

Novel Indenylzirconium Complexes as Supported Catalysts in the Polymerization of Ethylene

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A series of substituted indene [C_9H_7R-3 [$R = CH_2CH_2CH_2O-SiMe_3$ (**1**), $CH_2CH_2CH_2OCH_2C_6H_5$ (**2**), $CH_2CH_2CH_2OSiMe_2-tBu$ (**3**)], and *ansa*-indene compounds [$Me_2Si(C_9H_6R-3)_2-1$ [$R = CH_2CH_2CH_2OSiMe_3$ (**4**)], $Me_2Si(C_9H_6R-3)-1(C_5HMe_4)$ [$R = CH_2CH_2CH_2OSiMe_3$ (**5**), $CH_2CH_2CH_2OCH_2C_6H_5$ (**6**), $CH_2CH=CH_2$ (**7**), $CH_2CH_2CH_2OSiMe_2tBu$ (**8**)] have been prepared. The lithium derivatives of **1–8** were employed in the synthesis of the indenylzirconium complexes [$Zr(\eta^5-C_9H_6R-1)_2Cl_2$] [$R = CH_2CH_2CH_2OSiMe_3$ (**17**), $CH_2CH_2CH_2OCH_2C_6H_5$ (**18**), $CH_2CH_2CH_2OSiMe_2tBu$ (**19**)], *rac*-[$Zr\{Me_2Si(\eta^5-C_9H_5R-3)_2-1\}Cl_2$] [$R = CH_2CH_2CH_2OSiMe_3$ (**20**)], [$Zr\{Me_2Si(\eta^5-C_9H_5R-3)-1(\eta^5-C_5Me_4)\}Cl_2$] [$R = CH_2CH_2CH_2OSiMe_3$ (**21**), $CH_2CH_2CH_2OCH_2C_6H_5$ (**22**), $CH_2CH=CH_2$ (**23**), $CH_2CH_2CH_2OSiMe_2tBu$ (**24**)] and [$Zr(Me_2Si\{\eta^5-C_9H_5(CH_2CH_2CH_2O)-3\}-1\{\eta^5-C_5Me_4\})Cl$] (**21a**).

The alkyl complexes [$Zr(Me_2Si\{\eta^5-C_9H_5(CH_2CH_2CH_2O)-3\}-1\{\eta^5-C_5Me_4\})Me$] (**25**) and [$Zr\{Me_2Si(\eta^5-C_9H_5R-3)-1(\eta^5-C_5Me_4)\}Me_2$] [$R = CH_2CH_2CH_2OSiMe_2tBu$ (**26**)] have been synthesized by the reaction of the corresponding *ansa*-zirconocene derivative with the alkyl Grignard reagent. The molecular structure of [$(Zr\{C_9H_6(CH_2CH_2CH_2O)-1\}Cl_2)_2(Zr-O)$] (**17a**), a subproduct in the formation of **17** has been determined by single-crystal X-ray diffraction studies. The indenylzirconium complexes **17–24** have been immobilized on partially dehydroxylated SiO_2 , and these supported systems used to polymerize ethylene in the presence of methylaluminoxane. The catalytic activity of these compounds in both homogeneous and heterogeneous polymerization is reported. (© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2005)

Introduction

On the basis of production data for 2000, 85–95 million tons of polyolefins (essentially homopolymers and copolymers of ethylene and propylene) were produced globally. The worldwide polypropylene capacity is approximately 34 million tons, all of which is made with supported catalysts. Sixty percent of polyethylene is made with supported catalysts, bringing the current market for polyolefins produced on supported catalysts to a total of 65–70 million tons per year. This already impressive market is still in full growth.^[1,2]

Metallocene/MAO catalytic systems are highly efficient in producing polyolefins with defined microstructures and narrow molecular weight distributions,^[3,4] although to date,

these systems have generally been applied in solution. However, for most industrial applications, it is desirable to employ these catalysts in gas-phase reactions in order to take advantage of existing heterogeneous polymerization plant infrastructure and thus avoiding the costly modification needed for incorporating homogeneous systems. The single-site catalysts therefore need to be immobilized on a solid support in order to be active in gas-phase processes. Supported single-site catalysts are presently being used worldwide in the annual production of 1 billion kg of polyethylene.

The most common method of applying metallocene compounds to heterogeneous polymerization is to support the complexes on inorganic solids (in most cases silica gel).^[5–7] There are four different routes to supported catalysts: (i) Direct adsorption of the metallocene on the carrier surface leading to physisorption or chemisorption of the metallocene (direct heterogenization). (ii) Direct adsorption of the metallocene/MAO adduct on the support. (iii) Initial adsorption of MAO to the support followed by adsorption of the metallocene (indirect heterogenization). (iv) Covalent bonding between the ligands of the metallocene complex and the carrier surface followed by activation with external MAO.

Several metallocene compounds containing functional groups linked to cyclopentadienyl or indenyl ligands have

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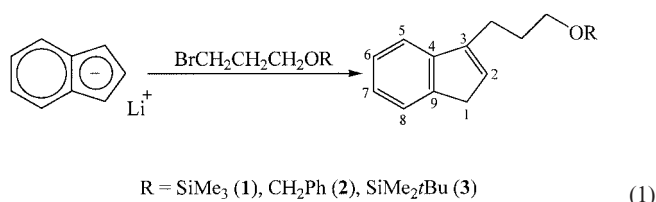
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been described.^[8] One of the most promising methods to obtain supported catalysts comes from the reaction between the functional group of these metallocene complexes and another functional group on the solid surface (route iv). This option was applied to obtain some supported mono- or bis(cyclopentadienyl) derivatives.^[8b,9–11] When silica is employed as a support, the surface hydroxy groups have frequently been used for immobilizing the catalyst although they can also cause some decomposition of the metallocene complex. A strained siloxane group generated by dehydroxylation has been shown to react with alkoxysilane groups,^[12] and this reactivity opens up the possibility of supporting metallocene complexes with pendant alkoxy or silyloxy groups on dehydroxylated silica.

In this paper we describe the synthesis and characterization of a series of alkoxy- and silyloxy-substituted indene compounds and their zirconium(IV) derivatives, and the successful immobilization of the metallocene catalysts on dehydroxylated silica.

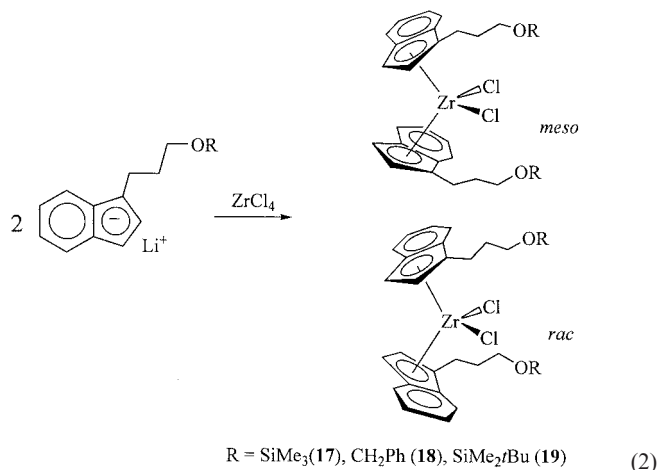
Results and Discussion

The preparation of the substituted indene precursors C_9H_7R-3 [$R = CH_2CH_2CH_2OSiMe_3$ (**1**), $CH_2CH_2CH_2OCH_2C_6H_5$ (**2**), $CH_2CH_2CH_2OSiMe_2tBu$ (**3**)] was achieved by the reaction of $BrCH_2CH_2CH_2OR$ ($R = SiMe_3$, $CH_2C_6H_5$, $SiMe_2tBu$) and indenyllithium [Equation (1)]. 1H NMR spectroscopy showed the isolated product of **1–3** to be virtually exclusively the 3-isomer (>98%). The 1-H signal for **1–3** was observed as a doublet, at $\delta \approx 3.2$ ppm, corresponding to two protons and 2-H as a triplet, at $\delta \approx 6.1$ ppm, corresponding to one proton. In addition, **1–3** were characterized by electron impact mass spectrometry (see Exp. Sect.).



Compounds **1–3** were lithiated in the normal manner with *n*-butyllithium giving the lithium derivatives $Li(C_9H_6R-1)$ [$R = CH_2CH_2CH_2OSiMe_3$ (**9**), $CH_2CH_2CH_2OCH_2C_6H_5$ (**10**), $CH_2CH_2CH_2OSiMe_2tBu$ (**11**)]. Compounds **9–11** were treated with $ZrCl_4$ to yield the zirconocene complexes $[Zr(\eta^5-C_9H_6R-1)_2Cl_2]$ [$R = CH_2CH_2CH_2OSiMe_3$ (**17**), $CH_2CH_2CH_2OCH_2Ph$ (**18**), $CH_2CH_2CH_2OSiMe_2tBu$ (**19**)] [Equation (2)].

The substituted indenyl ligands are prochiral and can yield two diastereomers for the zirconocene complexes. A *re, re* or *si, si* attachment gives rise to the two enantiomers of the *rac* diastereomer, whereas a *re, si* attachment leads to the *meso* diastereomer.^[13–15] The synthetic approach employed in this study gave, as shown by NMR spectroscopy, a 1:1 *rac/meso* isomer ratio.



1H and ^{13}C NMR spectra of **17–19** exhibit two sets of signals in a 1:1 ratio, corresponding to the presence of both diastereomers (see Exp. Sect.). The characterization was simplified by the fact that the *rac* isomer has C_2 symmetry which makes the two indenyl rings equivalent. This is also true for the *meso* isomer because of a mirror plane. In the 1H NMR spectra of **17–19**, the protons in position 2 and 3 of the indenyl ligand showed only vicinal coupling and were thus observed as doublets in the 1H NMR spectra. It was possible to assign the 2-H and 3-H signals to their respective diastereomers using NOE experiments. An interesting observation is that for a sample containing a mixture of the diastereomers, the “inner-pair” of 2-H and 3-H doublets were assigned to the *rac* isomer, whereas for the *meso* isomer the two doublets were the “outer-pair”. Because of the complex nature caused by overlapping signals we were not able to assign the multiplet systems observed for the protons of both the pendant chain and the indenyl C_6 fragment to their respective diastereomers.

During the preparation of **17**, a minor product was, at times, detected. We were able to isolate this subproduct, $[(Zr\{C_9H_6(CH_2CH_2CH_2O-1)Cl_2\}_2(Zr-O)]$ (**17a**), by fractional recrystallization and characterize it by single-crystal X-ray diffraction studies. The molecular structure and atomic numbering scheme are shown in Figure 1. Selected bond lengths and angles for **17a** are given in Table 1.

The structure consists of a dinuclear complex of zirconium. The metal atoms are bound to the indenyl ligand in an η^5 mode, to the oxygen atoms of the pendant chains which bridge the two zirconium atoms, and to two chlorine atoms in a four-legged piano-stool conformation. The indenyl ligands are in a *trans* disposition.

During the preparation of **9** it is possible that a second lithiation occurs at the oxygen atom of the pendant chain with the elimination of *n*BuSiMe₃ to give $Li[C_9H_6(CH_2CH_2CH_2OLi)-1]$. If this subproduct is present when the reaction of **9** is carried out with $ZrCl_4$, the presence of **17a** may be detected in the isolated product [Equation (3)].

The bridged bis(indene) compound, $\{Me_2Si[(C_9H_6R-3)-1]_2\}$ (**4**) ($R = CH_2CH_2CH_2OSiMe_3$), was prepared by

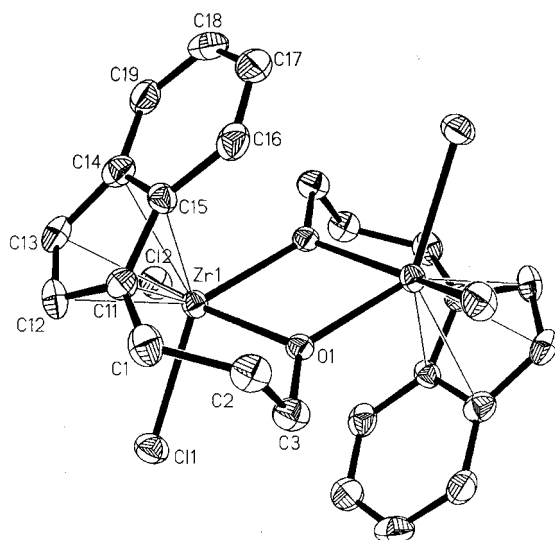
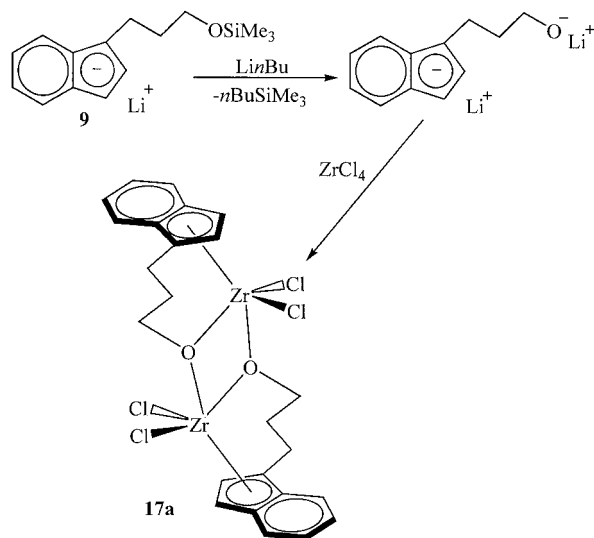


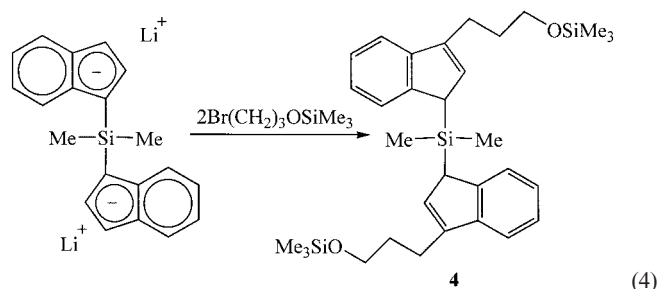
Figure 1. Molecular structure and atom labelling scheme for $[(\text{Zr}\{\text{C}_9\text{H}_6(\text{CH}_2\text{CH}_2\text{CH}_2\text{O})\text{-}1\}\text{Cl}_2)_2(\text{Zr-O})]$ (**17a**) with thermal ellipsoids at 30% probability.

Table 1. Selected bond lengths [$\text{\AA}$] and angles [$^\circ$] for **17a**; Cent(1) is the centroid of C(11)–C(15); * refers to the average bond length between Zr(1) and the carbon atoms of the C_5 ring of the indenyl moiety.

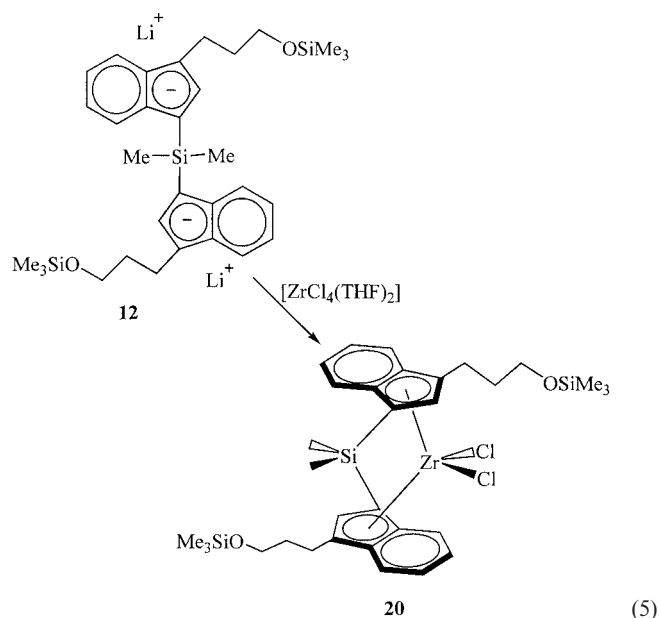
Zr(1)–Cent(1)	2.188
av Zr(1)–C[Cent(1)]*	2.486(9)
Zr(1)–Cl(1)	2.415(2)
Zr(1)–Cl(2)	2.447(2)
Zr(1)–O(1)	2.131(5)
Cent(1)–Zr(1)–O(1)	105.2
Cent(1)–Zr(1)–Cl(1)	109.0
Cent(1)–Zr(1)–Cl(2)	109.7
O(1)–Zr(1)–Cl(1)	88.13(15)
O(1)–Zr(1)–Cl(2)	143.8(2)
O(1)–Zr(1)–O(1)'	70.1(2)
Cl(1)–Zr(1)–Cl(2)	88.90(3)
Zr(1)–O(1)–C(3)	122.08(5)



the reaction of 2 equiv. of $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{OSiMe}_3$, with $\text{Li}_2[\text{Me}_2\text{Si}(\text{C}_9\text{H}_6)_2\text{-}1]$ and isolated as a mixture of its *meso* and *rac* isomers [Equation (4)].



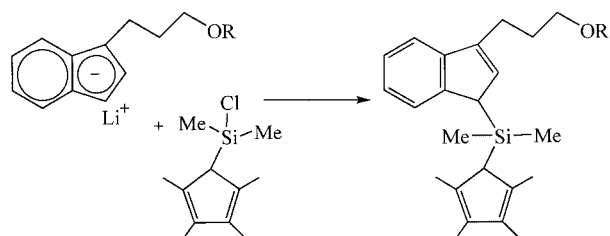
^1H NMR spectroscopy showed the isolated product of **4** to be virtually exclusively ($>98\%$) the symmetrically substituted indenyl isomer. In addition, **4** was characterized by electron impact mass spectrometry (see Exp. Sect.). Double deprotonation of **4** with 2 equiv. of *n*-butyllithium gave the corresponding dilithium derivative, $\text{Li}_2[\text{Me}_2\text{Si}(\text{C}_9\text{H}_5\text{R-}3)_2\text{-}1]$ (**12**) ($\text{R} = \text{CH}_2\text{CH}_2\text{CH}_2\text{OSiMe}_3$), whose reaction with $[\text{ZrCl}_4(\text{THF})_2]$ in toluene gave the *ansa*-indenyl complex, $[\text{Zr}\{\text{Me}_2\text{Si}(\eta^5\text{-C}_9\text{H}_5\text{R-}3)_2\text{-}1\}\text{Cl}_2]$ ($\text{R} = \text{CH}_2\text{CH}_2\text{CH}_2\text{OSiMe}_3$ (**20**)), exclusively as the *rac* isomer [Equation (5)]. Use of $[\text{ZrCl}_4(\text{THF})_2]$ as the zirconium source has been suggested to modify the ratio of the diastereomers formed.^[14] This proposal is reinforced by the observation that the reaction of **12** with ZrCl_4 gave **20** as a 3:2 *rac/meso* mixture.



Compound **20** was characterized by NMR spectroscopy. The proton signal assignments were made according to a procedure using ^1H and ^{13}C NMR correlated spectroscopy (HETCOR) (see Exp. Sect.).

The preparation of the asymmetrically substituted *ansa* ligand precursors $[\text{Me}_2\text{Si}(\text{C}_9\text{H}_6\text{R-}3)\text{-}1(\text{C}_5\text{HMe}_4)]$ [$\text{R} = \text{CH}_2\text{CH}_2\text{CH}_2\text{OSiMe}_3$ (**5**), $\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{C}_6\text{H}_5$ (**6**),

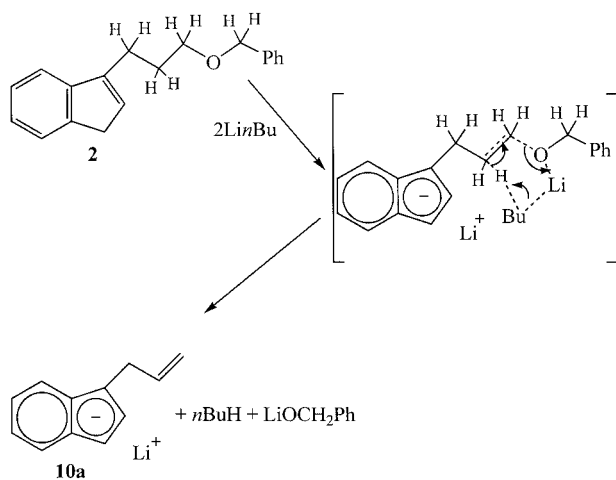
$\text{CH}_2\text{CH}_2\text{CH}_2\text{OSiMe}_2t\text{Bu}$ (**8**) was achieved by the reaction of $\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4\text{H})\text{Cl}$ and the corresponding lithium derivatives **9–12** [Equation (6)].



$\text{R} = \text{SiMe}_3$ (**5**), CH_2Ph (**6**), SiMe_2tBu (**8**)

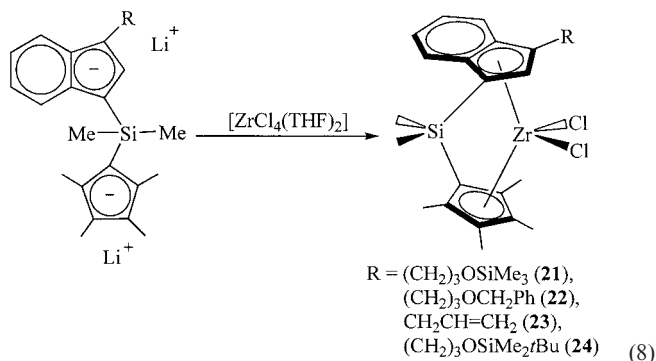
(6)

The reaction of **2** with an excess of $n\text{BuLi}$ gave the lithium derivative $\text{Li}[\text{C}_9\text{H}_6(\text{CH}_2\text{CH}=\text{CH}_2)\text{-1}]$ (**10a**) by a bimolecular elimination [Equation (7)]. The subsequent reaction of **10a** with $\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4\text{H})\text{Cl}$ yielded the asymmetrically substituted *ansa* ligand precursor, $\{\text{Me}_2\text{Si}[\text{C}_9\text{H}_6(\text{CH}_2\text{CH}=\text{CH}_2)\text{-3}]\text{-1}(\text{C}_5\text{HMe}_4)\}$ (**7**). ^1H NMR spectroscopy showed the isolated products **5–8** to be virtually exclusively (>98%) the regioisomer where the SiMe_2 *ansa* bridge is situated in position 1 in both the indenyl and cyclopentadienyl moieties. In addition, **5–8** were characterized by electron impact mass spectrometry (see Exp. Sect.).

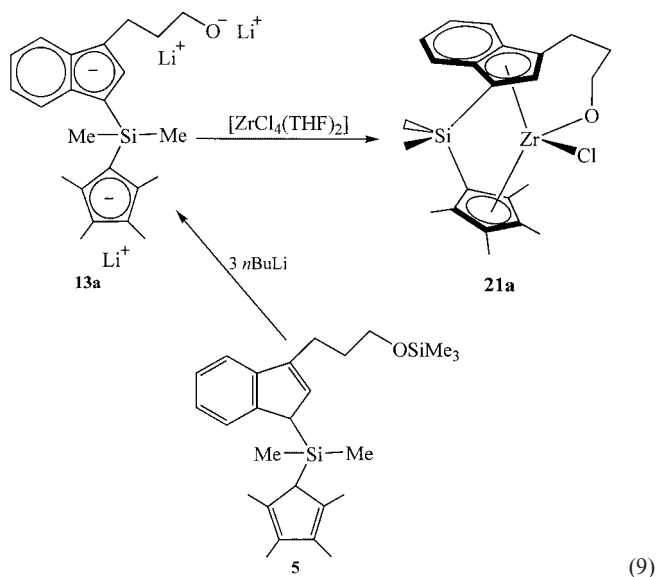


(7)

Compounds **5–8** were then lithiated in the normal way with n -butyllithium to give the corresponding dilithium derivatives, $\text{Li}_2[\text{Me}_2\text{Si}(\text{C}_9\text{H}_5\text{R-3})\text{-1}(\text{C}_5\text{Me}_4)]$ [$\text{R} = \text{CH}_2\text{CH}_2\text{CH}_2\text{OSiMe}_3$ (**13**), $\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{C}_6\text{H}_5$ (**14**), $\text{CH}_2\text{CH}=\text{CH}_2$ (**15**), $\text{CH}_2\text{CH}_2\text{CH}_2\text{OSiMe}_2t\text{Bu}$ (**16**)] whose reaction with $[\text{ZrCl}_4(\text{THF})_2]$ gave the *ansa*-zirconocene complexes $[\text{Zr}\{\text{Me}_2\text{Si}(\eta^5\text{-C}_9\text{H}_5\text{R-3})\text{-1}(\eta^5\text{-C}_5\text{Me}_4)\}\text{Cl}_2]$ [$\text{R} = \text{CH}_2\text{CH}_2\text{CH}_2\text{OSiMe}_3$ (**21**), $\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{C}_6\text{H}_5$ (**22**), $\text{CH}_2\text{CH}=\text{CH}_2$ (**23**), $\text{CH}_2\text{CH}_2\text{CH}_2\text{OSiMe}_2t\text{Bu}$ (**24**)] [Equation (8)].



When the lithiation reaction of **5** was carried out in the presence of excess of n -butyllithium, the trillithium derivative, $\text{Li}_2[\text{Me}_2\text{Si}[\text{C}_9\text{H}_5(\text{CH}_2\text{CH}_2\text{CH}_2\text{OLi})\text{-3}]\text{-1}(\text{C}_5\text{Me}_4)]$ (**13a**) was formed through the elimination of the SiMe_3 moiety [Equation (9)]. Compound **13a** was characterized by ^1H NMR spectroscopy which confirmed the loss of the SiMe_3 group. The reaction of **13a** with $[\text{ZrCl}_4(\text{THF})_2]$ gave the *ansa*-zirconocene complex $[\text{Zr}(\text{Me}_2\text{Si}\{\eta^5\text{-C}_9\text{H}_5(\text{CH}_2\text{CH}_2\text{CH}_2\text{O})\text{-3}\}\text{-1}\{\eta^5\text{-C}_5\text{Me}_4\})\text{Cl}(\text{Zr-O})]$ (**21a**), where the oxygen atom of the pendant chain is directly bonded to the metal center [Equation (9)].



(9)

Compounds **21–24** were characterized spectroscopically (see Exp. Sect.). The ^1H NMR spectra show the lack of symmetry in these chiral complexes, with four singlets being observed for the cyclopentadienyl methyl groups, two singlets for the *ansa*-bridge methyl groups, a singlet for the proton of the indenyl C_5 ring and four multiplets corresponding to the protons of the C_6 ring of the indenyl moiety. In addition signals were observed for the pendant alkyl chain.

The alkyl derivatives, $[\text{Zr}(\text{Me}_2\text{Si}\{\eta^5\text{-C}_9\text{H}_5(\text{CH}_2\text{CH}_2\text{CH}_2\text{O})\text{-3}\}\text{-1}\{\eta^5\text{-C}_5\text{Me}_4\})\text{Me}(\text{Zr-O})]$ (**25**) and $[\text{Zr}\{\text{Me}_2\text{Si}(\eta^5\text{-C}_9\text{H}_5\text{R-3})\text{-1}(\eta^5\text{-C}_5\text{Me}_4)\}\text{Me}_2]$ [$\text{R} = \text{CH}_2\text{CH}_2\text{CH}_2\text{OSi}$

Me_2tBu (**26**) were prepared by the reaction of the Grignard reagent MeMgBr with the corresponding mono- or dihalo *ansa*-zirconocene complexes **21a** and **24**, respectively [Equations (10) and (11)]. Compounds **25** and **26** were charac-

terized by spectroscopic methods (see Exp. Sect.). The ^1H NMR spectrum for **25** is similar to that recorded for its parent compound **21a** but in addition a singlet for the metal-bonded methyl group is observed. For **26**, two signals, assigned to the inequivalent metal-bonded methyl groups, were recorded.

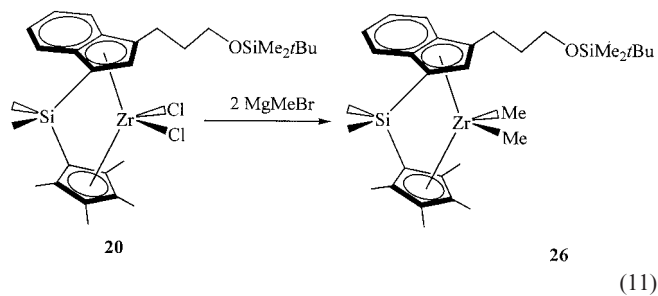
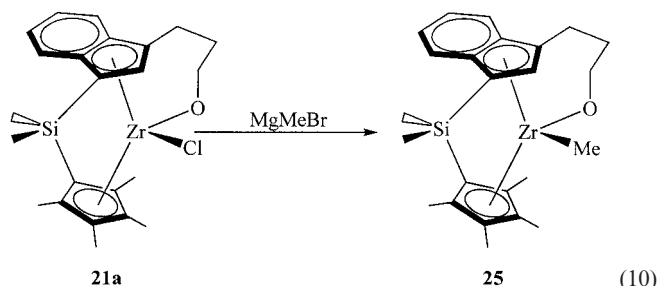


Figure 2 shows IR spectra corresponding to the reaction between a toluene solution of $[\text{Zr}\{\text{Me}_2\text{Si}(\eta^5\text{-C}_9\text{H}_5\text{R-3-1}(\eta^5\text{-C}_5\text{Me}_4)\}\text{Cl}_2]$ [$\text{R} = \text{CH}_2\text{CH}_2\text{CH}_2\text{OSiMe}_2t\text{Bu}$ (**17**)] and the surface of a partially dehydroxylated silica, after removal of solvent (see Exp. Sect.). The spectrum of silica preheated at 773 K has a sharp band at 3747 cm^{-1} (assigned to isolated OH groups) with a small broad shoulder at 3670 cm^{-1} , which can be attributed to silanols that are perturbed due to interparticle contact^[16] or to OH groups retained deep within the pores^[17] (Figure 2a). The magnitude of the silanol number, which is independent of the origin and structural characteristics of amorphous silica, is considered to be ca. 1.8 OH nm^{-2} for a silica dehydroxylated at 733 K.^[18] Bands at 1866 cm^{-1} and 1640 cm^{-1} are combination and overtone bands of Si–O network bonds. After contact with the metallocene solution and removal of the solvent (Figure 2b), new bands can be seen in the 2900 and 1400 cm^{-1} regions and these correspond to stretching and bending modes of the cyclopentadienyl ligands. The OH groups that were initially isolated are now partially perturbed, generating broad $\nu(\text{OH})$ bands at lower frequencies due to an interaction with the cyclopentadienyl π -electron system through

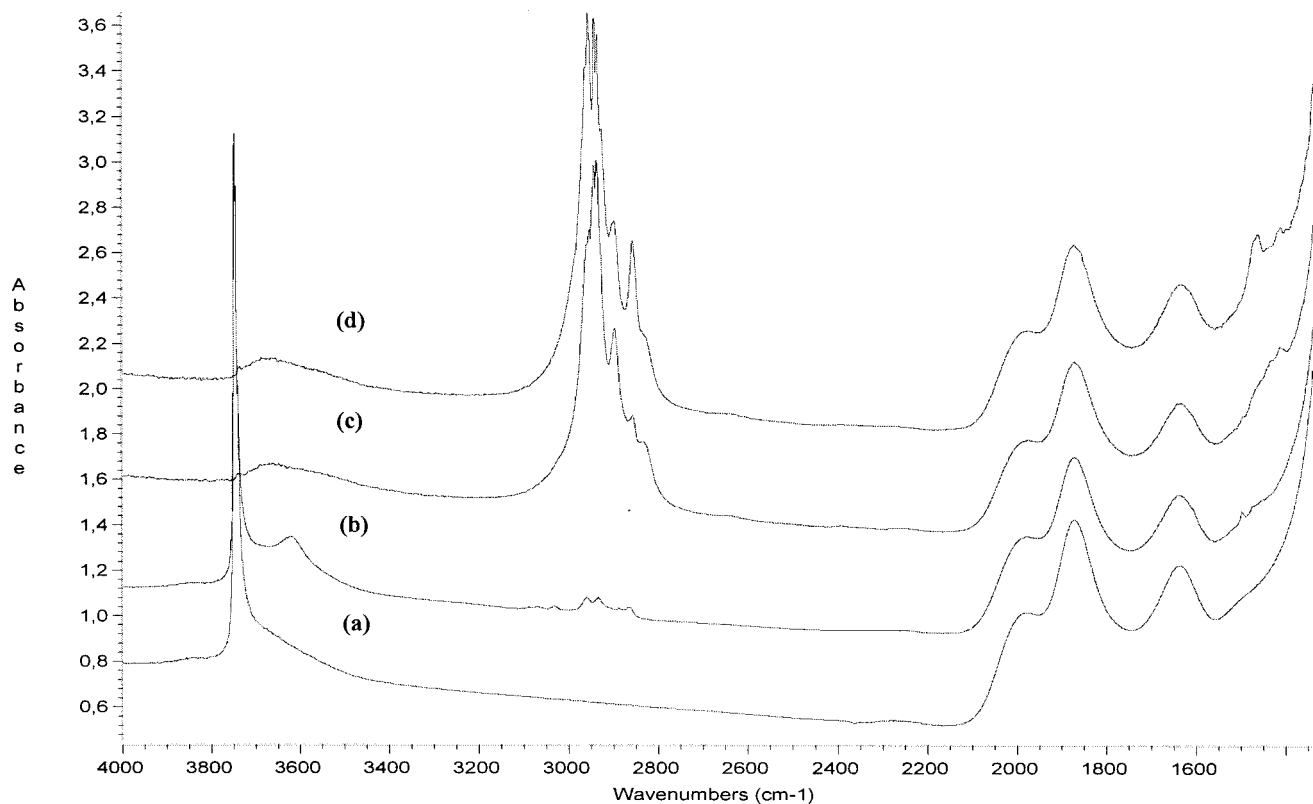


Figure 2. (a) SiO_2 dehydroxylated; (b) after grafting of **17**; (c) after addition of MAO; (d) after contact with C_2H_4 .

hydrogen bonding.^[19] The total intensity of the band due to the hydroxy groups was slightly modified after the addition of an excess of metallocene solution, a situation also observed by dos Santos and co-workers in the reaction between partially dehydroxylated silica and $[\text{Zr}(\eta^5\text{-C}_5\text{H}_4\text{-}n\text{Bu})_2\text{Cl}_2]$.^[20]

It is well established that the surface hydroxy group density on silica decreases with thermal activation as a result of an increase in the number of siloxane reactive bridges. These strained groups can activate covalent bonds such as the Si–O bond in silicon ethers or N–H in ammonia.^[21] We could propose a similar behavior with our silicon ether metallocene derivatives. Similar results were found in the reaction of $[\text{Zr}(\eta^5\text{-C}_5\text{H}_5)_2\text{Cl}_2]$ and dehydroxylated silica.^[22]

The behavior of the catalyst system after the addition of the MAO cocatalyst was also studied by FT-IR spectroscopy. The IR spectrum of a sample of **17**-SiO₂ treated with MAO (Al/Zr = 100) is shown in Figure 2c. After addition of MAO at room temperature, the infrared band attributed to the isolated silanol groups (at 3747 cm⁻¹) disappeared completely, indicating a reaction between some basic methyl groups of MAO and the acidic silanol moieties of the silica. New infrared bands were observed in the ν(CH) region (one intense band at 2940 cm⁻¹ and three weak bands at 2898, 2856 and 2838 cm⁻¹). These signals were assigned to stretching vibrations of the C–H bonds of the methyl groups in MAO. The grafted MAO should be able to activate neighboring surface zirconocene molecules.^[23] The catalytic activity of **17**-SiO₂, after treatment with MAO, towards ethylene polymerization was confirmed, using FT-IR spectroscopy, by monitoring the appearance of vibrations due to polyethylene in the regions 3000–2800 and 1500–1300 cm⁻¹ (Figure 2d). Intense bands were observed at 2970, 2850 and 1380 cm⁻¹, which correspond to the ν(CH) and δ(CH) vibrations of polyethylene, respectively.

The polymerization of ethylene, under homogeneous conditions and using **9–13** and **15–17** as the catalyst, with metal/MAO catalyst ratios of 1:100 (in order to compare with supported catalysts) or 1:500, has been carried out. The polymerization experiments were carried out at 70 °C and at an olefin pressure of 1.5 bar. The results of the experiments are given in Table 2.

In all the cases, as expected, higher activities were found for the 500:1 Al/Zr ratio. The highest catalytic activities were recorded for **19**, **22** and **23**. In comparison, **20** gave a notably low catalytic activity. The activities recorded for the *ansa*-zirconocene complexes **22** and **23** are higher than their unsubstituted analogue, $[\text{Zr}\{\text{Me}_2\text{Si}(\eta^5\text{-C}_9\text{H}_6)(\eta^5\text{-C}_5\text{Me}_4)\}\text{Cl}_2]$, although **24** gave a similar value. Only compound **19** shows a higher value than its corresponding unsubstituted reference complex.

The complexes **17–24** were supported on dehydroxylated silica and, in the presence of MAO (Zr/Al 1:100), were employed as heterogeneous catalysts in the polymerization of ethylene. The experiments were carried out at 70 °C and at an olefin pressure of 1.5 bar and the results are given in Table 3.

The amount of supported metallocene was verified by surface elemental analyses (Zr). The average results of several samples are summarized in Table 3.

Supported substituted complexes **17**, **21**, and **24** show similar or higher activities than their reference unsubstituted complexes. We could propose that, at least in these cases, more active surface species were obtained than those obtained from “conventional” unsubstituted complexes. Later complexes could be fixed on the surface by reaction between Zr–Cl moieties and Si–OH acidic groups, to give strong Zr–O–Si bonding, hard to activate by MAO. In contrast, the new complexes could be fixed by the reaction be-

Table 2. Homogeneous ethylene polymerization results for **17–24**, $[\text{Zr}(\eta^5\text{-C}_9\text{H}_7)_2\text{Cl}_2]$, $[\text{Zr}\{\text{Me}_2\text{Si}(\eta^5\text{-C}_9\text{H}_6)_2\text{-1,1'}\}\text{Cl}_2]$ and $[\text{Zr}\{\text{Me}_2\text{Si}(\eta^5\text{-C}_9\text{H}_6)(\eta^5\text{-C}_5\text{Me}_4)\}\text{Cl}_2]$ as references. Polymerization conditions: 70 °C, 1.5 bar monomer pressure, 33 μmol Zr, 250 mL toluene, t_{pol} = 30 min.

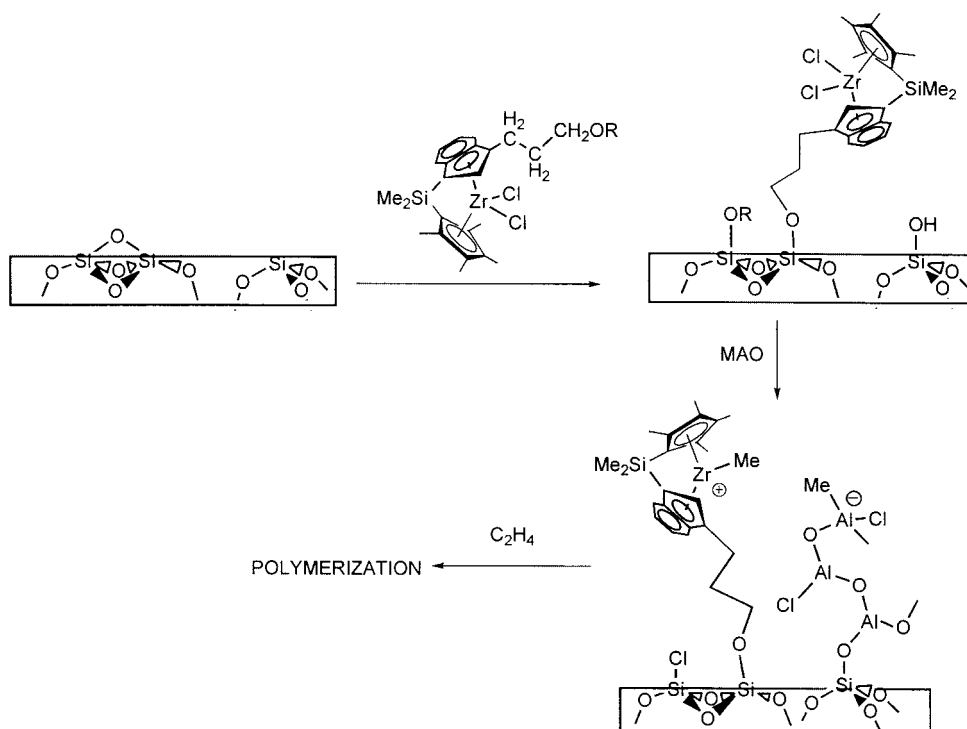
Complex	Activity ^[a,c]	Activity ^[a,b]
$[\text{Zr}(\eta^5\text{-C}_9\text{H}_7)_2\text{Cl}_2]$	598	352
$[\text{Zr}(\eta^5\text{-C}_9\text{H}_6\text{R-1})_2\text{Cl}_2]$ R = CH ₂ CH ₂ CH ₂ OSiMe ₃ (17)	287	21
$[\text{Zr}(\eta^5\text{-C}_9\text{H}_6\text{R-1})_2\text{Cl}_2]$ R = CH ₂ CH ₂ CH ₂ OCH ₂ Ph (18)	388	145
$[\text{Zr}(\eta^5\text{-C}_9\text{H}_6\text{R-1})_2\text{Cl}_2]$ R = CH ₂ CH ₂ CH ₂ OSiMe ₂ tBu (19)	725	76
$[\text{Zr}\{\text{Me}_2\text{Si}(\eta^5\text{-C}_9\text{H}_6)_2\text{-1,1'}\}\text{Cl}_2]$ <i>rac</i> - $[\text{Zr}\{\text{Me}_2\text{Si}(\eta^5\text{-C}_9\text{H}_5\text{R-3})_2\text{-1,1'}\}\text{Cl}_2]$	485	280
R = CH ₂ CH ₂ CH ₂ OSiMe ₃ (20)	88	26
$[\text{Zr}\{\text{Me}_2\text{Si}(\eta^5\text{-C}_9\text{H}_6)(\eta^5\text{-C}_5\text{Me}_4)\}\text{Cl}_2]$	558	180
$[\text{Zr}\{\text{Me}_2\text{Si}(\eta^5\text{-C}_9\text{H}_5\text{R-3})\text{-1}(\eta^5\text{-C}_5\text{Me}_4)\}\text{Cl}_2]$ R = CH ₂ CH ₂ CH ₂ OSiMe ₃ (21)	212	114
$[\text{Zr}\{\text{Me}_2\text{Si}(\eta^5\text{-C}_9\text{H}_5\text{R-3})\text{-1}(\eta^5\text{-C}_5\text{Me}_4)\}\text{Cl}_2]$ R = CH ₂ CH ₂ CH ₂ OCH ₂ Ph (22)	831	115
$[\text{Zr}\{\text{Me}_2\text{Si}(\eta^5\text{-C}_9\text{H}_5\text{R-3})\text{-1}(\eta^5\text{-C}_5\text{Me}_4)\}\text{Cl}_2]$ R = CH ₂ CHCH ₂ (23)	787	387
$[\text{Zr}\{\text{Me}_2\text{Si}(\eta^5\text{-C}_9\text{H}_5\text{R-3})\text{-1}(\eta^5\text{-C}_5\text{Me}_4)\}\text{Cl}_2]$ R = CH ₂ CH ₂ CH ₂ OSiMe ₂ tBu (24)	525	259

[a] In kg PE (mol Zr) h⁻¹. [b] Al/Zr 100:1. [c] Al/Zr 500:1.

Table 3. Heterogeneous ethylene polymerization results. Polymerization conditions: 70 °C, 1.5 bar monomer pressure, 250 mL toluene, 33 μmol Zr (approx. 300 mg of supported catalyst), Al/Zr 100:1, t_{pol} = 30 min.

Complex	% Zr	Activity ^[a]
$[\text{Zr}(\eta^5\text{-C}_9\text{H}_7)_2\text{Cl}_2]$	0.60	96
$[\text{Zr}(\eta^5\text{-C}_9\text{H}_6\text{R-1})_2\text{Cl}_2]$ R = CH ₂ CH ₂ CH ₂ OSiMe ₃ (17)	0.81	85
$[\text{Zr}(\eta^5\text{-C}_9\text{H}_6\text{R-1})_2\text{Cl}_2]$ R = CH ₂ CH ₂ CH ₂ OCH ₂ Ph (18)	0.67	15
$[\text{Zr}(\eta^5\text{-C}_9\text{H}_6\text{R-1})_2\text{Cl}_2]$ R = CH ₂ CH ₂ CH ₂ OSiMe ₂ tBu (19)	0.72	32
$[\text{Zr}\{\text{Me}_2\text{Si}(\eta^5\text{-C}_9\text{H}_6)_2\text{-1,1'}\}\text{Cl}_2]$ <i>rac</i> - $[\text{Zr}\{\text{Me}_2\text{Si}(\eta^5\text{-C}_9\text{H}_5\text{R-3})_2\text{-1,1'}\}\text{Cl}_2]$	0.84	104
R = CH ₂ CH ₂ CH ₂ OSiMe ₃ (20)	0.85	19
$[\text{Zr}\{\text{Me}_2\text{Si}(\eta^5\text{-C}_9\text{H}_6)(\eta^5\text{-C}_5\text{Me}_4)\}\text{Cl}_2]$	0.94	97
$[\text{Zr}\{\text{Me}_2\text{Si}(\eta^5\text{-C}_9\text{H}_5\text{R-3})\text{-1}(\eta^5\text{-C}_5\text{Me}_4)\}\text{Cl}_2]$ R = CH ₂ CH ₂ CH ₂ OSiMe ₃ (21)	0.76	122
$[\text{Zr}\{\text{Me}_2\text{Si}(\eta^5\text{-C}_9\text{H}_5\text{R-3})\text{-1}(\eta^5\text{-C}_5\text{Me}_4)\}\text{Cl}_2]$ R = CH ₂ CH ₂ CH ₂ OCH ₂ Ph (22)	0.89	35
$[\text{Zr}\{\text{Me}_2\text{Si}(\eta^5\text{-C}_9\text{H}_5\text{R-3})\text{-1}(\eta^5\text{-C}_5\text{Me}_4)\}\text{Cl}_2]$ R = CH ₂ CH ₂ CH ₂ OSiMe ₂ tBu (24)	0.82	199

[a] In kg PE (mol Zr) h⁻¹.



Scheme 1. Proposed mechanism in the immobilization of the catalyst at the siloxane bridge and its subsequent activation with MAO.

tween the $(\text{CH}_2)_2\text{OR}$ group and the siloxane bridges, to give surface species, which remember the structure of the analogous molecular complexes, to give more active catalysts (Scheme 1).

In addition, it is noteworthy that supported complexes **17**, **21** and **24** show similar or higher activities than their corresponding homogeneous catalysts, with a 100:1 Al/Zr ratio, showing both the advantages of supporting the complexes (reduced MAO addition to activate), and the use of pendant reactive chains (more active species).

Conclusions

We have carried out the synthesis of indenyl-containing zirconium complexes with pendant chains capable of interacting with dehydroxylated silica. We have successfully immobilized the complexes on silica and tested the activity of these supported catalysts in the polymerization of ethylene and compared the results with the reference unsubstituted complexes.

Experimental Section

General Remarks: All reactions were prepared using standard Schlenk tube techniques under dry nitrogen. Solvents were distilled from appropriate drying agents and degassed before use. $[\text{ZrCl}_4(\text{THF})_2]$, ZrCl_4 , C_9H_8 , $\text{Me}_2\text{Si}(\text{C}_5\text{HMe}_4)\text{Cl}$, SiMe_2Cl_2 , $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{OH}$ and $(\text{Me}_3\text{Si})_2\text{NH}$ were purchased from Aldrich and used directly. Grace Davison XPO 2407 silica (200 m^2/g , according to data from supplier) was dehydroxylated under vacuum (10^{-2} Torr) at 773 K for 16 h, cooled and stored under dry nitrogen.

Ethylene (Alphagaz), $i\text{Bu}_3\text{Al}$ (TIBA, Aldrich) and MAO (EURECENE, 10, Crompton) were used without further purification. ^1H and ^{13}C spectra were recorded with Varian UNITY FT-300, Varian GEMINITY FT-400 and Varian INNOVA FT-500 spectrometers and referenced to the residual deuterated solvent. Microanalyses were carried out with a Perkin–Elmer 2400 microanalyzer. Mass spectrometric analyses were performed with a Vg Autospec instrument or a Hewlett–Packard 5988A ($m/z = 50$ –1000) (electron impact). Infrared spectra were recorded with a Nicolet Magna 550-FT spectrophotometer using an infrared cell equipped with CaF_2 or KBr windows; this setup allowed in situ studies. A total of 32 scans were typically accumulated for each spectrum (resolution 2 cm^{-1}). The samples consisted of ca. 20 mg of silica pressed into a self-supported disc of 1 cm diameter. The samples were dehydroxylated at 773 K for 16 h. Zirconocene grafting was performed using a 10^{-2} M solution of the metallocene in toluene to give approximately 1% Zr/ SiO_2 . The samples were warmed at 333 K for 1 h, washed with toluene and dried in vacuo at 343 K until no further change was observed (sublimation of the excess complex was observed).

Preparation of $\text{C}_9\text{H}_7(\text{CH}_2\text{CH}_2\text{CH}_2\text{OSiMe}_3)\text{-3 (1)}$: $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{OSiMe}_3$ (9.04 g, 43.04 mmol) was added to a solution of $\text{Li}(\text{C}_9\text{H}_7)$ (5.25 g, 43.04 mmol) in Et_2O at -78°C . The reaction mixture was allowed to warm to room temperature and stirred for 15 h. The solvent was removed in vacuo and hexane (100 mL) was added. The mixture was filtered and the solvent removed from the filtrate under reduced pressure to yield the title compound as a yellow oil. Compound **1** was purified by flash distillation (8.47 g, 80%). ^1H NMR (400 MHz, CDCl_3 , 25°C): $\delta = 0.20$ (s, 9 H, OSiMe_3), 1.65 and 2.08 (2 m, each 2 H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$), 3.40 (m, 2 H, 1-H), 3.82 (t, $J = 6.3$ Hz, 2 H, $\text{CH}_2\text{OSiMe}_3$), 6.32 (m, 1 H, 2-H), 7.26 and 7.33 (2 t, $J = 7.3$ Hz, each 1 H, 5-H and 8-H), 7.50 and 7.58 (2 d, $J = 7.3$ Hz, each 1 H, 6-H and 7-H) ppm. EI MS: m/z (%) = 246 (30) [M^+ , $\text{C}_9\text{H}_7(\text{CH}_2\text{CH}_2\text{CH}_2\text{OSiMe}_3)^+$], 130 (100) [$\text{M}^+ - \text{C}_9\text{H}_7$], 115 (24) [$\text{M}^+ - \text{CH}_2\text{CH}_2\text{CH}_2\text{OSiMe}_3$].

Preparation of $C_9H_7(CH_2CH_2CH_2OCH_2Ph)$ -3 (2**):** The synthesis of **2** was carried out in an identical manner to **1**: $Li(C_9H_7)$ (5.25 g, 43.04 mmol) and $BrCH_2CH_2CH_2OCH_2Ph$ (12.87 g, 43.04 mmol). Yield (7.39 g, 65%). 1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 2.43 and 2.76 (2 m, each 2 H, $CH_2CH_2CH_2O$), 3.41 (m, 2 H, 1-H), 3.66 (t, J = 6.3 Hz, 2 H, CH_2OCH_2Ph), 4.62 (s, 2 H, CH_2OCH_2Ph), 6.29 (m, 1 H, 2-H), 7.29–7.56 (m, 9 H, 5-H–8-H and OCH_2Ph) ppm. EI MS: m/z (%) = 264 (27) [M^+ , $C_9H_7(CH_2CH_2CH_2OCH_2Ph)^+$], 173 (100) [M^+ – CH_2Ph], 91 (40) [M^+ – $C_9H_7CH_2CH_2CH_2O$].

Preparation of $C_9H_7(CH_2CH_2CH_2OSiMe_2tBu)$ -3 (3**):** The synthesis of **3** was carried out in an identical manner to **1**: $Li(C_9H_7)$ (5.25 g, 43.04 mmol) and $BrCH_2CH_2CH_2OSiMe_2tBu$ (10.90 g, 43.04 mmol). Yield (7.81 g, 63%). 1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.18 (s, 6 H, $OSiMe_2tBu$), 1.00 (s, 9 H, $OSiMe_2tBu$), 2.01 and 2.68 (2 m, each 2 H, $CH_2CH_2CH_2O$), 3.38 (m, 2 H, 1-H), 3.79 (t, J = 6.3 Hz, 2 H, CH_2OSiMe_2tBu), 6.28 (m, 1 H, 2-H), 7.58 and 7.65 (2 t, J = 7.3 Hz, each 1 H, 5-H and 8-H), 7.80 and 7.86 (2 d, J = 7.3 Hz, each 1 H, 6-H and 7-H) ppm. EI MS: m/z (%) = 287 (7) [M^+ , $C_9H_7(CH_2CH_2CH_2OSiMe_2tBu)^+$], 231 (100) [M^+ – tBu], 115 (45) [M^+ – $CH_2CH_2CH_2OSiMe_2tBu$].

Preparation of $\{Me_2Si[C_9H_6(CH_2CH_2CH_2OSiMe_3)-3]_2-1,1'\}$ (4**):** $BrCH_2CH_2CH_2OSiMe_3$ (8.37 g, 38.14 mmol) was added to a solution of $Li_2[Me_2Si(C_9H_6)_2]$ (5.73 g, 19.07 mmol) in Et_2O (50 mL) at –78 °C. The mixture was allowed to warm to 25 °C and stirred for 15 h. The solvent was removed in vacuo and hexane (100 mL) was added. The mixture was filtered and the solvent removed from the filtrate under reduced pressure to yield the title compound as a yellow oil. Compound **4** was purified by flash distillation (6.28 g, 60%). 1H NMR (400 MHz, $CDCl_3$, 25 °C, two isomers): δ = 0.06 and 0.07 (2 s, each 18 H, $4 \times OSiMe_3$), –0.64 and –0.22 [2 s, each 3 H, $SiMe_2$ (*meso*)], –0.49 [s, 6 H, $SiMe_2$ (*rac*)], 1.75 and 2.50 (2 m, each 8 H, $4 \times CH_2CH_2CH_2O$), 3.24 and 3.35 (2 d, J = 1.6 Hz, each 2 H, $4 \times 1-H$), 3.54 (m, 8 H, $4 \times CH_2OSiMe_3$), 5.97 and 6.17 (2 d, J = 1.6 Hz, each 2 H, $4 \times 2-H$), 7.14–7.46 (m, 16 H, $4 \times 5-H$, 6-H, 7-H and 8-H) ppm. EI MS: m/z (%) = 548 (17) [M^+ , $Me_2Si(C_9H_6CH_2CH_2CH_2OSiMe_3)_2^+$], 230 (70) [M^+ – $C_9H_6CH_2CH_2CH_2OSiMe_3$ – $SiMe_3$], 130 (100) [M^+ – $Me_2Si(C_9H_6CH_2CH_2CH_2OSiMe_3)(C_9H_6)$].

Preparation of $\{Me_2Si[C_9H_6(CH_2CH_2CH_2OSiMe_3)-3]-1(C_5HMe_4)\}$ (5**):** $ClMe_2Si(C_5HMe_4)$ (4.43 g, 20.8 mmol) in Et_2O (50 mL) was added to a solution of $Li[C_9H_6(CH_2CH_2CH_2OSiMe_3)-1]$ (**9**) (5.25 g, 20.80 mmol) in Et_2O (50 mL) at –78 °C. The reaction mixture was allowed to warm to room temperature and stirred for 15 h. The solvent was removed in vacuo and hexane (100 mL) was added to the resulting yellow oil. The mixture was filtered and the solvent removed from the filtrate under reduced pressure to yield the title compound as a yellow oil (6.19 g, 70%). 1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = –0.31 and –0.59 (2 s, each 3 H, $SiMe_2$), 0.01 (s, 9 H, $OSiMe_3$), 1.68, 1.73, 1.86 and 1.88 (4 s, each 3 H, C_5Me_4), 1.80 and 2.50 (2 m, each 2 H, $CH_2CH_2CH_2O$), 2.91 and 3.39 (2 m, each 1 H, C_5HMe_4 and 1-H), 3.56 (t, J = 6.3 Hz, 2 H, CH_2OSiMe_3), 6.10 (d, J = 1.6 Hz, 1 H, 2-H), 7.04–7.34 (m, 4 H, 5-H–8-H) ppm. EI MS: m/z (%) = 424 (14) [M^+ , $\{Me_2Si[C_9H_6(CH_2CH_2CH_2OSiMe_3)](C_5HMe_4)\}^+$], 303 (24) [M^+ – C_5HMe_4], 179 (100) [M^+ – $C_9H_6CH_2CH_2CH_2OSiMe_3$].

Preparation of $\{Me_2Si[C_9H_6(CH_2CH_2CH_2OCH_2Ph)-3]-1(C_5HMe_4)\}$ (6**):** The synthesis of **6** was carried out in an identical manner to **5**. $ClMe_2Si(C_5HMe_4)$ (4.33 g, 20.30 mmol) and $Li[C_9H_6(CH_2CH_2CH_2OCH_2Ph)-1]$ (5.12 g, 20.30 mmol). Yield 5.39 g, 60%. 1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = –0.55 and –0.27 (2 s, each 3 H, $SiMe_2$), 1.77, 1.89, 1.91 and 1.92 (4 s, each 3 H, C_5Me_4), 1.82

and 2.56 (2 m, each 2 H, $CH_2CH_2CH_2O$), 2.94 and 3.22 (2 m, each 1 H, C_5HMe_4 and 1-H), 3.49 (t, J = 6.3 Hz, 2 H, CH_2OCH_2Ph), 4.44 (m, 2 H, OCH_2Ph), 6.13 (d, J = 1.6 Hz, 1 H, 2-H), 7.02–7.33 (m, 9 H, 5-H–8-H and OCH_2Ph) ppm. EI MS: m/z (%) = 442 (26) [M^+ , $\{Me_2Si[C_9H_6(CH_2CH_2CH_2OCH_2Ph)](C_5HMe_4)\}^+$], 321 (15) [M^+ – C_5HMe_4], 179 (100) [M^+ – $C_9H_6CH_2CH_2CH_2OCH_2Ph$].

Preparation of $\{Me_2Si[C_9H_6(CH_2CH=CH_2)-3]-1(C_5HMe_4)\}$ (7**):** The synthesis of **7** was carried out in an identical manner to **5**. $ClMe_2Si(C_5HMe_4)$ (3.97 g, 10.15 mmol) and $Li[C_9H_6(CH_2CH=CH_2)-1]$ (**10a**) (1.64 g, 10.15 mmol). Yield 2.55 g, 75%. 1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = –0.59 and –0.28 (2 s, each 3 H, $SiMe_2$), 1.67, 1.72, 1.84 and 1.88 (4 s, each 3 H, C_5Me_4), 2.88 and 3.20 (2 m, each 1 H, C_5HMe_4 and 1-H), 3.22 (m, 2 H, $CH_2CH=CH_2$), 5.06 (m, 2 H, $CH_2CH=CH_2$), 5.87 (m, 1 H, $CH_2CH=CH_2$), 6.08 (d, J = 1.6 Hz, 1 H, 2-H), 7.00–7.27 (m, 4 H, 5-H–8-H) ppm. EI MS: m/z (%) = 334 (12) [M^+ , $\{Me_2Si[C_9H_6(CH_2CH=CH_2)](C_5HMe_4)\}^+$], 213 (41) [M^+ – C_5HMe_4], 179 (100) [M^+ – $C_9H_6CH_2CH=CH_2$].

Preparation of $\{Me_2Si[C_9H_6(CH_2CH_2CH_2OSiMe_2tBu)-3]-1(C_5HMe_4)\}$ (8**):** The synthesis of **8** was carried out in an identical manner to **5**. $ClMe_2Si(C_5HMe_4)$ (4.11 g, 16.98 mmol) and $Li[C_9H_6(CH_2CH_2CH_2OSiMe_2tBu)-1]$ (5.10 g, 16.98 mmol). Yield 5.35 g, 60%. 1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = –0.58 and –0.28 (2 s, each 3 H, $SiMe_2$), –0.05 (s, 6 H, $OSiMe_2tBu$), 0.80 (s, 9 H, $OSiMe_2tBu$), 1.74, 1.78, 1.87 and 1.89 (4 s, each 3 H, C_5Me_4), 1.82 and 2.54 (2 m, each 2 H, $CH_2CH_2CH_2O$), 2.93 and 3.39 (2 m, each 1 H, C_5HMe_4 and 1-H), 3.60 (t, J = 6.3 Hz, 2 H, CH_2OSiMe_2tBu), 6.10 (d, J = 1.6 Hz, 1 H, 2-H), 7.05–7.31 (m, 4 H, 5-H–8-H) ppm. EI MS: m/z (%) = 467 (25) [M^+ , $\{Me_2Si[C_9H_6(CH_2CH_2CH_2OSiMe_2tBu)](C_5HMe_4)\}^+$], 345 (35) [M^+ – C_5HMe_4], 179 (100) [M^+ – $C_9H_6CH_2CH_2CH_2OSiMe_2tBu$].

Preparation of $Li[C_9H_6(CH_2CH_2CH_2OSiMe_3)-1]$ (9**):** $nBuLi$ (1.60 M in hexane) (15.22 mL, 24.35 mmol) was added to a solution of **1** (5.00 g, 20.29 mmol) in Et_2O (100 mL) at –78 °C. The mixture was allowed to warm to 25 °C and stirred for 15 h. The solvent was removed in vacuo to give a yellow solid which was washed with hexane (2×50 mL) and dried under vacuum to yield a yellow solid of the title complex (4.35 g, 85%). $C_{15}H_{21}LiOSi$ (252.4): calcd. C 71.39, H 8.39; found C 71.03, H 8.30.

Preparation of $Li[C_9H_6(CH_2CH_2CH_2OCH_2Ph)-1]$ (10**):** The synthesis of **10** was carried out in an identical manner to **9**: **2** (5.25 g, 19.86 mmol) and $nBuLi$ (1.60 M in hexane) (14.90 mL, 23.83 mmol). Yield (3.49 g, 65%). 1H NMR (400 MHz, $C_6D_6/[D_8]-THF$, 25 °C): δ = 2.01 and 3.05 (2 m, each 2 H, $CH_2CH_2CH_2O$), 3.45 (t, J = 6.3 Hz, 2 H, CH_2OCH_2Ph), 4.19 (s, 2 H, CH_2OCH_2Ph), 6.08 and 6.58 (2 m, each 1 H, 3-H and 2-H), 6.77–7.62 (m, 9 H, 5-H–8-H and OCH_2Ph) ppm. $C_{19}H_{19}LiO$ (270.29): calcd. C 84.43, H 7.09; found C 84.63, H 7.07.

Preparation of $Li[C_9H_6(CH_2CH=CH_2)-1]$ (10a**):** The synthesis of **10a** was carried out in an identical manner to **9**: **2** (5.25 g, 33.60 mmol) and $nBuLi$ (1.60 M in hexane) (63.00 mL, 100.80 mmol). Yield (4.08 g, 75%). 1H NMR (400 MHz, $C_6D_6/[D_8]-THF$, 25 °C): δ = 3.75 (m, 2 H, $CH_2CH=CH_2$), 4.92 (m, 2 H, $CH_2CH=CH_2$), 6.20 (m, 1 H, $CH_2CH=CH_2$), 6.13 and 6.60 (2 m, each 1 H, 3-H and 2-H), 6.81–7.64 (m, 4 H, 5-H–8-H) ppm. $C_{12}H_{11}Li$ (162.2): calcd. C 88.88, H 6.84; found C 88.52, H 6.75.

Preparation of $Li[C_9H_6(CH_2CH_2CH_2OSiMe_2tBu)-1]$ (11**):** The synthesis of **11** was carried out in an identical manner to **9**: **3** (5.00 g, 17.33 mmol) and $nBuLi$ (1.60 M in hexane) (13.00 mL, 20.80 mmol). Yield (3.67 g, 72%). $C_{18}H_{27}LiOSi$ (294.4): calcd. C 73.43, H 9.24; found C 73.11, H 9.27.

Preparation of $\text{Li}_2[\text{Me}_2\text{Si}(\text{C}_9\text{H}_5\text{R}-3)_2-1]$ ($\text{R} = \text{CH}_2\text{CH}_2\text{CH}_2\text{OSiMe}_3$) (12): The synthesis of **12** was carried out in an identical manner to **9: 4** (5.00 g, 9.11 mmol) and *n*BuLi (1.60 M in hexane) (13.67 mL, 21.86 mmol). Yield (4.00 g, 78%). $\text{C}_{32}\text{H}_{46}\text{Li}_2\text{O}_2\text{Si}_3$ (560.8): calcd. C 68.53, H 8.27; found C 68.21, H 8.24.

Preparation of $\text{Li}_2[\text{Me}_2\text{Si}(\text{C}_9\text{H}_5\text{R}-3)-1(\text{C}_5\text{Me}_4)]$ ($\text{R} = \text{CH}_2\text{CH}_2\text{CH}_2\text{OSiMe}_3$) (13): The synthesis of **13** was carried out in an identical manner to **9: 5** (5.00 g, 11.77 mmol) and *n*BuLi (1.60 M in hexane) (17.65 mL, 28.25 mmol). Yield (4.16 g, 81%). $\text{C}_{26}\text{H}_{38}\text{Li}_2\text{OSi}_2$ (436.6): calcd. C 71.52, H 8.77; found C 71.33, H 8.71.

Preparation of $\text{Li}_2[\text{Me}_2\text{Si}[\text{C}_9\text{H}_5(\text{CH}_2\text{CH}_2\text{CH}_2\text{OLi})-3]-1(\text{C}_5\text{Me}_4)]$ (13a): The synthesis of **13a** was carried out in an identical manner to **9: 5** (5.00 g, 11.77 mmol) and *n*BuLi (1.60 M in hexane) (22.10 mL, 35.31 mmol). Yield (3.13 g, 72%). ^1H NMR (400 MHz, $\text{C}_6\text{D}_6/[\text{D}_8]\text{THF}$, 25 °C): $\delta = -0.30$ and -0.58 (2 s, each 3 H, *SiMe}_2*), 1.68, 1.70, 1.82 and 1.86 (4 s, each 3 H, *C}_5\text{Me}_4*), 1.76 and 2.59 (2 m, each 2 H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$), 3.53 (t, $J = 6.3$ Hz, 2 H, $\text{CH}_2\text{OSiMe}_3$), 6.14 (s, 1 H, 2-H), 6.98 (m, 2 H, 5-H, 8-H), 7.29 (m, 2 H, 6-H, 7-H) ppm. $\text{C}_{23}\text{H}_{29}\text{Li}_2\text{OSi}$ (370.40): calcd. C 74.58, H 7.89; found C 74.12, H 7.92.

Preparation of $\text{Li}_2[\text{Me}_2\text{Si}(\text{C}_9\text{H}_5\text{R}-3)-1(\text{C}_5\text{Me}_4)]$ ($\text{R} = \text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{Ph}$) (14): The synthesis of **14** was carried out in an identical manner to **9: 6** (5.00 g, 10.57 mmol) and *n*BuLi (1.60 M in hexane) (15.85 mL, 25.36 mmol). Yield (3.27 g, 68%). $\text{C}_{30}\text{H}_{36}\text{Li}_2\text{OSi}$ (454.6): calcd. C 79.27, H 7.98; found C 79.34, H 7.96.

Preparation of $\text{Li}_2[\text{Me}_2\text{Si}(\text{C}_9\text{H}_5\text{R}-3)-1(\text{C}_5\text{Me}_4)]$ ($\text{R} = \text{CH}_2\text{CH}=\text{CH}_2$) (15): The synthesis of **15** was carried out in an identical manner to **9: 7** (5.00 g, 14.95 mmol) and *n*BuLi (1.60 M in hexane) (22.43 mL, 35.88 mmol). Yield (4.14 g, 80%). $\text{C}_{23}\text{H}_{28}\text{Li}_2\text{Si}$ (346.4): calcd. C 79.74, H 8.15; found C 79.29, H 8.11.

Preparation of $\text{Li}_2[\text{Me}_2\text{Si}(\text{C}_9\text{H}_5\text{R}-3)-1(\text{C}_5\text{Me}_4)]$ ($\text{R} = \text{CH}_2\text{CH}_2\text{CH}_2\text{OSiMe}_2\text{tBu}$) (16): The synthesis of **16** was carried out in an identical manner to **9: 8** (5.00 g, 10.71 mmol) and *n*BuLi (1.60 M in hexane) (16.10 mL, 25.70 mmol). Yield (4.00 g, 78%). $\text{C}_{29}\text{H}_{44}\text{Li}_2\text{OSi}_2$ (478.7): calcd. C 72.76, H 9.26; found C 72.54, H 9.17.

Preparation of $[\text{Zr}\{\eta^5\text{-C}_9\text{H}_6(\text{CH}_2\text{CH}_2\text{CH}_2\text{OSiMe}_3)_2\text{Cl}_2]$ (17): Toluene (100 mL) was added to a solid mixture of ZrCl_4 (1.15 g, 4.95 mmol) and $\text{Li}[\text{C}_9\text{H}_6(\text{CH}_2\text{CH}_2\text{CH}_2\text{OSiMe}_3)_2-1]$ (**9**) (2.50 g, 9.90 mmol). The resulting pale yellow solution was stirred for 15 h. The mixture was filtered and the solvent removed in vacuo to yield a yellow oil of the title complex (1.87 g, 58%). ^1H NMR (300 MHz, CDCl_3 , 25 °C, two isomers): $\delta = 0.15$, 0.18 (2 s, each 18 H, $4\times\text{OSiMe}_3$), 1.60–2.00 and 2.60–3.15 (2 m, each 8 H, $4\times\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$), 3.45–3.80 (2 m, each 4 H, $4\times\text{CH}_2\text{OSiMe}_3$), 5.75 (d, $J = 3$ Hz, 2 H, *meso*-3-H), 5.88 (d, $J = 3$ Hz, 2 H, *rac*-3-H), 6.13 (d, $J = 3$ Hz, 2 H, *rac*-2-H), 6.37 (d, $J = 3$ Hz, 2 H, *meso*-2-H), 7.20–7.70 (m, 16 H, $4\times 5\text{-H-8-H}$) ppm. $^{13}\text{C}\{^1\text{H}\}$ (75 MHz, CDCl_3 , 25 °C, two isomers): $\delta = -0.3$ (OSiMe_3), 24.3 and 24.6 ($\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$), 30.5 ($\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$), 61.9 ($\text{CH}_2\text{OSiMe}_3$), 99.1 (*meso*-C-3), 99.29 (*rac*-C-3), 120.2 (*meso*-C-2), 121.8 (*rac*-C-2), 118.8–139.0 (C-5–C-8) (C-4, C-9 not observed) ppm. EI MS: m/z (%) = 652 (13) [$\text{M}^+ - \text{C}_9\text{H}_6\text{CH}_2\text{CH}_2\text{CH}_2\text{OSiMe}_3 - \text{Cl}_2$], 297 (100) [$\text{M}^+ - \text{C}_9\text{H}_6\text{CH}_2\text{CH}_2\text{CH}_2\text{OSiMe}_3 - \text{Cl}$]. $\text{C}_{30}\text{H}_{42}\text{Cl}_2\text{O}_2\text{Si}_2\text{Zr}$ (652.95): calcd. C 55.18, H 6.48; found C 55.36, H 6.45.

Preparation of $[\text{Zr}\{\eta^5\text{-C}_9\text{H}_6(\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{Ph})_2\text{Cl}_2]$ (18): The synthesis of **18** was carried out in identical manner to **17**. ZrCl_4 (1.16 g, 4.96 mmol) and $\text{Li}[\text{C}_9\text{H}_6(\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{Ph})_2-1]$ (**10**) (2.50 g, 9.91 mmol). Yield: 2.33 g, 68%. ^1H NMR (300 MHz,

CDCl_3 , 25 °C, two isomers): $\delta = 1.84$ –2.07 and 2.40–3.13 (2 m, each 8 H, $4\times\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$), 3.36–3.62 (m, 8 H, $4\times\text{CH}_2\text{OCH}_2\text{Ph}$), 4.03–4.58 (2 m, each 4 H, $4\times\text{OCH}_2\text{Ph}$), 5.68 (d, $J = 3$ Hz, 2 H, *meso*-3-H), 5.88 (d, $J = 3$ Hz, 2 H, *rac*-3-H), 6.10 (d, $J = 3$ Hz, 2 H, *rac*-2-H), 6.33 (d, $J = 3$ Hz, 2 H, *meso*-2-H), 7.14–7.68 (m, 36 H, $4\times 5\text{-H-8-H}$ and $4\times\text{OCH}_2\text{Ph}$) ppm. $^{13}\text{C}\{^1\text{H}\}$ (75 MHz, CDCl_3 , 25 °C, two isomers): $\delta = 24.4$ and 24.7 ($\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$), 29.9 ($\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$), 69.4 ($\text{CH}_2\text{OCH}_2\text{Ph}$), 72.9 (OCH_2Ph), 99.1 (*meso*-C-3), 99.3 (*rac*-C-3), 120.4 (*meso*-C-2), 122.0 (*rac*-C-2), 117.9–144.4 (C-5–C-8 and OCH_2Ph) (C-4, C-9 not observed) ppm. EI MS: m/z (%) = 688 (15) [$\text{M}^+ - \text{C}_9\text{H}_6\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{Ph} - \text{Cl}_2$], 388 (73) [$\text{M}^+ - \text{C}_9\text{H}_6\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{Ph} - \text{Cl}$], 261 (100) [$\text{M}^+ - \text{C}_9\text{H}_6\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{Ph} - 2\text{Cl} - \text{CH}_2\text{Ph}$]. $\text{C}_{38}\text{H}_{38}\text{Cl}_2\text{O}_2\text{Zr}$ (688.84): calcd. C 66.26, H 5.56; found C 66.46, H 5.52.

Preparation of $[\text{Zr}\{\eta^5\text{-C}_9\text{H}_6(\text{CH}_2\text{CH}_2\text{CH}_2\text{OSiMe}_2\text{tBu})_2\text{Cl}_2]$ (19): The synthesis of **19** was carried out in identical manner to **17**. ZrCl_4 (0.99 g, 4.25 mmol) and $\text{Li}[\text{C}_9\text{H}_6(\text{CH}_2\text{CH}_2\text{CH}_2\text{OSiMe}_2\text{tBu})_2-1]$ (**11**) (2.50 g, 8.49 mmol). Yield: 1.66 g, 53%. ^1H NMR (300 MHz, CDCl_3 , 25 °C, two isomers): $\delta = 0.03$, 0.05 (2 s, each 12 H, OSiMe_2), 0.89, 0.91 (2 s, each 18 H, OSiMe_2tBu), 1.57–1.87 and 2.62–3.04 (2 m, each 8 H, $4\times\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$), 3.57–3.71 (m, 8 H, $4\times\text{CH}_2\text{OSiMe}_2\text{tBu}$), 5.68 (d, $J = 3$ Hz, 2 H, *meso*-3-H), 5.84 (d, $J = 3$ Hz, 2 H, *rac*-3-H), 6.07 (d, $J = 3$ Hz, 2 H, *rac*-2-H), 6.30 (d, $J = 3$ Hz, 2 H, *meso*-2-H), 7.16–7.63 (m, 16 H, $4\times 5\text{-H-8-H}$) ppm. $^{13}\text{C}\{^1\text{H}\}$ (75 MHz, CDCl_3 , 25 °C, two isomers): $\delta = -5.2$ (OSiMe_2tBu), 24.1 and 24.4 ($\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$), 26.0 (OSiMe_2tBu), 32.3 ($\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$), 62.3 ($\text{CH}_2\text{OSiMe}_2\text{tBu}$), 99.0 (*meso*-C-3), 99.2 (*rac*-C-3), 120.39 (*meso*-C-2), 212.89 (*rac*-C-2), 120.5–139.3 (C-5–C-8) (C-4, C-9 not observed) ppm. EI MS: m/z (%) = 737 (15) [$\text{M}^+ - \text{Zr}(\text{C}_9\text{H}_6\text{CH}_2\text{CH}_2\text{CH}_2\text{OSiMe}_2\text{tBu})_2\text{Cl}_2$], 699 (14) [$\text{M}^+ - \text{Cl}$], 261 (100) [$\text{M}^+ - \text{C}_9\text{H}_6\text{CH}_2\text{CH}_2\text{CH}_2\text{OSiMe}_2\text{tBu} - \text{Cl} - \text{SiMe}_2\text{tBu}$]. $\text{C}_{36}\text{H}_{54}\text{Cl}_2\text{O}_2\text{Si}_2\text{Zr}$ (773.11): calcd. C 58.66, H 7.38; found C 58.39, H 7.33.

Preparation of $\text{rac-}[\text{Zr}(\text{Me}_2\text{Si}\{\eta^5\text{-C}_9\text{H}_5(\text{CH}_2\text{CH}_2\text{CH}_2\text{OSiMe}_3)_2-1,1'\}\text{Cl}_2]$ (20): Toluene (100 mL) was added to a solid mixture of $[\text{ZrCl}_4(\text{THF})_2]$ (2.06 g, 5.47 mmol) and $\text{Li}_2[\text{Me}_2\text{Si}[\text{C}_9\text{H}_5(\text{CH}_2\text{CH}_2\text{CH}_2\text{OSiMe}_3)_2-1,1']]$ (**12**) (3.09 g, 5.47 mmol). The resulting pale yellow solution was stirred for 15 h. The mixture was filtered and the filtrate concentrated (10 mL) and cooled to -30 °C to yield an orange solid of the title complex (1.16 g, 30%). ^1H NMR (500 MHz, CDCl_3 , 25 °C): $\delta = 0.09$ (s, 18 H, $2\times\text{OSiMe}_3$), 1.12 (s, 6 H, *SiMe}_2*), 1.77 and 2.86 (2 m, each 4 H, $4\times\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$), 3.55 (m, 4 H, $2\times\text{CH}_2\text{OSiMe}_3$), 5.81 (s, 2 H, $2\times 2\text{-H}$), 7.05 and 7.30 (2 t, $J = 8.6$ Hz, each 2 H, $2\times 6\text{-H}$ and 7-H), 7.40 and 7.53 (2 d, $J = 8.6$ Hz, each 2 H, $2\times 5\text{-H}$ and 8-H) ppm. $^{13}\text{C}\{^1\text{H}\}$ (75 MHz, CDCl_3 , 25 °C): $\delta = -1.2$ (*SiMe}_2*), -0.2 (OSiMe_3), 24.7, ($\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$), 32.9 ($\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$), 62.3 ($\text{CH}_2\text{OSiMe}_3$), 77.4 and 85.4 (C-1 and C-3) (C-4, C-9 not observed), 117.2 (C-2), 124.5, 124.9, 126.7 and 126.8 (C-5–C-8) ppm. $\text{C}_{32}\text{H}_{46}\text{Cl}_2\text{O}_2\text{Si}_2\text{Zr}$ (709.1): calcd. C 54.20, H 6.54; found C 54.35, H 6.57.

Preparation of $[\text{Zr}(\text{Me}_2\text{Si}\{\eta^5\text{-C}_9\text{H}_5(\text{CH}_2\text{CH}_2\text{CH}_2\text{OSiMe}_3)_2-1\}\eta^5\text{-C}_5\text{Me}_4)\text{Cl}_2]$ (21): Toluene (100 mL) was added to a solid mixture of $[\text{ZrCl}_4(\text{THF})_2]$ (2.46 g, 6.53 mmol) and $\text{Li}_2[\text{Me}_2\text{Si}[\text{C}_9\text{H}_5(\text{CH}_2\text{CH}_2\text{CH}_2\text{OSiMe}_3)_2-1(\text{C}_5\text{Me}_4)]]$ (**13**) (2.57 g, 6.53 mmol). The resulting pale yellow solution was stirred for 15 h. The mixture was filtered and the filtrate concentrated to 10 mL and cooled to -30 °C to yield yellow solid of the title complex (0.76 g, 20%). ^1H NMR (500 MHz, CDCl_3 , 25 °C): $\delta = 0.08$ (s, 9 H, OSiMe_3), 0.94 and 1.17 (2 s, each 3 H, *SiMe}_2*), 1.90, 1.94, 1.95 and 2.00 (4 s, each 3 H, *C}_5\text{Me}_4*), 1.98 and 3.00 (2 m, each 2 H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$), 3.63 (m, 2

H, $\text{CH}_2\text{OSiMe}_3$), 5.59 (s, 1 H, 2-H), 7.06 and 7.33 (2 t, $J = 8.6$ Hz, each 1 H, 6-H and 7-H), 7.45 and 7.57 (2 d, $J = 8.6$ Hz, each 1 H, 5-H and 8-H) ppm. $^{13}\text{C}\{^1\text{H}\}$ (125 MHz, CDCl_3 , 25 °C): $\delta = -0.5$ (OSiMe_3), 1.0 and 1.1 (SiMe_2), 12.1, 12.6, 14.6, 15.3 (C_5Me_4), 24.9 ($\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$), 32.7 ($\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$), 62.1 ($\text{CH}_2\text{OSiMe}_3$), 116.3 (C-2), 124.3 and 125.4 (C-5 and C-8), 126.1 and 126.3 (C-6 and C-7), 84.3, 95.6, (C-1, C-3) (C-4, C-9 not observed), 124.0–135.3 (C_5Me_4) ppm. $\text{C}_{26}\text{H}_{38}\text{Cl}_2\text{OSi}_2\text{Zr}$ (584.9): calcd. C 53.39, H 6.55; found C 53.22, H 6.52.

Preparation of $[\text{Zr}(\text{Me}_2\text{Si}\{\eta^5\text{-C}_9\text{H}_5(\text{CH}_2\text{CH}_2\text{CH}_2\text{O})\text{-3}\}\text{-1}\{\eta^5\text{-C}_5\text{Me}_4\})\text{Cl}(\text{Zr-O})]$ (21a): The synthesis of **21a** was carried out in identical manner to **21**. $\text{Li}_2\{\text{Me}_2\text{Si}[\text{C}_9\text{H}_5(\text{CH}_2\text{CH}_2\text{CH}_2\text{OSiMe}_3)\text{-3}\}\text{-1}(\text{C}_5\text{HMe}_4)\}$ (**13a**) (2.42 g, 6.53 mmol) and $[\text{ZrCl}_4(\text{THF})_2]$ (2.46 g, 6.53 mmol). Yield: 0.29 g, 29%. ^1H NMR (500 MHz, CDCl_3 , 25 °C): $\delta = 0.86$ and 1.00 (2 s, each 3 H, SiMe_2), 1.64, 1.82, 1.86 and 2.01 (4 s, each 3 H, C_5Me_4), 1.82 and 2.96 (2 m, each 2 H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$), 3.95 (m, 2 H, CH_2O), 5.91 (s, 1 H, 2-H), 6.94 and 7.18 (2 t, $J = 8.6$ Hz, each 1 H, 6-H and 7-H), 7.34 and 7.41 (2 d, $J = 8.6$ Hz, each 1 H, 5-H and 8-H) ppm. $^{13}\text{C}\{^1\text{H}\}$ (125 MHz, CDCl_3 , 25 °C): $\delta = 0.0$ and 0.6 (SiMe_2), 9.8, 10.9, 13.2 and 13.3 (C_5Me_4), 24.5 ($\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$), 29.6 ($\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$), 68.9 (CH_2O), 114.4 (C-2), 122.4 and 123.6 (C-5 and C-8), 124.2 and 124.3 (C-6 and C-7), 89.2, 98.4 (C-1, C-3) (C-4, C-9 not observed), 120.0–130.9 (C_5Me_4) ppm. $\text{C}_{23}\text{H}_{29}\text{ClOSiZr}$ (476.2): calcd. C 58.01, H 6.14; found C 58.31, H 6.12.

Preparation of $[\text{Zr}(\text{Me}_2\text{Si}\{\eta^5\text{-C}_9\text{H}_5(\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{Ph})\text{-3}\}\text{-1}\{\eta^5\text{-C}_5\text{Me}_4\})\text{Cl}_2]$ (22): The synthesis of **22** was carried out in identical manner to **21**. $\text{Li}_2\{\text{Me}_2\text{Si}[\text{C}_9\text{H}_5(\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{Ph})\text{-3}\}\text{-1}(\text{C}_5\text{HMe}_4)\}$ (**14**) (1.96 g, 5.65 mmol) and $[\text{ZrCl}_4(\text{THF})_2]$ (2.13 g, 5.65 mmol). Yield: 0.86 g, 26%. ^1H NMR (500 MHz, CDCl_3 , 25 °C): $\delta = 0.89$ and 1.09 (2 s, each 3 H, SiMe_2), 1.80, 1.87, 1.90 and 1.94 (4 s, each 3 H, C_5Me_4), 1.89 and 2.98 (2 m, each 2 H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$), 3.44 (m, 2 H, $\text{CH}_2\text{OCH}_2\text{Ph}$), $\delta_A = 4.50$, $\delta_B = 4.48$ (AB, $J_{AB} = 12.3$ Hz, 2 H, OCH_2Ph), 5.50 (s, 1 H, 2-H), 6.98 and 7.25 (2 t, $J = 8.6$ Hz, each 1 H, 6-H and 7-H), 7.41 and 7.52 (2 d, $J = 8.6$ Hz, each 1 H, 5-H and 8-H), 7.21–7.30 (m, 5 H, OCH_2Ph) ppm. $^{13}\text{C}\{^1\text{H}\}$ (125 MHz, CDCl_3 , 25 °C): $\delta = 1.1$ and 1.4 (SiMe_2), 12.3, 12.5, 14.7, 15.3 (C_5Me_4), 25.2 ($\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$), 29.9 ($\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$), 72.9 ($\text{CH}_2\text{OCH}_2\text{Ph}$), 77.4 (OCH_2Ph), 116.4 (C-2), 124.3 and 125.4 (C-5 and C-8), 126.2 and 126.3 (C-6 and C-7), 84.5, 95.6 (C-1, C-3) (C-4, C-9 not observed), 124.0–138.5 (C_5Me_4) ppm. $\text{C}_{30}\text{H}_{36}\text{Cl}_2\text{OSiZr}$ (602.8): calcd. C 59.77, H 6.02; found C 59.51, H 5.95.

Preparation of $[\text{Zr}(\text{Me}_2\text{Si}\{\eta^5\text{-C}_9\text{H}_5(\text{CH}_2\text{CH}=\text{CH}_2)\text{-3}\}\text{-1}\{\eta^5\text{-C}_5\text{Me}_4\})\text{Cl}_2]$ (23): The synthesis of **23** was carried out in identical manner to **21**. $\text{Li}_2\{\text{Me}_2\text{Si}[\text{C}_9\text{H}_5(\text{CH}_2\text{CH}=\text{CH}_2)\text{-3}\}\text{-1}(\text{C}_5\text{HMe}_4)\}$ (**15**) (2.59 g, 7.47 mmol) and $[\text{ZrCl}_4(\text{THF})_2]$ (2.82 g, 7.47 mmol). Yield: 0.85 g, 23%. ^1H NMR (500 MHz, CDCl_3 , 25 °C): $\delta = 0.93$ and 1.17 (2 s, each 3 H, SiMe_2), 1.84, 1.93, 1.94 and 2.00 (4 s, each 3 H, C_5Me_4), $\delta_A = 3.72$, $\delta_A' = 3.68$ (AA'BB'C, $J_{AA'} = 16.4$ Hz, 2 H, $\text{CH}_2\text{CH}=\text{CH}_2$), $\delta_B = 5.06$, $\delta_B' = 5.09$ (AA'BB'C, $J_{BB'} = 1.1$, $J_{BC} = 2.4$, $J_{BC'} = 10$ Hz, 2 H, $\text{CH}_2\text{CH}=\text{CH}_2$), 5.61 (s, 1 H, 2-H), $\delta_C = 5.98$ (AA'BB'C, $J_{AC} = J_{A'C} = 6.3$ Hz, 1 H, $\text{CH}_2\text{CH}=\text{CH}_2$), 7.05 and 7.34 (2 t, $J = 8.6$ Hz, each 1 H, 6-H and 7-H), 7.47 and 7.57 (2 d, $J = 8.6$ Hz, each 1 H, 5-H and 8-H) ppm. $^{13}\text{C}\{^1\text{H}\}$ (125 MHz, CDCl_3 , 25 °C): $\delta = 1.1$ and 1.4 (SiMe_2), 12.1, 12.5, 14.9, 15.3 (C_5Me_4), 33.4 ($\text{CH}_2\text{CH}=\text{CH}_2$), 116.3 ($\text{CH}_2\text{CH}=\text{CH}_2$), 136.0 ($\text{CH}_2\text{CH}=\text{CH}_2$), 117.1 (C-2), 124.3 and 125.5 (C-5 and C-8), 126.4 and 126.5 (C-6 and C-7), 84.5, 98.3 (C-1, C-3) (C-4, C-9 not observed), 124.1–137.0 (C_5Me_4) ppm. $\text{C}_{23}\text{H}_{28}\text{Cl}_2\text{SiZr}$ (494.7): calcd. C 55.84, H 5.71; found C 55.92, H 5.73.

Preparation of $[\text{Zr}(\text{Me}_2\text{Si}\{\eta^5\text{-C}_9\text{H}_5(\text{CH}_2\text{CH}_2\text{CH}_2\text{OSiMe}_2\text{tBu})\text{-3}\}\text{-1}\{\eta^5\text{-C}_5\text{Me}_4\})\text{Cl}_2]$ (24): The synthesis of **24** was carried out in identical

manner to **21**. $\text{Li}_2\{\text{Me}_2\text{Si}[\text{C}_9\text{H}_5(\text{CH}_2\text{CH}_2\text{CH}_2\text{OSiMe}_2\text{tBu})\text{-3}\}\text{-1}(\text{C}_5\text{HMe}_4)\}$ (**16**) (2.56 g, 5.36 mmol) and $[\text{ZrCl}_4(\text{THF})_2]$ (2.02 g, 5.36 mmol). Yield: 1.00 g, 30%. ^1H NMR (500 MHz, CDCl_3 , 25 °C): $\delta = 0.08$ (s, 6 H, OSiMe_2tBu), 0.96 and 1.18 (2 s, each 3 H, SiMe_2), 0.90 (s, 9 H, OSiMe_2tBu), 1.90, 1.93, 1.94 and 2.00 (4 s, each 3 H, C_5Me_4), 1.85 and 3.02 (2 m, each 2 H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$), 3.64 (m, 2 H, $\text{CH}_2\text{OSiMe}_2\text{tBu}$), 5.61 (s, 1 H, 2-H), 7.05 and 7.33 (2 t, $J = 8.6$ Hz, each 1 H, 6-H and 7-H), 7.48 and 7.60 (2 d, $J = 8.6$ Hz, each 1 H, 5-H and 8-H) ppm. $^{13}\text{C}\{^1\text{H}\}$ (125 MHz, CDCl_3 , 25 °C): $\delta = -5.0$ (OSiMe_2tBu), 1.4 and 1.7 (SiMe_2), 12.4, 12.7, 14.9, 15.5 (C_5Me_4), 25.1 ($\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$), 26.2 and 18.6 (OSiMe_2tBu), 33.1 ($\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$), 62.8 ($\text{CH}_2\text{OSiMe}_2\text{tBu}$), 116.7 (C-2), 124.6 and 125.7 (C-5 and C-8), 126.3 and 126.5 (C-6 and C-7), 84.6, 95.9 (C-1, C-3) (C-4, C-9 not observed), 119.2–138.1 (C_5Me_4) ppm. $\text{C}_{29}\text{H}_{44}\text{Cl}_2\text{OSi}_2\text{Zr}$ (627.0): calcd. C 55.56, H 7.07; found C 55.61, H 7.08.

Preparation of $[\text{Zr}(\text{Me}_2\text{Si}\{\eta^5\text{-C}_9\text{H}_5(\text{CH}_2\text{CH}_2\text{CH}_2\text{O})\text{-3}\}\text{-1}\{\eta^5\text{-C}_5\text{Me}_4\})\text{Me}(\text{Zr-O})]$ (25): The synthesis of **25** was carried out in identical manner to **26**. MgMeBr (3 M in THF) (0.21 mL, 0.63 mmol) and **21a** (0.30 g, 0.63 mmol). Yield: 0.24 g, 83%. ^1H NMR (500 MHz, C_6D_6 , 25 °C): $\delta = -1.13$ (s, 3 H, Zr-Me), 0.67 and 0.71 (2 s, each 3 H, SiMe_2), 1.70, 1.84, 1.87 and 2.03 (4 s, each 3 H, C_5Me_4), 1.56 and 2.65 (2 m, each 2 H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$), 3.89 (m, 2 H, CH_2O), 5.97 (s, 1 H, 2-H), 6.91 and 7.14 (2 t, $J = 8.6$ Hz, each 1 H, 6-H and 7-H), 7.32 and 7.36 (2 d, $J = 8.6$ Hz, each 1 H, 5-H and 8-H) ppm. $^{13}\text{C}\{^1\text{H}\}$ (125 MHz, C_6D_6 , 25 °C): $\delta = -3.1$ and -3.0 (SiMe_2), 10.7, 11.8, 14.0 and 14.6 (C_5Me_4), 24.5 (Zr-Me), 25.9 ($\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$), 32.0 ($\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$), 68.3 (CH_2O), 115.7 (C-2), 123.9 and 124.0 (C-5 and C-8), 126.1 and 126.2 (C-6 and C-7), 82.20, 93.11 (C-1, C-3) (C-4, C-9 not observed), 117.66–128.74 (C_5Me_4) ppm. $\text{C}_{24}\text{H}_{32}\text{OSiZr}$ (455.8): calcd. C 63.24, H 7.08; found C 63.34, H 7.09.

Preparation of $[\text{Zr}(\text{Me}_2\text{Si}\{\eta^5\text{-C}_9\text{H}_5(\text{CH}_2\text{CH}_2\text{CH}_2\text{OSiMe}_2\text{tBu})\text{-3}\}\text{-1}\{\eta^5\text{-C}_5\text{Me}_4\})\text{Me}_2]$ (26): MgMeBr (3 M in THF) (0.38 mL, 1.15 mmol) was added to a solution of **24** (0.30 g, 0.48 mmol) in THF (50 mL) at -78 °C. The reaction mixture was allowed to warm to room temperature and stirred for 4 h. The solvent was removed in vacuo and hexane (25 mL) added. The mixture was filtered and the solvent was removed from the filtrate in vacuo to yield the title complex (0.24 g, 87%). ^1H NMR (500 MHz, C_6D_6 , 25 °C): $\delta = -1.42$ and -0.36 (2 s, each 3 H, Zr-Me), 0.04 (s, 6 H, OSiMe_2tBu), 0.98 and 1.83 (2 s, each 3 H, SiMe_2), 0.97 (s, 9 H, OSiMe_2tBu), 1.61, 0.50, 0.67 and 1.74 (4 s, each 3 H, C_5Me_4), 1.80 and 3.00 (2 m, each 2 H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$), 3.55 (m, 2 H, $\text{CH}_2\text{OSiMe}_2\text{tBu}$), 5.45 (s, 1 H, 2-H), 6.88 and 7.16 (2 t, $J = 8.6$ Hz, each 1 H, 6-H and 7-H), 7.26 and 7.57 (2 d, $J = 8.6$ Hz, each 1 H, 5-H and 8-H) ppm. $^{13}\text{C}\{^1\text{H}\}$ (125 MHz, C_6D_6 , 25 °C): $\delta = -5.0$ (OSiMe_2tBu), 11.5 and 25.5 (SiMe_2), 1.0, 1.3, 14.9, 18.4 (C_5Me_4), 24.6 ($\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$), 25.5 and 21.4 (OSiMe_2tBu), 33.7 ($\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$), 36.5 and 36.7 (Zr-Me), 62.3 ($\text{CH}_2\text{OSiMe}_2\text{tBu}$), 117.5 (C-2), 126.3 and 124.2 (C-5 and C-8), 124.0 and 127.7 (C-6 and C-7), 80.11, 90.38 (C-1, C-3) (C-4, C-9 not observed), 120.8–129.5 (C_5Me_4) ppm. $\text{C}_{31}\text{H}_{50}\text{OSi}_2\text{Zr}$ (586.1): calcd. C 63.52, H 8.60; found C 63.68, H 8.64.

X-ray Crystal-Structure Determination of $[(\text{Zr}\{\text{C}_9\text{H}_6(\text{CH}_2\text{CH}_2\text{CH}_2\text{O})\text{-1}\}\text{Cl}_2)_2(\text{Zr-O})]$ (17a): Intensity data were collected with a NONIUS-MACH3 diffractometer equipped with a graphite monochromator and a Mo- K_α radiation source ($\lambda = 0.71073$ Å) using an $\omega/2\theta$ -scan technique. The final unit-cell parameters were determined from 25 well-centered reflections and refined by least-squares methods. Data were corrected for Lorentz and polarization effects but not for absorption. The structure was solved by direct methods using the SHELXS computer program^[24]

and refined on F^2 by full-matrix least squares (SHELXL-97).^[25] All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were included in calculated positions and were refined with an overall isotropic temperature factor using a riding model. Weights were optimized in the final cycles. Crystallographic data are given in Table 4. CCDC-259059 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 4. Crystal data and structure refinement for **17a**.

Empirical formula	C ₁₂ H ₁₂ Cl ₂ OZr
Formula mass	334.34
T [K]	293(2)
Crystal system	orthorhombic
Space group	P_{bca}
a [Å]	12.2690(10)
b [Å]	13.4540(10)
c [Å]	14.4320(10)
V [Å ³]	2382.2(3)
Z	8
D_c [g cm ⁻³]	1.864
μ [mm ⁻¹]	1.345
$F(000)$	1328
Crystal dimensions [mm]	0.3 × 0.2 × 0.1
θ range [°]	2.65 to 24.27
hkl ranges	$0 \leq h \leq 14, 0 \leq k \leq 15, 0 \leq l \leq 17$
No. of reflections measured	2096
Reflections observed	1084
Goodness-of-fit on F^2	0.965
Final R indices [$I > 2\sigma(I)$] ^[a]	$R_1 = 0.0522, wR_2 = 0.1015$
Largest difference peak [e/Å ³]	0.509/−0.502

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma(w(F_o^2)^2)]^{0.5}$.

Homogeneous Polymerization Experiments: Polymerizations were carried out in a 1-L glass reactor using toluene as a solvent (250 mL). Catalysts (33 μ mol) were treated with the appropriate quantity of a solution of MAO in toluene (10% Al) for 15 min. Toluene (230 mL), TIBA scavenger (2 mL) and activated catalyst were introduced, in this order, into the reactor and the temperature was fixed at 343 K. The nitrogen was removed and a continuous flow of ethylene (1.5 bar) was introduced over 30 min. The reaction mixture was then quenched by the addition of acidified methanol. The polymer was collected by filtration, washed with methanol and dried under vacuum at room temperature for 24 h.

Heterogeneous Polymerization Experiments: The supported catalysts were prepared under an inert gas using Schlenk techniques and a glove-box. A solution of the zirconocene complex (quantity needed to obtain a theoretical level of 1% Zr/SiO₂) in toluene (30 mL) was added to partially dehydroxylated silica (1.00 g) and the mixture was stirred at 333 K for 16 h. The slurries were filtered through fritted discs and washed with toluene (10 × 20 mL). The resultant solids were carefully washed with toluene and dried under vacuum. Polymerizations were carried out in a 1-L glass reactor using toluene as a solvent (250 mL). The supported catalysts (approx. 300 mg) were treated with the appropriate quantity of a solution of MAO in toluene (10% Al) for 15 min. The solvent and the volatiles were removed in vacuo. Toluene (230 mL), TIBA scavenger (2 mL) and activated catalyst in freshly distilled toluene (20 mL) were introduced, in this order, into the reactor and the temperature was fixed at 343 K. The nitrogen was removed and a continuous flow of ethylene (1.5 bar) was introduced over 30 min.

The reaction mixture was then quenched by the addition of acidified methanol. The polymer was collected by filtration, washed with methanol and dried under vacuum at room temperature for 24 h.

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