Titanocene and Zirconocene Complexes containing Dendrimer-Substituted Cyclopentadienyl Ligands − Synthesis and Ethylene Polymerization

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

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This paper describes the synthesis of a series of titanium and zirconium metallocenes bearing one or two first-generation silane dendritic wedges as bulky substituents at their cyclopentadienyl rings. Wedges $(R_2R'SiCH_2CH_2)_3SiCl$ [R = R′ = Et (**1**); R = Ph, R′ = Me (**2**)] were prepared by hydrosilylation of chlorotrivinylsilane with $R_2R'SiH$. They were reacted with $K(C_5H_5)$ and, subsequently, with KH to give $K[(R_2R'SiCH_2CH_2)_3Si(C_5H_4)]$ [R = R′ = Et (**3**); R = Ph, R′ = Me (**4**)]. The dendronized cyclopentadienides **3** and **4** were the starting materials for preparation of the mixed-ring titanocenes $[\{(R_2R'SiCH_2CH_2)_3SiC_5H_4\}(C_5R''_5)TiCl_2]$ [R = R′ = Et, R′′ = H (**5**), R′′ = Me (**6**); R = Ph, R′ = Me, R′′ = H (**7**), R′′ = Me (**8**)] or the symmetrically substituted metallocenes $[\{(Ph_2MeSiCH_2CH_2)_3SiC_5H_4\}_2MCl_2]$ [M = Ti (**9**), Zr (**10**)]. Cyclic voltammograms and catalytic behavior of all the new metallocenes in ethylene polymerization, using MAO as a cocatalyst, have been studied and compared to that of related non-dendritic complexes. Polyethylene polydispersities increase with the number of dendritic wedges in the catalyst, while activities decrease. Bimodal molecular weight distributions were clearly observed for the bis-dendritic titanocene **9**.

Introduction

The modification of cyclopentadienyl (Cp) ligands has played a crucial role in improving the usefulness of group 4 metallocenes as catalysts in olefin polymerization. It has proved to be especially relevant to the microstructure of polymers obtained from α-olefins.[1] Control of the stereochemistry requires some conformational constraint because it arises mainly from steric interactions between the incoming olefin monomer and the Cp ligand; bridged cyclopentadienyl ligands (*ansa*-metallocenes) have often been used for this purpose.[2] However, some degree of stereocontrol is in principle possible without a rigid ligand framework if rotation of the Cp ligands is hindered,[3] for example by means of sterically demanding substituents.[4]

We are currently studying the chemistry of titanium and zirconium metallocenes located at the focal point of one or two dendritic wedges. Our interest is focused on their use as precursors for olefin polymerization. In these complexes, the dendrimers[5] act as ligand modifiers that introduce steric hindrance around the cyclopentadienyl rings, and their behavior can be compared to that of other sterically encumbered metallocenes.

Cyclopentadienyl complexes have been employed for the peripheral functionalization of dendrimers and, in particular, group 4 derivatives have been already synthesized[6,7] and tested in olefin polymerization.[6a,7c] We have observed[7c] that, in such cases, dendrimers are more than mere supports of active sites and may significantly modify activities and molecular weights. Less attention has been paid to dendrimers, such as those reported here, that are metallated at their core or focal-point with cyclopentadienyl complexes.[8] However, the ability of dendritic shells to encapsulate functional core moieties and to create specific site-isolated nanoenvironments,[9] a concept taken from biological systems, has already been exploited in catalysis using a variety of metal complexes.[9,10]

In the present report, we describe the syntheses of titanium and zirconium metallocenes bearing one or two first generation carbosilane dendritic wedges, together with their behavior in ethylene polymerization using MAO as a cocatalyst.

Results and Discussion

The new dendritic titano- and zirconocenes were synthesized following the pathway depicted in Scheme 1. The reactions described below fulfil two conditions in order to warrant pure final products: high yields in every step and at least one step involving enough differences in solubility between the target compound and by-products. These conditions are required since the separation of by-products accumulated in these multistep preparations is complicated by

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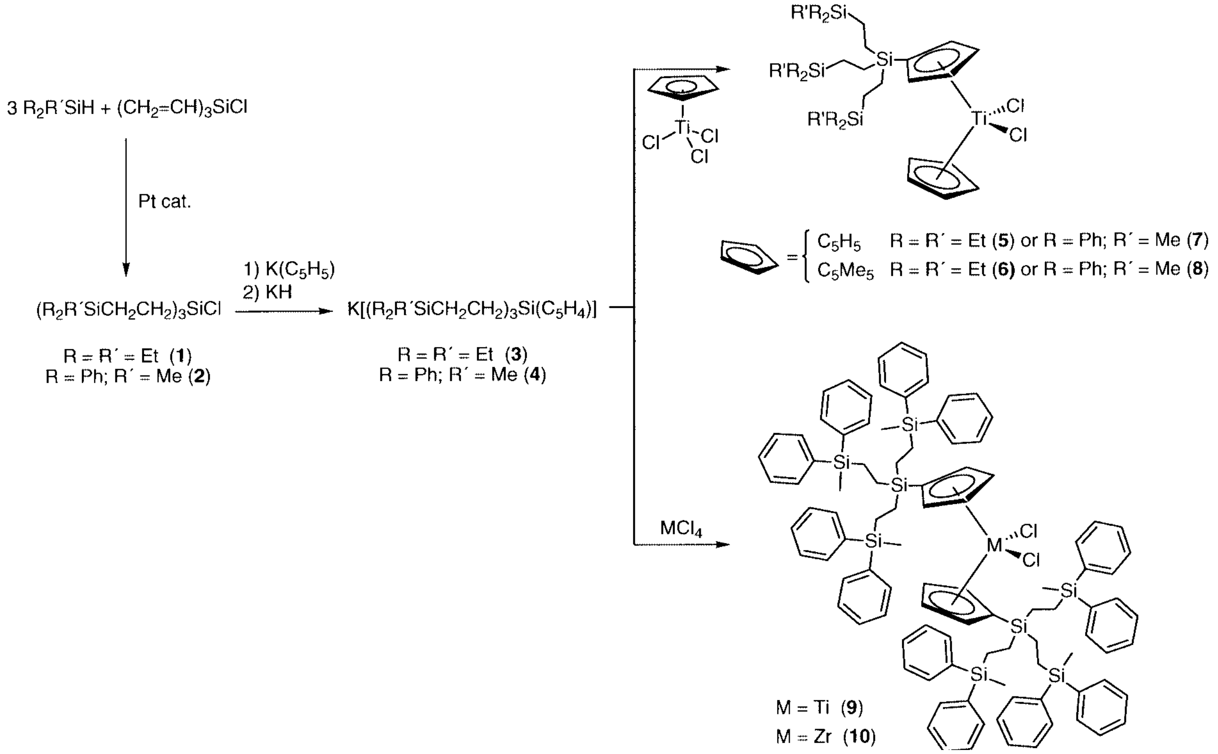
[a] Departamento de Química Inorgánica, Universidad de Alcalá,
Campus Universitario,
28871 Alcalá de Henares (Madrid), Spain
Fax: (internat.) +34-91/885-4683
E-mail: ernesto.dejesus@uah.es



Scheme 1

the high solubility and oily nature of these dendritic compounds.

The chlorosilanes $(R_2R'SiCH_2CH_2)_3SiCl$ [R = R′ = Et (**1**); R = Ph, R′ = Me (**2**)] were obtained from a solvent-free reaction in which chlorotrivinylsilane was hydrosilylated with an excess of the corresponding silane $R_2R'SiH$, using hydrogen hexachloroplatinate(IV) as a catalyst (Scheme 1). Only the formation of β-silylated compounds was observed. Silane **1** was obtained as a colorless oil after removal of volatiles in vacuo, whereas compound **2** was recrystallized from pentane at −30 °C as an off-white solid. The dendronized cyclopentadienides **3** and **4** were synthesized as their potassium salts by reaction of **1** or **2** with $K(C_5H_5)$ in THF and subsequent treatment of the cyclopentadienes with KH. Compound **3** separated from pentane at −30 °C as an oily pale yellow product whereas **4** was precipitated from hexane at room temperature as a white solid.

The mixed-ring titanocenes **5−8** were prepared by reaction of **3** or **4** and one equiv. of $[(C_5H_5)TiCl_3]$ or $[(C_5Me_5)TiCl_3]$. The symmetrically substituted metallocenes **9** (Ti) and **10** (Zr) were obtained from the reaction of **4** and $TiCl_4$ or $[ZrCl_4]\cdot 2THF$ in a 2:1 ratio. The reactions were carried out in THF and products were initially isolated as oils. Complexes **5−8** crystallized after workup whereas all attempts to crystallize **9** and **10** failed. Compounds **5−10** are rather stable to air and the analytical and spectroscopic data are in agreement with their proposed structure (see Exp. Sect.).

Among electrochemical methods, cyclic voltammetry has been widely used to study the influence of substituents on the electronic density at the metal center of complexes.[11,12] Cyclic voltammograms of metallocene derivatives **5−10** were recorded in THF solution. Each complex shows a quasi-reversible electrode process due to a one-electron reduction of the titano- and zirconocene derivatives at the potentials summarized in Table 1 vs. the ferricinium/ferrocene couple. The potential of the reference complex $[(C_5H_5)_2TiCl_2]$ is within the narrow range in which potentials of C_5H_5 complexes **5**, **7**, and **9** are observed (1.34−1.40 V). The same is true for $[(C_5H_5)(C_5Me_5)TiCl_2]$ and the range of C_5Me_5 compounds **6** and **8** (1.64−1.66 V), and for $[(C_5H_5)_2ZrCl_2]$ and **10**. These data can be interpreted in the sense that dendritic silane substituents have a minor influence on the electron-donating properties of the cyclopentadienyl ring and therefore on the electronic density of the metal center. Similar results have been obtained for the $SiMe_3$-substituted complexes $[(C_5H_4SiMe_3)_2TiCl_2]$ and $[(C_5H_3(SiMe_3)_2]_2TiCl_2]$, whose potentials are not shifted from those observed for $[(C_5H_5)_2TiCl_2]$.[13] It has been pointed out that steric hindrance between cyclopentadienyl substituents, when they are placed at the hinge positions of titanocene dichlorides, decreases the dihedral angle (φ) formed by the ring planes. This change results in LUMO orbitals of lower energy, and therefore in the observation of a decreased absolute value of the reduction potential.[12] The absence of a significant shift in the potential values of the dendritic titanocenes **5−9** (and for **10**) compared to their non-dendritic counterparts $\{[(C_5H_5)_2MCl_2]$ or $[(C_5H_5)(C_5Me_5)TiCl_2]\}$ is compatible with a dynamic model in which the rotating Cp ligands are preferentially accommodated in conformations in which the intramolecular steric strain is relieved; obviously these conformations are those with the dendritic wedges occupying the lateral positions of the molecule. However, the rotation of the Cp rings is far from being fully stopped in solution, as demonstrated by the fact that only two types of cyclopentadienyl protons are observed in the ^{1}H NMR spectrum of **9** even at −90 °C.

Upon activation with an excess of methylaluminoxane (MAO), complexes **5−10** catalyze the polymerization of ethylene. These results are summarized in Table 2 and details of the polymerization procedure are given in the Exp. Sect. As a reference, polymerization with $[(C_5H_5)_2MCl_2]$ (M = Ti, Zr) and $[(C_5H_5)(C_5Me_5)TiCl_2]$ was also carried out under the same conditions. Every dendritic catalyst displayed a lower activity than its reference complex.

For the titanium series, we can establish the following order of activity according to the type of cyclopentadienyl ligands: $(C_5H_5)_2 > (C_5H_4R)(C_5H_5) >> (C_5H_4R)_2 \approx (C_5H_5)(C_5Me_5) >> (C_5H_4R)(C_5Me_5)$, where each $>>$ corresponds to an activity reduction of one order of magnitude. What it is remarkable in these data is that replacement of a $C_5H_5^-$ ligand by a dendritic cyclopentadienide in **5** and **7** only causes a moderate decrease in activity (from 4320 in $[(C_5H_5)_2TiCl_2]$ to 2064 and 1728 kg/mol·h, respectively). Steric hindrance might cause the later decrease and an argument for this hypothesis is based on the CV results (see above) that show slight electronic density differences between their metal centers. The lower activity of bis-dendritic Cp system **9** might be interpretable in steric terms assuming that interaction between both dendritic wedges restricts the conformations in which they are kept far away from the metal center. In the case of zirconium, much less appreciable effects might be expected because of the bigger size of the metal center. In fact, the activity of the bis-dendritic Zr complex **10** is similar to that of $[(C_5H_5)_2ZrCl_2]$ with a decrease (from 8016 to 5472 kg/mol·h) far away from the one order of magnitude decrease observed for the analogous pair of titanium complexes. This result seems to contradict the data reported by Alt and Köppl in a recent review on the polymerization activity of ethylene with metallocenes. For complex $[(C_5H_4SiMe_2Ph)_2ZrCl_2]$ the activity found was less than 10% that of $[(C_5H_5)_2ZrCl_2]$.[1f] However, in this case an interaction of the aromatic end group of the substituent with the Lewis-acid center of the catalyst could be responsible for such an effect because of the additional stabilization of the active site. In the above discussion, it has been assumed that the concentration of active centers is the same for all the compared catalysts (and ideally equal to the precursor concentration). This is a general obstacle in the discussion of results in polymerization with metallocene/MAO catalysts.[14,15] In any case, the practical question is that dendritic wedges can be used as cyclopentadienyl substituents without hindering the closest metal environment to such an extent that the polymerization process is prevented.

Table 1. Cyclic voltammetric data for metallocene derivatives **5−10** in THF/Bu_4NPF_6[a]

Complex	Half-wave potentials[b]
$[(C_5H_5)_2TiCl_2]$	−1.39
$[\{(Et_3SiCH_2CH_2)_3SiC_5H_4\}(C_5H_5)TiCl_2]$ (**5**)	−1.34
$[\{(Ph_2MeSiCH_2CH_2)_3SiC_5H_4\}(C_5H_5)TiCl_2]$ (**7**)	−1.39
$[\{(Ph_2MeSiCH_2CH_2)_3SiC_5H_4\}_2TiCl_2]$ (**9**)	−1.40
$[(C_5H_5)(C_5Me_5)TiCl_2]$	−1.65
$[\{(Et_3SiCH_2CH_2)_3SiC_5H_4\}(C_5Me_5)TiCl_2]$ (**6**)	−1.66
$[\{(Ph_2MeSiCH_2CH_2)_3SiC_5H_4\}(C_5Me_5)TiCl_2]$ (**8**)	−1.64
$[(C_5H_5)_2ZrCl_2]$	−2.26
$[\{(Ph_2MeSiCH_2CH_2)_3SiC_5H_4\}_2ZrCl_2]$ (**10**)	−2.20

[a] Concentration 2×10^{-4} M; scan rate 0.1 V s^{-1}. [b] $(E_p^{red} + E_p^{ox})/2$ in volts vs. $(C_5H_5)_2Fe^+/(C_5H_5)_2Fe$.

The polyethylene samples generated with complexes **5**, **7**, **9**, and **10** were analyzed by gel-permeation chromatography (GPC). The molecular weights of the polymers obtained with dendritic systems are near to 400×10^3, a normal region for metallocenes, although the titanium dendrimers **5−9** gave polymers somewhat larger than those produced with $[(C_5H_5)_2TiCl_2]$/MAO. More remarkable are the molecular weight distributions of the samples obtained from the titanium complexes: the polydispersity values increase with the number of dendritic substituents on the catalyst precursor (from 1.86 for non-dendritic to 5.81 for bis-dend-

Table 2. Ethylene Polymerization results with complexes **5−10**[a]

Precatalyst	Yield (mg)	Activity (kg_{PE}/mol_M h)	M_w ($\times 10^{-3}$)	M_w/M_n
$[(C_5H_5)_2ZrCl_2]$	1670	8016	380	2.18
$[\{(Ph_2MeSiCH_2CH_2)_3SiC_5H_4\}_2ZrCl_2]$ (**10**)	1140	5472	410	2.80
$[(C_5H_5)_2TiCl_2]$	900	4320	244	1.86
$[\{(Et_3SiCH_2CH_2)_3SiC_5H_4\}(C_5H_5)TiCl_2]$ (**5**)	430	2064	434	2.51
$[\{(Ph_2MeSiCH_2CH_2)_3SiC_5H_4\}(C_5H_5)TiCl_2]$ (**7**)	360	1728	398	3.33
$[\{(Ph_2MeSiCH_2CH_2)_3SiC_5H_4\}_2TiCl_2]$ (**9**)	120	576	376	5.81
$[(C_5H_5)(C_5Me_5)TiCl_2]$	118	566	−	−
$[\{(Et_3SiCH_2CH_2)_3SiC_5H_4\}(C_5Me_5)TiCl_2]$ (**6**)	11	53	−	−
$[\{(Ph_2MeSiCH_2CH_2)_3SiC_5H_4\}(C_5Me_5)TiCl_2]$ (**8**)	10	48	−	−

[a] Conditions: MAO cocatalyst, Al/M = 1000, 1.25 μmol of catalyst dissolved in 50 mL of toluene, 10 minutes, 293 K, 1 bar of constant monomer pressure.

ritic). As shown in Figure 1, these values reflect the appearance of bimodal molecular weight distributions, especially for polymer yielded by the bis-dendritic system **9**. In contrast, the zirconium complex **10** produces polyethylene of low polydispersity. Bimodal distributions may result for several reasons, such as a multistate catalyst with slow interconversion of states,[16] or the presence of traces of impurities (for example, unsubstituted metal complexes).

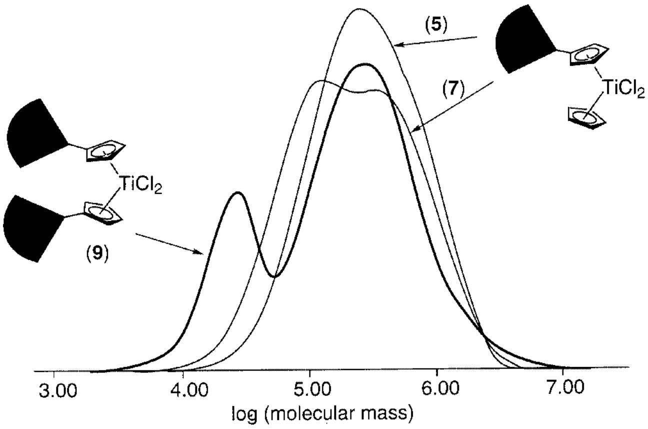


Figure 1. Molecular weight distributions for polyethylene samples obtained from **5**, **7**, and **9**/MAO catalytic systems

Conclusion

In this paper, we have modified the metal environment in titanium and zirconium metallocenes by the incorporation of first-generation carbosilane dendritic wedges into Cp ligands. An effect of such a modification in ethylene polymerization is the observed correlation between polyethylene polydispersities and the number of dendritic wedges in the titanium catalysts. Bimodal molecular weight distributions have been observed for several of the reported complexes, especially for the bis-dendritic titanocene **9**. On the other hand, the activity decreases caused by the bulky substituents are moderate, especially for zirconium complex **10**, suggesting that the metal centers remain quite accessible. In contrast to other bulky substituents, the long range of their space-filling properties is a distinctive feature of dendritic wedges (Figure 2) that may be truly useful for polymer stereocontrol. Work on the effects of growing dendritic generations on the polymerization of α-olefins is under way in our laboratory.

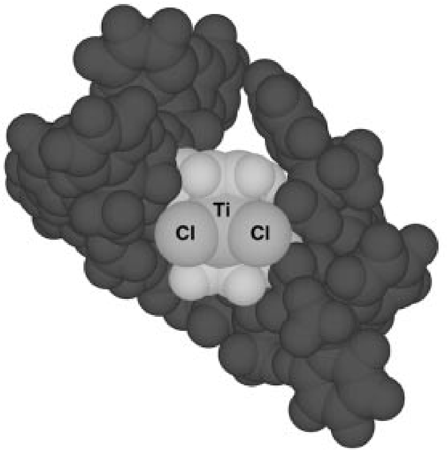


Figure 2. Space-filling model for complex [{(Ph$_2$MeSiCH$_2$CH$_2$)$_3$SiC$_5$H$_4$}$_2$TiCl$_2$] (**9**) in a bis-lateral arrangement; the wedges are shown in dark colors

Experimental Section

Reagents and General Techniques: All operations were performed under an argon atmosphere using Schlenk or dry box techniques. Solvents were dried and distilled under argon as described elsewhere.[17] Unless otherwise stated, reagents were obtained from commercial sources and used as received. MAO was obtained in toluene solution 1.5 M from Witco. K(C$_5$H$_5$) was prepared from freshly distilled cyclopentadiene and KH in THF. [M(C$_5$H$_5$)$_2$Cl$_2$] (M = Ti, Zr),[18] [Ti(C$_5$H$_5$)(C$_5$Me$_5$)Cl$_2$],[19] [Ti(C$_5$H$_5$)Cl$_3$],[20] and [Ti(C$_5$Me$_5$)Cl$_3$][21] were prepared according to reported procedures. ^{1}H, ^{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 ^{1}H resonances), or by the substitution method from the ^{29}Si resonance of SiMe$_4$. C, H and N analyses were performed in a Heraeus CHN-O-Rapid microanalyzer by the Microanalytical Services of the Universidad de Alcalá. Cyclic voltammograms were obtained with an AMEL 553 Potentiostat, an AMEL 567 Wave Generator, and a three-platinum-electrode cell. [Bu$_4$N][PF$_6$] (0.2 M in THF) was used as supporting electrolyte and potentials were zeroed to the ferricinium/ferrocene couple used as internal reference.

Synthesis of (Et$_3$SiCH$_2$CH$_2$)$_3$SiCl (1): A mixture of trivinylchlorosilane (2.0 mL, 13 mmol), an excess of Et$_3$SiH (8.2 mL, 52 mmol), and a hydrosilylation Pt catalyst (4 drops of a 2×10^{-3} M solution of H$_2$PtCl$_6$ in 2-propanol) was stirred for 24 h at 70 °C. After completion of the reaction (^{1}H NMR monitoring) the volatiles were removed under vacuum to give **1** (5.7 g, 89%) as a colorless oil. The sample was not analytically pure but was suitable for further preparations. ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C): δ = 0.91 (t, 27 H, CH_3CH$_2$), 0.70 and 0.46 [A and B parts of an A$_2$B$_2$ spin system, 12 H, Si(CH_2)$_2$Si], 0.50 (quart, 18 H, CH$_3$CH_2) ppm. ^{13}C{^{1}H} NMR (300 MHz, CDCl$_3$, 25 °C): δ = 7.4 (CH$_3$CH$_2$), 7.0 [Si(CH$_2$)$_2$Si], 2.8 (CH$_3$$CH_2$), 2.5 [Si($CH_2$)$_2$Si] ppm. ^{29}Si{^{1}H} NMR (500 MHz, CDCl$_3$, 25 °C): δ = 35.2 (*Si*Cl), 8.5 (Et$_3$*Si*) ppm.

Synthesis of (Ph$_2$MeSiCH$_2$CH$_2$)$_3$SiCl (2): This compound was prepared by the procedure described above for **1** from trivinylchlorosilane (1.9 mL, 12.5 mmol) and Ph$_2$MeSiH (10 mL, 50 mmol). After completion of the reaction, pentane (50 mL) was added to the solution and then cooled at −30 °C overnight. Sometimes an oil, instead of a solid, separated from the solution. In that case, the mixture was shaken vigorously, cooled again to −30 °C for several hours, and the process repeated until precipitation of a white solid. The mixture was filtered and the solid dried in vacuo and characterized as **2**. Further crops of **2** were collected from the pentane solution by repeated (2−3 times) concentration and crystallization, giving an overall yield of 7.0 g (76%). C$_{45}$H$_{51}$ClSi$_4$ (739.7): calcd. C 73.07, H 6.95; found C 72.68, H 7.17. ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C): δ = 7.45 (m, 12 H, C$_6$$H_5$), 7.31 (m, 18 H, C$_6$$H_5$), 0.91 and 0.73 [A and B parts of an A$_2$B$_2$ spin system, 12 H, Si(CH_2)$_2$Si], 0.51 (s, 9 H, CH$_3$) ppm. ^{13}C{^{1}H} NMR (300 MHz, CDCl$_3$, 25 °C): δ = 136.5 (C$_{ipso}$, C_6H$_5$), 134.4 (C$_{meta}$, C_6H$_5$), 129.2 (C$_{para}$, C_6H$_5$), 127.8 (C$_{ortho}$, C_6H$_5$), 7.2 and 5.7 [Si(CH$_2$)$_2$Si], −5.0

($C\mathrm{H_3}$) ppm. $^{29}\mathrm{Si}\{^1\mathrm{H}\}$ NMR (500 MHz, $\mathrm{CDCl_3}$, 25 °C): δ = 35.8 ($Si\mathrm{Cl}$), −5.5 ($\mathrm{Ph_2Me}Si$) ppm.

Synthesis of $\mathbf{K[(Et_3SiCH_2CH_2)_3Si(C_5H_4)]}$ (3): This compound was prepared by the same procedure described below for **4** from potassium cyclopentadienide (0.58 g, 6.0 mmol), **1** (3.0 g, 6.0 mmol) and KH (0.24 g, 6.0 mmol). However, its high solubility in hexane prevented its crystallization. Compound **3** was obtained as a pale yellow oil by evaporation of the final solution in vacuo to dryness (2.8 g, 85% yield). $^1\mathrm{H}$ NMR (300 MHz, $\mathrm{C_6D_6}$, 25 °C): δ = 6.07 and 6.04 (AA′ and BB′ parts of an AA′BB′ spin system, 4 H, $\mathrm{C_5}H_4$), 1.20 (t, 27 H, $\mathrm{C}H_3\mathrm{CH_2}$), 1.06 and 0.68 [A and B parts of an $\mathrm{A_2B_2}$ spin system, 12 H, $\mathrm{Si(C}H_2\mathrm{)_2Si}$], 0.79 (quart, 18 H, $\mathrm{CH_3C}H_2$) ppm. $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (300 MHz, $\mathrm{C_6D_6}$, 25 °C): δ = 114.2 and 109.3 ($C_5\mathrm{H_4}$), 8.2 ($C\mathrm{H_3CH_2}$), 7.8 and 5.9 [$\mathrm{Si(}C\mathrm{H_2)_2Si}$], 3.5 ($\mathrm{CH_3}C\mathrm{H_2}$) ppm; $\mathrm{C_{ipso}}$ of $C_5\mathrm{H_4}$ not found.

Synthesis of $\mathbf{K[(Ph_2MeSiCH_2CH_2)_3Si(C_5H_4)]}$ (4): Potassium cyclopentadienide (0.42 g, 4.0 mmol) was added to a solution of **2** (3.0 g, 4.0 mmol) in THF (50 mL). The mixture was stirred for 24 h at room temperature. Then the mixture was treated with solid KH (0.16 g, 4.0 mmol) and stirred until evolution of $\mathrm{H_2}$ ceased. After addition of hexane (10 mL), the mixture was filtered off and the solution was concentrated (up to ca. 5 mL). Hexane (100 mL) was added again to the metastable solution, and the stirring continued until precipitation of **4** as a white solid. The precipitate was filtered, washed with hexane and dried in vacuo (2.3 g, 72%). $^1\mathrm{H}$ NMR (300 MHz, $\mathrm{C_6D_6}$, 25 °C): δ = 7.67 (m, 12 H, $\mathrm{C_6}H_5$), 7.22 (m, 18 H, $\mathrm{C_6}H_5$), 5.85 and 5.71 (AA′ and BB′ parts of an AA′BB′ spin system, 4 H, $\mathrm{C_5}H_4$), 1.15 and 0.85 [A and B parts of an $\mathrm{A_2B_2}$ spin system, 12 H, $\mathrm{Si(C}H_2\mathrm{)_2Si}$], 0.71 (s, 9 H, $\mathrm{C}H_3$) ppm. $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (300 MHz, $\mathrm{C_6D_6}$, 25 °C): δ = 137.8 ($\mathrm{C_{ipso}}$, $C_6\mathrm{H_5}$), 135.1 ($\mathrm{C_{meta}}$, $C_6\mathrm{H_5}$), 129.5 ($\mathrm{C_{para}}$, $C_6\mathrm{H_5}$), 128.3 ($\mathrm{C_{ortho}}$, $C_6\mathrm{H_5}$), 114.2 ($C_5\mathrm{H_4}$), 109.1 ($C_5\mathrm{H_4}$), 7.7 and 5.9 [$\mathrm{Si(}C\mathrm{H_2)_2Si}$], −4.51 ($C\mathrm{H_3}$) ppm; $\mathrm{C_{ipso}}$ of $C_5\mathrm{H_4}$ not found.

Synthesis of $\mathbf{[\{(Et_3SiCH_2CH_2)_3SiC_5H_4\}(C_5H_5)TiCl_2]}$ (5): $[\mathrm{(C_5H_5)TiCl_3}]$ (0.50 g, 2.3 mmol) was added to a solution of the substituted potassium cyclopentadienide **3** (1.30 g, 2.3 mmol) in THF (20 mL). The mixture was stirred at room temperature for 4 h. After filtration, the THF solution was evaporated in vacuo to dryness. The crude red oil was dissolved in the minimum amount of pentane and **5** was crystallized as a red solid (0.97 g, 61%) at −30 °C. $\mathrm{C_{34}H_{66}Cl_2Si_4Ti}$ (706.0): calcd. C 57.84, H 9.42; found C 57.54, H 9.48. $^1\mathrm{H}$ NMR (300 MHz, $\mathrm{CDCl_3}$, 25 °C): δ = 6.83 and 6.60 (AA′ and BB′ parts of an AA′BB′ spin system, 4 H, $\mathrm{C_5}H_4$), 6.51 (s, 5 H, $\mathrm{C_5}H_5$), 0.90 (t, 27 H, $\mathrm{C}H_3\mathrm{CH_2}$), 0.70 and 0.42 [A and B parts of an $\mathrm{A_2B_2}$ spin system, 12 H, $\mathrm{Si(C}H_2\mathrm{)_2Si}$], 0.50 (quart, 18 H, $\mathrm{CH_3C}H_2$) ppm. $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (300 MHz, $\mathrm{CDCl_3}$, 25 °C): δ = 132.3 ($\mathrm{C_{ipso}}$, $\mathrm{C_5H_4}$), 128.6 ($\mathrm{C_5H_4}$), 121.6 ($\mathrm{C_5H_4}$), 120.0 ($\mathrm{C_5H_5}$), 7.5 ($C\mathrm{H_3CH_2}$), 4.6 and 3.6 [$\mathrm{Si(}C\mathrm{H_2)_2Si}$], 2.8 ($\mathrm{CH_3}C\mathrm{H_2}$) ppm. $^{29}\mathrm{Si}\{^1\mathrm{H}\}$ NMR (500 MHz, $\mathrm{CDCl_3}$, 25 °C): δ = 8.3 ($\mathrm{Et_3}Si$), 0.0 ($Si\mathrm{C_5H_4}$) ppm.

Synthesis of $\mathbf{[\{(Et_3SiCH_2CH_2)_3SiC_5H_4\}(C_5Me_5)TiCl_2]}$ (6): This complex was prepared by the same procedure described for **5**, starting from $[\mathrm{(C_5Me_5)TiCl_3}]$ (0.49 g, 1.7 mmol) and **3** (0.95 g, 1.7 mmol) in THF (20 mL). Due to its high solubility in pentane, compound **6** was obtained as a dark red oil (1.0 g, 78%) by removal of the solvent in vacuo. Crystals grew inside the oily samples when stored at room temperature for several days. Unfortunately, they were not suitable for X-ray diffraction studies. $\mathrm{C_{39}H_{76}Cl_2Si_4Ti}$ (776.2): calcd. C 60.35, H 9.87; found C 60.60, H 10.09. $^1\mathrm{H}$ NMR (300 MHz, $\mathrm{CDCl_3}$, 25 °C): δ = 6.40 and 6.07 (AA′ and BB′ parts of an AA′BB′ spin system, 4 H, $\mathrm{C_5}H_4$), 2.02 (s, 15 H, $\mathrm{C_5Me_5}$), 0.88 (t, 27 H, $\mathrm{C}H_3\mathrm{CH_2}$), 0.76 and 0.43 (A and B parts of an $\mathrm{A_2B_2}$ spin system, 12 H, $\mathrm{Si(C}H_2\mathrm{)_2Si}$), 0.47 (quart, 18 H, $\mathrm{CH_3C}H_2$) ppm. $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (300 MHz, $\mathrm{CDCl_3}$, 25 °C): δ = 136.0 ($\mathrm{C_{ipso}}$, $C_5\mathrm{H_4}$), 129.4 ($C_5\mathrm{Me_5}$), 128.7 and 117.3 ($C_5\mathrm{H_4}$), 13.5 ($\mathrm{C_5}Me_5$), 7.5 ($C\mathrm{H_3CH_2}$), 4.3 and 3.5 [$\mathrm{Si(}C\mathrm{H_2)_2Si}$], 2.8 ($\mathrm{CH_3}C\mathrm{H_2}$) ppm. $^{29}\mathrm{Si}\{^1\mathrm{H}\}$ NMR (500 MHz, $\mathrm{CDCl_3}$, 25 °C): δ = 8.3 ($\mathrm{Et_3}Si$), −0.6 ($Si\mathrm{C_5H_4}$) ppm.

Synthesis of $\mathbf{[\{(Ph_2MeSiCH_2CH_2)_3SiC_5H_4\}(C_5H_5)TiCl_2]}$ (7): This complex was prepared by the same procedure described for **5**, from $[\mathrm{(C_5H_5)TiCl_3}]$ (0.13 g, 0.62 mmol) and **4** (0.50 g, 0.62 mmol) in THF (20 mL). Due to its high solubility in pentane, compound **7** was obtained by removal of the solvent in vacuo as a dark red oil, which solidified after several weeks at room temperature (0.48 g, 81%). $\mathrm{C_{55}H_{60}Cl_2Si_4Ti}$ (952.2): calcd. C 69.38, H 6.35; found C 69.22, H 6.63. $^1\mathrm{H}$ NMR (300 MHz, $\mathrm{CDCl_3}$, 25 °C): δ = 7.53 (m, 12 H, $\mathrm{C_6}H_5$), 7.40 (m, 18 H, $\mathrm{C_6}H_5$), 6.63 and 6.51 (AA′ and BB′ parts of an AA′BB′ spin system, 4 H, $\mathrm{C_5}H_4$), 6.29 (s, 5 H, $\mathrm{C_5}H_5$), 0.91 and 0.81 [A and B parts of an $\mathrm{A_2B_2}$ spin system, 12 H, $\mathrm{Si(C}H_2\mathrm{)_2Si}$], 0.53 (s, 9 H, $\mathrm{CH_3}$) ppm. $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (300 MHz, $\mathrm{CDCl_3}$, 25 °C): δ = 136.8 ($\mathrm{C_{ipso}}$, $C_6\mathrm{H_5}$), 134.5 ($\mathrm{C_{meta}}$, $C_6\mathrm{H_5}$), 130.5 ($\mathrm{C_{ipso}}$, $C_5\mathrm{H_4}$), 129.1 ($\mathrm{C_{para}}$, $C_6\mathrm{H_5}$), 128.5 ($C_5\mathrm{H_4}$), 127.8 ($\mathrm{C_{ortho}}$, $C_6\mathrm{H_5}$), 121.7 ($C_5\mathrm{H_4}$), 119.9 ($C_5\mathrm{H_5}$), 6.5 and 4.5 [$\mathrm{Si(}C\mathrm{H_2)_2Si}$], −5.1 ($\mathrm{CH_3}$) ppm. $^{29}\mathrm{Si}\{^1\mathrm{H}\}$ NMR (500 MHz, $\mathrm{CDCl_3}$, 25 °C): δ = 0.7 ($Si\mathrm{C_5H_4}$), −5.7 ($\mathrm{Ph_2Me}Si$) ppm.

Synthesis of $\mathbf{[\{(Ph_2MeSiCH_2CH_2)_3SiC_5H_4\}(C_5Me_5)TiCl_2]}$ (8): This complex was prepared by the same procedure described for **5**, from $[\mathrm{(C_5Me_5)TiCl_3}]$ (0.18 g, 0.62 mmol) and **4** (0.50 g, 0.62 mmol) in THF (20 mL). Due to its high solubility in pentane, compound **8** was obtained, after removal of the solvent in vacuo, as a dark red oil, which solidified after several weeks at room temperature (0.54 g, 86%). $\mathrm{C_{60}H_{70}Cl_2Si_4Ti}$ (1022.4): calcd. C 70.49, H 6.90; found C 70.31, H 6.99. $^1\mathrm{H}$ NMR (300 MHz, $\mathrm{CDCl_3}$, 25 °C): δ = 7.40 (m, 12 H, $\mathrm{C_6}H_5$), 7.25 (m, 18 H, $\mathrm{C_6}H_5$), 6.26 and 6.00 (AA′ and BB′ parts of an AA′BB′ spin system, 4 H, $\mathrm{C_5}H_4$), 1.95 (s, 15 H, $\mathrm{C_5}Me_5$), 0.88 and 0.81 [A and B parts of an $\mathrm{A_2B_2}$ spin system, 12 H, $\mathrm{Si(C}H_2\mathrm{)_2Si}$], 0.48 (s, 9 H, $\mathrm{CH_3}$) ppm. $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (300 MHz, $\mathrm{CDCl_3}$, 25 °C): δ = 137.4 ($\mathrm{C_{ipso}}$, $\mathrm{C_6H_5}$), 134.6 ($\mathrm{C_{meta}}$, $C_6\mathrm{H_5}$), 129.54 ($C_5\mathrm{Me_5}$), 129.48 ($\mathrm{C_{ipso}}$, $C_5\mathrm{H_4}$), 129.0 ($\mathrm{C_{para}}$, $C_6\mathrm{H_5}$), 128.8 ($C_5\mathrm{H_4}$), 127.7 ($\mathrm{C_{ortho}}$, $C_6\mathrm{H_5}$), 117.2 ($C_5\mathrm{H_4}$), 13.5 ($\mathrm{C_5}Me_5$), 6.4 and 4.5 [$\mathrm{Si(}C\mathrm{H_2)_2Si}$], −5.01 ($\mathrm{CH_3}$) ppm. $^{29}\mathrm{Si}\{^1\mathrm{H}\}$ NMR (500 MHz, $\mathrm{CDCl_3}$, 25 °C): δ = 0.2 ($Si\mathrm{C_5H_4}$), −5.8 ($\mathrm{Ph_2Me}Si$) ppm.

Synthesis of $\mathbf{[\{(Ph_2MeSiCH_2CH_2)_3SiC_5H_4\}_2TiCl_2]}$ (9): $[\mathrm{TiCl_4}]$ (68 mL, 0.62 mmol) was added via syringe to a solution of **4** (1.00 g, 1.24 mmol) in toluene (25 mL). The solution was stirred overnight at room temperature. After filtration of the KCl precipitate, the solution was evaporated in vacuo to dryness yielding **9** (0.94 g, 92%) as a dark red oil. $\mathrm{C_{100}H_{110}Cl_2Si_8Ti}$ (1655.5): calcd. C 72.55, H 6.70; found C 72.61, H 6.79. $^1\mathrm{H}$ NMR (300 MHz, $\mathrm{CDCl_3}$, 25 °C): δ = 7.40 (m, 12 H, $C_6\mathrm{H_5}$), 7.25 (m, 18 H, $C_6\mathrm{H_5}$), 6.39 and 6.17 (AA′ and BB′ parts of an AA′BB′ spin system, 4 H, $\mathrm{C_5}H_4$), 0.85 and 0.75 [A and B parts of an $\mathrm{A_2B_2}$ spin system, 12 H, $\mathrm{Si(C}H_2\mathrm{)_2Si}$], 0.49 (s, 9 H, $\mathrm{CH_3}$) ppm. $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (300 MHz, $\mathrm{CDCl_3}$, 25 °C): δ = 136.9 ($\mathrm{C_{ipso}}$, $C_6\mathrm{H_5}$), 134.4 ($\mathrm{C_{meta}}$, $C_6\mathrm{H_5}$), 129.1 ($\mathrm{C_{para}}$, $C_6\mathrm{H_5}$), 131.5 ($\mathrm{C_{ipso}}$, $C_5\mathrm{H_4}$), 128.5 ($C_5\mathrm{H_4}$), 127.8 ($\mathrm{C_{ortho}}$, $C_6\mathrm{H_5}$), 120.2 ($C_5\mathrm{H_4}$), 6.6 and 4.7 [$\mathrm{Si(}C\mathrm{H_2)_2Si}$], −5.0 ($C\mathrm{H_3}$) ppm. $^{29}\mathrm{Si}\{^1\mathrm{H}\}$ NMR (500 MHz, $\mathrm{CDCl_3}$, 25 °C): δ = 0.6 ($Si\mathrm{C_5H_4}$), −5.7 ($\mathrm{Ph_2Me}Si$) ppm.

Synthesis of $\mathbf{[\{(Ph_2MeSiCH_2CH_2)_3SiC_5H_4\}_2ZrCl_2]}$ (10): This complex was obtained as a colorless oil (0.49 g, 94%) by the same procedure described for **9** from $\mathrm{ZrCl_4{\cdot}2THF}$ (0.12 g, 0.31 mmol) and **4** (0.50 g, 0.62 mmol) in toluene (25 mL). $\mathrm{C_{100}H_{110}Cl_2Si_8Zr}$ (1698.8):

calcd. C 70.70, H 6.53; found C 70.53, H 6.62. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 7.42$ (m, 12 H, C_6H_5), 7.26 (m, 18 H, C_6H_5), 6.28 and 6.14 (AA′ and BB′ parts of an AA′BB′ spin system, 4 H, C_5H_4), 0.85 and 0.74 [A and B parts of an A_2B_2 spin system, 12 H, $Si(CH_2)_2Si$], 0.49 (s, 9 H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 136.9$ (C_{ipso}, C_6H_5), 134.4 (C_{meta}, C_6H_5), 129.1 (C_{para}, C_6H_5), 127.7 (C_{ortho}, C_6H_5), 125.3 (C_5H_4), 124.3 (C_{ipso}, C_5H_4), 116.3 (C_5H_4), 6.5 and 4.6 [$Si(CH_2)_2Si$], -5.0 (CH_3) ppm. $^{29}Si\{^1H\}$ NMR (500 MHz, $CDCl_3$, 25 °C): $\delta = 0.0$ (SiC_5H_4), -5.7 (Ph_2MeSi) ppm.

Ethylene Polymerization: A 250 mL flask charged with toluene (50 mL) and equipped with a magnetic stirrer was evacuated four times 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 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 ethylene 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. Molecular weights were determined by gel-permeation chromatography (GPC).

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