Ethylene polymerization behavior of monometallic complexes and metallodendrimers based on cyclopentadienyl-aryloxy titanium units

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Abstract

Titanium-containing carbosilane dendrimers of type nG-Si[(CH$_2$)$_3$[{C$_6$H$_{4-y}$(OMe)$_y$}O]Ti(C$_5$H$_5$)Cl$_2$]$_x$, in which phenoxy group is anchored to the dendritic skeleton in *para* position through eugenol or 2-allyl-2,6-dimethoxyphenol precursors, were used in ethylene polymerization. Fresh toluene solutions of these dendrimers in conjunction with MAO behaved as moderate active systems. However, their aged toluene solutions, when they were activated with MAO became highly active catalysts as result of dendrimer aggregation processes. However, when the peripheral unit are replaced by [Ti(C$_5$Me$_5$)Cl$_2$] or [M(C$_5$H$_5$)$_2$Cl] groups or 2-allyl-6-methylphenol are incorporated to the peryphery of a carbosilane dendrimer no aggregation was observed upon aging.
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1. Introduction

The interest of dendrimers functionalized with metals at the periphery as catalysts, arises mainly from their ability to combine the advantages of homogeneous and heterogeneous catalysis in one system [1]. Moreover, their shape and size make them more suitable for recycling than soluble polymer-supported catalysts. The multiple reaction sites located at their surfaces may afford reaction rates comparable to those shown in homogeneous systems due to the accessibility for the substrate. However, catalytic efficiency of dendrimers concerning olefin polymerization is often lower than that of their monomeric counterparts, due to factors as, for instance, the congestion of the surface or the improvement of bimetallic deactivation mechanisms. In this context, Seyferth synthesized carbosilane dendrimers with eight peripheral zirconocene groups that showed considerable activity in the polymerization of ethylene [2], although they were ten times less active than monomeric zirconocenes. In contrast, for some other homogeneous processes, higher activities respecting to the mononuclear counterparts have been observed [3]. Recently we have published the synthesis of aryloxo cyclopentadienyl titanium-containing carbosilane dendrimers [4,5] of type nG-Si[(CH$_2$)$_3$[{C$_6$H$_{4-y}$(OMe)$_y$}O]Ti(C$_5$R$_5$)Cl$_2$]$_x$ (see an example in Fig. 1) using as precursor 4-allyl-2-methoxyphenol (commonly called eugenol) or 4-allyl-2,6-dimethoxyphenol, although no catalytic applications were described.

In this paper, we report on the use of these systems in the polymerization of ethylene and the different behavior observed depending on the aging of the precatalyst solution. As a comparison, the synthesis and catalytic behavior of new and analogous aryloxo cyclopentadienyl group 4 complexes based on the more encumbered precursor 2-allyl-6-methylphenol are also presented.

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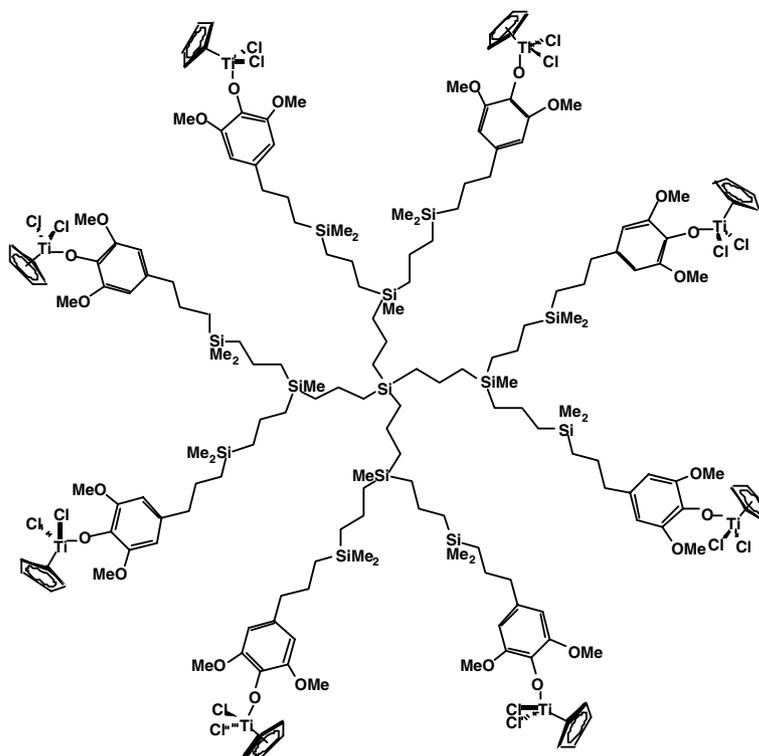   *E-mail address:* javier.delamata@uah.es (F.J. de la Mata).

Fig. 1. Molecular representation of the second generation organotitanium-containing dendrimer $Si[(CH_2)_3[\{C_6H_2(OMe)_2\}O]Ti(C_5H_5)Cl_2]_8$ (**4**).

2. Results and discussion

Fresh toluene solutions of the dendrimers nG-$Si[(CH_2)_3[\{C_6H_{4-y}(OMe)_y\}O]Ti(C_5H_5)Cl_2]_x$ ($n = 1$, $x = 4$, $y = 1$ (**1**), $y = 2$ (**2**); $n = 2$, $x = 8$, $y = 1$ (**3**), $y = 2$ (**4**); $n = 4$, $x = 32$, $y = 1$ (**5**), $y = 2$ (**6**)) [4] and the monometallic derivatives $[Ti(C_5H_5)\{OC_6H_{4-y}(OMe)_y(C_3H_5)\}Cl_2]$ ($y = 1$ (**7**); $y = 2$ (**8**)) [4] in which the aliphatic aryloxy substituent is in *para* position to the O function, polymerized ethylene upon activation with methylaluminoxane (MAO) at 1 bar of ethylene pressure with moderate efficiency, according to Gibson classification [6]. Metallodendrimers of first generation performed activities (101 gPE mmol^{-1} h^{-1} (**1**) and 134 gPE mmol^{-1} h^{-1} (**2**)) comparable to that shown by monometallic complexes **7** (144 gPE mmol^{-1} h^{-1}) and **8** (154 gPE mmol^{-1} h^{-1}), $[Ti(C_5H_5)Cl_3]$ (173 gPE mmol^{-1} h^{-1}), $[Ti(C_5H_5)Cl_2\{O\text{-}2,6\text{-}^iPr_2(C_6H_3)\}]$ [7], or silsesquioxane derivatives [8]. However, the catalytic activities dropped down to 29–34 gPE mmol^{-1} h^{-1} for second and fourth generation dendrimers, probably for the same reasons mentioned above. Nevertheless, when toluene solutions of dendritic precatalysts **1–6** were aged alone, prior to be added to a toluene solution containing MAO as cocatalyst, significant changes in the activities were detected. In three weeks, the first generation dendrimers doubled their activities while a dramatic increase, more than 40 times, was observed for second and fourth generation (525–800 gPE mmol^{-1} h^{-1}). During the aging of the precatalyst solutions, it was observed the slow precipitation of red oils which could not be redissolved by heating or with polar solvents for their spectroscopic characterization by NMR and reduces the concentration of titanium center in the solution. The positive behavior in terms of activity, cannot be ascribed either to changes in the Al/Ti ratio, because polymerization experiments carried out at different molar proportions do not produce significant increases, or to heterogeneous processes caused by the insoluble precipitate which do not polymerize ethylene. Another explanation may be the existence of different species arising from the transformation of the metallodendrimers during the aging process, for instance the presence of titanocene as a result of a ligand exchange, or µ-oxo titanium species along with dendrimers including phenol ended branches due to partial hydrolysis. For the later example, some authors have published the enhancement of the productivity and molecular weight by modification of MAO with phenols [9]. However, chemical transformation of the aged precatalysts can be ruled out because the ^{1}H MNR spectra of the soluble part of the precatalysts remain unchanged over the course of the aging process. Besides, the molecular weights of the polymers are more than ten times higher than those obtained with the titanocene derivative [10]. The changes in activity and molecular weights seem to be too high for an undetectable or partial hydrolysis suffered for these dendrimers.

In a systematic study, a toluene solution of dendrimer **4** was aged before activation with MAO, to accomplish ethylene polymerization at different aging times (see Table 1 and Section 4 for procedure). The activity reached a maximum at 5 weeks (entry 5, activity 1365 gPE mmol^{-1} h^{-1}). At this point, the dendrimer became a highly active catalyst [6]. From this time onwards, the activity decay was probably due to the presence of very low titanium concentrations resulting from the precipitation of the red oils above mentioned. The molecular weights (M_w = 663,000–1,000,400) and polydispersities (M_w/M_n = 1.5–1.6), measured at the same aging times, are shown in Table 1. The values obtained are of the same order or even higher than those found for the monometallic complex **8** (M_w = 826,000, M_w/M_n = 1.5). Hence, these values suggest that the aging process is not responsible of the high molecular weights and low polydispersities. Instead of that, the environment around the metal centers may be responsible of such effects. Indeed, the presence of alkyl substituents in *ortho* position of the aryloxy ligand like in Nomura complex [Ti(C$_5$H$_5$)Cl$_2${O-2,6-^{i}Pr$_2$(C$_6$H$_3$)}] [7], afforded polyethylene of lower molecular weight and higher polydispersity (M_w = 597,300, M_w/M_n = 3.3) under 4 atm of ethylene pressure and 60 °C. Other authors have published lower values of M_w = 336,866, M_w/M_n = 2.65 using the same precatalyst at 1 atm and room temperature [11]. It is possible to assume that the presence of *ortho* OMe groups in the aryloxy fragment allows an additional electronic stabilization of the active species increasing the propagation rate. Respecting the polydispersities, these are consistent with a single-site catalyst, ruling out the possibility of other type of polymerization being the responsible of the behavior observed after the aging time. In Table 1 are also recorded the melting points and enthalpies as well as the crystallinity percentage measured by differential scanning calorimetry (DSC). Both, monometallic complex **8** and the different entries of **4** afforded melting point values in a range of 135–137 °C consistent with high density polyethylene (HDPE) [12]. The most noticeable feature was the higher crystallinity percentage (57%) induced by the

dendrimer **4**, even with a freshly prepared catalyst, compared to monometallic derivative **8** (39%) and hence independent of the aging processes but reliant on the dendritic nature.

Dynamic light-scattering experiments on a 6 mM toluene solution of dendrimer **4** at different aging times showed the presence of time-dependent aggregates (see Fig. 2) [13]. The average hydrodynamic diameters were too small to be determined with accuracy at the initial
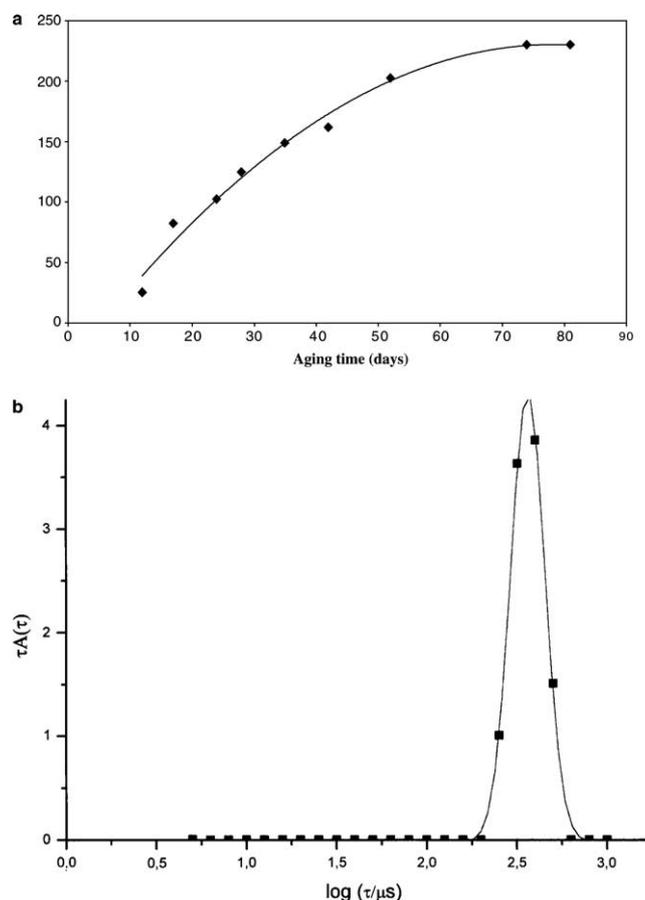

Fig. 2. (a) Plot of hydrodynamic diameter of dendrimer **4** aggregates versus aging time. (b) Distribution function of relaxation time for the dendrimer **4** with 28 days of aging time.

Table 1
Ethylene polymerization with dendrimer **4** and the monometallic derivative **8** using aged precatalyst solutions[a]

Entry	Precatalyst	Aging time (weeks)	Yield (mg)	Activity (gPE mmol^{-1} h^{-1})	M_w	M_w/M_n	T_m (°C)	ΔH (J g^{-1})	Crystallinity α (%)
1	**4**	0	7.0	34			136	−155	54
2	**4**	1	90.7	435	663,000	1.51	135	−164	57
3	**4**	3	173.2	831	732,300	1.61	137	−169	59
4	**4**	5	284.3	1365	1,004,000	1.56	135	−170	59
5	**4**	6	219.3	1053	784,600	1.51	135	−165	57
6	**4**	7	148.3	712			136	−165	57
7	**8**[b]	0	32.0	154	826,000	1.50	136	−113	39

[a] Conditions: Al/Ti: 1000/1, [Ti] = 25 μM, 50 mL of toluene, t = 10 min, T = 20 °C, p = 1 atm, MAO as cocatalyst.
[b] No significant changes observed when precatalyst is aged.

stages in which dendrimer **4** should be mainly unaggregated. The aggregate growth reached a plateau at ca. 74 days with hydrodynamic diameters of 229 nm. In addition, the polydispersity of the particle sizes was low as determined by the quality factor (less than 0.07). This feature was confirmed by the function of the relaxation time distribution from which only one dynamic process with a narrow distribution was observed (see Fig. 2). This result evidences the physical nature of the aggregation process and rules out the hydrolysis reaction mentioned above or other type of chemical aggregations.

Interestingly, when [Ti(C$_5$H$_5$)Cl$_2$] was replaced by [Ti(C$_5$Me$_5$)Cl$_2$] or [Ti(C$_5$H$_5$)$_2$Cl] as peripheral units [5], and the toluene solutions were aged before activation with MAO, no aggregation and no changes in the catalytic activities, were observed. The activities found for all these systems are comparable to those obtained with the well established compounds [Ti(C$_5$Me$_5$)Cl$_3$] or [Ti(C$_5$H$_5$)$_2$Cl$_2$].

In an attempt to shed light on the behavior above described, we prepared new aryloxo-cyclopentadienyl group 4 complexes based on the ligand precursor 2-allyl-6-methyphenol (Scheme 1). In these complexes

the aliphatic aryloxy substituent is in *ortho* position to the O function, which means altered electronic and steric properties. The reaction of 2-allyl-6-methylphenol with one equivalent of [Ti(C$_5$H$_5$)Cl$_3$] in toluene or one equivalent of [M(C$_5$H$_5$)$_2$Cl$_2$] (M = Ti, Zr) in tetrahydrofuran and in the presence of triethylamine, leads to the monometallic aryloxo mono- and bis-cyclopentadienyl complexes [Ti(C$_5$H$_5$){OC$_6$H$_3$(Me)(C$_3$H$_5$)}Cl$_2$] (**9**) and [M(C$_5$H$_5$)$_2${OC$_6$H$_3$(Me)(C$_3$H$_5$)}Cl] (M = Ti (**10**); Zr (**11**)) in high yields. Complex **9** has been previously reported elsewhere [14] using a different synthetic approach with lower yields. Hydrosilylation of the allyl group of the phenol with the carbosilane system [Si(CH$_2$CH$_2$CH$_2$SiMe$_2$H)$_4$] [15] using the Karstedt catalyst [16], affords the polyphenol ligand 1G-Si[(CH$_2$)$_3$ {C$_6$H$_3$(Me)}OH]$_4$ (**12**). Reaction of **12** with four equivalents of [Ti(C$_5$H$_5$)Cl$_3$] gives the polymetallic complex 1G-Si[(CH$_2$)$_3$[{C$_6$H$_3$(Me)}O]Ti(C$_5$H$_5$)Cl$_2$]$_4$ (**13**) as an oily red solid in very good yield. Analogously, **12** reacts with four equivalents of [Zr(C$_5$H$_5$)$_2$Cl$_2$] to give the zirconium derivative 1G-Si[(CH$_2$)$_3$[{C$_6$H$_3$-(Me)}O]Zr(C$_5$H$_5$)$_2$Cl]$_4$ (**14**). However, a similar reaction with [Ti(C$_5$H$_5$)$_2$Cl$_2$] does not lead to a polymetallic
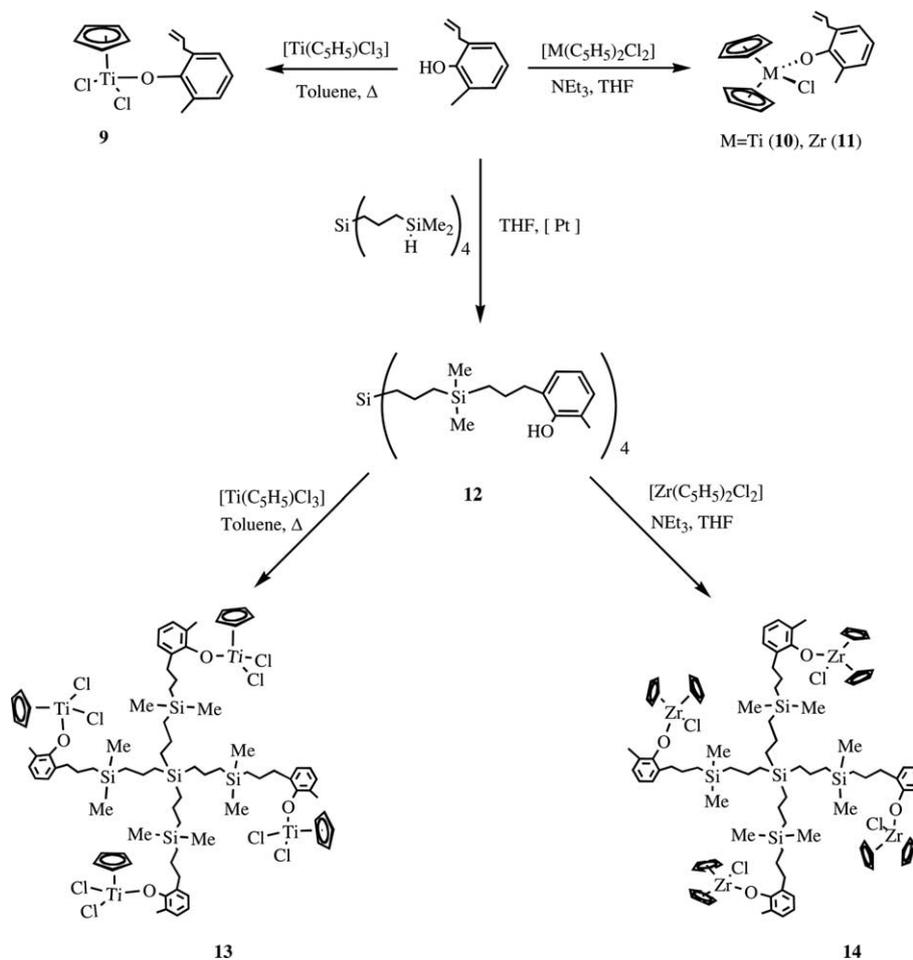
Scheme 1.

complex of titanium analogous to **6**. This behavior must be attributed to steric hindrance caused by the proximity of the phenol functionality to the carbosilylated chain. The same argument is valid to explain why it is not possible to prepare the second generation dendrimer of **13** similar to those that we obtained when, for instance, eugenol is used instead of 2-allyl-6-methylphenol [4,5].

The steric requirement of the 2-allyl-6-methylphenoxy group causes also the fluxional behavior observed in solution for complex **10** due to the spin restriction around the O–Ph bond. The ^{1}H NMR resonances assigned to the methyl and allyl substituents of the phenol group appear clearly broadened when the spectrum of the titanocene **10** is registered in a 300 MHz spectrometer at room temperature in chloroform-d_1. The dynamical origin of this broadening was confirmed lowering the temperature to $-50\,°C$, at which point methyl and allyl resonances are split in two sets of well-defined resonances with a ca. 2/1 integral ratio (see Section 4). This dynamical behavior is explained by the steric restrictions imposed by the *ortho* substituents on the O–Ph bond rotation, which allows the observation of two rotamers, one with the methyl and another with the allyl group in the *endo* position of the titanocene molecule. The activation barrier for the O–Ph bond rotation is estimated in 52 ± 2 kJ mol^{-1} in CD_2Cl_2. On other hand, only a set of well-defined resonances was observed for zirconocene **11** even at $-80\,°C$ ($\Delta G^{\ddagger} < 30$ kJ mol^{-1}), in agreement with the steric nature of the rotational restrictions.

\{^{1}H–^{29}Si\}-HMBC experiments were used to locate silicon atom resonances for **12–14**, which are centered at 1.44 ppm (inner Si) and at 1.55 ppm (outer Si). IR spectra of complexes **10** and **13** show a band at ca. 560 cm^{-1} corresponding to ν(Ti–O) and three signals at ca. 1210, 1020 and 910 cm^{-1} due to the presence of the C_{Ph}–O bond.

Compounds **9–14** are soluble in chlorinated and aromatic solvents and insoluble in saturated hydrocarbons. The organometallic compounds are thermally stable but moisture sensitive. Spectroscopic and analytical data of all complexes are collected in Section 4 and are consistent with the proposed formulation.

Complexes **9** and **13** showed very low or negligible activity as catalysts in ethylene polymerization after activation with an excess of MAO. No time-dependent aggregation was observed for **13**, in contrast with the behavior described above with related dendrimers containing aryloxide units derived from eugenol or 4-allyl-2,6-dimethoxylphenol ligands.

3. Conclusions

In conclusion, in the cases of systems having [Ti(C$_5$H$_5$)Cl$_2$] as peripheral unit in *para* position to

the aliphatic substituent, the presence of *ortho*-OMe group in the aryloxy ligand afforded polyethylene of high molecular weights and low polydispersity indistinctly if monometallic or metallodendrimers precursors were used. However, the dendritic nature enforced higher crystallinity percentage of the polymer, although for freshly prepared toluene solutions moderate activities were found. Surprisingly, these titanium ended carbosilane dendrimers spontaneously form in toluene time dependent aggregates when eugenol or 4-allyl-2,6-dimethoxylphenol are used as ligand precursors, and after activation with MAO behaved as highly active catalysts. However, when the peripheral units are replaced by [Ti(C$_5$Me$_5$)Cl$_2$] or [M(C$_5$H$_5$)$_2$Cl] fragments or 2-allyl-6-methylphenol are incorporated to the periphery of a carbosilane dendrimer, no aggregation was observed upon aging. Therefore, the electronic and/or the steric effects induced by different organometallic units or phenolic ligands have a big influence in the synthesis and catalytic activity of their organometallic derivatives.

4. Experimental

4.1. Reagents and general techniques

4.2. Synthesis of [Ti(C$_5$H$_5$){OC$_6$H$_3$(CH$_3$)-(CH$_2$CH=CH$_2$)}Cl$_2$] (**9**)

A solution of 2-allyl-6-methylphenol (0.43 g, 2.87 mmol) in toluene (20 mL) was slowly added to a

solution of $[Ti(C_5H_5)Cl_3]$ (0.63 g, 2.87 mmol) in toluene (20 mL). The mixture was heated up to 80 °C for 6 h and subsequently stirred at room temperature overnight. The solvent was removed at reduced pressure and the product was washed with hexane to give **9** as a crystalline orange solid (0.89 g, 94%). ^{1}H NMR (CDCl$_3$): δ 6.90–7.10 (m, 3H, C$_6$H$_3$), 6.71 (s, 5H, C$_5$H$_5$), 5.98 (m, 1H, –CH$_2$C*H*=CH$_2$), 5.10 (m, 2H, –CH$_2$CH=C*H*$_2$), 3.40 (m, 2H, –C*H*$_2$CH=CH$_2$), 2.29 (s, 3H, –CH$_3$). ^{13}C {^{1}H} NMR (CDCl$_3$): δ 166.0 (C$_{ipso}$ bonded to –OTi), 136.9 (CH$_2$CH=CH$_2$), 128.9 (C$_{ipso}$ bonded to –CH$_2$CH=CH$_2$), 124.1 (C$_{ipso}$ bonded to –CH$_3$), 119.2, 120.5, 127.9 (C$_6$H$_3$), 120.9 (C$_5$H$_5$), 116.0 (–CH$_2$CH=CH$_2$), 34.0 (–CH$_2$CH=CH$_2$), 17.5 (–CH$_3$). Anal. Calc. for C$_{15}$H$_{16}$OCl$_2$Ti: C, 54.42; H, 4.87. Found: C, 54.53; H, 4.60.

4.3. Synthesis of [Ti(C$_5$H$_5$)$_2${OC$_6$H$_3$(CH$_3$)-(CH$_2$CH=CH$_2$)}Cl] (10)

A solution of 2-allyl-6-methylphenol (0.81 g, 5.46 mmol) in THF (20 mL) was added to a solution of [Ti(C$_5$H$_5$)$_2$Cl$_2$] (1.36 g, 5.46 mmol) in THF (20 mL). To this mixture was added a slight excess of NEt$_3$ (0.84 mL, 6.0 mmol). The reaction mixture was stirred overnight, the solvent removed in vacuo and the residue extracted with toluene (30 mL). This mixture was filtered through Celite to remove NEt$_3 \cdot$ HCl. The resulting orange solution was evaporated under reduced pressure to give **10** as a dark orange oil (1.62 g, 83%). ^{1}H NMR (CDCl$_3$, 300 MHz, 298 K): δ 6.93–7.00 (m, 3H, C$_6$H$_3$), 6.31 (s, 10H, C$_5$H$_5$), 5.99 (m, 1H, –CH$_2$C*H*=CH$_2$), 5.03 (m, 2H, –CH$_2$CH=C*H*$_2$), 3.28 (m, 2H, –C*H*$_2$CH=CH$_2$), 2.11 (s broad, 3H, –CH$_3$). ^{13}C {^{1}H} NMR (CDCl$_3$): δ 168.1 (C$_{ipso}$ bonded to –OTi), 137.7 (–CH$_2$CH=CH$_2$), 129.1 (C$_{ipso}$ bonded to –CH$_2$CH=CH$_2$), 125.16 (C$_{ipso}$ bonded to –CH$_3$), 120.0, 128.0, 128.9 (C$_6$H$_3$), 117.7 (C$_5$H$_5$), 116.6 (–CH$_2$CH=CH$_2$), 34.6 (–CH$_2$CH=CH$_2$), 18.7 (–CH$_3$). Anal. Calc. for C$_{20}$H$_{21}$OClTi: C, 66.59; H, 5.87. Found: C, 66.01; H, 5.78.

^{1}H NMR (CD$_2$Cl$_2$, 500 MHz, 223 K, two rotamers in a 2/1 ratio): δ 7.0–6.7 (m, 3H, C$_6$H$_3$, overlapping resonances of both rotamers), 6.33 (s, 10H, C$_5$H$_5$, both rotamers), 5.97 and 5.89 (m, 1H, –CH$_2$C*H*=CH$_2$, minor and major rotamer), 5.16–4.97 (m, 2H, –CH$_2$CH=C*H*$_2$, overlapping resonances of both rotamers), 3.37 and 3.07 (d, 2H, –C*H*$_2$CH=CH$_2$, major and minor rotamer), 2.16 and 2.05 (s, 3H, –CH$_3$, minor and major rotamer).

4.4. Synthesis of [Zr(C$_5$H$_5$)$_2${OC$_6$H$_3$(CH$_3$)-(CH$_2$-CH=CH$_2$)}Cl] (11)

A solution of 2-allyl-6-methylphenol (0.26 g, 1.73 mmol) in THF (20 mL) was added to a solution of [Zr(C$_5$H$_5$)$_2$Cl$_2$] (0.51 g, 1.73 mmol) in THF (20 mL).

To this mixture was added a slight excess of NEt$_3$ (0.25 mL, 1.91 mmol). The reaction mixture was stirred overnight, the solvent removed in vacuo and the residue extracted with toluene (30 mL). This mixture was filtered through Celite to remove NEt$_3 \cdot$ HCl. The resulting orange solution was evaporated under reduced pressure to give **11** as a yellow oil (0.64 g, 92%). ^{1}H NMR (CDCl$_3$): δ 6.90–7.03 (m, 3H, C$_6$H$_3$), 6.34 (s, 10H, C$_5$H$_5$), 6.00 (m, 1H, –CH$_2$C*H*=CH$_2$), 5.08 (m, 2H, –CH$_2$CH=C*H*$_2$), 3.26 (m, 2H, –C*H*$_2$CH=CH$_2$), 2.15 (s, 3H, –CH$_3$). ^{13}C {^{1}H} NMR (CDCl$_3$): δ 161.6 (C$_{ipso}$ bonded to –OZr), 137.4 (–CH$_2$CH=CH$_2$), 128.7 (C$_{ipso}$ bonded to –CH$_2$CH=CH$_2$), 125.2 (C$_{ipso}$ bonded to –CH$_3$), 119.6, 127.7, 128.7 (C$_6$H$_3$), 114.6 (C$_5$H$_5$), 113.7 (–CH$_2$CH=CH$_2$), 34.2 (–CH$_2$CH=CH$_2$), 18.2 (–CH$_3$). Anal. Calc. for C$_{20}$H$_{21}$OClZr: C, 59.45; H, 5.24. Found: C, 58.97; H, 5.18.

4.5. Synthesis of 1G-Si[(CH$_2$)$_3${C$_6$H$_3$(Me)}OH]$_4$ (12)

[Si(CH$_2$CH$_2$CH$_2$SiMe$_2$H)$_4$] (0.14 g, 0.31 mmol) and two drops of the poly(dimethylsiloxane) solution of the Karstedt catalyst (3–3.5% Pt) were slowly added to a solution of 2-allyl-6-methylphenol (0.185 g, 1.25 mmol) in THF (5 mL). The resulting mixture was heated up to 70 °C for 7 h and subsequently stirred at room temperature overnight. Then, the solvent was removed at reduced pressure to give **12** as a yellow-brown solid. ^{1}H NMR (CDCl$_3$): δ 6.75–6.95 (m, 3H, C$_6$H$_3$), 4.59 (s, 1H, –O*H*), 2.58 (m, 2H, SiCH$_2$CH$_2$C*H*$_2$Ph), 2.23 (s, 3H, –C*H*$_3$), 1.58 (m, 2H, SiCH$_2$C*H*$_2$CH$_2$Ph), 1.28 (m, 2H, SiCH$_2$C*H*$_2$CH$_2$Si), 0.56 (m, 6H, SiC*H*$_2$CH$_2$C*H*$_2$Si and SiC*H*$_2$CH$_2$CH$_2$Ph overlapping), −0.61 (s, 6H, Si–C*H*$_3$). ^{13}C {^{1}H} NMR (CDCl$_3$): δ 142.9 (C$_{ipso}$ bonded to –OH), 132.1 (C$_{ipso}$ bonded to –CH$_2$CH$_2$CH$_2$Si), 122.0 (C$_{ipso}$ bonded to –CH$_3$), 120.5 (C$_5$H$_5$), 128.9, 127.7, 124.3 (C$_6$H$_3$), 34.7 (SiCH$_2$CH$_2$CH$_2$Ph), 25.5 (SiCH$_2$CH$_2$CH$_2$Ph), 15.5 (SiCH$_2$CH$_2$CH$_2$Ph), 17.5 (–CH$_3$), 20.1, 18.4, 12.6 (SiCH$_2$CH$_2$CH$_2$Si), −3.20 (Si–CH$_3$). ^{29}Si {^{1}H} NMR (CDCl$_3$): δ 1.55 (G1–Si), 1.44 (G0–Si). Silicon resonances assigned by {^{1}H–^{29}Si}-HMBC experiments. Anal. Calc. for C$_{60}$H$_{100}$O$_4$Si$_5$: C, 70.25; H, 9.83. Found: C, 69.87; H, 9.45.

4.6. Synthesis of 1G-Si[(CH$_2$)$_3$[{C$_6$H$_3$(Me)}O]-Ti(C$_5$H$_5$)Cl$_2$]$_4$ (13)

A solution of **12** (0.052 g, 0.05 mmol) was slowly added to a solution of [Ti(C$_5$H$_5$)Cl$_3$] (0.044 g, 0.20 mmol) in toluene (20 mL). The resulting mixture was heated up to 80 °C for 6 h and subsequently stirred at room temperature overnight.The solvent was removed at reduced pressure and the product washed with hexane to give **13** as an orange oil (0.078 g, 89%). ^{1}H NMR (CDCl$_3$): δ 6.67 (s, 5H, C$_5$H$_5$), 2.56 (m, 2H,

SiCH$_2$CH$_2$CH_2Ph), 2.27 (s, 3H, –CH$_3$), 1.50 (m, 2H, SiCH$_2$CH_2CH$_2$Ph), 1.25 (m, 2H, SiCH$_2$CH_2CH$_2$Si), 0.54 (m, 6H, SiCH_2CH$_2$CH_2Si and SiCH_2CH$_2$CH$_2$Ph overlapping), −0.07 (s, 6H, –SiMe$_2$–). ^{13}C {^{1}H} NMR (CDCl$_3$): δ 166.5 (C$_{ipso}$ bonded to –OTi), 132.2 (C$_{ipso}$ bonded to –CH$_2$CH$_2$CH$_2$Si), 122.2 (C$_{ipso}$ bonded to –CH$_3$), 120.8 (C$_5$H$_5$), 124.1, 127.8, 128.5 (C$_6$H$_3$), 34.9 (SiCH$_2$CH$_2$CH_2Ph), 25.7 (SiCH$_2$CH_2CH$_2$Ph), 15.6 (SiCH_2CH$_2$CH$_2$Ph), 17.5 (–CH$_3$), 12.5, 18.6, 20.3 (SiCH$_2$CH$_2$CH$_2$Si), −3.23 (Si–CH$_3$). ^{29}Si {^{1}H} NMR (CDCl$_3$): δ 1.53 (G1–Si), 1.42 (G0–Si). Anal. Calc. for C$_{80}$H$_{116}$Cl$_8$O$_4$Si$_5$Ti$_4$: C, 54.67; H, 6.60. Found: C, 53.85; H, 6.38.

4.7. Synthesis of 1G-Si[(CH$_2$)$_3$[{C$_6$H$_3$(Me)}O]-Zr(C$_5$H$_5$)$_2$Cl]$_4$ (14)

A solution of **12** (0.056 g, 0.055 mmol) in THF (10 mL) was added to a solution of [Zr(C$_5$H$_5$)$_2$Cl$_2$] (0.064 g, 0.22 mmol) in THF (20 mL). A slight excess of NEt$_3$ (0.03 mL, 0.23 mmol) was added to this mixture. The reaction mixture was stirred overnight, the solvent removed in vacuo and the residue extracted with toluene (30 mL). This mixture was filtered through Celite to remove NEt$_3 \cdot$HCl. The resulting solution was evaporated under reduced pressure to give **14** as a yellow oil (0.093 g, 83%). ^{1}H NMR (CDCl$_3$): δ 6.31 (s, 10H, C$_5$H$_5$), 2.52 (m, 2H, SiCH$_2$CH$_2$CH_2Ph), 2.28 (s, 3H, –CH$_3$), 1.48 (m, 2H, SiCH$_2$CH_2CH$_2$Ph), 1.23 (m, 2H, SiCH$_2$CH_2CH$_2$Si), 0.50 (m, 6H, SiCH_2CH$_2$CH_2Si and SiCH_2CH$_2$CH$_2$Ph overlapping) −0.06 (s, 6H, –SiMe$_2$–). ^{13}C {^{1}H} NMR (CDCl$_3$): δ 162.0 (C$_{ipso}$ bonded to –OZr), 133.4 (C$_{ipso}$ bonded to –CH$_2$CH$_2$CH$_2$Si), 122.6 (C$_{ipso}$ bonded to –CH$_3$), 121.3 (C$_5$H$_5$), 123.8, 127.4, 128.6 (C$_6$H$_3$), 34.6 (SiCH$_2$CH$_2$CH_2Ph), 25.1 (SiCH$_2$CH_2CH$_2$Ph), 15.2 (SiCH_2CH$_2$CH$_2$Ph), 13.7, 18.2, 20.1 (SiCH$_2$CH$_2$CH$_2$Si), −3.17 (Si–CH$_3$). ^{29}Si{^{1}H} NMR (CDCl$_3$): δ 1.52 (G1–Si), 1.42 (G0–Si). Anal. Calc. for C$_{80}$H$_{116}$Cl$_8$O$_4$Si$_5$Zr$_4$: C, 49.77; H, 6.06. Found: C, 49.53; H, 5.82.

4.8. Ethylene polymerization

A 250 mL flask charged with toluene (50 mL) and equipped with a magnetic stirrer was four times evacuated and refilled with pre-dried ethylene gas. Keeping the flask pressurized with ethylene (1 bar) and stirred at room temperature, a toluene solution of methylaluminoxane (MAO, 0.83 mL, 1.5 M) was syringed through a septum. After 5 min, a toluene solution of the fresh or aged precatalyst (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 ethylene feeding, 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.

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