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Titanacalixarenes in Homogeneous Catalysis: Synthesis, Conformation and Catalytic Activity in Ethylene Polymerisation

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Variously substituted titanacalixarenes were synthesised and tested for their performance as catalysts in ethylene polymerisation: *p-tert*-butylcalix[4]arene was derivatised to afford distal diether *p-tert*-butylcalix[4]arenes **L1**–**L4**, distal dihydroxy-depleted **L5**, proximal dihydroxy-depleted **L6**, proximal diether *p-tert*-butylcalix[4]arene **L7**, proximal intrabridged disiloxane **L8** and proximal monoether **L9**. (Dichlorotitana)-*p-tert*-butylcalix[4]arenes **1**–**8** and (monochlorotitana)-*p*-tertbutylcalix[4]arene **9** have been successfully synthesised by reacting **L1**–**L4** with $TiCl_4 \cdot 2THF$ or **L5**–**L9** with $TiCl_4$. The structural conformation of complexes **1**–**9** in solution were determined by ^1H NMR, ^{13}C NMR, NOESY and COSY spectroscopic studies. Compounds **2**, **3** and **4** have been structurally characterised by single-crystal X-ray diffraction. Upon activation with methylaluminoxane, compounds **1**–**8** revealed low to moderate activities for the production of high-density polyethylene (HDPE) to ultra-high-molecular-weight polyethylene (UHMWPE). **6/MAO** gave the best activity at 770 $kg_{PE}\,(mol\,Ti)^{-1}\,h^{-1}$.

Introduction

In the search for new homogeneous, heterogeneous or supported olefin polymerisation catalysts that are more active, the use of group 4 transition-metal complexes has undergone dramatic development over the past few decades. Numerous electronically flexible "molecular" or "surface" ligands have been coordinated to early transition metals.[1–10] The simultaneous use of σ- and π-donor atoms (i.e., N, O) has led to catalysts exhibiting remarkable performances in olefin polymerisation.

In the field of homogeneous catalysis Fujita et al. have reported bis(phenoxy–ether) catalysts, in which ligands contain both phenoxy and ether functionalities, exhibiting in some particular cases, very high[11] productivity of high-density polyethylene (HDPE). Various groups have reported new systems in which a group 4 metal is coordinated to at least one phenoxy ligand. Of particular interest with this type of ligand is the modification of the aryl framework as a way to tune catalytic performance by changing steric or electronic properties or the coordination mode to the metal. For instance, noncoordinating bridging moieties (i.e., methylene, ethylene) have been employed with the result of the catalytic activity being controlled by tuning of the O–M–O bite angle.[12,13] Furthermore, the activity can be highly increased when a donor atom (e.g., S, Te, P, N, O, etc.) is introduced as a bridge.[14] Schaverien et al.[15] used sterically hindered chelating binaphthoxy titanium catalysts showing moderate activity for the polymerisation of ethylene.

Interestingly, the surface of oxides (silica, alumina) has also been extensively used in industry to tune the activity and selectivity of supported group 4 metals,[16,17] and in particular titanium.[18] In this case, the surface of the oxide also supplies one or several O σ bonds and sometimes several O π bonds to the very oxophilic early transition metal with a reasonable control of the O–Ti–O bite angle. Many publications have also been devoted to silsesquioxanes as molecular models of these supported early-transition-metal catalysts.[19]

In this context, calixarenes that can provide variously substituted phenoxy and ether functionalities to a transition metal can serve as ideal ligands to generate new active catalysts or molecular models of heterogeneous catalysts: their corresponding phenoxy units can be easily tuned to modify their coordination mode, steric environment and electronic effect on the metal.[20] Interestingly, although they have been known to generate active catalysts with several transi-

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tion metals, such as Cr, V, and so forth,[21–25] calixarenes have hardly been employed with group 4 metals for the polymerisation of olefins. Matt et al. reported a new titanacalixarene complex in which the calixarene can provide two ether and two phenoxy ligands for the coordination with titanium dichloride. Upon methylaluminoxane (MAO) activation, the catalyst displayed activity in the production of ultra-high-molecular-weight polyethylene (UHMWPE).[26]

We aim to monitor the catalytic performances of titanium-based catalysts bearing calixarene ligands since these ligands present a number of advantages: (i) they can be easily derivatised to form different coordination modes, (ii) the flexibility of the backbone allows, in principle, a designed control of the steric bulk around the metal.

Two families of complexes differing by the relative position of the two Ti–O σ bonds have been designed: 1,2 versus 1,3 (or proximal vs. distal; see Figure 1: ***A***, ***B***, ***C*** vs. ***D***, ***E***, ***F***). For each of these configurations the remaining phenolic oxygen atoms can potentially be selectively etherified with the number of ether substituents varying between 0 and 3 (see Figure 1).

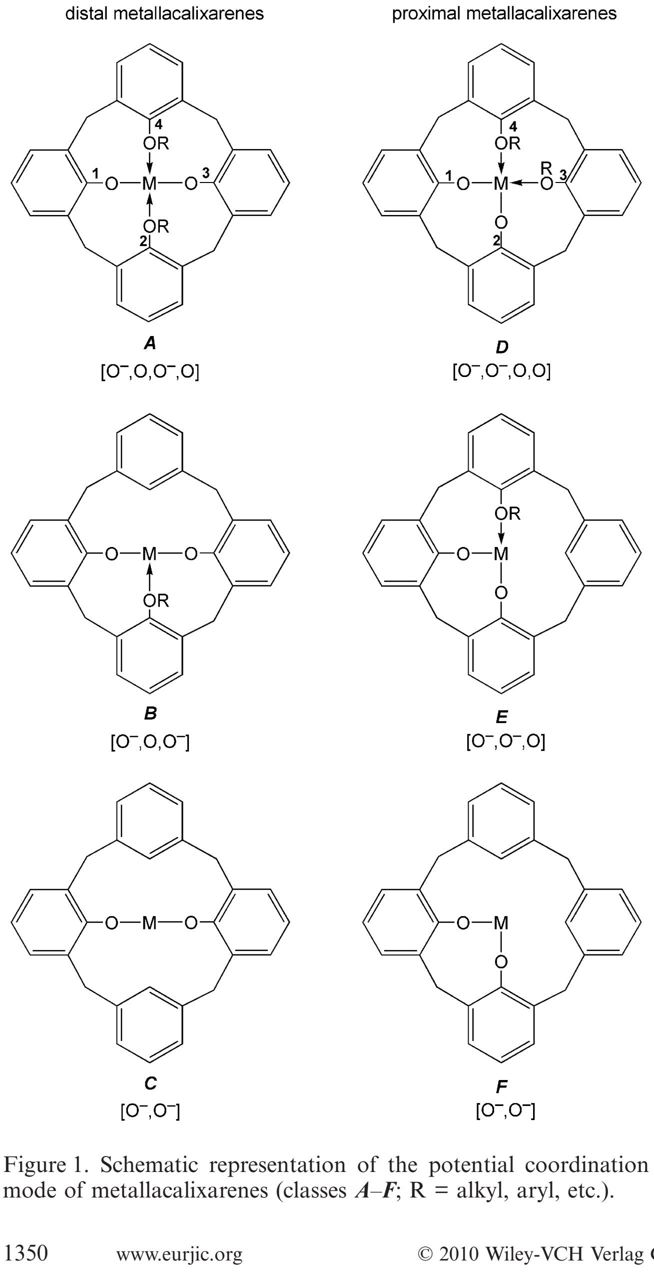


Figure 1. Schematic representation of the potential coordination mode of metallacalixarenes (classes ***A***–***F***; R = alkyl, aryl, etc.).

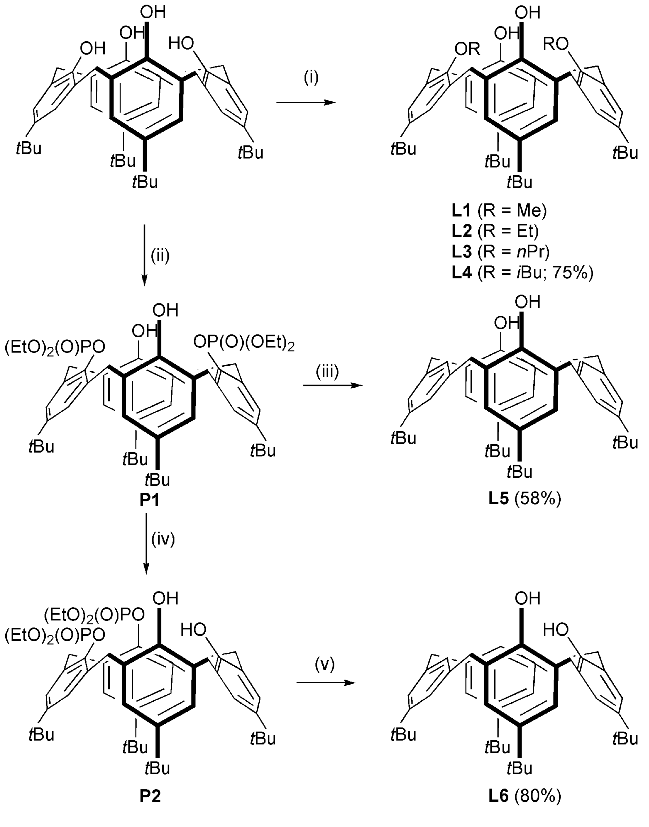
With the aim of understanding the role of steric hindrance, bite angle and coordination of titanium towards polymerisation of ethylene, we report the preparation and the characterisation of a series of new calixarene/titanium systems belonging to classes ***A***–***F***. Our attempts to prepare at least one member of each of this class have been partially successful. The performance of all the systems in the polymerisation of ethylene was assessed and the resulting polymers were characterised. A discussion of the relationship between the structure and the activity is provided when possible.

Results and Discussion

Synthesis of the Calix[4]arene Ligands

A series of proximal and distal *p-tert*-butylcalix[4]arene derivatives (**L1**–**L9**) have been prepared using different synthetic strategies with a view to being coordinated with titanium dichloride.

The 1,3-alkoxy-functionalised *p-tert*-butylcalix[4]arene compounds **L1**,[27] **L2**[28] and **L3**[29] (Scheme 1) have been synthesised following the classic procedure. The *p-tert*-but-



Scheme 1. Synthetic route for distal and proximal derivatised calix[4]arenes **L1**–**L6**. Reagents and conditions: (i) K_2CO_3, excess XI, CH_3CN, 82 °C, 16 h; (ii) NEt_3 (4 equiv.), $ClP(O)(OEt)_2$ (4 equiv.), toluene, room temp., 2 h; (iii) excess K, NH_3, diethyl ether, –78 °C, 1 h; (iv) 1.5 NaH, THF, 65 °C, 2 h; (v) K, NH_3, diethyl ether, –78 °C, 1 h.

ylcalix[4]arene was treated with K_2CO_3 as base in dry acetonitrile before addition of the corresponding haloalkane. After optimisation of the same protocol, a 1,3-diisobutoxy-*p-tert*-butylcalix[4]arene compound (**L4**) was prepared and isolated in an improved yield (75%).[30] The 1,3-diOH-depleted *p-tert*-butylcalix[4]arene (**L5**) was also synthesised by adapting the two-step methodology reported by Biali and co-workers.[31] Firstly, the diethyl diphosphate ester precursor **P1** was prepared by treatment of the *p-tert*-butylcalix[4]arene with $ClP(O)(OEt)_2$ and NEt_3 in toluene at room temperature in good yield (76%). Secondly, the reductive cleavage of the phosphate groups in the presence of potassium in liquid ammonia at –78 °C led to **L5**. The use of dichloromethane as an extraction solvent afforded an improved yield from 15 to 58%.

A new and easy method to synthesize the 1,2-diOH-depleted *p-tert*-butylcalix[4]arene **L6**[32] was developed (Scheme 1). Firstly, the proximal diethyl diphosphate ester precursor **P2** was obtained from the distal diethyl diphosphate ester precursor **P1** a in quantitative yield by phosphorotropic rearrangement as described by Markovsky et al.[33] Compound **P2** was then used without further purification to obtain **L6** (80% yield) by reductive cleavage of the phosphate groups. 1,2-Functionalised *p-tert*-butylcalix[4]arene compounds (**L7** and **L8**) have also been prepared by adapting the method described by Narumi et al.[34] The mono-OH-depleted monomethoxy-*p-tert*-butylcalix[4]arene (**L9**) was synthesised according to the method previously described by Fukazawa and co-workers.[35]

Synthesis of (Dichlorotitana)calix[4]arene Complexes

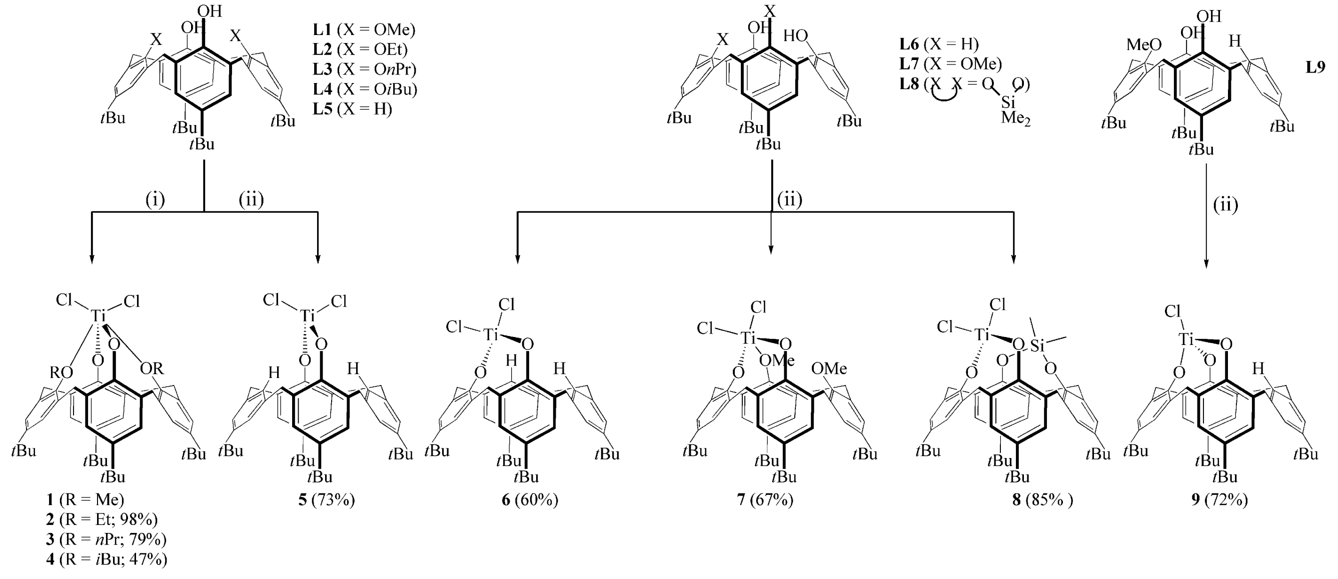
The 1,2- and 1,3-(dichlorotitana)-*p-tert*-butylcalix[4]arenes **1**–**8** have been synthesised in moderate to good yield (47–98%) by treating the corresponding calix[4]arene derivative with a tetrachlorotitanium precursor ($TiCl_4{\cdot}2THF$ or $TiCl_4$) at ambient temperature (Scheme 2). $TiCl_4$ was expected to be a better precursor for the synthesis of **5**–**9** than its corresponding THF adduct $TiCl_4{\cdot}2THF$, as it is assumed to afford the titanacalixarenes uncoordinated to any spectator ligand. All the corresponding complexes **1**–**8** were characterised by elemental analysis, with the conformation and coordination modes being determined using 1D and 2D ^{1}H and ^{13}C NMR spectroscopy (Figures S4–42 in the Supporting Information). Recrystallisation from toluene was attempted for all complexes, and resulted in crystals suitable for X-ray diffraction studies for **2**–**4**. To the best of our knowledge, **2** and **4**–**7** are new or unreported complexes. Characterisations of **1**,[36] **3**[26] and **8**[22,37] are consistent with literature data.

To obtain a monomethoxy-1,3-(dichlorotitana)-*p-tert*-butylcalix[4]arene complex, **L9** was treated with $TiCl_4$ to afford the unexpected tris-chelated (chlorotitana)calix[4]arene complex **9**.

Conformational Studies of (Dichlorotitana)-*p-tert*-Butylcalix[4]arenes (1–9)

The structure of the titanacalixarenes will be discussed based on the coordination modes of titanium and the conformation of the calixarene ligand using NMR spectroscopy and X-ray diffraction results.

Complexes 1–4: ^{1}H NMR spectra of **1**–**4** display a similar pattern of signals with two sets of doublets attributed to the methylene protons ($ArCH_2Ar$), consistent with the calixarene being in a cone conformation. Moreover, the sets of two signals for $C(CH_3)_3$ and for ArH and the signals for each proton of the alkoxyl chain are characteristic of C_{2v} symmetry. It is noteworthy that in the ^{1}H NMR spectrum



Scheme 2. Synthetic route for distal and proximal titanacalix[4]arenes **1**–**9**. Reagents and conditions: (i) $TiCl_4{\cdot}2THF$, toluene; (ii) $TiCl_4$, toluene.

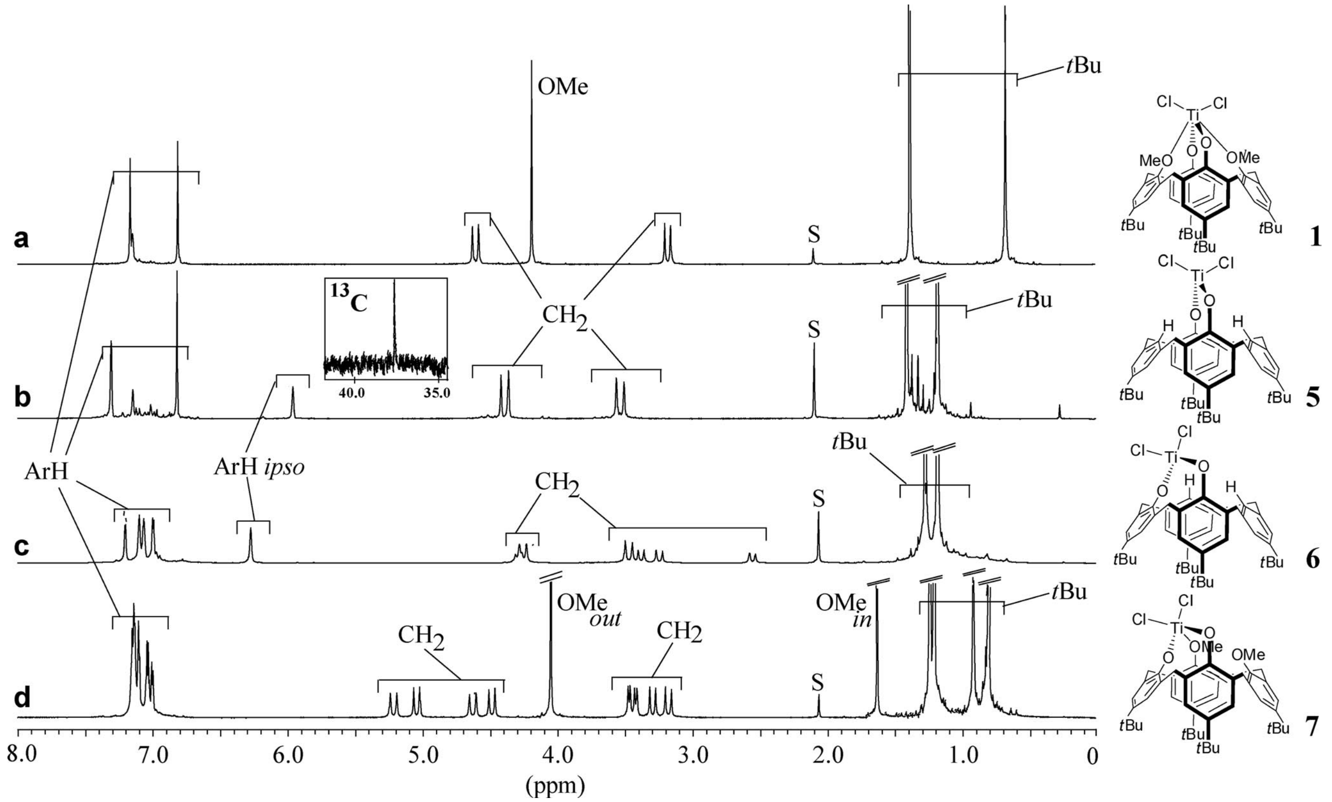


Figure 2. ^{1}H NMR spectra of complexes (a) **1**, (b) **5**, (c) **6** and (d) **7** recorded in C_6D_6 at 298 K. Residual solvent is noted "S".

of **1** (Figure 2, a) the methoxy groups are equivalent, as supported by a single singlet around 4.1 ppm. Finally, the significant shift ($\Delta\delta$) of the α protons of the alkoxy chains observed between the free ligands **L1**–**L4** and the corresponding complexes **1**–**4** indicates that the oxygen atoms of the alkoxy chains participate as ancillary ligands in the coordination with the titanium atom (Figure S43 in the Supporting Information).

Complexes **1**–**4** display original electronic features that can be attributed to both the electroattractivity of the titanium atom and the anisotropic effect due to the calixarene cavity and the chlorine atoms. Analysis of the chemical induced shift (CIS) observed in ^{1}H NMR spectra of the alkoxy chains of complexes **1**–**4** is presented in the Supporting Information. Suitable crystals of **2**–**4** were obtained by cooling saturated solutions of the complexes in toluene to –30 °C (Table S1 in the Supporting Information). The molecular structures of **2**–**4** have a similar arrangement (Figures 3, 4 and 5): the calixarene ligand adopts a cone conformation and is coordinated to a single titanium atom. Hexacoordinated titanium is thus bound to two phenoxy groups, two ether groups and two terminal chlorine atoms. The resulting geometry is a distorted octahedron (relevant distances and angles are reported in Table 1). The molecular structures of **2**–**4** have not been documented but that of **1** has previously been reported by Radius.[36] The O–Ti–O bite angle (a) lies in the same range for all the complexes with values consistent with those of **1** (i.e., $a = 94.83°$).

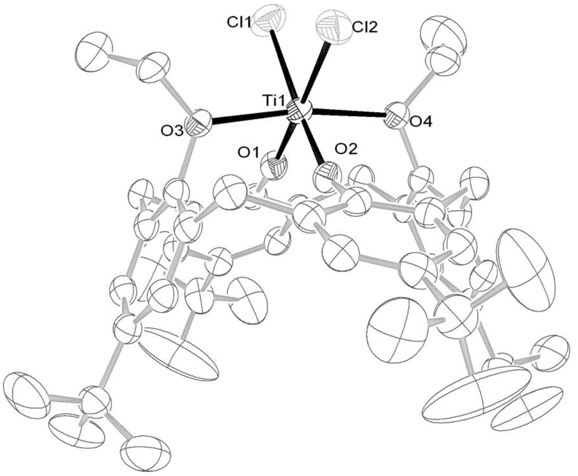


Figure 3. Molecular structure of **2** (only one of the two molecules of the unit cell is shown). For clarity H atoms and solvent molecules were omitted.

Complex 5: In the ^{13}C NMR spectrum, a single signal at $\delta = 38$ ppm is assigned to ArCH_2 (inset, Figure 2, b). This value is typical of calixarenes that have pairs of neighbouring phenoxy groups *anti*-oriented. The ^{1}H NMR spectrum displays three sets of two signals for the methylene, for the *t*Bu and for the ArH protons, which indicates a plane of symmetry in the structure (Figure 2, b). These observations led us to consider that complex **5** adopts a 1,3-alternated

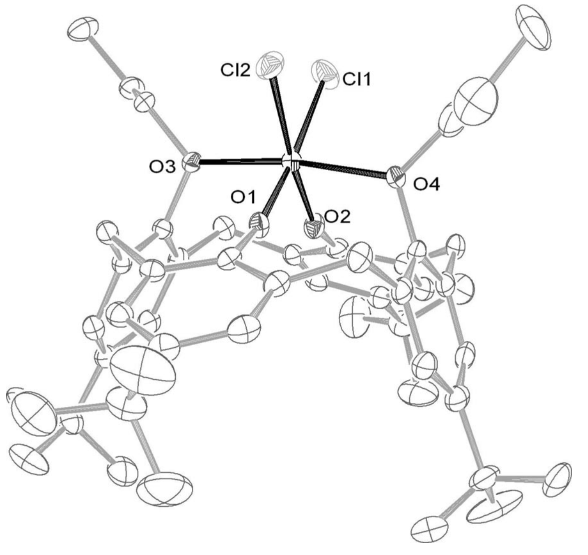


Figure 4. Molecular structure of **3** (only one of the two molecules of the unit cell is shown). For clarity H atoms and solvent molecules were omitted.

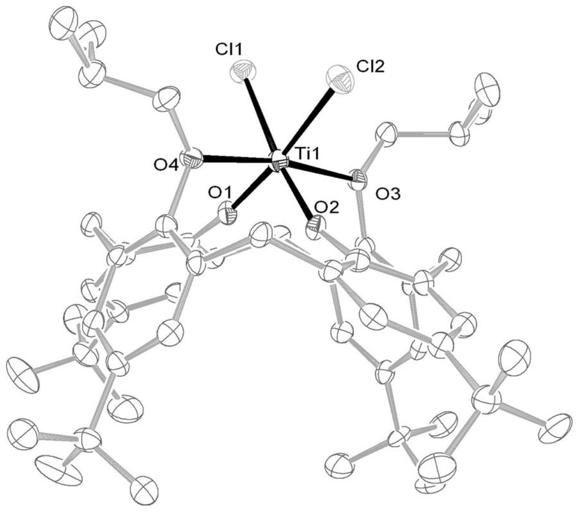


Figure 5. Molecular structure of **4** (only one of the two molecules of the unit cell is shown). For clarity H atoms and solvent molecules were omitted.

Table 1. Selected bonds lengths [Å] and bite angle [°] for **2**, **3** and **4**.

	2	**3**	**4**
Ti···O1	1.77(6)	1.78(6)	1.77(6)
Ti···O2	1.80(9)	1.81(0)	1.78(2)
Ti···O3	2.11(0)	2.12(2)	2.16(7)
Ti···O4	2.12(5)	2.09(7)	2.15(6)
Ti···Cl1	2.31(9)	2.34(0)	2.34(6)
Ti···Cl2	2.37(1)	2.36(9)	2.35(0)
O1–Ti–O2	95.3(2)	95.4(0)	97.0(7)

conformation.[38] This receives further support from 2D experiments as the NOESY spectrum of complex **5** reveals a spatial interaction between the *ipso* proton of one aryl group and the *meta* proton of its neighbouring aryl group, which confirms the 1,3-alternated conformation (Figures S29–30 in the Supporting Information).

Complex 6: The corresponding ligand **L6** (1,2-OH depleted), due to its high flexibility, is in a fast equilibrium, on the NMR spectroscopy timescale, between the cone and 1,2-alternated conformations.[32] In the ^{1}H NMR spectrum of complex **6**, two sets of signals that can be assigned to *t*Bu protons indicate a plane of symmetry in the complex. Moreover, the six sets of signals for the methylene protons (1,2,2,1,1,1 integration) and the four thin signals for ArH (2,2,2,2 + $2ArH_o$) confirm a frozen 1,2-alternated conformation (Figure 2, c). All the signals of **6** have been attributed by means of H–C correlation in 2D NMR spectroscopy. Finally, the NOESY spectrum of **6** shows a correlation between the proximal $C(CH_3)_3$ groups and is in full agreement with such a 1,2-alternated conformation. The conformational behaviour of **6** can be directly compared with the parent compound **8**, which was described in the same locked 1,2-alternated conformation.

Complex 7: The ^{1}H NMR spectrum signature of **7**, with a series of eight signals for the methylene protons, clearly indicates an asymmetrical species (Figure 2, d). Two singlets, at $\delta = 1.67$ and 4.09 ppm, can be assigned to the protons of the two methoxy groups of **L7**; the value of the latter is consistent with the oxygen of the methoxy group being coordinated to the titanium atom (OMe_{out}). The drastic upfield shift observed for the other methoxy group ($\Delta\delta = -2.2$ ppm) indicates that the corresponding aromatic ring remains uncoordinated and can undergo an inversion, thus orienting the OMe deep inside the cavity (OMe_{in}). 2D NMR spectroscopic investigations were undertaken to determine the conformation of **7** (Figures S38–39 in the Supporting Information). If it is assumed that the titanium atom is coordinated by the proximal alkoxyl units, calixarene **7** can adopt a partial cone conformation. This is in contrast with the ^{1}H NMR spectrum of the free ligand **L7** that adopts a classical cone conformation with only minor conformations being observed on the NMR timescale.[34]

Complex 9: In the case of monomethoxy-*p*-*tert*-butylcalix[4]arene **L9**, the titanium atom is close enough to the methoxy oxygen atom to substitute the methyl fragment and form an O–Ti σ bond, thus leading to complex **9**. This unexpected reactivity can be explained by the lack of stability provided by tris-chelating **L9** relative to the tetra-chelating ligands (**L1**–**L4**).

Using the classes of coordination modes introduced in Figure 1, the synthesized complexes can be ranked as follows: class ***A*** (**1**–**4**), class ***C*** (**5**), class ***E*** (**7**) and class ***F*** (**6** and **8**). It is noteworthy that the relative disposition of the alkoxy groups of the calixarene ligand appears to be highly influential towards the reactivity of the titanium metal centre, thus affecting the conformation and the coordination mode of the resulting titanacalixarene. For instance, the solid-state structure of class ***A*** (**1**–**4**) complexes shows that the titanium centre is tetra-chelated by the four oxygen atoms of the calixarene. The bis-chelated titanacalixarene of class ***C*** (**5**) has also been characterised by NMR spectroscopy. In contrast, the tris-chelating ligand (**L9**) provides a less stable titanacalixarene that can undergo σ-bond metathesis on the methoxy group to form **9**, which cannot be classified by our system.

The reactivity of proximal titanacalixarenes **6**–**8** seems to differ significantly from their distal counterparts. Whereas **6** belongs to class ***F*** as was originally targeted, the other proximal complexes **7** and **8** do not allow access to the targeted titanacalixarenes. For instance, **7** does not belong to the tetracoordinating class ***D*** for which it was designed, but seems to prefer a tris-chelating coordination mode (class ***E***). Complex **8** also could potentially be tetracoordinate but prefers a bis-chelating coordination mode.

Ethylene Polymerisation by Titanium Precatalyst/MAO Systems

The prepared (dichlorotitana)calixarene complexes (**1**–**8**) were screened for ethylene polymerisation under our standard conditions (Figure S44 in the Supporting Information). Table 2 summarises the activities that were observed with different complexes (**1**–**8/MAO**) while the experimental conditions were kept constant (P = 30 bar and T = 50 °C). In addition, **6/MAO** has been submitted to a series of runs in which both the temperature and the pressure of the test were systematically modified. The performance of the different catalysts will be first discussed before moving on to the optimisation of the polymerisation conditions.

Table 2. Ethylene polymerisation results for **1**–**8/MAO**.[a]

Entry	Catalyst precursor	Yield [g]	Activity[b]	M_n[c]	M_w/M_n	T_m[d] [°C]
1	**1**	0.028	14	2.9	2.7	132.0
2	**2**	0.034	16	2.7	2.5	132.4
3	**3**	0.045	21	3.2	2.9	131.8
4	**4**	0.033	16	2.3	3.0	131.4
5	**5**	0.388	185	2.6	3.3	133.2
6	**6**	0.735	350	1.4	5.4	134.6
7	**7**	0.174	83	n.d.[e]	n.d.[e]	133.6
8	**8**	0.238	113	1.7	4.4	137.4

[a] All polymerisation experiments were conducted at 50 °C under 30 bar of ethylene for 120 min, using the catalyst precursor (1.05 µmol) in toluene (50 mL). [Ti] = 2.1×10^{-5} M. [b] Average activity in $\mathrm{kg_{PE}(mol\,Ti)^{-1}\,h^{-1}}$ calculated over the whole polymerisation time (120 min). [c] Masses ($\times 10^6\,\mathrm{g\,mol^{-1}}$) were determined by HTSEC in 1,2,4-trichlorobenzene at 150 °C; measured with a relative calibration based on standard polystyrene. [d] Melting temperatures were determined by DSC (second heating). [e] n.d.: not determined.

Polymer Characterisation: For all runs (entries 1–8, Table 2), the melting temperatures (T_m) of the polymers are similar (from 131.4 to 134.6 °C). All systems produced a similar type of polyethylene (Figure S48 in the Supporting Information) consistent with the range observed for high-density polyethylene (HDPE) or UHMWPE.

The average molar mass (M_n) and the molar mass distribution (M_w/M_n) of PE measured with high-temperature size-exclusion chromatography (HTSEC) suggest the occurrence of two different types of catalytic performance. For **1**–**5/MAO** (entries 1–5, Table 2), the M_n values are the highest, ranging from 2.3×10^6 to $3.2 \times 10^6\,\mathrm{g\,mol^{-1}}$, which is typical of UHMWPE. In the case of **6/MAO** and **8/MAO**, the M_n values are significantly lower (1.4×10^6 and $1.7 \times 10^6\,\mathrm{g\,mol^{-1}}$, respectively), consistent with HDPE. It is well established that increased protection around the catalytically active centre hinders the rate of chain transfer thus leading to the production of higher molecular weights.[39] The variation observed in the centre of the molecular-weight distribution can be attributed to the different steric protection imparted by the calixarene backbone toward the titanium catalyst (**1**–**5/MAO** vs. **6**–**8/MAO**).

Catalyst Productivity: The activities observed for the polymerisation of ethylene span from 14 to 350 $\mathrm{kg_{PE}(mol\,Ti)^{-1}\,h^{-1}}$.

For **6**–**8/MAO** species, the titanium atom is supported in a proximal position by *p*-*tert*-butylcalix[4]arenes. In these cases, good catalytic activities for ethylene polymerisation have been observed (entries 6–8, Table 2), with **6/MAO** exhibiting the highest and unprecedented activity for titanacalixarene [350 $\mathrm{kg_{PE}(mol\,Ti)^{-1}\,h^{-1}}$]. Species **5/MAO** [185 kg $\mathrm{kg_{PE}(mol\,Ti)^{-1}\,h^{-1}}$], **8/MAO** [113 $\mathrm{kg_{PE}(mol\,Ti)^{-1}\,h^{-1}}$] and **7/MAO** [83 $\mathrm{kg_{PE}(mol\,Ti)^{-1}\,h^{-1}}$] show reduced activities, with **1**–**4/MAO** displaying comparably low activities of up to 21 $\mathrm{kg_{PE}(mol\,Ti)^{-1}\,h^{-1}}$ (entries 1–4, Table 2). These results suggest that a similar active species occurs in all four cases regardless of the nature of the alkoxy groups in distal positions. It appears that under these experimental conditions the steric effect of the various alkoxy ligands in distal positions affects neither the activities nor the polymer properties.

Influence of the Coordination Mode on the Catalytic Performance: In terms of the relative disposition of the titanacalixarene, the direct comparison between **5/MAO** and **6/MAO** suggests that proximal geometry leads to better activity that that of distal. It is noteworthy that, when comparing the bond angle O1–Ti–O2 of these titanium complexes, it is significantly larger in a proximal titanium calixarene such as **6**, with 106.4°, than in a distal counterpart (i.e., O1–Ti–O2 = 96.2° in **1**).[22] This means that **6** adopts a geometry closer to tetrahedral or distorted square planar in comparison with **5**, which seems to be close to octahedral. Species **5/MAO** (class ***C***) displays a much higher activity [185 $\mathrm{kg_{PE}(mol\,Ti)^{-1}\,h^{-1}}$] and leads to a higher molecular weight (entry 5, Table 2) relative to **1**–**4/MAO** (class *A*). This difference of behaviour is probably due to the octahedral geometry of **1**–**4**, which prevents olefin coordination after alkylation and Ti cation formation. In comparison, the coordinative unsaturations of **5**, especially after alkylation and cationic formation due to the presence of MAO, could lead to a highly unsaturated and very electrophilic titanium centre. In other words, the presence of two electron-donating oxygen atoms from the alkoxy groups, coordinated to the metal, increase both the coordination number and electron density of the titanium centre by π donation to the active site. Accordingly, these geometric and electronic parameters make the coordination of ethylene to the metal centre more difficult, which reduces the catalytic activity. In proximal systems (**6/MAO–8/MAO**) as in distal systems (**1/MAO–5/MAO**), increasing the number of the substituents on the proximal positions seems to also decrease the catalytic activity.[40]

Species **6/MAO**, due to its good performance, was retained to optimise the temperature and pressure conditions. Polymerisation was performed firstly at constant pressure (30 bar) while increasing the temperature from 50 to 80 °C (Table 3). In a second experiment, the temperature was maintained at 70 °C with different pressures ranging from 5 to 30 bar (Figures S45–46 in the Supporting Information). Finally, the initial activity was determined by shortening the length of the run to 15 min under the optimal conditions of pressure and temperature.

Table 3. Ethylene polymerisation results for **6/MAO**.[a]

Entry	T [°C]	P [bar]	Yield [g]	Activity[b]	M_n[c]	M_w/M_n	T_m[d] [°C]
1	50	30	0.735	350	1.4	5.4	134.6
2	60	30	1.23	586	2.3	3.5	136.6
3	70	30	1.62	770	1.0	4.9	133.9
4	80	30	1.45	690	0.6	3.0	134.9
5	70	5	0.11	52	0.6	5.9	133.9
6	70	10	0.28	131	0.8	3.9	134.0
7	70	20	0.82	390	1.3	3.5	134.0
8	70	30	1.62	770	1.0	4.7	135.5
9[e]	70	30	0.7	667	1.2	5.4	135.5

[a] All polymerisation experiments were conducted for 120 min, using catalyst precursor **6** (1.05 µmol) in toluene (50 mL). [Ti] = 2.1×10^{-5} M. [b] Average activity in $\mathrm{kg_{PE}\,(mol\,Ti)^{-1}\,h^{-1}}$ calculated over the whole polymerisation time (120 min). [c] Masses ($\times 10^6\ \mathrm{g\,mol^{-1}}$) were determined by HTSEC in 1,2,4-trichlorobenzene at 150 °C; measured with a relative calibration based on standard polystyrene. [d] Determined by DSC (first heating). [e] Run quenched after 15 min.

The activity of **6/MAO** was found to be maximal at 70 °C and 30 bar, giving an unprecedented value of 770 $\mathrm{kg_{PE}\,(mol\,Ti)^{-1}\,h^{-1}}$. A significant decrease in this value was observed at higher temperature, probably due to thermal decomposition. The produced PE seems to be largely unaffected by the change of temperature as T_m for all runs spans from 133.9 to 136.6 °C. However, M_n showed significant variation with the higher molecular weight ($2.3 \times 10^{-6}\ \mathrm{g\,mol^{-1}}$) produced at 60 °C and the lower at 80 °C (Table 3). This suggests that the rate of chain termination or chain transfer increases much faster than the chain propagation with the increase of polymerisation temperature.

The influence of the ethylene pressure on the activity was also studied at 70 °C. As the ethylene pressure was raised from 5 to 30 bar, both the yield and catalyst activity increased as expected for such systems (Table 3, entries 5–8).

Conclusion

A series of titanacalixarenes derivatives **1–9** was synthesised and characterised by NMR spectroscopy and single-crystal X-ray diffraction studies (for **2–4**) to determine their conformation and their coordination mode. Distal titanacalixarenes were identified as tetracoordinate, class ***A*** (**1–4**), or tricoordinate, class ***C*** (**5**). Proximal titanacalixarenes were tris-chelating, class ***E*** (**7**), and bis-chelating, class ***F*** (**6** and **8**). To evaluate the influence of the coordination sphere of the titanacalixarene on its catalytic activity, **1–8** were screened for ethylene polymerisation under our standard conditions. The difference in catalytic performance (i.e., activity and molecular-weight distribution) between the distal and the proximal calixarene (classes ***A*** and ***C*** vs. classes ***E*** and ***F***) derivatives suggests the formation of two different active species. This is probably due to the bite angle of O–Ti–O being wider. In both distal and proximal titanacalixarenes, increasing the number of ether oxygen atoms coordinated to the titanacalixarene decreases their productivity.

Experimental Section

General: All manipulations were carried out under a dry argon atmosphere using standard Schlenk techniques. All solvents were dried by standard methods and were freshly distilled before use. NMR spectra were recorded on DRX400 and DRX300 Bruker instruments. High-purity ethylene was purchased from Air Liquide and was dried with a deoxo catalyst (BASF R3-11 and 4-Å molecular sieves) prior to use.

General Procedure for Ethylene Polymerisations: Solid MAO was obtained by removing toluene and $\mathrm{AlMe_3}$ under vacuum at 50 °C overnight from a commercially available solution (10 wt.-%, Aldrich). A stock solution of MAO (100 $\mathrm{mg\,L^{-1}}$) was prepared by dissolving the resulting white solid in toluene and this was used for two weeks. All loadings were carried out in a glove box. Toluene (50 mL) and the MAO solution (0.9 mL, 100 $\mathrm{mg\,L^{-1}}$) were charged to a 80 mL autoclave. After 10 min, the precatalyst solution (1 mL, 1.05×10^{-3} M) was injected and the reactor was heated to the desired temperature. Under magnetic stirring, the desired ethylene pressure was established and kept constant for 120 min. The reaction was quenched by removing ethylene and pouring the mixture into a solution of EtOH (40 mL), H_2O (140 mL) and HCl (20 mL, 37%). After 2 h of being stirred, the resulting solid polymer was filtered off and washed successively with water (80 mL) and EtOH (80 mL) and dried at 50 °C under vacuum until the mass was constant.

Differential scanning calorimetry measurements for the determination of the melting transition temperature were performed on Perkin–Elmer Pyris 1 and Mettler DSC1 apparatus. Samples were heated from 40 to 150 °C at 5 $\mathrm{°C\,min^{-1}}$. In both cases, two successive heating and cooling cycles of the samples were performed. We have considered data obtained during the second run. High-temperature SEC analyses were performed using a Waters Alliance GPCV 2000 chromatograph equipped with three columns (PLgel Olexis 7 × 300 mm, Polymer Laboratories). Samples (1 $\mathrm{mg\,mL^{-1}}$) were eluted with trichlorobenzene with a flow rate of 1 $\mathrm{mL\,min^{-1}}$ at 150 °C. Online detection was performed by refractometry and viscosimetric measurements using Waters equipments. The system was calibrated with polystyrene standards in the range of 500 to 7106 $\mathrm{g\,mol^{-1}}$.

5,11,17,23-Tetra-*tert*-butyl-25,27-dihydroxy-26,28-bis[(2-methylpropyl)oxy]calix[4]arene (L4): *p-t*Bu-calix[4]arene (1.500 g, 2.311 mmol) and K_2CO_3 (0.352 g, 2.543 mmol) were suspended in dry CH_3CN (40 mL). *i*BuI (1.34 mL, 11.557 mmol) was then added and the mixture was stirred under reflux for 24 h. To complete the reaction, the same amounts of K_2CO_3 and *i*BuI were added again and the mixture was stirred under reflux for 24 h. After evaporation of the solvent, the residue was dissolved in CH_2Cl_2 (30 mL), washed twice with aqueous HCl (1 M) and brine and dried ($MgSO_4$). The solvent was removed under vacuum and the solid was washed with cold MeOH to give a white powder (1.317 g, 75%). ^{1}H NMR ($CDCl_3$, 300 MHz, 298 K): δ = 0.97 (s, 18 H, *t*Bu), 1.22 [d, ^3J(H,H) = 6.9 Hz, 12 H, *i*Bu], 1.27 (s, 18 H, $C\mathit{H}_3$-*t*Bu), 2.31 (m, 2 H, C*H*-*i*Bu), 3.28 [d, ^2J(H,H) = 12.9 Hz, 4 H, calix-$C\mathit{H}_2$], 3.73 [d, ^3J(H,H) = 6.0 Hz, 4 H, $C\mathit{H}_2$-*i*Bu], 4.28 [d, ^2J(H,H) = 12.9 Hz, 4 H, calix-CH_2], 6.82 (s, 4 H, Ar-H), 7.03 (s, 4 H, Ar-H), 7.79 (s, 2 H, OH) ppm. ^{13}C NMR (DEPT, HSQC, HMBC; $CDCl_3$, 125 MHz): δ = 19.47 (CH_3-*i*Bu), 29.39 (CH-*t*Bu), 31.02 (CH_3-*t*Bu), 31.70 (CH_3-*t*Bu, CH_2-calix), 33.77 (*t*Bu-quat), 33.92 (*t*Bu-quat), 82.97 (CH_2-*i*Bu), 124.96 (Ar-*meta*), 125.44 (Ar-*meta*), 127.60 (Ar-*ortho*), 132.68 (Ar-*ortho*), 141.16 (Ar-*para*), 146.68 (Ar-*para*), 159.72 (Ar-O), 150.99 (Ar-O) ppm. LRMS (ES$^+$): *m*/*z* = 783.5 [M + Na]$^+$. HRMS (ES$^+$): calcd. for $C_{52}H_{72}O_4Na$ [M + Na]$^+$ 783.5328; found 783.5327.

5,11,17,23-Tetra-*tert*-butyl-25,27-dihydroxy-26,28-bis[(diethoxyphosphanyl)oxy]calix[4]arene (P1): *p*-*t*Bu-calix[4]arene (5.000 g, 7.705 mmol) and NEt_3 (4.3 mL, 30.821 mmol) were dissolved in toluene (125 mL). $ClP(O)(OEt)_2$ (4.45 mL, 30.821 mmol) was added dropwise to the solution and the mixture was stirred for 60 h at room temperature. The resulting mixture was then successively washed with HCl (3 N), 10% NaOH and brine and dried with $MgSO_4$. After evaporation of the solvent, the residue was washed with cold MeOH to provide a white powder (5.393 g, 76%). ^{1}H NMR ($CDCl_3$, 300 MHz, 298 K): δ = 0.87 (s, 18 H, *t*Bu), 1.33 (s, 18 H, *t*Bu), 1.36 (m, 12 H, $OCH_2C\mathit{H}_3$), 3.41 [d, ^2J(H,H) = 14.0 Hz, 4 H, CH_2], 4.28 (m, 8 H, $OC\mathit{H}_2CH_3$), 4.40 [d, ^2J(H,H) = 14.0 Hz, 4 H, CH_2], 5.14 (s, 2 H, OH), 6.71 (s, 4 H, Ar-H), 7.13 (s, 4 H, Ar-H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz, 298 K): δ = 15.97 ($OCH_2\mathit{C}H_3$), 30.61 (CH_3-*t*Bu), 31.45 (CH_3-*t*Bu), 32.09 (-CH_2), 33.59 (*t*Bu-quat), 33.68 (*t*Bu-quat), 64.60 ($O\mathit{C}H_2CH_3$), 125.15 (Ar-*meta*), 125.79 (Ar-*meta*), 127.90 (Ar-*para*), 131.23 (Ar-*ortho*), 142.15 (Ar-*ortho*), 147.55 (Ar-O), 149.93 (Ar-O) ppm. ESI-MS: *m*/*z* = 921.2 [M + H]$^+$.

5,11,17,23-Tetra-*tert*-butyl-25,27-dihydroxycalix[4]arene (L5): Under argon, NH_3 was condensed over K (1.220 g, 31.267 mmol) at –78 °C to give a dark blue solution (100 mL). A solution of **P1** (4.800 g, 5.211 mmol) in of dry diethyl ether (30 mL) was added dropwise to the stirred blue solution. After 40 min, the reaction was slowly quenched with NH_4Cl until the blue colour was discharged and the ammonia solution became white. After evaporation of the ammonia, the residue was treated with CH_2Cl_2 (200 mL). After filtration of the salts, the filtrate was washed twice with water and dried with $MgSO_4$. After evaporation of the solvent, the residue was triturated and washed with cold MeOH to provide a white powder (1.852 g, 58%). ^{1}H NMR ($CDCl_3$, 300 MHz, 298 K): δ = 1.24 (s, 18 H, *t*Bu), 1.34 (s, 18 H, *t*Bu), 3.94 (s, 8 H, CH_2), 4.14 (s, 2 H, OH), 6.11 (s, 2 H, Ar-H-*ipso*), 6.99 (s, 4 H, Ar-H), 7.21 (s, 4 H, Ar-H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz, 298 K): δ = 31.41 (CH_3-*t*Bu), 31.59 (CH_3-*t*Bu), 33.85 (*t*Bu-quat), 34.54 (*t*Bu-quat), 37.37 (-CH_2), 122.40 (Ar-*ipso*), 123.86 (Ar-*meta*), 125.34 (Ar-*ortho*), 127.02 (Ar-*meta*), 140.39 (Ar-*ortho*), 143.10 (Ar-*para*), 150.24 (Ar-*para*), 151.45 (Ar-O) ppm. ESI-MS: *m*/*z* = 617.20 [M + H]$^+$.

5,11,17,23-Tetra-*tert*-butyl-25,26-dihydroxycalix[4]arene (L6): Under argon, NH_3 was condensed over K (2.300 g, 58.626 mmol) at –78 °C to give a dark blue solution (75 mL). A solution of **P2** (0.540 g, 0.586 mmol) in dry diethyl ether (10 mL) was added dropwise to the blue solution and the mixture was stirred for 1 h at –78 °C. After quenching of the solution with NH_4Cl until complete transformation of the blue solution into a white suspension, NH_3 was left to evaporate at room temperature. The resulting residue was extracted with CH_2Cl_2 (3 × 30 mL) and the filtrate was washed with water (70 mL), brine, dried with $MgSO_4$ and the solvents were evaporated. The solid was triturated with cold MeOH and filtered to provide a white solid (0.290 g, 80%). ^{1}H NMR (C_6D_6, 300 MHz, 298 K): δ = 1.25 (s, 18 H, *t*Bu), 1.31 (s, 18 H, *t*Bu), 3.07 (s, 2 H, CH_2), 3.90 (s, 2 H, CH_2), 3.94 (s, 4 H, CH_2), 6.24 (s, 2 H, OH), 6.53 (s, 2 H, Ar-H), 7.08–7.15 (m, 6 H, Ar-H), 7.40 [d, ^4J(H,H) = 2.4 Hz, 2 H, Ar-H] ppm. ^{13}C NMR DEPT (C_6D_6, 75 MHz, 298 K): δ = 31.48 (CH_3-*t*Bu), 31.74 (CH_3-*t*Bu), 32.18 (calix-CH_2), 34.17 (*t*Bu-quat), 34.57 (*t*Bu-quat), 38.14 (calix-CH_2), 42.69 (calix-CH_2), 123.51 (C_{Ar}), 124.03 (C_{Ar}), 125.03 (C_{Ar}), 126.61 (C_{Ar}), 126.74 (C_{Ar}; overlapped with C_6H_6), 128.00 (C_{Ar}), 128.84 (C_{Ar}), 140.06 (C_{Ar}), 142.92 (C_{Ar}), 143.99 (C_{Ar}), 149.63 (C_{Ar}), 151.46 (C_{Ar}) ppm. LRMS (ES$^-$): *m*/*z* = 615.6 [M – H]$^-$. HRMS (ES$^-$): calcd. for $C_{44}H_{55}O_2$ 615.4202; found 615.4200.

5,11,17,23-Tetra-*tert*-butyl-25,27-dioxo-26,28-diethyloxycalix[4]arenetitanium(IV) Dichloride (2): A slurry of **L2** (0.827 g, 1.173 mmol) and $TiCl_4\cdot 2THF$ (0.392 g, 1.173 mmol) in toluene (20 mL) was stirred for 24 h at 60 °C. After evaporation of the volatiles, the residue was washed with pentane (10 mL) to provide a dark red solid (0.971 g, 98%). ^{1}H NMR (C_6D_6, 300 MHz, 298 K): δ = 0.69 (s, 18 H, *t*Bu), 1.21 [t, ^3J(H,H) = 6.9 Hz, 6 H, $C\mathit{H}_3$-CH_2], 1.40 (s, 18 H, *t*Bu), 3.16 [d, ^2J(H,H) = 13.2 Hz, 4 H, calix-$C\mathit{H}_2$], 4.75 [d, ^2J(H,H) = 13.2 Hz, 4 H, calix-$C\mathit{H}_2$], 4.95 [q, ^3J(H,H) = 6.9 Hz, 4 H, CH_3-$C\mathit{H}_2$], 6.83 (s, 4 H, Ar-H), 7.16 (s, 4 H, Ar-H) ppm. ^{13}C NMR DEPT (C_6D_6, 75 MHz, 298 K): δ = 14.22 ($\mathit{C}H_3$-Et), 30.58 ($\mathit{C}H_3$-*t*Bu), 31.88 ($\mathit{C}H_3$-*t*Bu), 33.76 (*t*Bu-quat), 34.52 (*t*Bu-quat), 35.20 (CH_2-calix), 82.34 (CH_2-Et), 124.55 (Ar-*meta*), 127.20 (Ar-*meta*), 130.98 (Ar-*ortho*), 132.50 (Ar-*ortho*), 144.36 (Ar-*para*), 149.31 (Ar-*para*), 155.53 (Ar-O), 165.64 (Ar-O) ppm. Suitable crystals for X-ray analysis were obtained at –30 °C from a saturated solution in toluene. $C_{48}H_{62}Cl_2O_4Ti$ (821.18)·(toluene)$_{0.28}$: calcd. C 70.80, H 7.64; found C 70.71, H 7.49.

5,11,17,23-Tetra-*tert*-butyl-25,27-dioxo-26,28-dipropyloxycalix[4]arenetitanium(IV) Dichloride (3): A slurry of **L3** (0.595 g, 0.812 mmol) and $TiCl_4\cdot 2THF$ (0.271 g, 0.812 mmol) in toluene (10 mL) was stirred for 20 h at 60 °C. After evaporation of the volatiles, the residue was washed with pentane (2 × 5 mL) to provide a dark red solid (0.520 g, 79%). ^{1}H NMR (C_6D_6, 300 MHz, 298 K): δ = 0.32 [t, ^3J(H,H) = 7.2 Hz, 6 H, $C\mathit{H}_3$-CH_2-CH_2-O], 0.70 (s, 18 H, *t*Bu), 1.41 (s, 18 H, *t*Bu), 1.98 (m, 4 H, CH_3-$C\mathit{H}_2$-CH_2-O), 3.21 [d, ^2J(H,H) = 13.2 Hz, 4 H, calix-$C\mathit{H}_2$], 4.83 [d, ^2J(H,H) = 13.2 Hz, 4 H, calix-$C\mathit{H}_2$], 4.96 (m, 4 H, CH_3-CH_2-$C\mathit{H}_2$-O), 6.88 (s, 4 H, Ar-H), 7.20 (s, 4 H, Ar-H) ppm. ^{13}C NMR DEPT (C_6D_6, 75 MHz, 298 K): δ = 8.60 ($\mathit{C}H_3$-CH_2-CH_2-O), 21.52 (CH_3-$\mathit{C}H_2$-CH_2-O), 30.59 ($\mathit{C}H_3$-*t*Bu), 31.89 ($\mathit{C}H_3$-*t*Bu), 33.78 (*t*Bu-quat), 34.54 (*t*Bu-quat), 35.26 (CH_2-calix), 87.50 ($\mathit{C}H_3$-CH_2-$\mathit{C}H_2$-O), 124.59 (Ar-*meta*), 127.26 (Ar-*meta*), 130.98 (Ar-*ortho*), 132.45 (Ar-*ortho*), 144.45 (Ar-*para*), 149.40 (Ar-*para*), 156.22 (Ar-O), 165.68 (Ar-O) ppm. Suitable crystals for X-ray analysis were obtained at – 30 °C from a saturated solution in toluene. $C_{50}H_{66}Cl_2O_4Ti$ (848.38)·(toluene)$_{0.5}$: calcd. C 71.72, H 7.88; found C 71.72, H 7.78.

5,11,17,23-Tetra-*tert*-butyl-25,27-dioxo-26,28-bis[(2-methylpropyl)oxy]calix[4]arenetitanium(IV) Dichloride (4): A slurry of **L4** (2.000 g, 2.628 mmol) and $TiCl_4\cdot 2THF$ (0.878 g, 2.628 mmol) in toluene (40 mL) was stirred for 24 h at 60 °C. The solution was reduced and left to crystallise at –30 °C for two days. After filtration, a dark red solid was obtained (1.090 g, 47%). ^{1}H NMR (C_6D_6, 300 MHz, 298 K): δ = 0.68 (s, 18 H, *t*Bu), 0.77 [d, ^3J(H,H) = 6.9 Hz, 12 H, $(\mathrm{C}H_3)_2$-CH-$\mathrm{CH_2}$-O], 1.41 (s, 18 H, *t*Bu), 2.52 [m, 2 H, $(\mathrm{CH_3})_2$-C*H*-$\mathrm{CH_2}$-O], 3.22 [d, ^2J(H,H) = 13.0 Hz, 4 H, calix-$\mathrm{C}H_2$], 4.92 [d, ^2J(H,H) = 13.2 Hz, 4 H, calix-$\mathrm{C}H_2$], 4.99 [d, ^3J(H,H) = 6.0 Hz, 4 H, $(\mathrm{CH_3})_2$-CH-$\mathrm{C}H_2$-O], 6.85 (s, 4 H, Ar-H), 7.19 (s, 4 H, Ar-H) ppm. ^{13}C NMR DEPT (C_6D_6, 75 MHz, 298 K): δ = 20.56 [$(C\mathrm{H_3})_2$-CH-$\mathrm{CH_2}$-O], 28.10 [$(\mathrm{CH_3})_2$-*C*H-$\mathrm{CH_2}$-O], 30.56 ($C\mathrm{H_3}$-*t*Bu), 31.86 ($C\mathrm{H_3}$-*t*Bu), 33.73 (*t*Bu-quat), 34.52 (*t*Bu-quat), 35.33 ($\mathrm{CH_2}$-calix), 93.49 [$(\mathrm{CH_3})_2$-CH-$C\mathrm{H_2}$-O], 124.58 (Ar-*meta*), 127.26 (Ar-*meta*), 130.98 (Ar-*ortho*), 132.18 (Ar-*ortho*), 144.53 (Ar-*para*), 149.22 (Ar-*para*), 157.19 (Ar-O), 165.67 (Ar-O) ppm. Suitable crystals for X-ray analysis were obtained at –30 °C from a saturated solution in toluene. $C_{52}H_{70}Cl_2O_4Ti$ (876.41)·(toluene)$_2$: calcd. C 74.63, H 8.16; found C 74.31, H 7.78.

5,11,17,23-Tetra-*tert*-butyl-25,27-dioxocalix[4]arenetitanium(IV) Dichloride (5): A solution of **L5** (0.800 g, 1.297 mmol) in toluene (20 mL) was added dropwise at 0 °C to a solution of $TiCl_4$ [1.43 mL, 1 M in toluene (18 mL)] and the resulting red solution was stirred for 72 h at room temperature. After evaporation of the volatiles under vacuum, the red-brown residue was washed with pentane (15 mL + 10 mL) and dried to give an orange powder (0.690 g, 73%). ^{1}H NMR (NOESY, COSY; C_6D_6, 300 MHz, 298 K): δ = 1.19 (s, 18 H, *t*Bu), 1.42 (s, 18 H, *t*Bu), 3.54 [d, ^2J(H,H) = 16.7 Hz, 4 H, $\mathrm{C}H_2$], 4.40 [d, ^2J(H,H) = 16.7 Hz, 4 H, $\mathrm{C}H_2$], 5.96 (s, 2 H, Ar-H), 6.82 (s, 4 H, Ar-H), 7.31 (s, 4 H, $\mathrm{H_{Ar}}$) ppm. ^{13}C NMR DEPT (C_6D_6, 75 MHz, 298 K): δ = 30.50 ($C\mathrm{H_3}$-*t*Bu), 30.57 ($C\mathrm{H_3}$-*t*Bu), 33.39 (*t*Bu-quat), 33.72 (*t*Bu-quat), 36.83 ($C\mathrm{H_2}$-calix), 120.18 (*Ar-Hipso*), 125.14 (Ar-*meta*), 126.18 (Ar-*meta*), 128.42 (Ar-*ortho*), 137.76 (Ar-*ortho*), 147.30 (Ar-*para*), 150.12 (Ar-*para*), 166.32 (Ar-OTi) ppm. $C_{44}H_{54}Cl_2O_2Ti$ (732.30): calcd. C 72.03, H 7.42; found C 71.87, H 7.50.

5,11,17,23-Tetra-*tert*-butyl-25,26-dioxocalix[4]arenetitanium(IV) Dichloride (6): $TiCl_4$ (0.51 mL, 0.511 mmol, 1 M in toluene) was added dropwise to a solution of **L6** (0.300 g, 0.486 mmol) in toluene (40 mL) at –40 °C and the resulting mixture was allowed to reach room temperature overnight. After evaporation of the volatiles, the residue was washed with pentane (2 × 5 mL) and dried to provide a dark red solid (0.215 g, 60%). ^{1}H NMR (C_6D_6, 300 MHz, 298 K): δ = 1.22 (s, 18 H, *t*Bu), 1.31 (s, 18 H, *t*Bu), 2.61 [d, ^2J(H,H) = 13.0 Hz, 1 H, $\mathrm{CH_2}$], 3.28 [d, ^2J(H,H) = 14.0 Hz, 1 H, $\mathrm{CH_2}$], 3.42 [d, ^2J(H,H) = 13.0 Hz, 1 H, $\mathrm{CH_2}$], 3.50 [d, ^2J(H,H) = 15.6 Hz, 2 H, $\mathrm{CH_2}$], 4.29 (d, 2 H, $\mathrm{CH_2}$) overlapped with 4.32 (d, 1 H, $\mathrm{CH_2}$), 6.32 (s, 2 H, Ar-H), 7.04 [d, ^4J(H,H) = 1.6 Hz, 2 H, Ar-H], 7.11 (s, 2 H, Ar-H), 7.15 (s, 2 H, Ar-H), 7.24 [d, ^4J(H,H) = 1.6 Hz, 2 H, Ar-H] ppm. ^{13}C NMR (DEPT, NOESY, HSQC; C_6D_6, 125 MHz, 298 K): δ = 31.40 ($\mathrm{CH_3}$-*t*Bu), 31.56 ($\mathrm{CH_3}$-*t*Bu), 34.53 (*t*Bu-quat), 34.61 (*t*Bu-quat), 34.73 (calix-$\mathrm{CH_2}$), 37.97 (calix-$\mathrm{CH_2}$), 42.88 (calix-$\mathrm{CH_2}$), 123.14 ($\mathrm{C_{Ar}}$), 123.40 ($\mathrm{C_{Ar}}$), 123.84 ($\mathrm{C_{Ar}}$), 125.72 ($\mathrm{C_{Ar}}$), 126.74 ($\mathrm{C_{Ar}}$), 127.10 ($\mathrm{C_{Ar}}$), 137.25 ($\mathrm{C_{Ar}}$), 139.87 ($\mathrm{C_{Ar}}$), 142.58 ($\mathrm{C_{Ar}}$), 148.49 ($\mathrm{C_{Ar}}$), 151.44 ($\mathrm{C_{Ar}}$), 163.22 ($\mathrm{C_{Ar}}$) ppm. $C_{44}H_{54}Cl_2O_2Ti$ (732.30): calcd. C 72.03, H 7.42; found C 71.64, H 7.07.

5,11,17,23-Tetra-*tert*-butyl-25,26-dioxo-27,28-methyloxycalix[4]-arene Titanium(IV) Dichloride (7): $TiCl_4$ (0.38 mL, 0.377 mmol, 1 M in toluene) was added dropwise to a solution of **L7** (0.243 g, 0.359 mmol) in toluene (20 mL) at –40 °C and the resulting mixture was allowed to reach room temperature overnight. After evaporation of the volatiles, the residue was triturated in hot pentane (10 mL), filtered and dried to provide a dark red solid (0.190 g, 67%). ^{1}H NMR (C_6D_6, 300 MHz, 298 K): δ = 0.85 (s, 9 H, *t*Bu), 0.96 (s, 9 H, *t*Bu), 1.25 (s, 9 H, *t*Bu), 1.28 (s, 9 H, *t*Bu), 1.67 (s, 3 H, OMe), 3.21 [d, ^2J(H,H) = 13.2 Hz, 1 H, $\mathrm{CH_2}$], 3.33 [d, ^2J(H,H) = 13.6 Hz, 1 H, $\mathrm{CH_2}$], 4.47 [d, ^2J(H,H) = 14.8 Hz, 1 H, $\mathrm{CH_2}$], 3.49 [d, ^2J(H,H) = 15.2 Hz, 1 H, $\mathrm{CH_2}$], 4.09 (s, 3 H, OMe), 4.52 [d, ^2J(H,H) = 13.2 Hz, 1 H, $\mathrm{CH_2}$], 4.67 [d, ^2J(H,H) = 14.8 Hz, 1 H, $\mathrm{CH_2}$], 5.08 [d, ^2J(H,H) = 13.6 Hz, 1 H, $\mathrm{CH_2}$], 5.25 [d, ^2J(H,H) = 15.2 Hz, 1 H, $\mathrm{CH_2}$], 7.04–7.20 (m, 8 H, Ar-H) ppm. ^{13}C NMR

Table 4. Crystallographic data for **2**, **3** and **4**.

	2	**3**	**4**
Colour	dark brown	dark red	dark brown
Formula	$C_{48}H_{62}Cl_2O_4Ti\cdot 2(C_7H_8)$	$C_{50}H_{66}Cl_2O_4Ti\cdot 3(C_7H_8)$	$C_{52}H_{70}Cl_2O_4Ti\cdot 2(C_7H_8)$
Formula weight	1006.05	1126.30	1062.21
Crystal size [mm]	0.39 × 0.18 × 0.16	0.48 × 0.29 × 0.18	0.22 × 0.17 × 0.15
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$	$P2_1/c$
a [Å]	12.9019(6)	12.8768(6)	15.206(2)
b [Å]	19.0460(7)	25.2620(10)	18.120(3)
c [Å]	23.8319(14)	19.8828(9)	21.850(4)
α [°]	90	90	90
β [°]	100.103(5)	92.164(4)	94.93(2)
γ [°]	90	90	90
V [Å^3]	5765.4(5)	6463.1(5)	5998.1(17)
Z	4	4	4
T [K]	200	150	180
ρ [g cm^{-3}]	1.159	1.157	1.176
F(000)	2152	2416	2280
μ(Mo-K_α) [mm^{-1}]	2.44	0.261	0.277
Reflections collected	21858	43245	33503
Independent reflections	9745	15513	14226
R_{int}	0.054	0.050	0.140
Restraints/parameters	66/622	18/731	98/658
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.093	R_1 = 0.0655	R_1 = 0.0711
	wR_2 = 0.2691	wR_2 = 0.1823	wR_2 = 0.1213
Final R indices (all data)	R_1 = 0.1026	R_1 = 0.0898	R_1 = 0.2638
	wR_2 = 0.2895	wR_2 = 0.1972	wR_2 = 0.3362
Goodness-of-fit on F^2	1.062	0.8039	1.1942

(DEPT, NOESY; C_6D_6, 125 MHz, 298 K): δ = 30.97 (CH_3-*t*Bu), 31.33 (CH_3-*t*Bu), 31.55 (CH_3-*t*Bu), 31.77 (CH_3-*t*Bu), 34.07 (*t*Bu-quat), 34.08 (*t*Bu-quat), 34.19 ($2\times$calix-CH_2), 34.52 (*t*Bu-quat), 34.73 (*t*Bu-quat), 36.76 (calix-CH_2), 37.12 (calix-CH_2), 67.23 (OMe), 68.51 (OMe), 124.44 (C_{Ar}), 125.63 (C_{Ar}), 126.25 (C_{Ar}), 126.48 (C_{Ar}), 126.52 (C_{Ar}), 126.88 (C_{Ar}), 127.44 (C_{Ar}), 127.52 (C_{Ar}), 128.53 (C_{Ar}), 128.64 (C_{Ar}), 131.83 (C_{Ar}), 131.89 (C_{Ar}), 133.28 (C_{Ar}), 133.45 (C_{Ar}), 134.14 (C_{Ar}), 135.89 (C_{Ar}), 146.32 (C_{Ar}), 147.03 (C_{Ar}), 149.33 (C_{Ar}), 149.88 (C_{Ar}), 155.52 (C_{Ar}), 159.46 (C_{Ar}), 165.42 (C_{Ar}), 168.11 (C_{Ar}) ppm. $C_{46}H_{58}Cl_2O_4Ti$ (792.32)·(toluene)$_{0.4}$: C 70.57, H 7.43; found C 70.94, H 7.15.

5,11,17,23-Tetra-*tert*-butyl-25,26,27-trioxocalix[4]arenetitanium(IV) Monochloride (9): *p*-*t*Bu-calix[4]arene (1.000 g, 1.580 mmol) and $TiCl_4$·2THF (0.580 g, 1.738 mmol) were dissolved in toluene (30 mL) and the mixture was stirred at 110 °C overnight. The clear solution was allowed to reach room temperature and was crystallised at –30 °C over 48 h. The dark red solid was then collected (0.660 g, 59 %). ^1H NMR ($CDCl_3$, 300 MHz): δ = 0.93 (s, 9 H, *t*Bu), 1.04 (s, 9 H, *t*Bu), 1.31 (s, 18 H, *t*Bu), 3.44 (d, *J* = 13.5 Hz, 2 H, CH_2), 3.50 (d, *J* = 13.1 Hz, 2 H, CH_2), 4.43 (d, *J* = 13.1 Hz, 2 H, CH_2), 4.62 (d, *J* = 13.5 Hz, 2 H, CH_2), 6.66 (s, 2 H, Ar-H), 6.81 (s, 2 H, Ar-H), 7.07 (s, 2 H, Ar-H), 7.08 (s, 2 H, Ar-H), 8.59 (s, 1 H, Ar-H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 31.06 ($2\times CH_3$-*t*Bu), 31.43 (CH_3-*t*Bu), 33.58 (calix-CH_2), 34.08 (*t*Bu-quat), 34.27 (*t*Bu-quat), 38.52 (calix-CH_2), 122.41 (C_{Ar}), 124.61 (C_{Ar}), 124.90 (C_{Ar}), 125.46 (C_{Ar}), 127.55 (C_{Ar}), 128.21 (C_{Ar}), 130.57 (*ipso*-C_{Ar}), 132.60 (C_{Ar}), 139.49 (C_{Ar}), 146.74 (C_{Ar}), 147.76 (C_{Ar}), 150.88 (C_{Ar}), 157.79 (C_{Ar}), 165.26 (C_{Ar}) ppm. $C_{44}H_{53}ClO_3Ti$ (712.32)·(toluene)$_3$: calcd. C 78.89, H 7.84; found C 79.08, H 7.54.

X-ray Crystallographic Study (Table 4): Data collection, cell refinement and data reduction: CrysalisPro;[41] program(s) used to solve structure: SIR97;[42] program(s) used to refine structure: CRYSTALS;[43] molecular graphics: ORTEP3;[44] software used to prepare material for publication: CRYSTALS.[43] Cu-K_α radiation, λ = 1.54184 Å, $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $w^{-1} = [\sigma^2(F_o)^2+(aP)^2]$, $P = [\max(F_o^2,0) + 2(F_c^2)]/3$, in which *a* is a constant adjusted by the program; goodness of fit = $[\Sigma(F_o^2 - F_c^2)2/(n - p)]^{1/2}$, in which *n* is the number of reflections and *p* the number of parameters.

CCDC-748976 (for **4**), -748977 (for **2**) and -748978 (for **3**) contain 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.

Supporting Information (see also the footnote on the first page of this article): NMR spectra of compounds and complexes (Figures S4–S42); chemical induced shift (CIS) (Figure S43); general procedure for ethylene polymerisations (Figure S44); ethylene polymerisation with **6**/MAO as catalyst at temperatures ranging from 50 to 90 °C and constant pressure (30 bar) (Figure S45); ethylene polymerisation with **6**/MAO as catalyst at pressures ranging from 5 to 30 bar and constant temperature (70 °C) (Figure S46); DSC spectrum of polyethylene obtained at 50 °C in the presence of **6**/MAO (Figure S47). ^{13}C NMR spectrum of PE (Figure S48).

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