Carbosilane Dendrons Functionalized at Their Focal Point

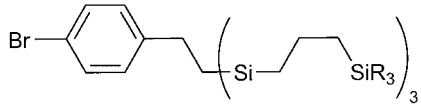
Román Andrés,*[a] Ernesto de Jesús,*[a] F. Javier de la Mata,[a] Juan C. Flores,[a] and Rafael Gómez[a]

Keywords: Dendrimers / Metallocenes / Silanes / Titanium / Zirconium

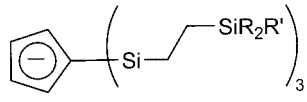
The Si–Ph bond of $PhSi[(CH_2)_3SiMe_2Bz]_3$ (**5**) is cleaved with triflic acid to give $TfOSi[(CH_2)_3SiMe_2Bz]_3$, which, in turn, reacts with triethylammonium chloride or potassium cyclopentadienide to give, respectively, $ClSi[(CH_2)_3SiMe_2Bz]_3$ (**8**) and $(C_5H_5)Si[(CH_2)_3SiMe_2Bz]_3$ (**10**). This strategy can be applied to the post-growth incorporation of nucleophiles to the focal point of carbosilane dendritic wedges. In this way, cyclopentadiene-functionalized dendritic wedges of second and third generation C_5H_5-G*n*-$[(CH_2)_3SiMe_2Bz]_x$ (*n* = 2, *x* = 9, **11**; *n* = 3, *x* = 27, **12**) have been obtained starting from Ph-G*n*-$[(CH_2)_3SiMe_2Bz]_x$ (**6**, **7**). The metallocenes $[\{(BzMe_2SiCH_2CH_2CH_2)_3SiC_5H_4\}_2MCl_2]$ (M = Ti, **14**; Zr, **15**) have also been obtained from **10** and their catalytic behavior in ethylene and propylene polymerization, using MAO as a cocatalyst, has been studied and compared to that of related non-dendritic complexes.

Introduction

The large number of dendrimers synthesized nowadays from a diversity of cores, repetitive units, and peripheral groups allows the design of macromolecules with tailored properties through the incorporation of suitable functions at the appropriate site of the dendritic molecule (i.e. core, framework, or periphery).[1] Transition metal catalysts are a good example of the relevance of the location of the functional group in the dendritic structure because of the different accessibility of the metal center to the substrate in core- and periphery-functionalized dendrimers.[2,3] In the vast majority of metal-functionalized carbosilane dendrimers the metal complexes reside in the periphery.[4] Some of the exceptions are represented by the metal complexes that van Leeuwen and al. have synthesized from phosphane ligands [triphenylphosphane, bis(diphenylphosphanyl)ferrocene (dppf), bis(diphenylphosphanyl)xanthene (xantphos), or *o*-(diphenylphosphanyl)phenol] located in the core of carbosilane dendrimers.[5] All these phosphanes have been obtained from a family of dendritic wedges whose first generation, **A**, is represented in Scheme 1 and which are grown from *p*-bromostyrene by the usual divergent methodology that alternates hydrosilylation and alkylation steps using $HSiCl_3$ and allylmagnesium bromide, respectively.[6] In the aforementioned dendritic phosphanes, prepared from the lithium derivative of **A**, a styrene spacer separates the phosphorus and the core silicon atoms.



A, R = allyl, Me



B, R = R' = Et; R = Ph, R' = Me

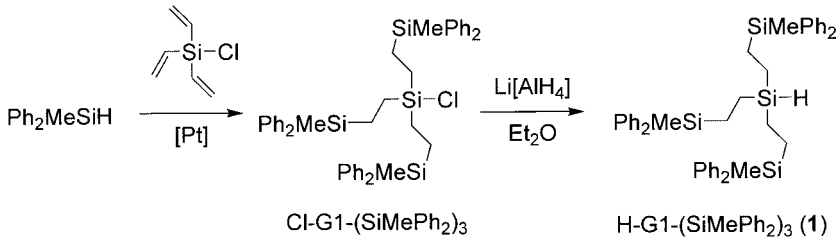
Scheme 1.

We have previously reported the synthesis of group 4 metallocenes derived from the first-generation dendron **B** that possesses a cyclopentadienide anion (Cp^-) directly linked to its focal point.[7] In contrast to the aryl bromide in **A**, the Cp group is not compatible with the hydrosilylation and alkylation steps and cannot be incorporated before the growth of the dendrimer. Here we describe a strategy for the post-synthetic modification of the focal point of a carbosilane dendritic wedge.

Results and Discussion

Fréchet introduced the term "dendritic wedge" in the description of the convergent strategy for the growth of dendrimers.[8] In this strategy, the dendrimer is assembled from the periphery and each successive generation is synthesized from a single reactive group located at the focal point of a dendritic wedge. The final reaction involves the attachment of the dendritic wedges to a core molecule. For this reason,

[a] Departamento de Química Inorgánica, Universidad de Alcalá, Campus Universitario, 28871 Alcalá de Henares, Madrid, Spain
Fax: +34-91-885-4683
E-mail: ernesto.dejesus@uah.es

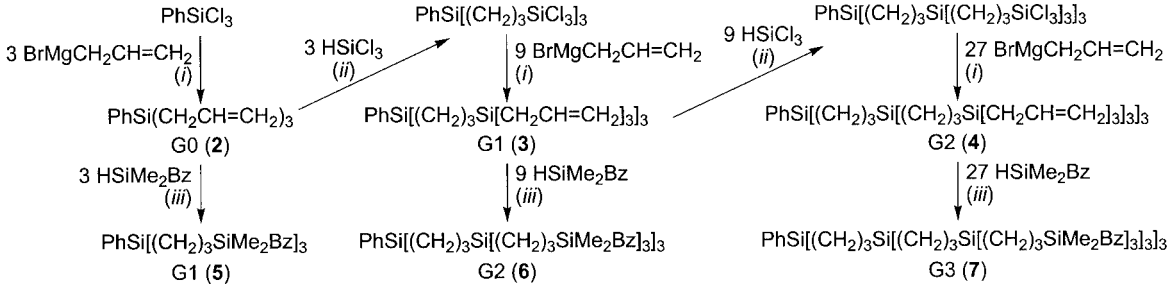


Scheme 2.

the convergent approach has been largely applied to the synthesis of core- or focal-point functionalized dendrimers. Carbosilane dendrimers are, in general, synthesized divergently by a repetitive sequence of hydrosilylation and alkylation steps.[6,9] The sequence of reactions depicted in Scheme 2 illustrates a possible route for the convergent preparation of carbosilane dendrimers in which the Si–Cl bond is reduced to Si–H instead of being alkylated as in a divergent synthesis. Thus, the carbosilane Cl-G1-$[(CH_2)_3SiMePh_2]_3$ was prepared by hydrosilylation of chlorotrivinylsilane with methyldiphenylsilane,[7] and reacted with lithium tetrahydridoaluminate to give H-G1-$[(CH_2)_3SiMePh_2]_3$ (**1**), the first-generation analog of the starting methyldiphenylsilane, quantitatively. The presence of a Si–H bond in **1** was confirmed by the septuplet observed in the ^1H NMR spectrum at $\delta = 3.64$ ppm ($^3J_{H,H} = 2.9$ Hz). Unfortunately, hydrosilylation of chlorotrivinylsilane with **1** always gave mixtures of the second-generation wedge Cl-G2-$[(CH_2)_3SiMePh_2]_3$ with partially hydrosilylated compounds, in spite of the variety of solvents, temperatures, and Pt catalysts (Speier, Karstedt, and Pt/C) tested. This result was not completely unexpected because it is known that both bulky and electron-donating substituents decrease the reactivity of silanes in the platinum-catalyzed hydrosilylation of olefins.[10] Both characteristics are combined in the silane **1** and in its progressively bulkier higher-generation analogs H-G*n*-$[(CH_2)_3SiMePh_2]_3$, which are required for this convergent strategy, in contrast to the divergent growth that uses activated silanes with electron-withdrawing chloro substituents.

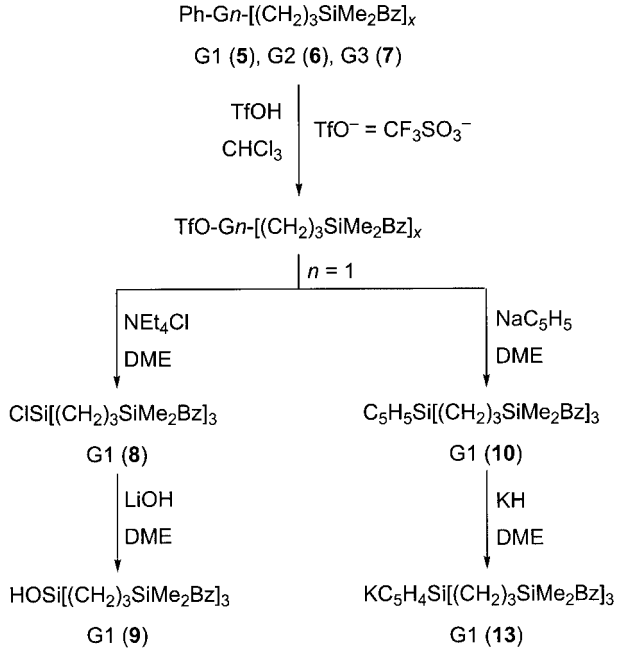
The desired focal-point functionalization can also be achieved by an approach in which a protecting group is linked to the core before the dendrimer growth and eliminated at the end of the growing process. In the case of a carbosilane dendrimer, the phenyl group fulfills the main requirements of a silicon-core protector: it is inert towards hydrosilylation and alkylation, but forms bonds with silicon that can undergo protolysis to give a by-product that is easily separable from the dendrimer. Thus, G0, G1, and G2 compounds Ph-G*n*-$(CH_2CHCH_2)_x$ (**2**–**4**, respectively) with 3, 9, and 27 allyl end-groups, respectively, were synthesized from $PhSiCl_3$ by successive allylation and hydrosilylation steps (Scheme 3).[11] The ^1H NMR olefinic resonances at around $\delta = 4.8$ and 5.7 ppm were used to follow the progress of the critical hydrosilylation steps in order to determine their completion and, therefore, the absence of defects in the branches of the final products. The growth was terminated at the desired generation by using benzyldimethylsilane instead of trichlorosilane as the hydrosilylating agent to give Ph-G*n*-$[(CH_2)_3SiMe_2Bz]_x$ (Bz = $CH_2C_6H_5$, **5**–**7**). The reaction of allyl-terminated dendrimers with trichlorosilane in the presence of H_2PtCl_6 as a catalyst occurred smoothly at room temperature, whereas the reaction mixture had to be gently heated for the activation of the trialkylsilane $HSiMe_2Bz$ (^1H NMR monitoring). Dendrimers **5**–**7** were obtained as colorless oils after removal of the volatiles in vacuo and were purified by chromatography on a silica-gel column prior to subsequent use. After isolation, the yields ranged from 93 to 96% for allyl-terminated dendrimers **2**–**4** (for **3** and **4** the values correspond to overall yields from the allyl dendrimer of the previous generation) and 82–83% for **5**–**7**.

Acid-induced cleavage of the Ph–Si bond was attempted with boron trichloride in hexane,[12] HCl and catalytic amounts of aluminum trichloride in diethyl ether,[13] or triflic acid (trifluoromethanesulfonic acid, TfOH) in chloro-

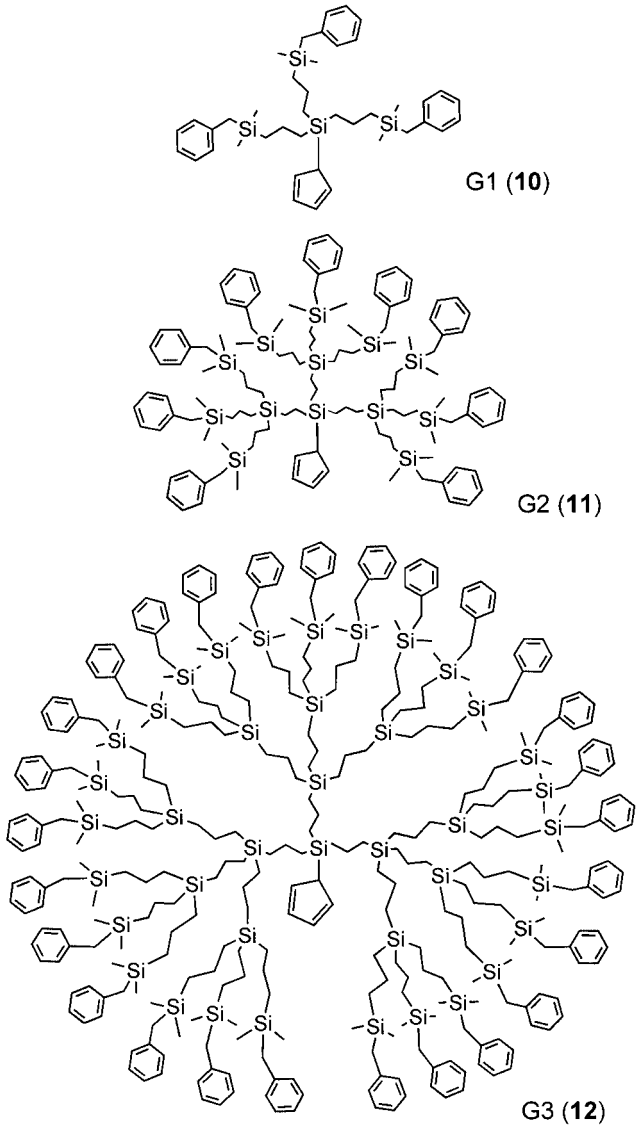


Scheme 3. Synthesis of carbosilane dendritic wedges **2**–**7** with a phenyl group attached to their focal point. Conditions: (*i*) diethyl ether, room temperature, overnight; (*ii*) solvent-free reaction, H_2PtCl_6 in 2-propanol, room temperature, 4 h; (*iii*) solvent-free reaction, H_2PtCl_6 in 2-propanol; see Exp. Sect. for details.

form.[14] Boron trichloride failed to react with both allyl- and benzyldimethylsilyl-terminated compounds **2** and **5** at room temperature, and protic acids such as HCl or TfOH reacted at the same time with the terminal allyl groups of dendrimers Ph-G*n*-$(CH_2CH{=}CH_2)_x$ (**2**–**4**).[15] Cleavage of the Si–Ph bond with HCl was slow in diethyl ether at room temperature (^{1}H NMR evidence), whereas the Si–Ph bond of dendrimers Ph-G*n*-$[(CH_2)_3SiMe_2Bz]_x$ (**5**–**7**) was cleanly and readily cleaved with triflic acid at 0 °C in chloroform (Scheme 4), with the advantage that the triflate anion TfO^- is a good leaving-group in silyl triflates, undergoing exchange with a wide range of nucleophiles.[16] For the reactions described below, compounds TfO-G*n*-$[(CH_2)_3SiMe_2Bz]_x$ were used without isolation. As shown in Scheme 4, the reaction of $TfOSi[(CH_2)_3SiMe_2Bz]_3$ with triethylammonium chloride in dimethoxyethane (DME) gave $ClSi[(CH_2)_3SiMe_2Bz]_3$ (**8**). Other nucleophiles can be introduced at the focal-point position either from the chlorosilane or directly from the silyl triflate, as exemplified by the preparation of the silanol $HOSi[(CH_2)_3SiMe_2Bz]_3$ (**9**) or the cyclopentadiene $(C_5H_5)Si[(CH_2)_3SiMe_2Bz]_3$ (**10**). The ^{1}H NMR spectrum of **10** shows, at room temperature, broadened temperature-dependent resonances for both types of cyclopentadiene protons, those bonded to sp^2 (δ = 6.4–6.7 ppm) and those bonded to sp^3 carbons (δ = 2.9–3.5 ppm). The related trimethylsilylcyclopentadiene ($C_5H_5SiMe_3$), which is present as a mixture of the three possible isomers, also shows broadened temperature-dependent ^{1}H resonances, which are ascribed to the interconversion of ring protons and isomers by sigmatropic $SiMe_3$ and proton shifts.[17] The ^{1}H NMR behavior of **10** is clearly similar to that of $C_5H_5SiMe_3$, especially in the distribution and temperature dependence of the C(sp^3)–H resonances. Thus, the major isomer of **10** (ca. 70–75%) corresponds to the cyclopentadiene with a C(sp^3)–Si bond (Scheme 5) and gives a broad resonance at δ = 3.4 ppm, whereas the minor isomers show resonances at around δ = 3.0 ppm which are sharper at room temperature. The usefulness of the described methodology for the synthesis of higher-generation dendritic wedges has been demonstrated by the synthesis of the G2 and G3 cyclopentadienes **11** and **12** (Scheme 5). They were obtained as yellow oils in the same conditions described above for **10**, starting from the corresponding triflate TfO-G*n*-$[(CH_2)_3SiMe_2Bz]_x$. The ^{1}H NMR resonances in the cyclopentadiene sp^3 region are similar to those described above for **10**, although they are accompanied by the general broadening of resonances that the restricted mobility of protons causes in higher generations.



Scheme 4.

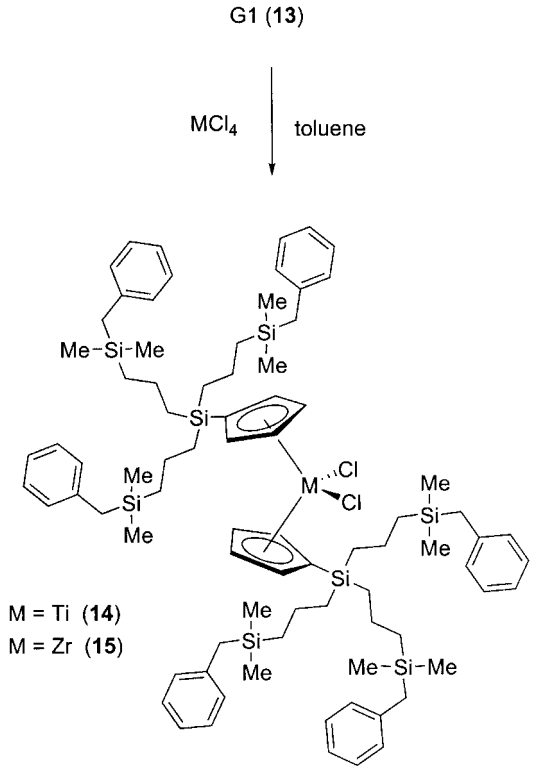


Scheme 5. Cyclopentadienes with carbosilane dendritic wedges of first (**10**), second (**11**), and third generation (**12**). Only the major isomers are represented.

Dendrimers **2**–**12** were characterized by elemental analysis and ^{1}H, ^{13}C{^{1}H}, and ^{29}Si{^{1}H} NMR spectroscopy. Three groups of methylene resonances are observed for the

$SiCH_2CH_2CH_2Si$ repeating unit in phenyl-protected dendrimers **5**–**7**, at $\delta \approx 0.8$ ppm for the methylene bonded to the core silicon, $\delta = 1.2$–1.3 ppm for the middle CH_2 groups, and $\delta \approx 0.5$ ppm for the rest. Only the core $SiCH_2$ resonance is affected by the modification of the focal-point group, and is progressively shifted to high field when Ph is replaced by Cl, OH, and C_5H_5. In the $^{29}Si\{^1H\}$ NMR spectra, a singlet is observed for every type of silicon atom present in the corresponding molecule. Mass spectra were obtained by ESI or APCI techniques for all the first-generation post-functionalized dendrimers **8**–**10**. Attempts to record MALDI-TOF mass spectra of second- and third-generation cyclopentadiene dendrimers **11** and **12** failed. The purity of phenyl-protected dendrimers **5**–**7**, as well as that of the post-modified cyclopentadienes **10**–**12**, was routinely checked by GPC chromatography in THF. Every chromatogram showed a unique peak with typical polydispersity values of about 1.02–1.03, according to the monodisperse nature of these molecules. As expected, the elution time of the dendrimers increases with the molecular weight. The molecular weights obtained after calibration with a standard of polystyrene were not in good agreement with the theoretical values because of the globular nature of dendrimers. However, a good linear relationship was shown between the logarithm of the theoretical molecular weights and the elution times on GPC traces ($R_2 = 0.984$).[18]

The first-generation cyclopentadienide **13** was synthesized as a potassium salt by reaction of **10** with KH in DME. Dendritic metallocenes **14** (Ti) and **15** (Zr) were subsequently obtained by reaction of two equivalents of cyclopentadienide **13** with $TiCl_4$ or $ZrCl_4$·2THF in toluene (Scheme 6). These products were isolated as red (Ti) or colorless (Zr) oils that were rather stable upon exposure to air. Upon activation with an excess of methylaluminoxane (MAO), complexes **14** and **15** catalyze the polymerization of ethylene. The results are summarized in Table 1 and compared with those of simple metallocenes $[(C_5H_5)_2MCl_2]$ (M = Ti, Zr) obtained under the same conditions. The activity is lowered by one order by the dendritic substituents in the titanocene catalyst, but noticeably there is no such decrease in the zirconocene case. We have previously reported a similar result with vinyl-type carbosilanes $[\{(Ph_2MeSiCH_2CH_2)_3SiC_5H_4\}_2MCl_2]$ (M = Ti, Zr), although in this example a small but significant decrease of 30% was observed for the zirconocene compound.[7] These results can be interpreted in steric terms by taking into account the bigger size of the zirconium atom, and the larger hindrance of vinyl-type carbosilanes when compared with the allyl type reported here. In polymerization of propylene (Table 1), the zirconium complex **15** displays a similar activity to that observed for $[(C_5H_5)_2ZrCl_2]$. Some degree of stereocontrol in the polymerization of α-olefins with metallocenes is, in principle, possible by restricting the rotation of the Cp ligand, for example by means of sterically demanding substituents.[19] The polypropylene obtained with **15**, at both 20 °C and –30 °C, shows the distribution of ^{13}C NMR resonances of a mainly atactic polymer,[20] similar to that obtained with $[(C_5H_5)_2ZrCl_2]$.



Scheme 6.

In view of these results, we tried the preparation of the second- and third-generation analogs of metallocenes **14** and **15**. Somewhat surprisingly, no reaction was observed between **11** or **12** and KH under the same conditions used for **10**. When *n*-buyllithium was employed instead as a deprotonating agent, the ^1H NMR spectra in C_6D_6 showed the disappearance of the resonances due to the $C(sp^3)$ protons, as expected for the formation of the lithium cyclopentadienides. However, the formation of either mono- or biscyclopentadienyl complexes was never observed when these

Table 1. Ethylene and propylene polymerization results with complexes **14** and **15**.[a]

Precatalyst	Ethylene Yield [g]	Activity [kg_{PE}/mol_M h]	Propylene Yield [g]	Activity [kg_{PP}/mol_M h]
$[Cp_2TiCl_2]$	1.150	5520	–	–
14	0.100	480	–	–
$[Cp_2ZrCl_2]$	2.459	11803	0.446	2141
15	2.549	12235	0.311	1493

[a] Conditions: MAO cocatalyst, Al/M = 1700, 1.25 mmol of catalyst dissolved in 50 mL of toluene, 10 min, 293 K, 1 bar of constant monomer pressure.

solutions were reacted with $TiCl_4$ or $ZrCl_4$ in the usual solvents (toluene or THF for zirconium), with reaction times of up to two days and temperatures up to 50 °C. The reason for this failure − steric hindrance or inappropriate reaction conditions − is not clear to us at this stage.

Conclusions

The post-synthetic modification of the focal point of a dendrimer is useful for the chemistry of dendrimers and hyperbranched polymers because it permits the incorporation of more-reactive cores.[21] In this paper, we have demonstrated a methodology for such a modification of carbosilane dendrimers that is based on the protolysis of Si–Ph bonds with triflic acid and allows the linking of functional nucleophiles to the focal point of carbosilane wedges. In this way, we have synthesized dendritic cyclopentadienes up to the third generation. We are currently exploring the utility of this strategy for the modification of a variety of ligands.

Experimental Section

Reagents and General Techniques: All operations were performed under argon by using Schlenk or dry-box techniques. Solvents were dried and distilled under argon as described elsewhere.[22] Unless otherwise stated, reagents were obtained from commercial sources and used as received. $Na(C_5H_5)$ was prepared from freshly distilled cyclopentadiene and NaH in THF. $HSiMe_2Bz$ was synthesized from $HSiMe_2Cl$ and BzMgCl in diethyl ether. $ClSi(CH_2CH_2SiMePh_2)_3$ was prepared as previously reported.[7] ^1H, ^{13}C, and ^{29}Si NMR spectra were recorded on Varian Unity 300 or 500 Plus spectrometers. Chemical shifts (δ, ppm) are relative to $SiMe_4$, and were measured by internal referencing to the deuterated solvent (^{13}C and residual ^1H resonances), or by the substitution method (^{29}Si). Coupling constants (J) are given in hertz. The Analytical Services of the Universidad de Alcalá performed the C, and H analyses with a Heraeus CHN–O-Rapid microanalyzer, and the mass spectra with an Automass Multi, ThermoQuest. GPC analyses were carried out with a Varian Inert 9012 and 9065 Polychrom chromatograph, and Polymer Laboratories PL-ELS 1000 Light Scattering detector, using Polymer Laboratories Plgel columns and tetrahydrofuran (THF) as the eluent.

Synthesis of $HSi(CH_2CH_2SiMePh_2)_3$ (1): A solution of $ClSi(CH_2CH_2SiMePh_2)_3$ (1.00 g, 1.35 mmol) in 10 mL of diethyl ether was added to a mixture of lithium aluminum hydride (25 mg, 0.67 mmol) in diethyl ether (25 mL). After stirring the mixture for 6 h at room temperature, the excess of lithium aluminum hydride was hydrolyzed with a 5% solution of HCl in water, and the ethereal and aqueous phases were separated. The aqueous phase was extracted with diethyl ether (2×10 mL) and the ethereal fractions were collected and dried with anhydrous $MgSO_4$. Then, the solvent was removed in vacuo and the residue characterized as $HSi(CH_2CH_2SiMePh_2)_3$ (0.85 g, 89%) as a colorless oil. $C_{45}H_{52}Si_4$ (705.24): calcd. C 76.64, H 7.43; found C 76.31, H 7.39. ^1H NMR ($CDCl_3$): δ = 7.45 (m, 12 H, Ph), 7.32 (m, 18 H, Ph), 3.64 (sept, $^3J_{H,H}$ = 2.9, 1 H, Si*H*), 1.50 (s, 9 H, Me), 0.88 (m, 6 H, $HSiCH_2$), and 0.54 (m, 6 H, $CH_2SiMePh_2$) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 137.1 (*ipso-Ph*), 134.5 (*meta-Ph*), 129.1 (*para-Ph*), 127.8 (*ortho-Ph*), 7.3 and 2.5 [$Si(CH_2)_2Si$], –5.1 (Me) ppm.

Synthesis of Ph-G*n*-(allyl)$_x$ (2–4): These compounds have been reported previously but complete preparative details were not given.[11] Here, the preparation of Ph-G2-$(allyl)_{27}$ (**4**) is described as representative. Ph-G1-$(allyl)_9$ (**3**; 3.7 g, 5.4 mmol) was added to an excess of trichlorosilane (10 mL, 99 mmol) in the presence of a 2×10^{-3} M solution of H_2PtCl_6 in 2-propanol (0.080 mL, 0.16 μmol) as catalyst. The solution was stirred for 4 h at room temperature and, after verification of the complete hydrosilylation of **3** by ^1H NMR spectroscopy, the excess of silane and other volatiles were removed under vacuum. Subsequently, the crude product was dissolved in diethyl ether (25 mL) and added dropwise (30 min) to an ice-cooled solution of allylmagnesium bromide (180 mmol) in diethyl ether (300 mL). When the addition was finished, the reaction mixture was allowed to warm to room temperature and the stirring was continued overnight. The excess of allylmagnesium bromide was then hydrolyzed with a concentrated aqueous solution of NH_4Cl (100 mL). The organic phase was separated by decantation and the aqueous solution was extracted again with diethyl ether (2×100 mL). The combined organic phase were dried with anhydrous $MgSO_4$, filtered, and the solvents evaporated in vacuo to yield **4** (10.7 g, 96%) as a colorless liquid that was pure by ^1H NMR spectroscopy.

Ph-G0-$(allyl)_3$ (**2**; 13.0 g, 96%) was obtained from $PhSiCl_3$ (9.5 mL, 59 mmol) and allylmagnesium bromide (200 mmol). Ph-G1-$(allyl)_9$ (**3**; 11.4 g, 93%) was obtained from Ph-G0-$(allyl)_3$ (**2**; 4.10 g, 18.0 mmol), trichlorosilane (10 mL, 99 mmol), and allylmagnesium bromide (190 mmol).

Ph-G0-$(allyl)_3$ (2): $C_{15}H_{20}Si$ (228.40): calcd. C 78.88, H 8.83; found C 78.80, H 8.81. ^1H NMR ($CDCl_3$): δ = 7.52 (m, 2 H, Ph), 7.36 (m, 3 H, Ph), 5.80 (m, 3 H, CH_2CH=CH_2), 4.89 (m, 6 H, CH_2CH=CH_2) 1.86 (m, 6 H, CH_2CH=CH_2) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 135.2 (*ipso*-Ph), 134.2 (CH_2CH=CH_2), 133.8 (*ortho*-Ph), 129.3 (*para*-Ph), 127.7 (*meta*-Ph), 114.3 (CH_2CH=CH_2), 19.5 (CH_2CH=CH_2) ppm. $^{29}Si\{^1H\}$ NMR ($CDCl_3$): δ = –7.90 ppm.

Ph-G1-$(allyl)_9$ (3): $C_{42}H_{68}Si_4$ (685.33): calcd. C 73.61, H 10.00; found C 73.57, H 9.98. ^1H NMR ($CDCl_3$): δ = 7.44 (m, 2 H, Ph), 7.34, (m, 3 H, Ph), 5.74 (m, 9 H, CH_2CH=CH_2), 4.84 (m, 18 H, CH_2CH=CH_2), 1.54 (m, 18 H, CH_2CH=CH_2), 1.37 (m, 6 H, $SiCH_2CH_2CH_2Si$), 0.84 (m, 6 H, $PhSiCH_2CH_2CH_2$), 0.66 (m, 6 H, $PhSiCH_2CH_2CH_2Si$) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 137.2 (*ipso*-Ph), 134.1 (CH_2CH=CH_2), 133.7 (*ortho*-Ph), 128.6 (*para*-Ph), 127.4 (*meta*-Ph), 113.3 (CH_2CH=CH_2), 19.9 (CH_2CH=CH_2), 18.4, 17.6, and 16.7 [$Si(CH_2)_3Si$] ppm. $^{29}Si\{^1H\}$ NMR ($CDCl_3$): δ = –1.14 (3 Si), –4.01 (1 Si) ppm.

Ph-G2-$(allyl)_{27}$ (4): $C_{123}H_{212}Si_{13}$ (2056.1): calcd. C 71.85, H 10.39; found C 71.81, H 10.36. ^1H NMR ($CDCl_3$): δ = 7.42 (m, 2 H, Ph), 7.30 (m, 3 H, Ph), 5.74 (m, 27 H, CH_2CH=CH_2), 4.85 (m, 54 H, CH_2CH=CH_2), 1.55 (m, 54 H, CH_2CH=CH_2), 1.28 (m, 24 H, $SiCH_2CH_2CH_2Si$), 0.84 (m, 6 H, $PhSiCH_2CH_2CH_2$), 0.54 (m, 42 H, $PhSiCH_2CH_2CH_2Si$ and $SiCH_2CH_2CH_2Si$) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 137.5 (*ipso*-Ph), 134.3 (CH_2CH=CH_2), 133.9 (*ortho*-Ph), 128.6 (*para*-Ph), 127.6 (*meta*-Ph), 113.4 (CH_2CH=CH_2), 19.8 (CH_2CH=CH_2), 18.6, 18.2, and 16.5 [G1-$Si(CH_2)_3Si$], 18.3, 17.6, and 16.7 [G2-$Si(CH_2)_3Si$] ppm. $^{29}Si\{^1H\}$ NMR ($CDCl_3$): δ = –4.21 (1 Si), 0.42 (3 Si), –1.02 (9 Si) ppm.

Synthesis of Ph-G*n*-[$(CH_2)_3SiMe_2Bz$]$_x$ (5–7): The preparation of Ph-G3-$[(CH_2)_3SiMe_2Bz]_{27}$ (**7**) is given as representative. An excess of benzyldimethylsilane (9.3 mL, 59 mmol) and a 2×10^{-3} M solution of H_2PtCl_6 in 2-propanol (0.080 mL, 0.16 μmol) were added to **4** (4.00 g, 1.95 mmol). The mixture was gently heated until reaction started (the solution became more viscous and turned slightly yellow) and then allowed to recover room temperature. The volatiles

were evaporated under vacuum at room temperature and the residue was purified by flash chromatography on a silica gel column with hexane as eluent. Dendrimer **7** (9.86 g, 83%) was obtained as a colorless liquid.

Ph-G1-[$(CH_2)_3SiMe_2Bz$]$_3$ (**5**; 4.89 g, 82%) was obtained from benzyldimethylsilane (5.0 mL, 31.6 mmol) and **2** (2.00 g, 8.76 mmol); Ph-G2-[$(CH_2)_3SiMe_2Bz$]$_9$ (**6**; 7.68 g, 83%) was obtained from benzyldimethylsilane (7,0 mL, 44.2 mmol) and **3** (3.10 g, 4.53 mmol).

Ph-G1-[$(CH_2)_3SiMe_2Bz$]$_3$ (5): $C_{42}H_{62}Si_4$ (679.28): calcd. C 74.26, H 9.20; found C 74.21, H 9.19. ^{1}H NMR ($CDCl_3$): δ = 7.44 (m, 2 H, SiPh), 7.35 (m, 3 H, SiPh), 7.18 (m, 6 H, CH_2Ph), 7.05 (m, 3 H, CH_2Ph), 6.95 (m, 6 H, CH_2Ph), 2.04 (s, 6 H, CH_2Ph), 1.33 (m, 6 H, $CH_2CH_2CH_2$), 0.81 (m, 6 H, PhSi$CH_2CH_2CH_2$Si), 0.57 (m, 6 H, PhSi$CH_2CH_2CH_2$Si), –0.07 (s, 18 H, CH_3) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 140.4 (*ipso*-CH_2Ph), 137.9 (*ipso*-Ph), 134.0 (*meta*-Ph), 128.7 (*para*-Ph), 128.1 (*ortho*-CH_2Ph), 128.0 (*meta*-CH_2Ph), 127.6 (*ortho*-*Ph*), 123.8 (*para*-CH_2Ph), 27.7 (CH_2Ph), 19.6, 18.3, and 17.3 [Si(CH_2)$_3$Si], –3.51 (Me) ppm. ^{29}Si{^{1}H} NMR ($CDCl_3$): δ = 1.53 (3 Si), –3.99 (1 Si) ppm.

Ph-G2-[$(CH_2)_3SiMe_2Bz$]$_9$ (6): $C_{123}H_{194}Si_{13}$ (2038.0): calcd. C 72.49, H 9.59; found C 72.47, H 9.55. ^{1}H NMR ($CDCl_3$): δ = 7.42 (m, 2 H, Ph), 7.26 (m, 3 H, Ph), 7.17 (m, 18 H, CH_2Ph), 7.03 (m, 9 H, CH_2Ph), 6.95 (m, 18 H, CH_2Ph), 2.04 (s, 18 H, $CH_2C_6H_5$), 1.24 (m, 24 H, Si$CH_2CH_2CH_2$Si), 0.82 (m, 6 H, PhSi$CH_2CH_2CH_2$), 0.50 (m, 42 H, PhSi$CH_2CH_2CH_2$Si and Si$CH_2CH_2CH_2$Si), –0.07 (s, 54 H, Me) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 140.4 (*ipso*-CH_2Ph), 137.8 (*ipso*-Ph), 134.0 (*ortho*-Ph), 128.7 (*para*-Ph), 128.1 (*ortho*-CH_2Ph), 128.0 (*meta*-CH_2Ph), 127.6 (*meta*-Ph), 123.8 (*para*-CH_2Ph), 25.8 (CH_2Ph), 19.6, 18.4, and 17.4 [G2-Si(CH_2)$_3$Si], 18.6, 17.8, and 17.7 [G1-Si(CH_2)$_3$Si], –3.5 (Me) ppm. ^{29}Si{^{1}H} NMR ($CDCl_3$): δ = 1.45 (9 Si), 0.47 (3 Si), –4.13 (1 Si) ppm.

Ph-G3-[$(CH_2)_3SiMe_2Bz$]$_{27}$ (7): $C_{366}H_{590}Si_{40}$ (6114.02): calcd. C 71.90, H 9,73; found C 71.60, H 8.75. ^{1}H NMR ($CDCl_3$): δ = 7.42 (m, 2 H, Ph), 7.20 (m, 3 H, Ph), 7.14 (m, 54 H, CH_2Ph), 7.00 (m, 27 H, CH_2Ph), 6.93 (m, 54 H, CH_2Ph), 2.03 (s, 54 H, $CH_2C_6H_5$), 1.24 (m, 78 H, Si$CH_2CH_2CH_2$Si), 0.80 (m, 6 H, PhSi$CH_2CH_2CH_2$), 0.51 (m, 150 H, PhSi$CH_2CH_2CH_2$Si and Si$CH_2CH_2CH_2$Si), –0.07 (s, 162 H, Me) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 140.3 (*ipso*-CH_2Ph), 137.8 (*ipso*-Ph), 134.1 (*ortho*-*Ph*), 128.4 (*para*-Ph), 128.1 (*ortho*-CH_2Ph), 128.0 (*meta*-CH_2Ph), 127.6 (*meta*-Ph), 123.9 (*para*-CH_2Ph), 25.8 (CH_2Ph), 18.7, 18.1, and 17.8 [G2-Si(CH_2)$_3$Si], 19.9, 18.5 and 17.5 [G3-Si(CH_2)$_3$Si], –3.4 (Me) ppm; [G1-Si(CH_2)$_3$Si] not found. ^{29}Si{^{1}H} NMR ($CDCl_3$): δ = 1.45 (27 Si), 0.44 (3 Si), 0.40 (9 Si), –4.11 (1 Si) ppm.

Synthesis of Cl-G1-[$(CH_2)_3SiMe_2Bz$]$_3$ (8): Compound **5** (1.00 g, 1.47 mmol) was dissolved in a small volume of chloroform (1 mL). Trifluoromethanesulfonic acid (0.14 mL, 1.6 mmol) was then added dropwise from a syringe to this solution previously cooled to 0 °C. Stirring was continued for 1 h at room temperature, the solvent was removed in vacuo, the residue was dissolved in dimethoxyethane (10 mL), and an excess of solid triethylammonium chloride (0.30 g, 2.2 mmol) was added. After stirring the reaction mixture for 2 h, the volatiles were removed in vacuo and the residue was extracted with hexane (10 mL), the mixture was filtered, and the solvent was evaporated to yield **8** (0.81 g, 86%) as a colorless oil. $C_{36}H_{57}ClSi_4$ (637.63): calcd. C 67.81, H 9.01; found C 67.35, H 9.10. MS (ESI–): *m*/*z* = 653 (calcd. for MOH^-: 653). ^{1}H NMR ($CDCl_3$): δ = 7.19 (m, 6 H, CH_2Ph), 7.04 (m, 3 H, CH_2Ph), 6.98 (m, 6 H, CH_2Ph), 2.06 (s, 6 H, $CH_2C_6H_5$), 1.37 (m, 6 H, Si$CH_2CH_2CH_2$Si), 0.79 (m, 6 H, ClSi$CH_2CH_2CH_2$Si), 0.57 (m, 6 H, ClSi$CH_2CH_2CH_2$), –0.04 (s, 18 H, Me) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 140.3 (*ipso*-CH_2Ph), 128.1 (*ortho*-CH_2Ph), 128.0 (*meta*-CH_2Ph), 123.9 (*para*-CH_2Ph), 25.7 ($CH_2C_6H_5$), 20.9, 19.1, and 17.6 [Si(CH_2)$_3$Si], –3.5 (Me) ppm. ^{29}Si{^{1}H} NMR ($CDCl_3$): δ = 30.50 (1 Si), 1.65 (3 Si) ppm.

Synthesis of HO-G1-[$(CH_2)_3SiMe_2Bz$]$_3$ (9): An excess of anhydrous lithium hydroxide (50 mg, 2.1 mmol) was added to a solution of **8** (0.50 g, 0.78 mmol) in dimethoxyethane (10 mL). After stirring the mixture for 3 h at room temperature, the solvent was removed in vacuo, the residue was extracted with hexane (10 mL), the mixture was filtered, and the solvent evaporated to yield **9** (0.41 g, 84%) as a colorless oil. Alternatively, compound **9** can be synthesized by hydrolysis of a solution of **8** in diethyl ether with several drops of water in the presence of an excess of triethylamine. $C_{36}H_{58}OSi_4$ (619.19): calcd. C 69.83, H 9.44; found C 69.43, H 9.43. MS (APCI–): *m*/*z* = 650 (calcd. for $MMeOH^-$: 650). ^{1}H NMR ($CDCl_3$): δ = 7.19 (m, 6 H, CH_2Ph), 7.04 (m, 3 H, CH_2Ph), 6.99 (m, 6 H, CH_2Ph), 2.06 (s, 6 H, $CH_2C_6H_5$), 1.33 (m, 6 H, Si$CH_2CH_2CH_2$Si), 1.20 (s, 1 H, O*H*), 0.61 and 0.54 (m, 12 H, Si$CH_2CH_2CH_2$Si), –0.05 (s, 18 H, Me) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 140.3 (*ipso*-CH_2Ph), 128.1 (*ortho*-CH_2Ph), 128.0 (*meta*-CH_2Ph), 123.8 (*para*-CH_2Ph), 25.8 ($CH_2C_6H_5$), 20.0, 19.5, and 17.7 [Si(CH_2)$_3$Si], –3.4 (Me) ppm. ^{29}Si{^{1}H} NMR ($CDCl_3$): δ = 15.49 (1 Si), 1.57 (3 Si) ppm.

Synthesis of C_5H_5-G*n*-[$(CH_2)_3SiMe_2Bz$]$_x$ (10–12): The preparation of C_5H_5-G3-[$(CH_2)_3SiMe_2Bz$]$_{27}$ (**12**) is given as representative. Compound **7** (10.0 g, 1.63 mmol) was dissolved in a small volume of chloroform (4 mL). Trifluoromethanesulfonic acid (0.245 g, 1.63 mmol) was added dropwise from a syringe to this solution previously cooled to 0 °C. Stirring was continued for 1 h at room temperature and then the solvent was removed in vacuo and the residue dissolved in dimethoxyethane (50 mL). Subsequently, solid NaC_5H_5 (0.144 g, 1.63 mmol) was added in a dry box. The reaction mixture was stirred for 3 h, the volatiles removed in vacuo, and the residue extracted with hexane (3 × 20 mL). After evaporation of the solvent, compound **12** (8.5 g, 85%) was obtained as a dark-yellow oil.

C_5H_5-G1-[$(CH_2)_3SiMe_2Bz$]$_3$ (**10**; 8.6 g, 80%) was obtained from **5** (11.0 g, 16.2 mmol), trifluoromethanesulfonic acid (2.43 g, 16.2 mmol), and NaC_5H_5 (1.43 g, 16.2 mmol). C_5H_5-G2-[$(CH_2)_3SiMe_2Bz$]$_9$ (**11**; 2.0 g, 80%) was obtained from **6** (2.50 g, 1.23 mmol), trifluoromethanesulfonic acid (0.184 g, 1.23 mmol), and NaC_5H_5 (0.108 g, 1.23 mmol).

Data for C_5H_5-G1-[$(CH_2)_3SiMe_2Bz$]$_3$ (10): $C_{41}H_{62}Si_4$ (667.27): calcd. C 73.80, H 9.37; found C 73.75, H 9.36. MS (ESI–): *m*/*z* = 666 (calcd. for $M–H^-$: 666). ^{1}H NMR ($CDCl_3$): δ = 7.19 (m, 6 H, CH_2Ph), 7.04 (m, 3 H, CH_2Ph), 6.96 (m, 6 H, CH_2Ph), 6.57, 3.42, and 2.96 (broad resonances, 5 H, C_5H_5), 2.05 (s, 6 H, $CH_2C_6H_5$), 1.27 (m, 6 H, Si$CH_2CH_2CH_2$Si), 0.53 and 0,46 (m, 12 H, Si$CH_2CH_2CH_2$Si), –0.06 (s, 18 H, Me) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 140.2 (*ipso*-CH_2Ph), 133.1 (C_5H_5), 129.9 (C_5H_5), 128.0 (*ortho*-CH_2Ph), 127.9 (*meta*-CH_2Ph), 123.8 (*para*-CH_2Ph), 49.7 (C_5H_5), 25.8 ($CH_2C_6H_5$), 19.7, 18.8, and 17.5 [Si(CH_2)$_3$Si], –3.3 (Me) ppm. ^{29}Si{^{1}H} NMR ($CDCl_3$): δ = 2.71 (1 Si), 1.54 (3 Si) ppm.

Data for C_5H_5-G2-[$(CH_2)_3SiMe_2Bz$]$_9$ (11): $C_{122}H_{194}Si_{13}$ (2026.0): calcd. C 72.33, H 9.65; found C 71.86, H 9.27. ^{1}H NMR ($CDCl_3$): δ = 7.16 (m, 18 H, CH_2Ph), 7.02 (m, 9 H, CH_2Ph), 6.95 (m, 18 H, CH_2Ph), 6.54, 3.40, and 2.97 (broad resonances, 5 H, C_5H_5), 2.04 (s, 18 H, $CH_2C_6H_5$), 1.26 (m, 24 H, Si$CH_2CH_2CH_2$Si), 0.51 (m, 48 H, Si$CH_2CH_2CH_2$Si), –0.07 (s, 54 H, Me) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 140.4 (*ipso*-CH_2Ph), 132.9 (C_5H_5), 130.1 (C_5H_5), 128.1 (*ortho*-CH_2Ph), 128.0 (*meta*-CH_2Ph), 123.9 (*para*-CH_2Ph),

49.9 (C_5H_5), 25.8 ($CH_2C_6H_5$), 19.9, 18.5, and 17.5 [G2-Si(CH_2)$_3$Si], 18.9, 18.0 and, 17.9 [G1-Si(CH_2)$_3$Si], –3.4 (Me) ppm. ^{29}Si{^{1}H} NMR ($CDCl_3$): δ = 2.70 (1 Si), 1.58 (9 Si), 0.55 (3 Si) ppm.

Data for C_5H_5-G3-[$(CH_2)_3SiMe_2Bz$]$_{27}$ (12): $C_{365}H_{590}Si_{40}$ (6102.0): calcd. C 71.84, H 9.75; found C 71.15, H 9.44. ^{1}H NMR ($CDCl_3$): δ = 7.14 (m, 54 H, CH_2Ph), 7.02 (m, 27 H, CH_2Ph), 6.92 (m, 54 H, CH_2Ph), 6.50, 3.35, 2.93 (broad resonances, 5 H, C_5H_5), 2.01 (s, 54 H, $CH_2C_6H_5$), 1.25 (m, 78 H, $SiCH_2CH_2CH_2Si$), 0.51 (m, 156 H, $SiCH_2CH_2CH_2Si$), –0.09 (s, 162 H, Me) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 140.2 (*ipso*-CH_2Ph), 133.0 (C_5H_5), 130.1 (C_5H_5), 128.1 (*ortho*-CH_2Ph), 127.9 (*meta*-CH_2Ph), 123.8 (*para*-CH_2Ph), 49.5 (C_5H_5), 25.8 ($CH_2C_6H_5$), 19.9, 18.6, and 17.5 [G3-Si(CH_2)$_3$Si], 18.8, 18.3, and 17.9 [G2-Si(CH_2)$_3$Si], –3.3 (Me) ppm; [G1-Si(CH_2)$_3$Si] not found. ^{29}Si{^{1}H} NMR ($CDCl_3$): δ = 2.60 (1 Si), 1.48 (27 Si), 0.43 (9 Si), 0.38 (3 Si) ppm.

Synthesis of KC_5H_4-G1-[$(CH_2)_3SiMe_2Bz$]$_3$ (13): In a dry box, solid potassium hydride (0.60 g, 15 mmol) was added to a solution of **10** (10 g, 15 mmol) in dimethoxyethane (50 mL). The reaction mixture was stirred overnight, filtered, and subsequently the solvent was evaporated in vacuo. Washing the resulting dark-yellow oil, which was insoluble in alkanes, with pentane (3 × 30 mL) yielded 8.7 g (82%) of pure **13**, which is stable enough to be characterized and stored for months in a dry box. MS (ESI+): *m*/*z* = 705 (calcd. for MH^+: 705). ^{1}H NMR (C_6D_6): δ = 7.24 (m, 6 H, CH_2Ph), 7.09 (m, 9 H, CH_2Ph), 6.01 (broad resonance, 4 H, C_5H_4), 2.20 (s, 6 H, $CH_2C_6H_5$), 1.64 (m, 6 H, $CH_2CH_2CH_2$), 0.90 (m, 12 H, $CH_2CH_2CH_2$), 0.17 (s, 18 H, Me) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ = 140.5 (*ipso*-CH_2Ph), 128.7 (*ortho*-CH_2Ph), 128.5 (*meta*-CH_2Ph), 124.5 (*para*-CH_2Ph), 114.0 (C_5H_5), 109.3 (C_5H_5), 26.6 ($CH_2C_6H_5$), 21.0, 20.8, and 20.3 [Si(CH_2)$_3$Si], –2.5 (Me) ppm; *ipso*-C_5H_4 not found. ^{29}Si{^{1}H} NMR (C_6D_6): δ = –12.03 (1 Si), 1.46 (3 Si) ppm.

Synthesis of [{C_5H_4-G1-[$(CH_2)_3SiMe_2Bz$]$_3$}$_2$TiCl$_2$] (14): A 0.20 M solution of $TiCl_4$ in toluene (3.0 mL, 0.60 mmol) was added from a syringe to a solution of the potassium cyclopentadienide **13** (0.85 g, 1.2 mmol) in toluene (20 mL). The mixture was stirred at room temperature overnight. After filtration, the solution was evaporated in vacuo to dryness. The crude red oil thus obtained was characterized as **14** (0.79 g, 91%). $C_{82}H_{122}Cl_2Si_8Ti$ (1451.3): calcd. C 67.86, H 8.47; found C 67.83, H 8.42. ^{1}H NMR ($CDCl_3$): δ = 7.17 (m, 6 H, CH_2Ph), 7.03 (m, 3 H, CH_2Ph), 6.95 (m, 6 H, CH_2Ph), 6.65 (pseudo t, AA′ part of an AA′BB′ spin system, 2 H, C_5H_4), 6.49 (pseudo t, BB′ part of an AA′BB′ spin system, 2 H, C_5H_4), 2.06 (s, 6 H, $CH_2C_6H_5$), 1.30 (m, 6 H, $SiCH_2CH_2CH_2Si$), 0.81 (m, 6 H, $C_5H_5SiCH_2CH_2CH_2Si$), 0.56 (m, 6 H, $C_5H_5SiCH_2CH_2CH_2Si$), –0.06 (s, 18 H, Me) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 140.1 (*ipso*-CH_2Ph), 129.2 (C_5H_4), 127.9 (*ortho*-CH_2Ph), 127.8 (*meta*-CH_2Ph), 123.6 (*para*-CH_2Ph), 119.1 (C_5H_4), 25.9 ($CH_2C_6H_5$), 20.0, 18.8, and 18.3, [Si(CH_2)$_3$Si], –3.1 (Me) ppm; *ipso*-C_5H_4 not found. ^{29}Si{^{1}H} NMR ($CDCl_3$): δ = –5.65 (1 Si), 1.53 (3 Si) ppm.

Synthesis of [{C_5H_4-G1-[$(CH_2)_3SiMe_2Bz$]$_3$}$_2$ZrCl$_2$] (15): Solid $ZrCl_4$·2THF (0.267 g, 0.71 mmol) was added, in a dry box, to a solution of **13** (1.00 g, 1.42 mmol) in toluene. The reaction mixture was stirred overnight, evaporated in vacuo, and extracted with hexane (3 × 10 mL). After filtration, the solvent was evaporated in vacuo to yield **15** (0.89 g, 84%) as a colorless oil. $C_{82}H_{122}Cl_2Si_8Zr$ (1494.66): calcd. C 65.89, H 8.23; found C 65.84, H 8.21. ^{1}H NMR ($CDCl_3$): δ = 7.19 (m, 6 H, CH_2Ph), 7.05 (m, 3 H, CH_2Ph), 6.95 (m, 6 H, CH_2Ph), 6.56 (pseudo t, AA′ part of an AA′BB′ spin system, 2 H, C_5H_4), 6.46 (pseudo t, BB′ part of an AA′BB′ spin system, 2 H, C_5H_4), 2.06 (s, 6 H, $CH_2C_6H_5$), 1.32 (m, 6 H, $SiCH_2CH_2CH_2Si$), 0.85 (m, 6 H, $C_5H_5SiCH_2CH_2CH_2Si$), 0.58 (m, 6 H, $C_5H_5SiCH_2CH_2CH_2Si$), –0.05 (s, 18 H, Me) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 140.1 (*ipso*-CH_2Ph), 127.9 (*ortho*-CH_2Ph), 125.5 (C_5H_4), 127.8 (*meta*-CH_2Ph), 123.6 (*para*-CH_2Ph), 115.5 (C_5H_4), 25.9 ($CH_2C_6H_5$), 19.9, 18.8, and 18.3 [Si(CH_2)$_3$Si], –3.1 (Me) ppm; *ipso*-C_5H_4 not found. ^{29}Si{^{1}H} NMR ($CDCl_3$): δ = –6.34 (1 Si), 1.54 (3 Si) ppm.

Ethylene and Propylene Polymerization: A 250-mL flask charged with toluene (50 mL) and equipped with a magnetic stirrer was evacuated and refilled with pre-dried ethylene or propylene gas four times. Whilst keeping the flask pressurized with the corresponding gas (1 bar) and stirring at room temperature, a toluene solution of methylaluminoxane (PMAO-IP 13% Akzo Nobel, 0.50 mL) was syringed through a septum. After 5 min, a toluene solution of the catalyst (0.50 mL, 2.5 mM) was injected into the flask with simultaneous starting of a stopwatch. The polymerization was quenched 10 min later by closing the gas feed, release of the overpressure, and addition of acidified methanol (4% v/v HCl). The mixture was stirred for 6 h and the polymer was filtered, washed with copious amounts of methanol, and dried in an oven to constant weight.

Acknowledgments

We gratefully acknowledge financial support from the DGI-Ministerio de Ciencia y Tecnología (Project BQU2001-1160 and Programa Ramón y Cajal), and the DGI-Comunidad de Madrid (Project GR/MAT/0733/2004).

[1] a) *Dendrimers and Other Dendritic Polymers* (Eds.: J. M. J. Frechet, D. A. Tomalia), Wiley-VCH, Weinheim, **2001**; b) G. R. Newkome, C. N. Moorefield, F. Vögtle, *Dendrimers: Concepts, Syntheses, Applications*, Wiley-VCH, Weinheim, **2001**.

[2] a) G. E. Oosterom, J. N. H. Reek, P. C. J. Kamer, P. W. N. M. van Leeuwen, *Angew. Chem. Int. Ed.* **2001**, *40*, 1828–1849; b) L. J. Twyman, A. S. H. King, I. K. Martin, *Chem. Soc. Rev* **2002**, *31*, 69–82.

[3] a) D. Astruc, F. Chardac, *Chem. Rev.* **2001**, *101*, 2991–3023; b) R. Kreiter, A. W. Kleij, R. J. M. Klein Gebbink, G. van Koten, *Top. Curr. Chem.* **2001**, *217*, 163–199.

[4] O. Rossell, M. Seco, I. Angurell, *C. R. Chimie* **2003**, *6*, 803–817.

[5] a) G. E. Oosterim, R. J. van Haaren, J. N. H. Reek, P. C. J. Kamer, P. W. N. M. van Leeuwen, *Chem. Commun.* **1999**, 1119–1120; b) G. E. Oosterom, S. Steffens, J. N. H. Reek, P. C. J. Kamer, P. W. N. M. van Leeuwen, *Top. Catal.* **2002**, *19*, 61–73; c) J. N. H. Reek, D. de Groot, G. E. Oosterom, P. C. J. Kamer, P. W. N. M. van Leeuwen, *C. R. Chimie* **2003**, *6*, 1061–1077; d) C. Müller, L. J. Ackerman, J. N. H. Reek, P. C. J. Kamer, P. W. N. M. van Leeuwen, *J. Am. Chem. Soc.* **2004**, *126*, 14960–14963.

[6] a) A. W. van der Made, P. W. N. M. van Leeuwen, *J. Chem. Soc., Chem. Commun.* **1992**, 1400–1401; b) A. W. van der Made, P. W. N. M. van Leeuwen, J. C. de Wilde, R. A. C. Brandes, *Adv. Mater.* **1993**, *5*, 466–468; c) L. L. Zhou, J. Rovers, *Macromolecules* **1993**, *26*, 963–968; d) A. M. Muzafarov, O. B. Gorbatsevich, E. A. Rebrov, G. M. Ignat'eva, T. B. Chenskaya, V. D. Myakushev, A. F. Bulkin, V. S. Papkov, *Vysokomol. Soedin.* **1993**, *35*, 1867–1872; *Polym. Sci. Ser A.* **1993**, *35*, 1575–1580; e) B. Alonso, I. Cuadrado, M. Morán, J. Losada, *J. Chem. Soc., Chem. Commun.* **1994**, 2575–2576.

[7] R. Andrés, E. de Jesús, F. J. de la Mata, J. C. Flores, R. Gómez, *Eur. J. Inorg. Chem.* **2002**, 2281–2286.

[8] a) C. Hawker, J. M. J. Fréchet, *J. Chem. Soc., Chem. Commun.* **1990**, 1010–1013; b) C. J. Hawker, J. M. J. Fréchet, *J. Am. Chem. Soc.* **1990**, *112*, 7638–7647.

[9] A convergent synthesis of ferrocene-containing carbosilane denderimers has been reported: I. Cuadrado, C. M. Casado, B.

Alonso, M. Morán, J. Losada, V. Belsky, *J. Am. Chem. Soc.* **1997**, *119*, 7613–7614.
[10] J. L. Speier, *Adv. Organomet. Chem.* **1979**, *17*, 407–447; L. N. Lewis, *J. Am. Chem. Soc.* **1990**, *112*, 5998–6004.
[11] D. Terumuna, T. Kato, R. Nishio, K. Matsuoka, H. Kuzuhara, Y. Aoki, H. Nohira, *Chem. Lett.* **1998**, 59–60.
[12] See for example: E. Hupe, M. I. Calaza, P. Knochel, *Chem. Commun.* **2002**, 1390–1391.
[13] B. Reiter, K. Hassler, *J. Organomet. Chem.* **1994**, *467*, 21–29.
[14] a) D. Häbich, F. Effenberger, *Synthesis* **1978**, 755–756. b) For a more recent reference see: J. O. Daiss, M. Penka, C. Burschka, R. Tacke, *Organometallics* **2004**, *23*, 4987–4994.
[15] Allyl is a still-better leaving group than phenyl; a) A. R. Bassindale, T. Stout, *J. Organomet. Chem.* **1984**, *271*, C1–C3; K. E. Ruehl, K. Matyjaszewski, *J. Organomet. Chem.* **1991**, *410*, 1–12; b) W. Uhlig, *J. Organomet. Chem.* **1993**, *452*, 29–32.
[16] H. Emde, D. Domsch, H. Feger, U. Frick, A. Götz, H. H. Hergott, K. Hofmann, W. Kober, K. Krägeloh, T. Oesterle, W. Steppan, W. West, G. Simchen, *Synthesis* **1982**, 1–26.
[17] A. J. Ashe, *J. Am. Chem. Soc.* **1970**, *92*, 1233–1235; E. W. Abel, M. O. Dunster, *J. Organomet. Chem.* **1971**, *33*, 161–167.
[18] A. Morikawa, M. Kakimoto, Y. Imai, *Macromolecules* **1992**, *25*, 3247–3253; M. Veith, R. Elsässer, R. P. Krüger, *Organometallics* **1999**, *18*, 656–661.
[19] G. W. Coates, R. M. Waymouth, *Science* **1995**, *267*, 217–219; M. D. Bruce, G. W. Coates, E. Hauptman, R. M. Waymouth, J. W. Ziller, *J. Am. Chem. Soc.* **1997**, *119*, 11174–11182; K. Kimura, K. Takaishi, T. Matsukawa, T. Yoshimura, H. Yamazaki, *Chem. Lett.* **1998**, 571–572.
[20] V. Busico, R. Cipullo, *Prog. Polym. Sci.* **2001**, *26*, 443–533.
[21] P. J. Gittins, L. J. Twyman, *J. Am. Chem. Soc.* **2005**, *127*, 1646–1647.
[22] D. D. Perrin, W. L. F. Armarego, *Purification of Laboratory Chemicals*, 3rd ed., Butterworth–Heinemann Ltd., Oxford, **1988**.

Received: March 1, 2005
Published Online: August 4, 2005

