Organometallics **2003,** *22,* 5109−5113

Synthesis of Aryloxo Cyclopentadienyl Group 4 Metal-Containing Dendrimers

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Received July 16, 2003

A quantitative procedure for the hydrosilylation of allylic $-SiMe_3$ protected phenols with Et_3SiH and Si−H terminated carbosilane dendrimers of first, second, and fourth generations have been performed to give nG-$[(CH_2)_3\{C_6H_{4-r}(OMe)_r\}OH]_m$. The subsequent treatment with $[Ti(C_5Me_5)Cl_2Me]$, $[Ti(C_5Me_5)Me_3]$, or $[M(C_5H_5)_2ClX]$ (M = Ti, X = Cl; M = Zr, X = H) afforded the corresponding organometallic metallodendrimers.

Introduction

An area of growing interest is the synthesis of metallodendrimers in which the metal has been attached to the surface for generating new inorganic/organic hybrid macromolecules with interesting advantages over both homogeneous and heterogeneous catalysis.[1] On the other hand, Ziegler−Natta polymerization of α-olefins by homogeneous catalysts has been the subject of both fundamental and applied studies, and the development of new “single-site” group 4 catalyst precursors for optimizing polymerization catalysis is one of the most striking subjects in the field of organometallic chemistry.[2] The combination of these two areas affords cyclopentadienyl group 4 metal derivatives as a family of attractive candidates for the attachment over a dendritic surface, providing in this way model systems for heterogenization of such complexes on, for example, silica supports. A few examples have been reported so far,[3,4] consisting of bis(cyclopentadienyl) group 4 metals, in which the metallocene units were linked to a carbosilane dendritic skeleton through the ancillary cyclopentadienyl ring.

We have recently reported the synthesis of carbosilane dendrimers with peripheral phenol functionalities that have proved to be useful supports for $[Ti(C_5H_5)Cl_3]$.[5] The extension reported here of this methodology to other cyclopentadienyl titanium and zirconium complexes is also explained by some observations about their catalytic activities.[6] However, the selectivity of the key reaction affording the phenol-functionalized dendrimers, i.e., the hydrosilylation of allylphenols with the terminal Si−H units of carbosilane dendrimers, was limited and an additional study was needed.

Results and Discussion

We have reported[5] that treatment of 4-allyl-2-methoxyphenol (**Ia**; eugenol) or 4-allyl-2,6-dimethoxyphenol (**Ib**) with Et_3SiH or Si−H terminated dendrimers using Karstedt’s catalyst[7] in THF produced the C-silylated derivatives (hydrosilylation of the olefin fragment) together with variable amounts of the O-silylated products (silylation of the phenol functionality) along with the 2-propenyl isomers of **I**, as a result of competitive isomerization reactions (see Scheme 1). The undesired products (O-silylated and 2-propenyl isomers) could be easily removed using chromatographic techniques. Nevertheless, the overall yield of the reaction was significantly diminished.

To increase the selectivity of the hydrosilylation reaction, we have conducted sets of experiments in which Et_3SiH, 1G-H_4, 2G-H_8, and 4G-H_{32} have been used in the hydrosilylation reaction of **Ia**,**b**: (i) varying the solvent (THF or toluene), (ii) changing reactant concentrations, (iii) using different catalyst concentrations, and (iv) repeating these experiments while protecting the phenolic function of **I** with the $-SiMe_3$ group. The percentage of C- and O-silylation was determined by ^1H NMR spectroscopy, as the *o*-methoxy substituent of the phenyl ring is sensitive to the presence of a hydroxy (δ 3.86) or siloxy group (δ 3.78). In a preliminary set of experiments, we observed that solvent polarity does not have an appreciable effect on selectivity and a high concentration of reagents favors the C-silylation versus the two side reactions. In the absence of solvent, the silane dendrimers form a gel and the reaction does not proceed. Thus, unless otherwise

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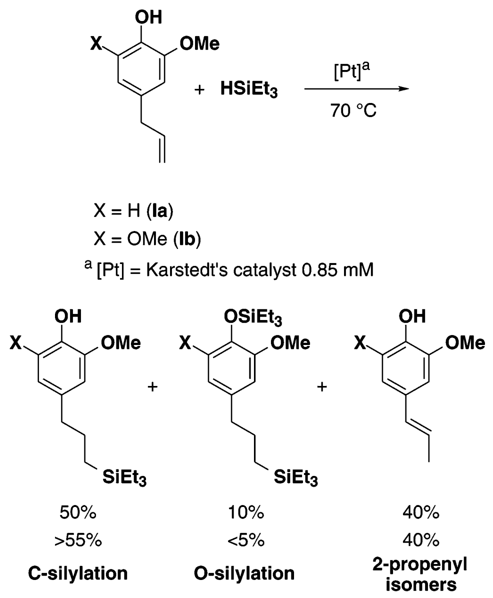
10.1021/om034042i CCC: $25.00
Publication on Web 10/25/2003

Scheme 1



[a] [Pt] = Karstedt's catalyst (0.85 mM).

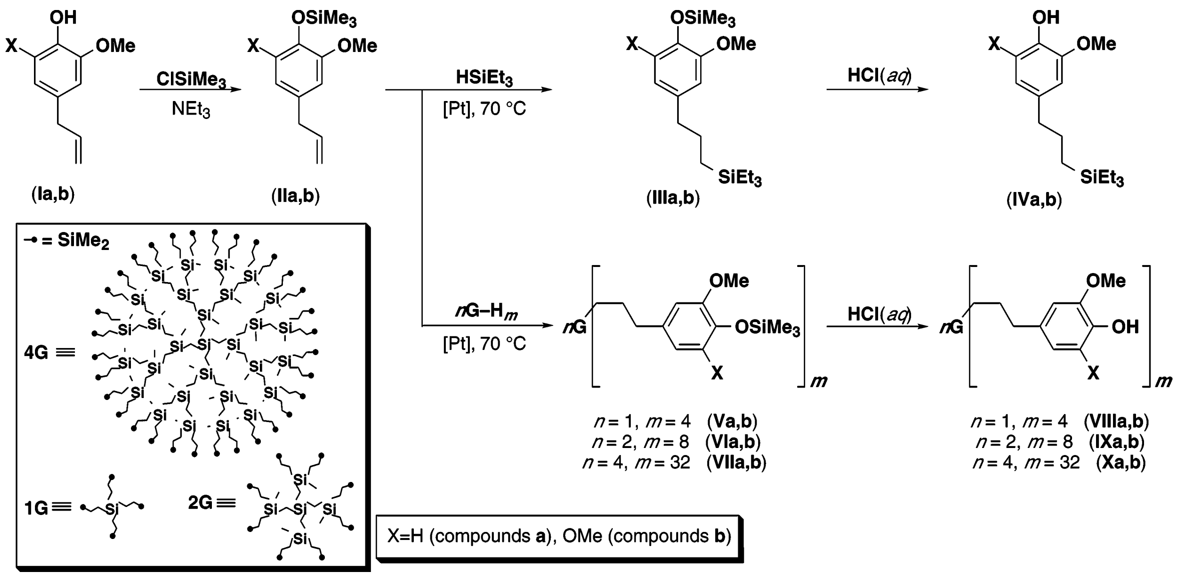
stated, the hydrosilylation reactions were carried out in a minimum amount of THF with Karstedt's catalyst (0.8 mM), under an argon atmosphere at 70 °C for 9 h and then at room temperature for 12 h. Under these conditions, Et_3SiH afforded O-silylated products (10−15% for **Ia** and <5% for **Ib**) and 40−50% of isomerized compounds, whereas negligible amounts of O-silylation and a lower percentage of isomerization (15−25%) were found for dendrimers 1G-H_4, 2G-H_8, and 4G-H_{32}. With regard to the catalyst concentration, when it is increased 2- or 3-fold (2.6 mM), the amounts employed above gave an increase of the O-silylation products in the cases of all the silane reagents used and a decrease of the isomerization products, which were negligible for the dendritic silanes. From these results we cannot make a proposal about the nature of the active species in the catalytic cycle, but it seems clear that the polyfunctional nature of the dendrimers strongly favors C-silylation versus O-silylation and isomerization, hence inferring a different mechanism with respect to the monofunctional Et_3SiH. A similar result was observed by Laine et al. using silsesquioxane silanes.[8]

With the intermediates described above, we carried out the hydrosilylation reactions using $-SiMe_3$ protected phenols **IIa**,**b**, which were easily prepared by addition of $SiMe_3Cl$ to the corresponding alcohol in the presence of NEt_3, and a Karstedt catalyst concentration of 2.6 mM (Scheme 2). As expected, no O-silylation products were found. For Et_3SiH, a dramatic decrease of isomerization reactions occurred, affording **IIIa**,**b** in high yields. For dendritic silanes, 1G-H_4, 2G-H_8, and 4G-H_{32}, isomerization products were not observed and dendrimers **V**−**VII** were quantitatively obtained.[9] The subsequent treatment of these siloxy derivatives with aqueous HCl afforded the previously reported[5] phenol-terminated carbosilane dendrimers **VIII**−**X** in 90−95% overall yield after purification by column chromatography.[5b]

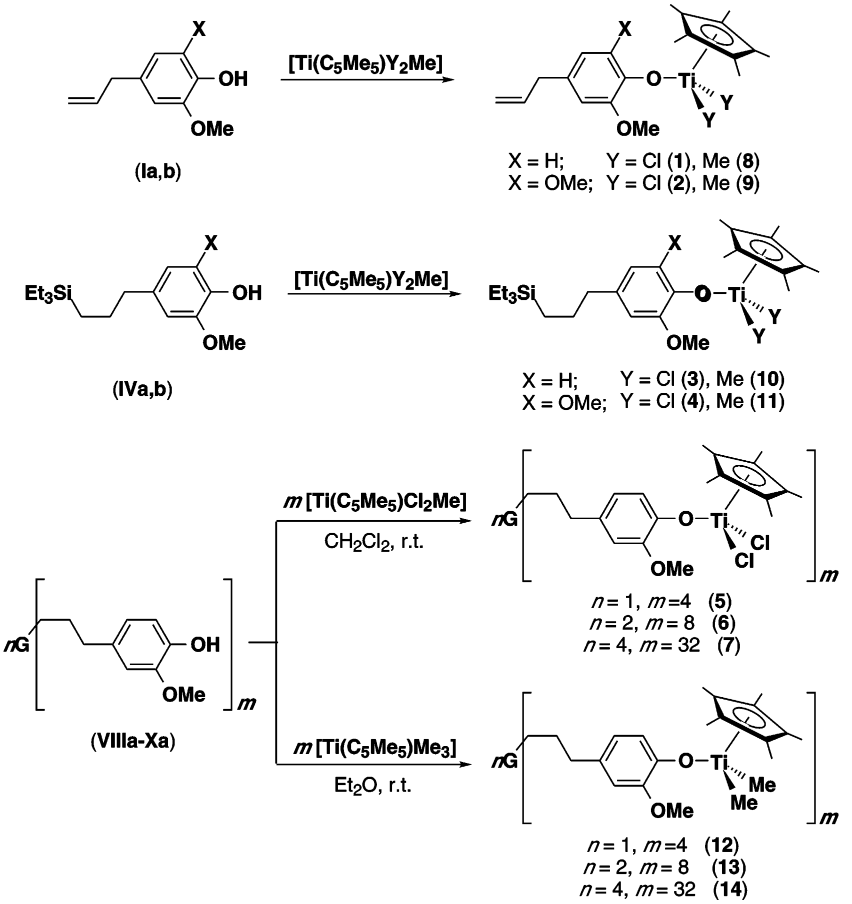
Titanium centers have been successfully incorporated at the surface of the carbosilane dendrimer containing phenol end groups via alcoholysis of a Ti−Cl bond in $[Ti(C_5H_5)Cl_3]$.[5] However, this approach is not appropriate for the synthesis of analogous dendrimers containing pentamethylcyclopentadienyl titanium units because of the enhanced stability of the Ti−Cl bond in $[Ti(C_5Me_5)Cl_3]$ toward alcoholysis. We have also reported[10] the synthesis in good yield of mononuclear pentamethylcyclopentadienyl aryloxo titanium complexes via reaction of $[Ti(C_5Me_5)Cl_3]$ with the dilithium salt of different hydroquinones or the lithium salt of eugenol. This second approach may be convenient for early-generation dendrimers but seems to be unsuitable for higher generations because the selectivity of lithiation decreases when the number of phenol groups increases. Here, we describe appropriate synthetic procedures for anchoring chloro and methyl pentamethylcyclopentadienyl titanium fragments to the periphery of phenol-ended dendrimers via reaction of such systems with $[Ti(C_5Me_5)Cl_2Me]$ or $[Ti(C_5Me_5)Me_3]$ or bis(cyclopentadienyl) titanium or zirconium units by using $[Ti(C_5H_5)_2Cl_2]$ or $[Zr(C_5H_5)_2HCl]$, respectively.

The reaction of monophenolic derivatives **I** and **IV** with $[Ti(C_5Me_5)Cl_2Me]$ in toluene at room temperature

Scheme 2



Scheme 3



proceeds with evolution of methane to form the corresponding aryloxo complexes **1**–**4** (see Scheme 3) as red solids in quantitative yields. The same procedure has been used for the synthesis of the corresponding dendrimers. Metathetical replacement of a methyl group by an aryloxo unit is readily achieved when phenol-ended dendrimers **VIIIa**–**Xa** react with 1 equiv (per phenol group) of [Ti(C_5Me_5)Cl_2Me] in toluene overnight, leading to the new organometallic dendrimers **5**–**7** (see Scheme 3). These metallodendrimers are obtained as red, moisture-sensitive oils, soluble in aromatic solvents and insoluble in aliphatic solvents.

Aryloxo methyl derivatives have been prepared by reaction of phenol derivatives **I** and **IV** or phenol-ended dendrimers **VIIIa**–**Xa** with 1 equiv (per phenol group) of [Ti(C_5Me_5)Me_3]. In this case, the reaction is carried out in hexane and is complete after 2 h at room temperature, giving the complexes **8**[10] and **9**–**14** (see Scheme 3). These methyl complexes are soluble in aromatic solvents and in saturated hydrocarbons. They are soluble in chlorinated solvents, but in these solvents Ti–Me bonds are transformed into Ti–Cl bonds. As reported for other aryloxo pentamethylcyclopentadienyl titanium derivatives,[11] these methyl derivatives cannot be prepared by methylation of chloro derivatives **1**–**7**, because methylating reagents such as $AlMe_3$ and MgClMe react with the Ti–aryloxo bonds of complexes **1**–**7** to give a mixture of [Ti(C_5Me_5)MeCl_2], [Ti(C_5Me_5)Me_3], and aryloxo aluminum or magnesium derivatives.[12]

Phenol-functionalized dendrimers have also been used to support bis(cyclopentadienyl) group 4 complexes at their surface. The preparation of these supported dendrimers requires different synthetic procedures for titanium and zirconium. Reaction of phenols **Ia**, **IVa**, **VIIIa**, and **IXa** with [Ti(C_5H_5)$_2$$Cl_2$] in the presence of NEt_3 affords monosubstituted aryloxides **15**–**18** (see Scheme 4). No disubstitution has been observed in any of these reactions, possibly due to steric hindrance at the titanium center relative to zirconium (see below). For the synthesis of mononuclear complexes a light excess of the phenol derivative can be used in order to ensure completion of the reaction. However, in the case of titanium dendrimers an accurate stoichiometry must be used in order to avoid the presence of unsubstituted phenol groups.

In contrast, the reaction of **Ia** with 1 equiv of [Zr(C_5H_5)$_2$$Cl_2$] in the presence of 1 equiv of NEt_3 affords a mixture of the starting zirconium precursor together with the mono- and disubstitution aryloxo derivatives, whereas the reaction of [Zr(C_5H_5)$_2$$Cl_2$] with 2 equiv of eugenol in the presence of 2 equiv of NEt_3 affords quantitatively the bis(aryloxide) compound **19**. This behavior can be attributed to the larger size of the

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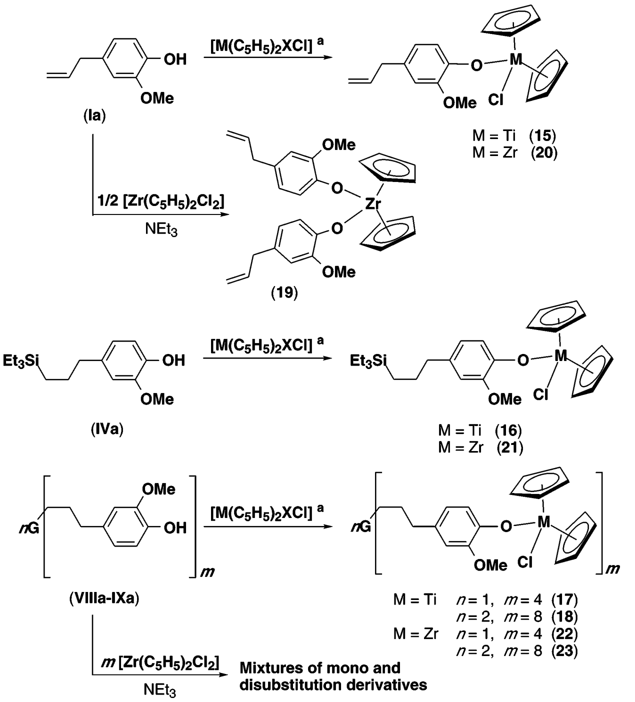
(12) For instance, the reaction of **Ib** with $AlMe_3$ allowed the isolation of an aryloxo aluminium derivative, {($AlMe_2$)$_2$[μ-{O[C_6H_2(OMe)$_2$-(C_3H_5)]}]$_2$}. ^{1}H NMR ($CDCl_3$): δ 6.37 (s, 4H, C_6H_2), 5.70 (m, 2H, $CH_2CH{=}CH_2$), 5.06 (m, 4H, $CH_2CH{=}CH_2$), 3.80 (s, 12H, OMe), 3.30 (m, 4H, $CH_2CH{=}CH_2$), -0.83 (s, 12H, Al–CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 147.4 (C_{ipso} bonded to –OMe), 137.4 ($CH_2CH{=}CH_2$), 131.9 (C_{ipso} bonded to –C_3H_5), 115.9 ($CH_2CH{=}CH_2$), 104.4 (C_6H_2), 56.4 (OMe), 40.3 ($CH_2CH{=}CH_2$), –9.2 (Al–CH_3).

Scheme 4[a]



[a] Conditions: M = Ti, X = Cl, toluene as solvent, NEt_3 must be added; M = Zr, X = H, THF as solvent.

zirconium center that allows the entry of a second aryloxo ligand to its coordination sphere.[13]

Nevertheless, we have been able to obtain monosubstituted aryloxo derivatives of zirconium by reaction of phenols **Ia**, **IVa**, **VIIIa**, and **IXa** with 1 equiv of $[Zr(C_5H_5)_2HCl]$ (per phenol group) to give **20**−**23** in quantitative yield with evolution of dihydrogen (see Scheme 4).

These bis(cyclopentadienyl) titanium and zirconium derivatives are moisture sensitive and in the presence of air decompose, giving the μ-oxo complexes $[\{M(C_5H_5)_2Cl\}_2(\mu\text{-}O)]$ (M = Ti,[14] Zr[15]), although they can be stored under an inert atmosphere for long time periods. All of them are soluble in chlorinated and aromatic solvents and completely insoluble in saturated hydrocarbons.

The organometallic compounds have been characterized using ^1H, ^{13}C, and ^{29}Si NMR spectroscopy and elemental analysis (full details are given in the Supporting Information). For complex **2** the solid-state structure has been determined by X-ray diffraction methods.

The ^1H NMR spectra of some metallodendrimers have shown small peaks of impurities (less than 2%) due to hydrolysis processes or solvent molecules, which were difficult to separate. The NMR spectra of all complexes **1**−**23** show singlets corresponding to the pentamethylcyclopentadienyl or cyclopentadienyl ligands in the expected region (see the Supporting Information). Methyl groups bonded to titanium appear as singlets in ^1H NMR (0.40 ppm) and in ^{13}C NMR (53.6 ppm). From these data it could be assumed that substitution of the eugenolate moiety for the 2,6-dimethoxyphenoxide fragment or hydrosilylation of the allyl fragment does not produce significant changes on the electronic density at the metal center.

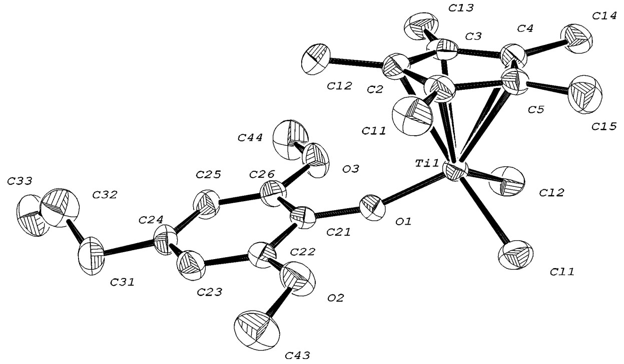


Figure 1. ORTEP (50% thermal ellipsoids) view of $[Ti(C_5Me_5)Cl_2\{O[C_6H_2(OMe)_2(CH_2CH{=}CH_2)]\}]$ (**2**). Selected bond lengths (Å) and angles (deg): Ti(1)−O(1) = 1.770(3), Ti(1)−Cl(1) = 2.2661(18), Ti(1)−Cp(1) = 2.026; Cp(1)−Ti(1)−O(1) = 118.9, Ti(1)−O(1)−C(21) = 163.1(3).

For complexes **1**, **2**, **8**, **9**, **15**, **19**, and **20**, the allyl group resonances were unambiguously assigned. The ^1H NMR data of the dendritic complexes show, in contrast, the presence of the $SiCH_2CH_2CH_2{-}Ph$ fragment as the result of an anti-Markovnikov addition of a Si−H bond to the allyl fragment. The resonance patterns for these methylene protons and for the methylene protons of the branches $-SiCH_2CH_2CH_2Si-$ present in the dendrimers are in agreement with the proposed formulation (full details of the assignment of these signals is given in the Experimental Section and the Supporting Information, and a more detailed discussion of this assignment can be found in ref 5b). The carbosilane fragments do not present significant changes, due to the nature and number of the cyclopentadienyl rings or to the presence of a titanium or zirconium metal center. In agreement with this, the ^{29}Si NMR data show no significant changes from the organic dendritic precursors or the metallodendrimers containing $[Ti(C_5H_5)Cl_2]$ units, as was expected.

Single crystals of **2** suitable for X-ray diffraction studies were obtained from a mixture of Et_2O and hexane cooled to −20 °C. An ORTEP drawing of the molecular structure is shown in Figure 1. The Ti−O bond (1.76 Å) and Ti−O−C angle (163.0°) are almost identical with those of other similar monometallic complexes such as $\{Ti(C_5Me_5)[O(2,6\text{-}Me_2C_6H_3)]Cl_2\}$[16] or an analogue containing the unsubstituted cyclopentadienyl ligand, $\{Ti(C_5H_5)[O(2,6\text{-}^iPr_2C_6H_3)]Cl_2\}$.[11,17]

In summary,we have developed a synthetic strategy to obtain selectively the C-silylation products of phenols having pendant allyl groups with Si−H terminated dendrimers and allowing the synthesis of phenol-ended carbosilane dendrimers in almost quantitative yields. These dendrimers can be used to anchor different mono- and bis(cyclopentadienyl) complexes of titanium and zirconium through the use of suitable organometallic

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precursors. In all cases, the dendritic framework seems to be chemically inert and spectroscopically invariable to the changes produced in the periphery, while the organometallic unit retains the spectroscopic, and hence chemical, properties of the mononuclear counterparts.

Experimental Section

General Procedures. All manipulations were performed under an inert atmosphere of argon using standard Schlenk techniques or a drybox. Solvents used were previously dried and freshly distilled under argon: tetrahydrofuran from sodium benzophenone ketyl, toluene from sodium, hexane from sodium−potassium, and methylene chloride over P_4O_{10}. Unless otherwise stated, reagents were obtained from commercial sources and used as received. $[Ti(C_5Me_5)Cl_3]$,[18] $[[Ti(C_5Me_5)Cl_2Me]$,[19] $[Ti(C_5Me_5)Me_3]$,[20] and G*n*-H dendrimers[21] were prepared according to reported methods.

^1H, ^{13}C, and ^{29}Si NMR spectra were recorded on Varian Unity VXR-300 and Varian 500 Plus instruments. Chemical shifts (δ, ppm) were measured relative to residual ^1H and ^{13}C resonances for chloroform-*d* and benzene-d_6 used as solvents, and ^{29}Si chemical shifts were referenced to external $SiMe_4$ (0.00 ppm). The integral values of the signals in the ^1H NMR spectra of dendrimer complexes represent only one-fourth of the total amount of hydrogen atoms. C, H analyses were carried out with a Perkin-Elmer 240 C microanalyzer. Thin-layer chromatography was accomplished using 0.25 mm silica gel plates from Alugram, and chromatography was performed on silica gel (35−70 mesh) for the organic dendrimers.

A selection of synthetic procedures and data are shown; for the rest, see the Supporting Information.

Synthesis of 4G-$[(CH_2)_3\{[C_6H_3(OMe)]O\}Ti(C_5Me_5)Cl_2]_{32}$ (7). A solution of 4G-$\{(CH_2)_3[C_6H_3(OMe)]OH\}_{32}$ (0.30 g, 2.75 × 10^{-2} mmol) in CH_2Cl_2 (10 mL) was slowly added to a solution of $[Ti(C_5Me_5)Cl_2Me]$ (0.24 g, 0.88 mmol) in CH_2Cl_2 (5 mL). The mixture was stirred overnight. The solvent was removed at reduced pressure, to obtain a foamy red solid. The product was washed with Et_2O (2 × 2 mL) to give **7** as a red foamy solid (0.39 g, 75% yield). ^1H NMR ($CDCl_3$): δ 6.84 (m, 8H, C_6H_3), 6.60 (m, 16H, C_6H_3), 3.77 (s, 24H, OMe), 2.52 (m, 16H, $SiCH_2CH_2CH_2Ph$), 2.16 (s, 120H, C_5Me_5), 1.54 (m, 16H, $SiCH_2CH_2CH_2Ph$), 1.24 (m, 30H, $SiCH_2CH_2CH_2Si$), 0.52 (m br, 76H, $SiCH_2CH_2CH_2Si$ and $SiCH_2CH_2CH_2Ph$ overlapping), −0.07 (m br, 69 H, $SiMe_2$ and SiMe overlapping). ^{13}C NMR ($CDCl_3$); δ 153.4 (C_{ipso} bonded to −OTi), 149.9 (C_{ipso} bonded to −OMe), 138.6 (C_{ipso} bonded to $-CH_2$), 132.7 (C_5Me_5), 120.6, 120.1, and 113.0 (C_6H_3), 56.3 (OMe), 39.9 ($SiCH_2CH_2CH_2Ph$), 26.1 ($SiCH_2CH_2CH_2Ph$), 15.3 ($SiCH_2CH_2CH_2Ph$), 20.2, 18.9, 18.5, and overlapped signals ($Si(CH_2)_3Si$), 12.8 (C_5Me_5), −3.2 ($SiMe_2$), −4.9 (SiMe). $^{29}Si\{^1H\}$ NMR ($CDCl_3$): δ 1.91 (G4-Si), 1.28 (G3-Si); the rest were not observed. Anal. Calcd for $C_{912}H_{1500}Cl_{64}O_{64}Si_{61}Ti_{32}$: C, 57.64; H, 7.95. Found: C, 56.82; H, 7.70.

Synthesis of 4G-$[(CH_2)_3\{[C_6H_3(OMe)]O\}Ti(C_5Me_5)Me_2]_{32}$ (14). A solution of 4G-$\{(CH_2)_3[C_6H_3(OMe)]OH\}_{32}$ (0.30 g, 2.75 × 10^{-2} mmol) in Et_2O (10 mL) was slowly added to a solution of $[Ti(C_5Me_5)Me_3]$ (0.20 g, 0.88 mmol) in Et_2O (5 mL). The reaction mixture was stirred for 2 h at room temperature. The solvent was removed at reduced pressure to obtain **14** as a brown-yellow oil in quantitative yield (0.48 g). Selected data are as follows. ^1H NMR ($CDCl_3$): δ 0.38 (s, 48H, $TiMe_2$). ^{13}C NMR ($CDCl_3$): δ 152.3 (C_{ipso} bonded to −OTi), 53.8 ($TiMe_2$). The rest of the data are almost invariable with respect to compound **7**; see the Supporting Information. $^{29}Si\{^1H\}$ NMR ($CDCl_3$): δ 1.94 (G4-Si), 1.31 (G3-Si); the rest were not observed. Anal. Calcd for $C_{976}H_{1692}O_{64}Si_{61}Ti_{32}$: C, 66.24; H, 9.64. Found: C, 65.02; H, 9.40.

Synthesis of 2G-$[(CH_2)_3\{[C_6H_3(OMe)]O\}Ti(C_5H_5)_2Cl]_8$ (18). A solution of 2G-$\{(CH_2)_3[C_6H_3(OMe)]OH\}_8$ (0.10 g, 0.04 mmol) in toluene (10 mL) was slowly added to a solution of $[Ti(C_5H_5)_2Cl_2]$ (0.08 g, 0.32 mmol) in toluene (50 mL). To this mixture was added a slight excess of NEt_3 (50 μL, 0.36 mmol). The reaction mixture was stirred for 12 h and then filtered through Celite to remove $NEt_3 \cdot HCl$. The resulting red solution was evaporated under reduced pressure to give **18** as a red microcrystalline solid (0.127 g, 79%). ^1H NMR ($CDCl_3$): δ 6.67−6.60 (m, 6H, C_6H_3), 6.32 (s, 20H, C_5H_5), 3.76 (s, 6H, OMe), 2.51 (m, 4H, $SiCH_2CH_2CH_2Ph$), 1.54 (m, 4H, $SiCH_2CH_2CH_2Ph$), 1.29 (m, 6H, $SiCH_2CH_2CH_2Si$), 0.50 (m, 16H, $SiCH_2CH_2CH_2Ph$ and $SiCH_2CH_2CH_2Si$ overlapping), −0.07 (s, 12H, $SiMe_2$), −0.09 (s, 3H, SiMe). ^{13}C NMR ($CDCl_3$): δ 159.1 (C_{ipso} bonded to −OTi), 145.8 (C_{ipso} bonded to −OMe), 134.9 (C_{ipso} bonded to $-CH_2$), 125.1, 120.5, and 111.8 (C_6H_3), 117.4 (C_5H_5), 55.9 (OCH_3), 39.9 ($SiCH_2CH_2CH_2Ph$), 26.4 ($SiCH_2CH_2CH_2Ph$), 15.6 ($SiCH_2CH_2CH_2Ph$), 22.7, 19.1, 18.7, and overlapped signals ($Si(CH_2)_3Si$), −2.9 ($SiMe_2$), −4.6 (SiMe). $^{29}Si\{^1H\}$ NMR ($CDCl_3$): δ 1.87 (G2-Si), 1.19 (G1-Si), 0.77 (G0-Si). Anal. Calcd for $C_{216}H_{308}Cl_8O_{16}Si_{13}Ti_8$: C, 61,88; H, 7,40. Found: C, 61.52; H, 7.46.

Synthesis of 2G-$[(CH_2)_3\{[C_6H_3(OMe)]O\}Zr(C_5H_5)_2Cl]_8$ (23). A solution of 2G-$\{(CH_2)_3[C_6H_3(OMe)]OH\}_8$ (0.05 g, 0.02 mmol) in THF (5 mL) was slowly added to a suspension of $[Zr(C_5H_5)_2HCl]$ (0.04 g, 0.17 mmol) in THF (5 mL). The reaction mixture was stirred for 15 min. After hydrogen evolution ceased, the resulting yellow solution was evaporated under reduced pressure, affording quantitatively **23** as a yellow oil (0.088 g). Selected data are as follows. ^1H NMR ($CDCl_3$): δ 6.33 (s, 20H, C_5H_5). ^{13}C NMR ($CDCl_3$): δ 152.6 (C_{ipso} bonded to −OZr), 114.4 (C_5H_5). The rest of the data are almost invariable with respect to those of compound **18**; see the Supporting Information. $^{29}Si\{^1H\}$ NMR ($CDCl_3$): δ 1.86 (G2-Si), 1.19 (G1-Si), 0.77 (G0-Si). Anal. Calcd for $C_{216}H_{308}Cl_8O_{16}Si_{13}Zr_8$: C, 57.18; H, 6.79. Found: C, 56.92; H, 6.56.

Acknowledgment. We acknowledge the Ministerio de Ciencia y Tecnología of Spain (Grant No. BQU2001-1160) and Consejería de Educación-Comunidad de Madrid (Grant No. 07N/0078/2001) for financial support.

Supporting Information Available: Text giving experimental procedures and NMR and analytical data of all the complexes, figures giving a selection of ^1H, ^{13}C, and ^{29}Si NMR spectra of titanium and zirconium mononuclear complexes and dendrimers, and tables of crystal and data collection parameters, atomic coordinates, bond lengths, bond angles, and thermal displacement parameters of compound **2**; X-ray crystal data are also available as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

OM034042I

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