $\delta$ , ppm) were measured relative to residual <sup>1</sup>H and <sup>13</sup>C resonances for chloroform-*d* used as solvent. The <sup>29</sup>Si chemical shifts were referenced to external SiMe<sub>4</sub> (0.00 ppm). C, H, and N analyses were carried out with a Perkin-Elmer 240 C microanalyzer. MALDI-TOF MS samples were prepared in a 1,8,9-trihydroxyanthracene (dithranol) matrix, and spectra were recorded on a Bruker Reflex II spectrometer equipped with a nitrogen laser emitting at 337 nm and operated in the reflector mode at an accelerating voltage in the range 23 000–25 000 V. Thin-layer chromatography was accomplished using 0.25 mm silica gel plates from ALUGRAM, and chromatography was performed on silica gel (35–70 mesh).

**Materials.** Solvents were dried prior to use and freshly distilled under argon: tetrahydrofuran and diethyl ether from sodium benzophenone ketyl, toluene from sodium, hexane from sodium–potassium alloy, and methylene chloride over P<sub>4</sub>O<sub>10</sub>. Unless otherwise stated, reagents were obtained from commercial sources and used as received. [Ti(C<sub>5</sub>H<sub>5</sub>)Cl<sub>3</sub>]<sup>24</sup> and GnH dendrimers<sup>11d,e</sup> were prepared according to reported methods.

(22) Morikawa, A.; Kakimoto, M.; Imai, Y. *Macromolecules* **1992**, *25*, 3247.

(23) Liao, Y.-H.; Moss, J. R. *Organometallics* **1995**, *14*, 2130.

(24) Cardoso, A. M.; Clark, R. J. H.; Moorhouse, S. *J. Chem. Soc., Dalton Trans.* **1980**, 1156.

**Synthesis of [Ti(C<sub>5</sub>H<sub>5</sub>)Cl<sub>2</sub>{O[C<sub>6</sub>H<sub>2</sub>(OMe)<sub>2</sub>(CH<sub>2</sub>CH=CH<sub>2</sub>)]} (2).** A solution of 4-allyl-2,6-dimethoxyphenol (0.88 g, 4.56 mmol) in toluene (20 mL) was slowly added to a solution of [Ti(C<sub>5</sub>H<sub>5</sub>)Cl<sub>3</sub>] (1.00 g, 4.56 mmol) in toluene (40 mL). The mixture was heated to 80 °C for 6 h and subsequently stirred overnight at room temperature. The solvent was removed under vacuum to obtain an oily red solid. The product was washed with hexane at  $-78$  °C to give **1** as red microcrystals (1.46 g, 85% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  6.71 (s, 5H, C<sub>5</sub>H<sub>5</sub>), 6.37 (s, 2H, C<sub>6</sub>H<sub>2</sub>), 5.92 (m, 1H,  $-\text{CH}_2\text{CH}=\text{CH}_2$ ), 5.08 (m, 2H, CH<sub>2</sub>CH=CH<sub>2</sub>), 3.84 (s, 6H, OMe), 3.32 (m, 2H, CH<sub>2</sub>CH=CH<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  150.8 (C<sub>ipso</sub> bonded to  $-\text{OMe}$ ), 148.7 (C<sub>ipso</sub> bonded to  $-\text{OTi}$ ), 136.8 (C<sub>ipso</sub> bonded to  $-\text{C}_5\text{H}_5$ ), 136.1 (CH<sub>2</sub>CH=CH<sub>2</sub>), 121.1 (C<sub>5</sub>H<sub>5</sub>), 116.3 (CH<sub>2</sub>CH=CH<sub>2</sub>), 105.8 (C<sub>6</sub>H<sub>2</sub>), 56.8 (OMe), 40.5 (CH<sub>2</sub>CH=CH<sub>2</sub>). Anal. Calcd for C<sub>16</sub>H<sub>18</sub>Cl<sub>2</sub>O<sub>3</sub>Ti: C, 50.96; H, 4.81. Found: C, 50.93; H, 4.83.

**Synthesis of [Ti(C<sub>5</sub>H<sub>5</sub>)Cl<sub>2</sub>{O[C<sub>6</sub>H<sub>3</sub>(OMe)(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-SiEt<sub>3</sub>)]} (3).** A solution of [HO{C<sub>6</sub>H<sub>3</sub>(OMe)(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-SiEt<sub>3</sub>)] (**5**) (see preparation below; 0.40 g, 1.43 mmol) in toluene (20 mL) was slowly added to a solution of [Ti(C<sub>5</sub>H<sub>5</sub>)Cl<sub>3</sub>] (0.31 g, 1.43 mmol) in toluene (40 mL). The mixture was heated to 80 °C for 6 h, and then, the solvent was removed under vacuum to obtain **3** as a red oil (0.66 g, 100% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  6.91 (m, 1H, C<sub>6</sub>H<sub>3</sub>), 6.74 (s, 5H, C<sub>5</sub>H<sub>5</sub>), 6.73 (m, 1H, C<sub>6</sub>H<sub>3</sub>), 6.63 (m, 1H, C<sub>6</sub>H<sub>3</sub>), 3.87 (s, 3H, OMe), 2.57 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Ph), 1.58 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Ph), 0.90 (t, 9H, SiCH<sub>2</sub>CH<sub>3</sub>), 0.50 (m, 8H, SiCH<sub>2</sub>CH<sub>3</sub> and SiCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Ph overlapping). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  157.3 (C<sub>ipso</sub> bonded to  $-\text{OTi}$ ), 149.8 (C<sub>ipso</sub> bonded to  $-\text{OMe}$ ), 140.0 (C<sub>ipso</sub> bonded to  $-\text{CH}_2$ ), 121.0 (C<sub>5</sub>H<sub>5</sub>), 120.4, 118.9, 113.1 (C<sub>6</sub>H<sub>3</sub>), 56.4 (OMe), 40.1 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Ph), 26.0 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Ph), 11.2 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Ph), 7.5 (SiCH<sub>2</sub>CH<sub>3</sub>), 3.3 (SiCH<sub>2</sub>CH<sub>3</sub>). Anal. Calcd for C<sub>22</sub>H<sub>32</sub>Cl<sub>2</sub>O<sub>2</sub>SiTi: C, 54.44; H, 6.96. Found: C, 54.23; H, 6.81.

**Synthesis of [Ti(C<sub>5</sub>H<sub>5</sub>)Cl<sub>2</sub>{O[C<sub>6</sub>H<sub>2</sub>(OMe)<sub>2</sub>(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-SiEt<sub>3</sub>)]} (4).** A solution of [HO{C<sub>6</sub>H<sub>2</sub>(OMe)<sub>2</sub>(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-SiEt<sub>3</sub>)] (**6**) (see preparation below; 0.40 g, 1.29 mmol) in toluene (20 mL) was slowly added to a solution of [Ti(C<sub>5</sub>H<sub>5</sub>)Cl<sub>3</sub>] (0.28 g, 1.29 mmol) in toluene (40 mL). The mixture was heated to 80 °C for 6 h, and then, the solvent was removed under vacuum to obtain **4** as a red oil (0.63 g, 100% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  6.71 (s, 5H, C<sub>5</sub>H<sub>5</sub>), 6.35 (s, 2H, C<sub>6</sub>H<sub>2</sub>), 3.84 (s, 6H, OMe), 2.54 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Ph), 1.55 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Ph), 0.90 (t, 9H, SiCH<sub>2</sub>CH<sub>3</sub>), 0.50 (m, 8H, SiCH<sub>2</sub>CH<sub>3</sub> and SiCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Ph overlapping). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  150.6 (C<sub>ipso</sub> bonded to  $-\text{OMe}$ ), 148.5 (C<sub>ipso</sub> bonded to  $-\text{OTi}$ ), 139.0 (C<sub>ipso</sub> bonded to  $-\text{CH}_2$ ), 121.1 (C<sub>5</sub>H<sub>5</sub>), 105.7 (C<sub>6</sub>H<sub>2</sub>), 56.8 (OMe), 40.6 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Ph), 25.9 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Ph), 11.2 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Ph), 7.5 (SiCH<sub>2</sub>CH<sub>3</sub>), 3.3 (SiCH<sub>2</sub>CH<sub>3</sub>). Anal. Calcd for C<sub>22</sub>H<sub>34</sub>Cl<sub>2</sub>O<sub>3</sub>SiTi: C, 53.56; H, 6.95. Found: C, 53.78; H, 6.87.

**Synthesis of [HO{C<sub>6</sub>H<sub>3</sub>(OMe)(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-SiEt<sub>3</sub>)] (5).** Two drops of the poly(dimethylsiloxane) solution of the Karstedt catalyst (3–3.5% Pt) were slowly added to a solution of 4-allyl-2-methoxyphenol (1.00 g, 6.1 mmol) in neat HSiEt<sub>3</sub> (2.0 mL, 12.6 mmol). The resulting mixture was stirred for 9 h at 70 °C and subsequently at room temperature overnight. The solvent was removed at reduced pressure, and the product was purified by chromatography on a silica gel column (35–70 mesh) with hexane as eluent to give **5** as a pale yellow oil (0.68 g, 40% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  6.81 (m, 1H, C<sub>6</sub>H<sub>3</sub>), 6.66 (m, 2H, C<sub>6</sub>H<sub>3</sub>), 5.44 (s, 1H, OH), 3.86 (s, 3H, OMe), 2.53 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Ph), 1.58 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Ph), 0.90 (t, 9H, SiCH<sub>2</sub>CH<sub>3</sub>), 0.50 (m, 8H, SiCH<sub>2</sub>CH<sub>3</sub> and SiCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Ph overlapping). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  146.3 (C<sub>ipso</sub> bonded to  $-\text{OMe}$ ), 143.5 (C<sub>ipso</sub> bonded to  $-\text{OH}$ ), 134.7 (C<sub>ipso</sub> bonded to  $-\text{CH}_2$ ), 121.0, 114.1, 111.0 (C<sub>6</sub>H<sub>3</sub>), 55.5 (OMe), 39.8 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Ph), 26.2 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Ph), 11.2 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Ph), 7.4 (SiCH<sub>2</sub>CH<sub>3</sub>), 3.3 (SiCH<sub>2</sub>CH<sub>3</sub>). Anal. Calcd for C<sub>16</sub>H<sub>28</sub>O<sub>2</sub>Si: C, 68.52; H, 10.06. Found: C, 68.31; H, 9.87.

**Synthesis of [HO{C<sub>6</sub>H<sub>2</sub>(OMe)<sub>2</sub>(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-SiEt<sub>3</sub>)] (6).** HSiEt<sub>3</sub> (2 mL, 12.6 mmol) and 2 drops of the poly(dimethyl-



siloxane) solution of the Karstedt catalyst (3–3.5% Pt) were slowly added to a solution of 4-allyl-2,6-dimethoxyphenol (1.00 g, 5.15 mmol) in THF (2 mL). The resulting mixture was stirred for 9 h at 70 °C and subsequently at room temperature overnight. Then, the solvent and the silane in excess were removed at reduced pressure, and the product was purified by chromatography (silica gel column (35–70 mesh)/hexane) to give **6** as a pale yellow oil (0.70 g, 44% yield).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  6.37 (s, 2H,  $\text{C}_6\text{H}_2$ ), 5.34 (s, 1H, OH), 3.86 (s, 6H, OMe), 2.53 (m, 2H,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{Ph}$ ), 1.56 (m, 2H,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{Ph}$ ), 0.90 (t, 9H,  $\text{SiCH}_2\text{CH}_3$ ), 0.50 (m, 8H,  $\text{SiCH}_2\text{CH}_3$  and  $\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Ph}$  overlapping).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  146.8 ( $\text{C}_{\text{ipso}}$  bonded to –OMe), 133.8 ( $\text{C}_{\text{ipso}}$  bonded to –OH), 132.7 ( $\text{C}_{\text{ipso}}$  bonded to – $\text{CH}_2$ ), 105.0 ( $\text{C}_6\text{H}_2$ ), 56.2 (OMe), 40.2 ( $\text{CH}_2\text{CH}_2\text{CH}_2\text{Ph}$ ), 26.3 ( $\text{CH}_2\text{CH}_2\text{CH}_2\text{Ph}$ ), 15.3 ( $\text{CH}_2\text{CH}_2\text{CH}_2\text{Ph}$ ), 20.1, 18.8, 18.5 and overlapped signals of ( $\text{Si}(\text{CH}_2)_3\text{Si}$ ), –3.3 (SiMe<sub>2</sub>), –5.0 (SiMe).  $^{29}\text{Si}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.86 (G2-Si), 1.19 (G1-Si), not observed (G0-Si). MALDI-TOF-MS:  $m/z$  2752.7 [ $\text{M} + \text{Na}$ ]<sup>+</sup> (calcd 2752.5). Anal. Calcd for  $\text{C}_{144}\text{H}_{252}\text{O}_{24}\text{Si}_{13}$ : C, 63.29; H, 9.29. Found: C, 62.52; H, 9.47.

**Synthesis of 4G-[(CH<sub>2</sub>)<sub>3</sub>{C<sub>6</sub>H<sub>3</sub>(OMe)}OH]<sub>32</sub> (**9**).** This fourth-generation dendrimer was prepared from 4G-H<sub>32</sub> (0.49 g, 0.087 mmol) and 4-allyl-2-methoxyphenol (0.48 g, 2.92 mmol) using 2 drops of the poly(dimethylsiloxane) solution of the Karstedt catalyst (3–3.5% Pt). The resulting mixture was stirred for 9 h at 70 °C and subsequently at room temperature overnight. The solvent was removed at reduced pressure, and the product was washed twice with hexane to eliminate mainly the olefinic isomer of **I** and then purified by chromatography (10 cm column of silica gel;  $\text{CH}_2\text{Cl}_2$  for higher weight components and then 10% ethyl acetate in  $\text{CH}_2\text{Cl}_2$ )<sup>18</sup> to give **9** as a pale yellow, thick oil (0.66 g, 70% yield).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  6.79 (m, 8H,  $\text{C}_6\text{H}_3$ ), 6.62 (m, 16H,  $\text{C}_6\text{H}_3$ ), 5.46 (s, 8H, OH), 3.81 (s, 24H, OMe), 2.50 (m, 16H,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{Ph}$ ), 1.53 (m, 16H,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{Ph}$ ), 1.28 (m, 30H,  $\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Si}$ ), 0.52 (m, 76H,  $\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Si}$  and  $\text{CH}_2\text{CH}_2\text{CH}_2\text{Ph}$  overlapping), –0.08 (s, 48H, SiMe<sub>2</sub>), –0.11 (broad, 21H, SiMe).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  146.2 ( $\text{C}_{\text{ipso}}$  bonded to –OMe), 143.5 ( $\text{C}_{\text{ipso}}$  bonded to –OH), 134.6 ( $\text{C}_{\text{ipso}}$  bonded to – $\text{CH}_2$ ), 120.9, 114.1, and 111.0 ( $\text{C}_6\text{H}_3$ ), 55.8 (OMe), 39.7 ( $\text{CH}_2\text{CH}_2\text{CH}_2\text{Ph}$ ), 26.4 ( $\text{CH}_2\text{CH}_2\text{CH}_2\text{Ph}$ ), 15.3 ( $\text{CH}_2\text{CH}_2\text{CH}_2\text{Ph}$ ), 20.1, 18.8, 18.5, and overlapped signals ( $\text{Si}(\text{CH}_2)_3\text{Si}$ ), –3.2 (SiMe<sub>2</sub>), –4.9, –5.0, and –5.1 (SiMe).  $^{29}\text{Si}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  2.06 (G4-Si), 1.46 (G3-Si), the rest were not observed. Anal. Calcd for  $\text{C}_{592}\text{H}_{1052}\text{O}_{64}\text{Si}_{61}$ : C, 65.19; H, 9.72. Found: C, 64.31; H, 9.67.

**Synthesis of 1G-[(CH<sub>2</sub>)<sub>3</sub>{C<sub>6</sub>H<sub>2</sub>(OMe)<sub>2</sub>}OH]<sub>4</sub> (**10**).** 4-Allyl-2,6-dimethoxyphenol (1.00 g, 5.12 mmol) and 2 drops of the poly(dimethylsiloxane) solution of the Karstedt catalyst (3–3.5% Pt) were added to a THF (3 mL) solution of 1G-H<sub>4</sub> (0.53 g, 1.22 mmol). The resulting mixture was stirred for 9 h at 70 °C and subsequently at room temperature overnight. The solvent was removed at reduced pressure, and the product was washed with hexane twice to eliminate mainly the olefinic isomer of **II** and then purified by chromatography (10 cm column of silica gel;  $\text{CH}_2\text{Cl}_2$  for higher weight components and then 10% ethyl acetate in  $\text{CH}_2\text{Cl}_2$ )<sup>18</sup> to give **10** as a pale yellow, thick oil (1.04 g, 70% yield).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  6.36 (s, 2H,  $\text{C}_6\text{H}_2$ ), 5.34 (s, 1H, OH), 3.84 (s, 6H, OMe), 2.51 (m, 2H,  $\text{CH}_2\text{CH}_2\text{Ph}$ ), 1.57 (m, 2H,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{Ph}$ ), 1.27 (m, 2H,  $\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Si}$ ), 0.53 (m, 6H,  $\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Si}$  and  $\text{CH}_2\text{CH}_2\text{CH}_2\text{Ph}$  overlapping), –0.07 (s, 6H, SiMe<sub>2</sub>).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  146.8 ( $\text{C}_{\text{ipso}}$  bonded to –OMe), 133.8 ( $\text{C}_{\text{ipso}}$  bonded to –OH), 132.7 ( $\text{C}_{\text{ipso}}$  bonded to – $\text{CH}_2$ ), 105.0 ( $\text{C}_6\text{H}_2$ ), 56.2 (OMe), 40.2 ( $\text{CH}_2\text{CH}_2\text{CH}_2\text{Ph}$ ), 26.4 ( $\text{CH}_2\text{CH}_2\text{CH}_2\text{Ph}$ ), 15.4 ( $\text{CH}_2\text{CH}_2\text{CH}_2\text{Ph}$ ), 20.3, 18.6, 17.6 ( $\text{Si}(\text{CH}_2)_3\text{Si}$ ), –3.3 (SiMe<sub>2</sub>).  $^{29}\text{Si}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.98 (G1-Si), 1.02 (G0-Si). MALDI-TOF-MS:  $m/z$  1209.5 [ $\text{M} + \text{H}$ ]<sup>+</sup> (calcd 1209.7). Anal. Calcd for  $\text{C}_{64}\text{H}_{108}\text{O}_{12}\text{Si}_5$ : C, 63.53; H, 9.00. Found: C, 63.60; H, 9.37.

**Synthesis of 2G-[(CH<sub>2</sub>)<sub>3</sub>{C<sub>6</sub>H<sub>2</sub>(OMe)<sub>2</sub>}OH]<sub>8</sub> (**11**).** This dendrimer was prepared by a method similar to that described for **10**, starting from 2G-H<sub>8</sub> (0.50 g, 0.42 mmol) and 4-allyl-2,6-dimethoxyphenol (0.68 g, 3.53 mmol). The product was purified as in the procedure for the preparation of **10**, giving **11** as a pale yellow, thick oil (0.83 g, 72% yield).  $^1\text{H}$  NMR

( $\text{CDCl}_3$ ):  $\delta$  6.36 (s, 4H,  $\text{C}_6\text{H}_2$ ), 5.35 (s, 2H, OH), 3.84 (s, 12H, OMe), 2.51 (m, 4H,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{Ph}$ ), 1.59 (m, 4H,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{Ph}$ ), 1.29 (m, 6H,  $\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Si}$ ), 0.53 (m, 16H,  $\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Si}$  and  $\text{CH}_2\text{CH}_2\text{CH}_2\text{Ph}$  overlapping), –0.07 (s, 12H, SiMe<sub>2</sub>), –0.10 (s, 3H, SiMe).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  146.8 ( $\text{C}_{\text{ipso}}$  bonded to –OMe), 133.8 ( $\text{C}_{\text{ipso}}$  bonded to –OH), 132.7 ( $\text{C}_{\text{ipso}}$  bonded to – $\text{CH}_2$ ), 105.0 ( $\text{C}_6\text{H}_2$ ), 56.2 (OMe), 40.2 ( $\text{CH}_2\text{CH}_2\text{CH}_2\text{Ph}$ ), 26.3 ( $\text{CH}_2\text{CH}_2\text{CH}_2\text{Ph}$ ), 15.3 ( $\text{CH}_2\text{CH}_2\text{CH}_2\text{Ph}$ ), 20.1, 18.8, 18.5 and overlapped signals of ( $\text{Si}(\text{CH}_2)_3\text{Si}$ ), –3.3 (SiMe<sub>2</sub>), –5.0 (SiMe).  $^{29}\text{Si}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.86 (G2-Si), 1.19 (G1-Si), not observed (G0-Si). MALDI-TOF-MS:  $m/z$  2752.7 [ $\text{M} + \text{Na}$ ]<sup>+</sup> (calcd 2752.5). Anal. Calcd for  $\text{C}_{144}\text{H}_{252}\text{O}_{24}\text{Si}_{13}$ : C, 63.29; H, 9.29. Found: C, 62.52; H, 9.47.

**Synthesis of 4G-[(CH<sub>2</sub>)<sub>3</sub>{C<sub>6</sub>H<sub>2</sub>(OMe)<sub>2</sub>}OH]<sub>32</sub> (**12**).** This dendrimer was prepared by a method similar to that described for **10**, starting from 4G-H<sub>32</sub> (0.44 g, 0.078 mmol) and 4-allyl-2,6-dimethoxyphenol (0.51 g, 2.62 mmol). The product was purified as in the procedure described above for **10**, giving **12** as a pale yellow, thick oil (0.63 g, 68% yield).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  6.34 (s, 16H,  $\text{C}_6\text{H}_2$ ), 5.36 (s, 8H, OH), 3.82 (s, 48H, OMe), 2.50 (m, 16H,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{Ph}$ ), 1.54 (m, 16H,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{Ph}$ ), 1.28 (m, 30H,  $\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Si}$ ), 0.52 (m, 76H,  $\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Si}$  and  $\text{CH}_2\text{CH}_2\text{CH}_2\text{Ph}$  overlapping), –0.07 (s, 48H, SiMe<sub>2</sub>), –0.11 (s broad, 21H, SiMe).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  146.8 ( $\text{C}_{\text{ipso}}$  bonded to –OMe), 133.7 ( $\text{C}_{\text{ipso}}$  bonded to –OH), 132.7 ( $\text{C}_{\text{ipso}}$  bonded to – $\text{CH}_2$ ), 105.0 ( $\text{C}_6\text{H}_2$ ), 56.2 (OMe), 40.2 ( $\text{CH}_2\text{CH}_2\text{CH}_2\text{Ph}$ ), 26.3 ( $\text{CH}_2\text{CH}_2\text{CH}_2\text{Ph}$ ), 15.3 ( $\text{CH}_2\text{CH}_2\text{CH}_2\text{Ph}$ ), 20.1, 18.8, 18.5 and overlapped signals ( $\text{Si}(\text{CH}_2)_3\text{Si}$ ), –3.2 (SiMe<sub>2</sub>), –5.0 (s broad, SiMe).  $^{29}\text{Si}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.91 (G4-Si), 1.28 (G3-Si), the rest were not observed (G1-Si, G0-Si). Anal. Calcd for  $\text{C}_{624}\text{H}_{1116}\text{O}_{96}\text{Si}_{61}$ : C, 63.15; H, 9.48. Found: C, 64.15; H, 9.10.

**Synthesis of 4G-[(CH<sub>2</sub>)<sub>3</sub>{C<sub>6</sub>H<sub>3</sub>(OMe)}O]Ti(C<sub>5</sub>H<sub>5</sub>)Cl<sub>2</sub>]<sub>32</sub> (**15**).** A solution of [Ti(C<sub>5</sub>H<sub>5</sub>)Cl<sub>3</sub>] (0.26 g, 1.18 mmol) in toluene (20 mL) was added to another solution containing **9** (0.40 g, 0.037 mmol) in toluene (10 mL). The mixture was heated at 80 °C for 6 h and subsequently stirred overnight at room temperature. Afterward, 1 drop of NEt<sub>3</sub> was added. Then, after filtration, the solvent was removed at reduced pressure to give **15** as a red oil in quantitative yield (0.61 g).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  6.89 (m, 8H,  $\text{C}_6\text{H}_3$ ), 6.72 (s, 40H,  $\text{C}_5\text{H}_5$ ), 6.64 (m, 16H,  $\text{C}_6\text{H}_3$ ), 3.84 (s, 24H, OMe), 2.54 (m, 16H,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{Ph}$ ), 1.55 (m, 16H,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{Ph}$ ), 1.29 (m, 30H,  $\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Si}$ ), 0.53 (m, 76H,  $\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Si}$  and  $\text{CH}_2\text{CH}_2\text{CH}_2\text{Ph}$  overlapping), –0.06 (s, 48H, SiMe<sub>2</sub>), –0.09 (s broad, 21H, SiMe).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  157.2 ( $\text{C}_{\text{ipso}}$  bonded to –OTi), 149.8 ( $\text{C}_{\text{ipso}}$  bonded to –OMe), 139.9 ( $\text{C}_{\text{ipso}}$  bonded to – $\text{CH}_2$ ), 121.1 ( $\text{C}_5\text{H}_5$ ), 120.2, 118.9, 113.0 ( $\text{C}_6\text{H}_3$ ), 56.3 (OMe), 39.9 ( $\text{CH}_2\text{CH}_2\text{CH}_2\text{Ph}$ ), 26.1 ( $\text{CH}_2\text{CH}_2\text{CH}_2\text{Ph}$ ), 15.4 ( $\text{CH}_2\text{CH}_2\text{CH}_2\text{Ph}$ ), 20.1, 18.8, 18.5 and overlapped signals ( $\text{Si}(\text{CH}_2)_3\text{Si}$ ), –3.2 (SiMe<sub>2</sub>), –4.8 (SiMe).  $^{29}\text{Si}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.94 (G4-Si), 1.31 (G3-Si), the rest were not observed. Anal. Calcd for  $\text{C}_{752}\text{H}_{1180}\text{Cl}_{64}\text{O}_{64}\text{Si}_{61}\text{Ti}_{32}$ : C, 53.89; H, 7.10. Found: C, 53.46; H, 7.17.

**Synthesis of 1G-[(CH<sub>2</sub>)<sub>3</sub>{C<sub>6</sub>H<sub>2</sub>(OMe)<sub>2</sub>}O]Ti(C<sub>5</sub>H<sub>5</sub>)Cl<sub>2</sub>]<sub>4</sub> (**16**).** A solution of [Ti(C<sub>5</sub>H<sub>5</sub>)Cl<sub>3</sub>] (0.33 g, 1.52 mmol) in toluene (20 mL) was added to a solution of **10** (0.46 g, 0.38 mmol) in toluene (10 mL). The mixture was heated at 80 °C for 6 h and subsequently stirred overnight at room temperature. Then, the solvent was removed at reduced pressure to obtain **16** as a red oil in quantitative yield (0.74 g).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  6.71 (s, 5H,  $\text{C}_5\text{H}_5$ ), 6.34 (s, 2H,  $\text{C}_6\text{H}_2$ ), 3.84 (s, 6H, OMe), 2.53 (m, 2H,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{Ph}$ ), 1.59 (m, 2H,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{Ph}$ ), 1.29 (m, 2H,  $\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Si}$ ), 0.53 (m, 6H,  $\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Si}$  and  $\text{CH}_2\text{CH}_2\text{CH}_2\text{Ph}$  overlapping), –0.06 (s, 6H, SiMe<sub>2</sub>).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  150.7 ( $\text{C}_{\text{ipso}}$  bonded to –OMe), 148.5 ( $\text{C}_{\text{ipso}}$  bonded to –OTi), 138.9 ( $\text{C}_{\text{ipso}}$  bonded to – $\text{CH}_2$ ), 121.1 ( $\text{C}_5\text{H}_5$ ), 105.7 ( $\text{C}_6\text{H}_2$ ), 56.8 (–OMe), 40.4 ( $\text{CH}_2\text{CH}_2\text{CH}_2\text{Ph}$ ), 26.0 ( $\text{CH}_2\text{CH}_2\text{CH}_2\text{Ph}$ ), 15.4 ( $\text{CH}_2\text{CH}_2\text{CH}_2\text{Ph}$ ), 20.3, 18.6, 17.6 ( $\text{Si}(\text{CH}_2)_3\text{Si}$ ), –3.3 (SiMe<sub>2</sub>).  $^{29}\text{Si}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.97 (G1-Si), 0.89 (G0-Si). Anal. Calcd for  $\text{C}_{84}\text{H}_{124}\text{Cl}_8\text{O}_{12}\text{Si}_5\text{Ti}_4$ : C, 51.97; H, 6.44. Found: C, 51.57; H, 6.43.

**Synthesis of 2G-[(CH<sub>2</sub>)<sub>3</sub>{C<sub>6</sub>H<sub>2</sub>(OMe)<sub>2</sub>O}Ti(C<sub>5</sub>H<sub>5</sub>)Cl<sub>2</sub>]<sub>8</sub> (17).** This metallodendrimer was prepared by a method similar to that described for **16**, starting from [Ti(C<sub>5</sub>H<sub>5</sub>)Cl<sub>3</sub>] (0.32 g, 1.46 mmol) and **11** (0.50 g, 0.18 mmol), to give **17** as a red oil in quantitative yield (0.76 g). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 6.70 (s, 10H, C<sub>5</sub>H<sub>5</sub>), 6.33 (s, 4H, C<sub>6</sub>H<sub>2</sub>), 3.83 (s, 12H, OMe), 2.53 (m, 4H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Ph), 1.56 (m, 4H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Ph), 1.27 (m, 6H, SiCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si), 0.52 (m, 16H, SiCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si and CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Ph overlapping), -0.06 (s, 12H, SiMe<sub>2</sub>), -0.09 (s, 3H, SiMe). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ 150.7 (C<sub>ipso</sub> bonded to -OMe), 148.5 (C<sub>ipso</sub> bonded to -OTi), 138.9 (C<sub>ipso</sub> bonded to -CH<sub>2</sub>), 121.0 (C<sub>5</sub>H<sub>5</sub>), 105.7 (C<sub>6</sub>H<sub>2</sub>), 56.8 (OMe), 40.4 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Ph), 26.0 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Ph), 15.4 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Ph), 20.1, 18.8, 18.5 and overlapped signals (Si(CH<sub>2</sub>)<sub>3</sub>Si), -3.2 (SiMe<sub>2</sub>), -4.9 (SiMe). <sup>29</sup>Si{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ 1.89 (G2-Si), 1.20 (G1-Si), not observed (G0-Si). Anal. Calcd for C<sub>184</sub>H<sub>284</sub>Cl<sub>16</sub>O<sub>24</sub>Si<sub>13</sub>Ti<sub>8</sub>: C, 52.67; H, 6.82. Found: C, 52.43; H, 6.51.

**Synthesis of 4G-[(CH<sub>2</sub>)<sub>3</sub>{C<sub>6</sub>H<sub>2</sub>(OMe)<sub>2</sub>O}Ti(C<sub>5</sub>H<sub>5</sub>)Cl<sub>2</sub>]<sub>32</sub> (18).** A solution of [Ti(C<sub>5</sub>H<sub>5</sub>)Cl<sub>3</sub>] (0.18 g, 0.81 mmol) in toluene (20 mL) was added to another solution containing **12** (0.30 g, 0.025 mmol) in toluene (10 mL). The mixture was heated to 80 °C for 6 h and subsequently stirred overnight at room temperature. Afterward, 1 drop of NEt<sub>3</sub> was added. Then, after filtration, the solvent was removed at reduced pressure to give **18** as a red oil in quantitative yield (0.44 g). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 6.68 (s, 40 H, C<sub>5</sub>H<sub>5</sub>), 6.32 (s, 16H, C<sub>6</sub>H<sub>2</sub>), 3.81 (s, 48H, OMe), 2.52 (m, 16H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Ph), 1.55 (m, 16H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Ph),

1.28 (m, 30H, SiCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si), 0.52 (m, 76H, SiCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si and CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Ph overlapping), -0.07 (s, 48H, SiMe<sub>2</sub>), 0.10 (broad, 21H, SiMe). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ 150.6 (C<sub>ipso</sub> bonded to -OMe), 148.4 (C<sub>ipso</sub> bonded to -OTi), 138.8 (C<sub>ipso</sub> bonded to -CH<sub>2</sub>), 121.1 (C<sub>5</sub>H<sub>5</sub>), 105.6 (C<sub>6</sub>H<sub>2</sub>), 56.7 (OMe), 40.4 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Ph), 26.0 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Ph), 15.4 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Ph), 20.2, 18.8, 18.5 and overlapped signals (Si(CH<sub>2</sub>)<sub>3</sub>Si), -3.2 (SiMe<sub>2</sub>), -4.9 (SiMe). <sup>29</sup>Si{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ 2.08 (G4-Si), 1.46 (G3-Si), the rest were not observed. Anal. Calcd for C<sub>784</sub>H<sub>1244</sub>Cl<sub>64</sub>O<sub>96</sub>Si<sub>61</sub>Ti<sub>32</sub>: C, 53.14; H, 7.08. Found: C, 52.68; H, 7.27.

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**Supporting Information Available:** Selected data as <sup>1</sup>H and <sup>13</sup>C NMR and MALDI-TOF spectra of derivatives **10** and **11**, <sup>29</sup>Si NMR spectra of 4G dendrimer generation **9**, **12**, **15**, and **18**, and GPC traces of derivatives **10–12**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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