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Alkylmono(cyclopentadienyl)titanium Complexes Containing the 2,2′-Methylenebis(6-*tert*-butyl-4-methylphenoxido) Ligand – Studies on the Nature of the Catalytic Species Present in α-Olefin Polymerisation Processes

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The mono(alkyl)bis(phenoxido)titanium complexes [TiR′(η^5-C_5R_5)(η^2-mbmp)] [R = H, R′ = Me (**4**), CH_2Ph (**5**), Ph (**6**), CH_2SiMe_3 (**7**); R = Me, R′ = Me (**8**), CH_2Ph (**9**), CH_2SiMe_3 (**10**); η^2-mbmp = 2,2′-methylenebis(6-*tert*-butyl-4-methylphenoxido)] have been prepared in good yields by reaction of the appropriate alkylating reagent with the corresponding chlorido(cyclopentadienyl)bis(phenoxido)titanium derivative. Compound **6** reacts in toluene with traces of water to afford the μ-oxidotitanium complex {Ti(η^5-C_5H_5)(η^2-mbmp)}$_2$(μ-O) (**11**). Compounds **8**, **9** and **11** have been characterised by single-crystal X-ray crystallography, and density functional calculations have been performed in order to elucidate the energetic and structural properties of these compounds. The activity of these complexes in the presence of methylaluminoxane (MAO), $B(C_6F_5)_3$ or $[Ph_3C][B(C_6F_5)_4]$ as co-catalysts in the polymerisation of propylene and styrene has been studied. In an effort to model the nature of the catalytic species generated from these precursors, the reactions of the mono(cyclopentadienyl)bis(phenoxido)chlorido- and -alkyltitanium derivatives with Lewis acids were examined. $B(C_6F_5)_3$ reacts with the neutral complexes [TiR′(η^5-C_5R_5)(η^2-mbmp)] by abstraction of the alkyl group R′ to give the highly stable species [Ti(η^5-C_5H_5)(η^2-mbmp)][$MeB(C_6F_5)_3$] (**12**), [Ti(η^5-C_5H_5)(η^2-mbmp)][$(PhCH_2)B(C_6F_5)_3$] (**13**), [Ti(η^5-C_5Me_5)(η^2-mbmp)][$MeB(C_6F_5)_3$] (**14**) and [Ti(η^5-C_5Me_5)(η^2-mbmp)][$(PhCH_2)B(C_6F_5)_3$] (**15**), which are inactive in propylene and styrene polymerisation. In contrast, the reaction between the neutral alkyl derivatives and $[CPh_3][B(C_6F_5)_4]$ affords species that are active in α-olefin polymerisation. Treatment of the mono(chlorido) compound [TiCl(η^5-C_5H_5)(η^2-mbmp)] with 1 equiv. of $AlMe_3$ affords the methyl derivative **4** as essentially the only reaction product. When an excess of $AlMe_3$ is used, transmetallation reactions of the bis(phenoxido) ligand from titanium to aluminium are observed. Reactions of the bis(phenol) mbmpH_2 with $AlMe_3$ or $AlClMe_2$ yield [AlMe(mbmp)]$_2$ (**16**) and [AlCl(mbmp)]$_2$ (**17**).

Introduction

Alkoxido derivatives of transition metals are used as catalysts in a wide range of homogeneous reactions, and early transition metal elements are strongly stabilized in high oxidation states by alkoxido (or phenoxido) ligands.[1–3] Alkoxidotitanium and -zirconium compounds combined with a co-catalyst (MAO) are highly active catalysts in α-olefin polymerisation.[4–9] The synthesis of dialkyl(alkoxido) derivatives of group 4 elements is very difficult as they are sensitive to atmospheric moisture and to light. The reaction of [$MR_{4-x}(OAr)_x$] complexes with the Lewis acid $B(C_6F_5)_3$ has been reported to give the zwitterionic species [$M(CH_2Ph)(OAr)_2$][B(η^6-$C_6H_5CH_2$)$(C_6F_5)_3$] for the benzyl derivatives and a mixture of [$Ti(C_6F_5)Me(OAr)_2$] and $BMe(C_6F_5)_2$ for the methyl complexes.[10]

In a previous paper we reported the synthesis and characterisation of the mono(cyclopentadienyl)titanium complexes [TiClCp′(η^2-mbmp)] [Cp′ = η^5-C_5H_5 (**1**), η^5-C_5Me_5 (**2**), η^5-$C_5H_4SiMe_2Cl$ (**3**)] containing the bis(phenoxido) bidentate dianionic ligand 2,2′-methylenebis(6-*tert*-butyl-4-methylphenoxido) (η^2-mbmp). Density functional calculations developed for these complexes provide remarkable conclusions about their structural behaviour, which were subsequently confirmed by X-ray diffraction studies in the solid state. After activation with MAO, these mono(cyclopentadienyl)titanium derivatives are suitable catalysts for olefin (propylene, styrene and isoprene) polymerisation.[11]

To elucidate the influence of the co-catalyst used in these studies on the activity of the catalyst, as well as on the poly-

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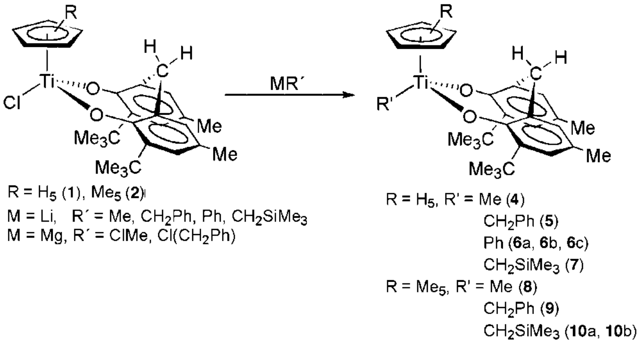
merisation mechanism, we have synthesised new alkylmono(cyclopentadienyl)titanium systems containing the mbmp ligand. Here we report the synthesis of [TiR′(η^5-C_5R_5)(η^2-mbmp)] (R = H, Me; R′ = Me, CH_2Ph, Ph, CH_2SiMe_3) derivatives, their reactions with Lewis acids {$AlMe_3$, $B(C_6F_5)_3$ and $[CPh_3][B(C_6F_5)_4]$} as well as their catalytic application in α-olefin polymerisation, in which different co-catalysts and temperature conditions were employed. The synthesis of a dinuclear μ-oxidotitanium derivative [{Ti(η^5-C_5H_5)(η^2-mbmp)}$_2$(μ-O)] and dinuclear aluminium compounds [AlX(mbmp)]$_2$ (X = Cl, Me) with a μ-η^1,η^2 disposition of the mbmp ligand are also reported. The X-ray molecular structures of [TiR′(η^5-C_5Me_5)(η^2-mbmp)] (R′ = Me, CH_2Ph) and [{Ti(η^5-C_5R_5)(η^2-mbmp)}$_2$(μ-O)] complexes were determined by diffraction methods and density functional calculations performed for [TiR′(η^5-C_5H_5)(η^2-mbmp)] (R′ = Me, CH_2Ph, Ph).

Results and Discussion

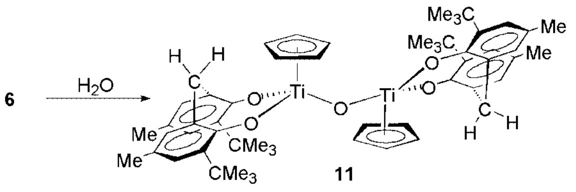
Synthesis of Complexes

The reaction of the chlorido derivatives [TiCl(η^5-C_5R_5)(η^2-mbmp)] [R = H (**1**), Me (**2**); η^2-mbmp = 2,2′-CH_2-bis(6-*t*Bu-4-$CH_3C_6H_2$-1-O)],[11] with 1.2 equiv. of MR′ (M = Li, R′ = Me, CH_2Ph, Ph, CH_2SiMe_3; M = Mg, R′ = $ClCH_2$, $ClCH_2Ph$), in hexane at –78 °C, affords the alkylmono(cyclopentadienyl) complexes [TiR′(η^5-C_5R_5)(η^2-mbmp)] [R = H, R′ = Me (**4**), CH_2Ph (**5**), Ph (**6**), CH_2SiMe_3 (**7**); R = Me, R′ = Me (**8**), CH_2Ph (**9**), CH_2SiMe_3 (**10**)] containing a bidentate bis(phenoxido) ligand (Scheme 1). The compounds were isolated as yellow-orange solids in 60–80% yield.



Scheme 1.

When compound **6** reacts in toluene with traces of water at room temperature crystals of a dimetallic complex with an oxygen atom bridging two titanium atoms and identified as [{Ti(η^5-C_5H_5)(η^2-mbmp)}$_2$(μ-O)] (**11**) were obtained (Scheme 2).



Scheme 2.

Compounds **4**–**10** are soluble in chlorinated solvents (chloroform and dichloromethane) and aromatic (benzene, toluene) and aliphatic hydrocarbons (pentane and hexane), while complex **11** only presents low solubility in toluene and chlorinated solvents (chloroform and dichloromethane). They can be stored under an inert gas in solution for months and are stable for some weeks in the solid state without decomposition. They were characterised by elemental analysis and NMR spectroscopy. The elemental analysis values found for **5** were inaccurate due to the presence of small amounts of impurities which could not be removed, although this compound has been characterised by spectroscopic methods. The analytical composition fits the proposed formulation exactly. The molecular structures of **8**, **9** and **11** have been determined by X-ray diffraction.

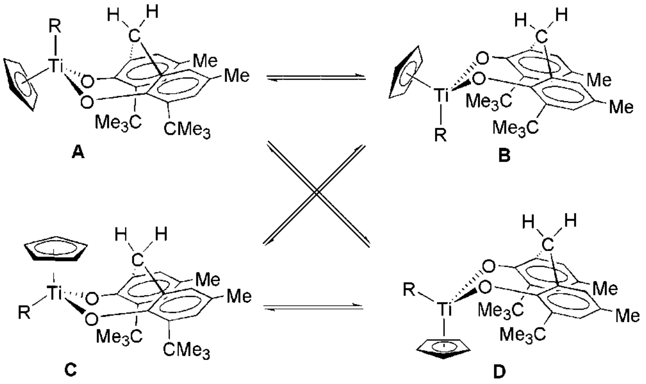
The NMR spectra (C_6D_6 and $CDCl_3$, room temperature) of complexes **4**–**10** show patterns for the mbmp fragment similar to those described for compounds containing the same bis(phenoxido) ligand.[11] The two CH_2 protons appear in the ^1H NMR spectra as a pair of doublets; the value of the chemical shift difference (Δδ, C_6D_6) between their chemical shifts varies between 2.13 and 0.28 ppm. This difference seems to be due to changes in the configuration of the metallacyclic ring in solution.[11] Both equivalent *tert*-butyl groups and the two methyl substituents on the phenyl rings appear as singlets between δ = 1.49–1.20 and 2.18–2.07 ppm in C_6D_6, respectively. The protons at the 3- and 5-positions on the phenyl ring give two doublets, corresponding to AA′ spin systems, with a $^4J_{H,H}$ coupling constant of 1.83 Hz. Singlets are observed for the cyclopentadienyl and the methylcyclopentadienyl ring protons in the expected region of the spectra. For all of these compounds, structural features similar to those determined by ^1H NMR spectroscopy can be deduced from the $^{13}C\{^1H\}$ NMR spectra (C_6D_6, room temperature). These spectroscopic data are consistent with C_s-symmetrical molecules. In the ^1H NMR spectra, the alkyl substituents at the titanium centre show the expected behaviour for this kind of group in C_s molecules, namely one singlet for the methyl group, two singlets that integrate for two and nine protons for the CH_2SiMe_3 substituent, one singlet and signals of aromatic protons for the CH_2Ph group and resonances of aromatic protons for the phenyl group, with the corresponding resonances in the $^{13}C\{^1H\}$ NMR spectra.

The ^1H NMR spectrum of **11** shows two doublets for the methylene protons with a chemical shift difference between them of 1.00 ppm (C_6D_6). The *tert*-butyl and methyl groups of each bis(phenoxido) ligand are not equivalent and appear as two singlets. The protons in the 3- and 5-positions on the phenyl rings are also not equivalent and appear as four doublets. However, the molecule is symmetric as a result of the presence of a C_2 axis through the bridging oxygen atom that runs perpendicular to the titanium–oxygen bonds. As a consequence, each fragment of the phenoxido ligand of one titanium centre is equivalent to the opposite fragment of the phenoxido ligand of the other titanium centre, as shown in Scheme 2. The molecular structure determined by X-ray diffraction confirms this proposed arrangement, thus indicating that the solid-state structure is maintained in solution.

The ^{1}H NMR spectra of analytically pure samples of **4**, **5** and **7** show only one pattern for the signals discussed. The study of the phenyl derivative **6** showed the presence of three different isomers (**6a**, **6b** and **6c**). Isomers **6a** and **6b** can be separated as pure samples by repeated recrystallisation from toluene because of their different solubility. A solution of **6b** in deuterated benzene evolves to a 1:1 molar ratio mixture of **6b** and **6c** at room temperature in 3 h, while a solution of **6a** under the same conditions remains unaltered for a long time. The formation of a single compound was observed spectroscopically for the pentamethylcyclopentadienyl derivatives **8** and **9**, while the ^{1}H NMR spectrum of **10** shows two sets of signals, thus indicating that this complex is obtained in solution as a mixture of two isomers (**10a/10b**) in a 10:1 molar ratio. Theoretical studies (see below) permitted us to understand this behaviour.

Study of the Molecular Structure – Theoretical and Conformational Studies and Crystal Structure of [TiMe(η^5-C_5Me_5)(η^2-mbmp)] (8), [Ti(CH_2Ph)(η^5-C_5Me_5)(η^2-mbmp)] (9) and [{Ti(η^5-C_5H_5)(η^2-mbmp)}$_2$(μ-O)] (11)

For the [TiR′Cp(η^2-mbmp)] type of compounds the existence of four possible conformers related by two different conformational change processes, i.e., by ring inversion and boat/chair interconversion (Scheme 3) can be proposed.[11]



Scheme 3.

The HF method with B3LYP hybrid exchange-correlation energy functional[12] implemented in the Gaussian suite of programs[13] using a 3-21g* basis set was employed in order to explore the potential energy surface (PES) and to locate the minima involved in the related processes. All the structures were optimised at this level of theory. To study the character of the stationary points found, an analysis of the approximate Hessian was made, which confirmed all these points as minima on the PES. In our search, three different conformers (**I**, **II**, and **III**) were found (Figure 1).

The equilibrium Ti–O bond length, the relative electronic energies and the relative population based on Boltzmann's equilibrium distribution at 298 K of these three conformers for compounds **4**–**6** and previously reported **1**[11] are listed in Table 1.

For almost all of the complexes studied, the most stable conformer (**I**) has a geometry intermediate between a boat and a chair conformation (intermediate between **C** and **B** in Scheme 3, although slightly closer to the boat than to the chair), with the Cp ligand close to the methylene bridge between the phenyl groups and short Ti–O bond lengths (1.78–1.807 Å).

The second calculated conformer (**II** in Figure 1, corresponding to a disposition similar to **A** in Scheme 3 but intermediate between **A** and **D**) has a similar arrangement to conformer **I**, with the Cp and alkyl ligands interchanged. The Ti–O bond lengths are analogous (1.79–1.803 Å) to those found for conformer **I**. These calculations suggest a clear degree of multiple bonding in the Ti–O link close to sp hybridisation for both conformers. For complex **6**, we can see how the high planarity of the C–O–Ti–O–C fragment makes isomers **I** and **II** very close in energy.

The third conformer (**III** in Figure 1, corresponding to a disposition close to **D** in Scheme 3) exhibits different behaviour to **I** and **II** as a result of its geometrical structure. It presents a closer sp^2 oxygen angle and a larger Ti–O bond length (1.81–1.814 Å).

As a result of the calculations, two boat conformers (**I** and **II**) related through a ring-inversion process could be expected. Conformer **III**, in which the oxygen atoms move toward sp^2 hybridisation, is the most unstable due to Ti–O bond weakening, which raises the energy by around 13 kcal mol^{-1} with respect to the most stable conformer for compounds **1** and **4**. The stability of each conformer is reflected in the Ti–O bond order in such a way that the shorter the bond the greater the stability. The preference to adopt conformation **I** or **II** depends on the steric impediment exerted by the cyclopentadienyl ring and the alkyl substituent at the titanium centre.

As shown in Table 1, **I** is the most stable conformer for compounds **1**, **4** and **6**, in which the Cp ligand is located towards the methylene bridge. A small difference in stability between **I** and **II** is predicted for compound **6**, while for compounds **1** and **4** higher differences in the related energies are deduced; only for complex **5** is conformation **II** more stable than **I** due to the high steric hindrance produced between the *t*Bu groups of the bis(phenoxido) ligand and the ring of the benzyl substituent. The high relative energies of conformations **I** and **III** for complex **5** are comparable as a result of this steric hindrance, which in **III** is due to the steric hindrance between the cyclopentadienyl

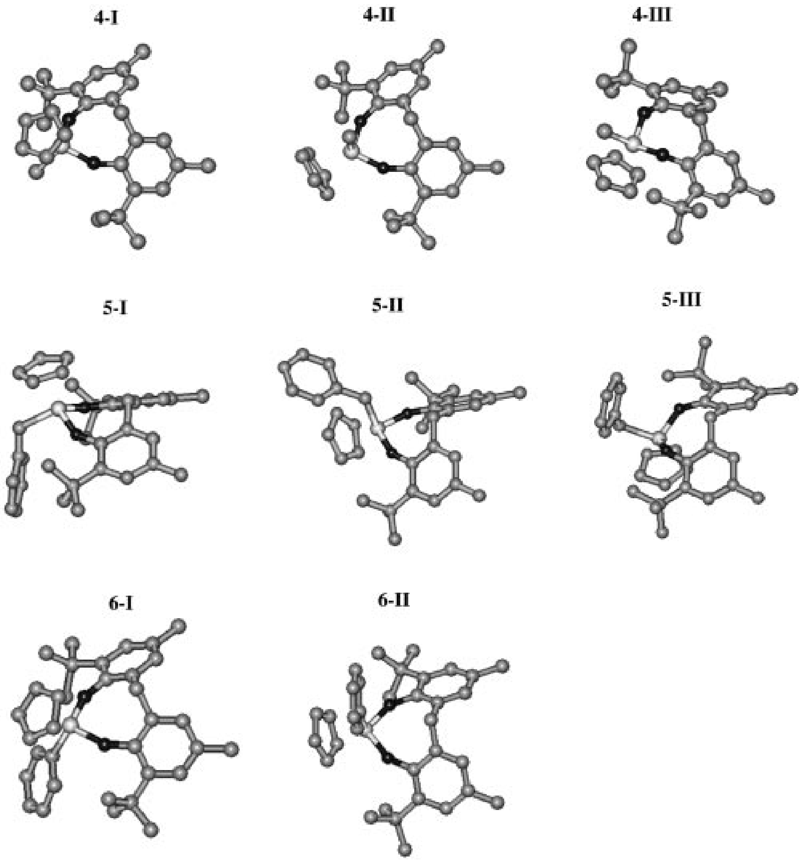


Figure 1. Optimised structures for [TiR′Cp(η^2-mbmp)] [R′ = Me (**4**), CH$_2$Ph (**5**), Ph (**6**)] complexes.

Table 1. Ti–O distances, energetics and Boltzmann populations for the calculated isomers.

	Ti–O distance [Å]				Relative energy[a] [kcal mol^{-1}]				Boltzmann equilibrium population[b]			
	1	**4**	**5**	**6**	**1**	**4**	**5**	**6**	**1**	**4**	**5**	**6**
I	1.78	1.797	1.807	1.799	0.0	0.0	5.02	0.0	98.5	99.9	ca. 0.0	81.3
II	1.79	1.801	1.801	1.803	2.5	4.30	0.0	0.86	1.5	0.1	<99.9	18.7
III	1.81	1.814	1.813	–	12.1	13.68	6.06	–	0.0	0.0	0.0	–

[a] Energy relative to the most stable conformer. [b] Percent populations of the different conformers at 298 K following a distribution of the energies according to Boltzman's distribution law.

ligand and the *t*Bu groups. These theoretical results are in agreement with the NMR experimental data. Although complexes **1**, **4** and **5** could exist in three different conformations, the high stability of disposition **I** for **1** and **4** (or **II** for **5**) is enough to make these the only preferred conformations, which leads to the formation of one unique isomer, as observed spectroscopically.

For complex **6**, the theoretical studies predict the possibility of two boat conformations (**I** and **II**) with similar energies and therefore both species can coexist in solution at room temperature. These theoretical studies explain the presence of two of the three patterns of signals found in the NMR spectra. In contrast, the value of the chemical shift difference for the two methylene protons of the bis(phenoxido) ligand in the ^{1}H NMR spectrum is initially an excellent probe for the detection of the metallacycle conformation.[11] Taking into account the relationship between this value and the conformation found in the X-ray structures elucidated for this type of complex (see below and ref.[11]), a $\Delta\delta_{CH_2}$ value of around or below 1.00 ppm points to a boat conformation. In this sense, conformations **I** and **II** would correspond to isomers **6a** and **6b**. The third pattern (**6c**) could correspond to conformer **III**, which, although it is not found by the theoretical calculations, is experimentally plausible and would explain why a pure solution of **6b** interconverts at room temperature to an equimolecular mixture of **6b** and **6c**.

To establish and to confirm the structural details of the molecular geometry in the solid state for this type of compound, X-ray crystal structure analyses of **8**, **9** and **11** were carried out. Single crystals of **8** obtained by slow recrystallisation from hexane solution were of good enough quality to be analysed by X-ray diffraction. The crystal structure of **8** is shown in Figure 2. Crystals of **9** were also obtained

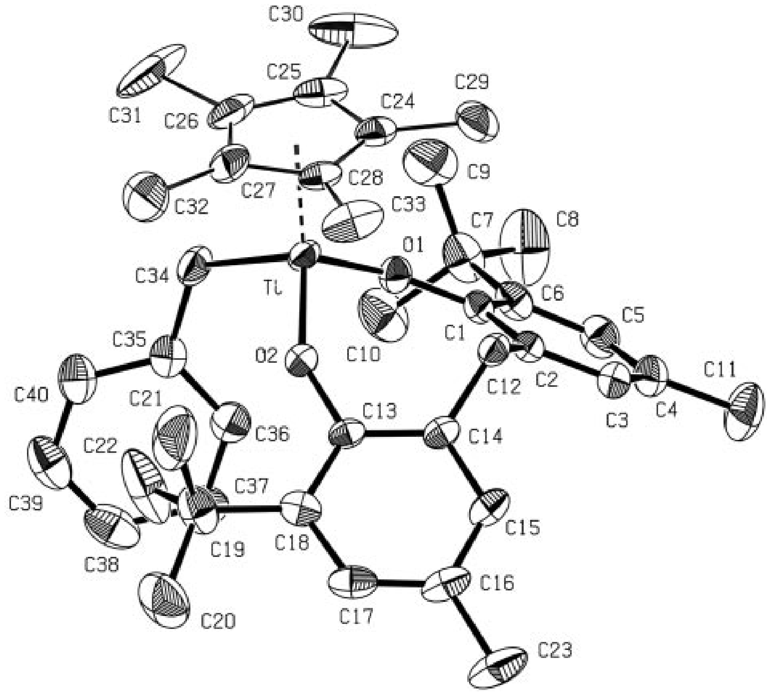


Figure 2. ORTEP plot of compound **8** in the solid state. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

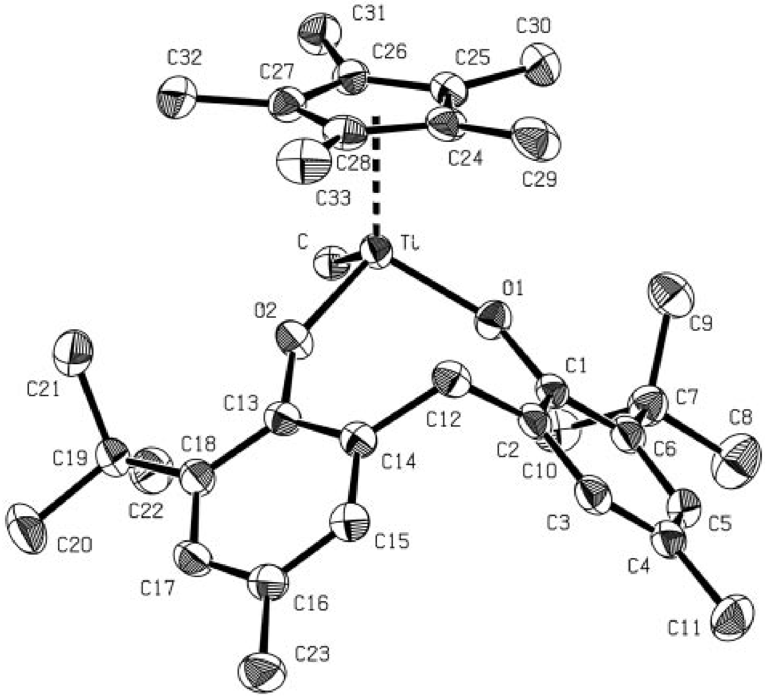


Figure 3. ORTEP plot of compound **9** in the solid state. The major part (82.1%) of the disordered Cp ligand is shown. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

from hexane solution at –20 °C but were not good enough for X-ray crystallography. However, it was possible to determine its molecular structure, which is depicted in Figure 3. Table 2 summarises selected bond lengths and angles.

The mbmp ligand adopts a puckered chelate disposition with the typical boat conformation in the solid state with the methylene bridge pointing toward the cyclopentadienyl ring.[9,14,15] The observed structural parameters correlate

Table 2. Selected bond lengths [Å] and bond angles [°] for **8** and **9**.

	8	**9**
Ti–O1	1.840(1)	1.828(2)
Ti–O2	1.834(1)	1.833(2)
Ti–C–C34	1.993(2)	2.154(2)
O1–C1	1.364(2)	1.365(2)
O2–C13	1.372(2)	1.362(3)
Ti–C24	2.370(2)	2.373(3)[a]
Ti–C25	2.404(2)	2.430(3)[a]
Ti–C26	2.436(2)	2.425(3)[a]
Ti–C27	2.403(2)	2.364(3)[a]
Ti–C28	2.373(2)	2.341(3)[a]
Ti···Cg[b]	2.071	2.064[a]
O1–Ti–O2	101.63(6)	102.96(7)
O1–Ti–C/C34	101.39(6)	97.15(7)
O1–Ti···Cg[b]	119.62	120.45[a]
O2–Ti–C/C34	101.07(7)	105.37(8)
O2–Ti···Cg[b]	119.37	118.11[a]
C–C34–Ti···Cg[b]	110.84	109.98[a]
Ti–O1–C1	148.9(1)	151.3(1)
Ti–O2–C13	149.1(1)	148.0(1)
C2–C12–C14	113.2(1)	117.2(2)

[a] Distances and angles to the major part (82.1%) of the disordered Cp ligand. [b] Cg denotes the cyclopentadienyl ring centroid.

well with those calculated for the most stable conformer determined by density functional calculations. This confirms that the preferred structure for these complexes in the solid state is the boat conformation, in agreement with the theoretical results, from which a similar boat conformation is predicted for the analogous complexes bearing an η^5-C_5H_5 ligand.

The coordination geometry around the titanium atom is a pseudo-three-legged piano stool, as expected for complexes of the type $TiCpL_3$.[16] The metal–oxygen bond lengths in **8** (av. 1.8367 Å) and **9** (av. 1.8300 Å) are in the expected range for titanium complexes with a linked bis(phenoxido) ligand with ($\sigma + \pi$) donor oxygen atoms.[3,17] Compared with the related structure of the chlorido derivative **2**,[11] the presence of a less electronegative alkyl group increases the electronic density at the metal centre, which leads to longer average Ti–O bonds and a more open O1–Ti–O2 angle.

The geometry adopted for these complexes is a compromise situation where the least steric hindrance between the pentamethylcyclopentadienyl ring and the methylene bridge is produced and the methyl substituent is located far away from the *tert*-butyl groups of the bis(phenoxido) ligand.

Crystals of compound **9** diffracted poorly, as indicated by the weak diffraction patterns, the high thermal parameters and the high *R* values. The pentamethylcyclopentadienyl ring is disordered but the refinement shows undoubtedly that complex **9** is present as described. As can be seen in Figure 3, complex **9** presents a boat conformation with the methylene bridge pointing toward the pentamethylcyclopentadienyl ring, in a similar manner to conformation **I** obtained in the theoretical study. This study for the analogous benzylmono(cyclopentadienyl) complex **5** predicted a boat conformation of type **II**, with the benzyl substituent far away from the *tert*-butyl groups of the bis(phenoxido) ligand. Nevertheless, the difference in steric relaxation between the benzyl group and the pentamethylcyclopentadienyl ring near the *tert*-butyl groups should not be significant for compound **9**, which prefers to adopt the most stable type-**I** conformation, which is the preferred conformation for the chlorido-, methyl- and phenyl(cyclopentadienyl) derivatives deduced from the theoretical study.

The structure of compound **11** was confirmed by X-ray diffraction analysis. A view of the molecular structure is given in Figure 4 and selected bond lengths and angles are listed in Table 3.

The coordination sphere around the metal centre is a four-legged piano stool. The bite angles of the bis(phenoxido) ligands [O(1)–Ti(1)–O(2) = 103.23(6)° and O(3)–Ti(2)–O(4) = 103.97(6)°] are larger than 90° and in the same range

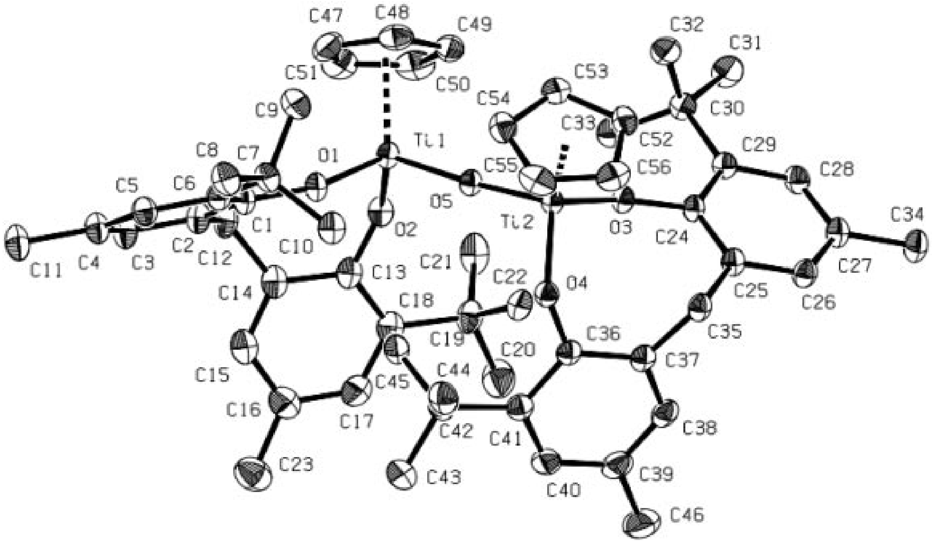


Figure 4. ORTEP plot of compound **11** in the solid state. Thermal ellipsoids are drawn at the 40% probability level. Hydrogen atoms are omitted for clarity.

Table 3. Selected bond lengths [Å] and bond angles [°] for **11**·0.75 C_6H_{14}.

Bond lengths [Å]		Bond angles [°]	
Ti1–O1	1.808(2)	O1–Ti1–O2	103.23(6)
Ti1–O2	1.843(2)	O1–Ti1···Cg1[a]	117.85
Ti2–O3	1.809(2)	O2–Ti1···Cg1[a]	111.56
Ti2–O4	1.857(2)	O5–Ti1···Cg1[a]	114.87
Ti1–O5	1.826(1)	O1–Ti1–O5	102.13(6)
Ti2–O5	1.816(1)	O2–Ti1–O5	105.80(6)
Ti1···Cg1[a]	2.069	O3–Ti2–O4	103.97(6)
Ti2···Cg2[a]	2.066	O3–Ti2···Cg2[a]	116.88
O1–C1	1.367(3)	O4–Ti2···Cg2[a]	111.83
O2–C13	1.352(3)	O5–Ti2···Cg2[a]	114.12
O3–C24	1.363(2)	O3–Ti2–O5	102.13(6)
O4–C36	1.360(3)	O4–Ti2–O5	106.76(6)
		Ti1–O5–Ti2	174.30(8)
		C14–C12–C2	115.9(2)
		C25–C35–C37	115.5(2)
		Ti1–O1–C1	152.9(1)
		Ti1–O2–C13	134.5(1)
		Ti2–O3–C24	152.3(1)
		Ti2–O4–C36	132.0(1)

[a] Cg denotes the cyclopentadienyl ring centroid.

as those obtained for complexes containing the mbmp ligand, such as [Ti(mbmp)$_2$] [106.24(7)° and 107.28(8)°],[3] [TiCl$_2$(mbmp)] [106.5(2)°],[18] [TiMe$_2$(mbmp)] [112.7(2)°],[18] [Ti(mbmp)(BH$_4$)$_2$] [103.9(2)°],[19] and the mono(cyclopentadienyl)bis(phenoxido)titanium complexes [CpTiX(OC$_6$H$_3$-*i*Pr$_2$)$_2$] [X = Cl, *t*Bu and Me; 103.0(3)°, 107.7(9)° and 109.0(5)°, respectively].[20] The dihedral angles between both phenyl rings are 115.92(19)° and 115.52(18)°, more open than those found for analogous ligands with different bridging units {S in tmbp and Te in tebp [tmbp = 2,2′-thiobis(6-*tert*-butyl-4-methylphenoxido), tebp = 2,2′-tellurobis(6-*tert*-butyl-4-methylphenoxido)]; [Ti(mbmp)(BH$_4$)$_2$] = 64.1(2)°,[19] [TiCl$_2$(mbmp)(thf)] = 113.4(3)°,[21] [TiCl$_2$(tmbp)]$_2$ = 102.9(3)°,[5] [CpTiCl(tmbp)] = 107.3(1)°[9] and [TiCl$_2$(tebp)]$_2$ = 96.0(2)°}.[15]

The mbmp ligand adopts a typical boat conformation in the solid state, with one of the methylene bridge protons pointing towards the metal centre and the other away from it and with both in the proximity of the cyclopentadienyl ring.[9,15] The metal–oxygen bond lengths [Ti(1)–O(1) = 1.808(2), Ti(1)–O(2) = 1.843(2), Ti(2)–O(3) = 1.809(2) and Ti(2)–O(4) = 1.857(2) Å] are short but in the expected range for titanium complexes with a linked bis(phenoxido) ligand with ($\sigma + \pi$) donor oxygen atoms, such as [Ti(mbmp)$_2$] [av. 1.802(6) Å],[3] [TiCl$_2$(mbmp)(thf)] [av. 1.791(2) Å],[21] [TiCl$_2$(tmbp)]$_2$ [av. 1.818(4) Å],[5] [TiCl$_2$(tebp)]$_2$ [av. 1.801(9) Å],[15] [CpTiCl(tmbp)] [av. 1.827(2) Å][9] and [Ti(CH$_2$Ph)$_2${2,2′-(4-MeO-6-*t*BuC$_6$H$_2$O)$_2$}] [av. 1.810(7) Å],[7] and slightly larger than those found in analogous compounds such as [TiCl$_2$(mbmp)] [av. 1.751(4) Å][18] and [TiBr$_2$(ebmp)] [ethylene-bridged analogue; av. 1.750(9) Å].[17] Similar results were found in titanium complexes with non-linked phenoxido ligands, such as [CpTiX(OC$_6$H$_3$*i*Pr$_2$)$_2$] [X = Cl, *t*Bu, Me; av. 1.801(5), 1.79(2) and 1.817(9) Å, respectively], due to the presence of a cyclopentadienyl ligand, which decreases the π-donation from the oxygen atoms to the metal centre.[20] Finally, the angle at the oxygen bridge atom is crystallographically restricted to 174.30(8)° and the metal–bridging oxygen bond lengths of 1.826(1) and 1.816(1) Å are typical for bridged titanium oxides.[22]

Olefin Polymerisation

Using MAO in excess or B(C$_6$F$_5$)$_3$ or [CPh$_3$][B(C$_6$F$_5$)$_4$] [1:1 molar ratio with respect to the precursor in the presence of triisobutylaluminium (TIBA) as scavenger] as co-catalysts, complexes **4**, **5**, **8** and **9** were studied as α-olefin polymerisation catalysts under various conditions.

Propylene polymerisation was investigated by using 27 μmol of catalyst in 150 mL total volume of toluene with a 1000:1 Al(MAO)/Ti or 250:1:1 Al(TIBA)/Ti/[CPh$_3$][B(C$_6$F$_5$)$_4$] molar ratio at different temperatures and monomer pressures (conditions and results are summarised in Tables 4 and 5). Only traces of polymer or no polymerisation was found when the reaction was carried out at 30 °C with 5 atm of monomer and MAO as co-catalyst (runs 1, 4, 7 and 10). However, polymer was found at 0 °C using liquid propylene and MAO as co-catalyst for complexes **4** and **5** (runs 2 and 5), while compounds **8** and **9** (runs 8 and 11) showed poor activity. Decomposition of the catalyst system in the presence of the monomer at high temperatures could be a possible explanation for this behaviour. The activity [7.4 kg PP (mol Ti)$^{-1}$ h^{-1}] at 0 °C for the chlorido(cyclopentadienyl) system **1**/MAO[11] is markedly higher than that found for the corresponding alkyl derivatives **4** and **5**. Polymerisation runs at 0 °C resulted in the formation of PP with a molecular weight (M_w) of around 10^5 for the pentamethylcyclopentadienyl derivatives **8** and **9** (2.5–5.6 × 10^5), one order of magnitude higher than the corresponding non-substituted alkyl(cyclopentadienyl) derivatives **4** and **5**, probably due to the more electron-donating capability of the η^5-C$_5$Me$_5$ ligand, which prevents β-elimination processes.

When the salt [CPh$_3$][B(C$_6$F$_5$)$_4$] was used as co-catalyst, complexes **4** and **5** exhibited analogous activity (runs 3 and 6), but the activity was greatly increased for compounds **8** and **9** (runs 9 and 12), producing around 20–40 kg PP (mol Ti)$^{-1}$ h^{-1}. A similar behaviour is observed with the molecular weight of the polymer synthesised, and the high value found with systems **8**/[CPh$_3$][B(C$_6$F$_5$)$_4$] and **9**/[CPh$_3$][B(C$_6$F$_5$)$_4$] is worthy of mention, with each reaching values of 2–3 × 10^6, with similar polydispersity values to those reported in the literature.[7,15,20,23] For these samples, values of T_g, T_m and ΔH similar to those found with the **1**/MAO system[11] are observed.

The use of the borane salt produces a decrease in the stereoselectivity of the process, as shown in Table 5 from an analysis of the degree of isotacticity in the samples by ^{13}C NMR spectroscopy. The activation of the precursors with MAO at 0 °C gives isotactic PP with an isotacticity (mmmm) of 24–30 % (runs 2 and 5) for the cyclopentadienyl complexes **4** and **5**. However, activation with

Table 4. Polymerisation of propylene with [TiR′(η^5-C_5R_5)(η^2-mbmp)] compounds.

Run	Catalyst[a]	Time [min]	Yield [mg]	Activity [kg PP (mol Ti)$^{-1}$ h^{-1}]	10^{-4} M_w	M_w/M_n	T_g [°C]	T_m [°C]	ΔH [J g^{-1}]
1	4[b]	120	traces	–	–	–	–	–	–
2	4[c]	120	189	3.5	3.8	1.86	–9.8	101	5.2
3	4[d]	120	158	3.0	–	–	–	–	–
4	5[b]	120	traces	–	–	–	–	–	–
5	5[c]	120	256	4.7	2.7	1.78	–9.0	80	5.4
6	5[d]	120	298	5.5	53	3.54	–	–	–
7	8[b]	120	79	1.5	25	3.57	–	–	–
8	8[c]	120	63	1.2	56	2.42	–	–	–
9	8[d]	120	2067	38.1	217	47.5	–	–	–
10	9[b]	120	traces	–	–	–	–	–	–
11	9[c]	120	141	2.6	25	1.86	–	–	–
12	9[d]	120	1159	21.5	301	37.0	–	–	–

[a] 27 µmol of catalyst. [b] Propylene gas (5 atm), 30 °C, co-catalyst: MAO. [c] Propylene liquid (40 mL), 0 °C, co-catalyst: MAO. [d] Propylene liquid (40 mL), 0 °C, co-catalyst: [CPh_3][$B(C_6F_5)_4$].

Table 5. Pentand distributions obtained for PP.

Run	Catalyst	% mmmm[a]	Run	Catalyst	% mmmm[a]
1	**4**	–	7	**8**	–
2	**4**	24.1	8	**8**	12.5
3	**4**	8.2	9	**8**	insoluble
4	**5**	–	10	**9**	–
5	**5**	30.2	11	**9**	17.9
6	**5**	5.0	12	**9**	insoluble

[a] From ^{13}C NMR spectra.

[CPh_3][$B(C_6F_5)_4$] produces atactic PP (runs 3 and 6). The pentamethylcyclopentadienyl complexes **8** and **9** activated with either MAO or [CPh_3][$B(C_6F_5)_4$] afford atactic PP. The high molecular weights of the samples obtained in runs 9 and 12 impeded the detection of their degree of isotacticity due to their lack of solubility in the deuterated solvents used for the spectroscopic analysis.

The results obtained at different temperatures and the microstructures of the polymers synthesised with MAO as co-catalyst are similar to those found with the **1**/MAO system[11] and resemble those reported by Ewen[24] for PP obtained with the achiral metallocene [$TiCp_2Ph_2$], which is very unusual for monocyclopentadienyl compounds. This analysis permits us to conclude that the polymer obtained at low temperature with precursors **4** and **5** activated with MAO contains large isotactic stereoblocks produced by a chain-end control mechanism with a certain atactic character due to 2,1-enchainments. Nevertheless, it is noteworthy that the activation of precursors **8** and **9** with [CPh_3][$B(C_6F_5)_4$] co-catalyst produces atactic PP with a high molecular weight of 10^6.

Styrene polymerisation was studied using 40 mL total volume of reaction and 5 mL of monomer (conditions and results are summarised in Table 6). When the precursors are activated with MAO (runs 3, 7, 11 and 15), the activity of the cyclopentadienyl complexes **4** and **5** is higher ($7–8 \times 10^5$) than the activity found for the pentamethylcyclopentadienyl compounds **8** and **9** ($2–3 \times 10^5$), in all cases leading to syndiotactic PS (>95% syndiotacticity). Increased activity can be achieved with donor substituents in

Table 6. Polymerisation of styrene with [TiR′(η^5-C_5R_5)(η^2-mbmp)] compounds.

Run		Catalyst	T [°C]	Time [min]	Al/Ti	Yield [g]	Activity [kg PS (mol Ti)$^{-1}$ h^{-1}]	Tacticity	10^{-4} M_w	M_w/M_n
13	1	4[a]	50	45	–	2.82	190	atactic	0.4	1.89
14	2	4[b]	50	45	20	0.02	1.6	atactic	[c]	[c]
15	3	4[d]	50	12	1000	3.36	840	syndiotactic	3.2	2.19
16	4	4[e]	50	30	–	–	–	–	–	–
17	5	5[a]	50	45	–	3.28	220	atactic	0.4	1.95
18	6	5[b]	50	45	20	0.03	2.3	atactic	[c]	[c]
19	7	5[d]	50	20	1000	4.58	700	syndiotactic	2.7	3.68
20	8	5[e]	50	30	–	–	–	–	–	–
21	9	8[a]	50	45	–	3.37	220	atactic	0.5	1.85
22	10	8[b]	50	45	20	0.15	9.5	atactic	0.9	1.70
23	11	8[f]	50	15	1000	2.00	160	syndiotactic	9.8	2.15
24	12	8[e]	50	30	–	–	–	–	–	–
25	13	9[a]	50	45	–	2.77	180	atactic	0.6	1.91
26	14	9[b]	50	45	20	0.05	3.0	atactic	[c]	[c]
27	15	9[f]	50	10	1000	2.57	308	syndiotactic	12.4	1.98
28	16	9[e]	50	30	–	–	–	–	–	–

[a] 20 µmol of catalyst; co-catalyst: [CPh_3][$B(C_6F_5)_4$]. [b] 20 µmol of catalyst; co-catalyst: [CPh_3][$B(C_6F_5)_4$]/TIBA; Al/Ti molar ratio: 20:1. [c] Not enough sample for analysis. [d] 20 µmol of catalyst; co-catalyst: MAO; Al/Ti molar ratio: 1000:1. [e] 20 µmol of catalyst; co-catalyst: $B(C_6F_5)_3$. [f] 50 µmol of catalyst; co-catalyst: MAO; Al/Ti molar ratio: 1000:1.

the cyclopentadienyl ring, while the presence of bulky substituents results in a decrease in activity. The bulky substituents would inhibit 2,1-insertion through steric effects and simultaneously inhibit the generation of the active species.

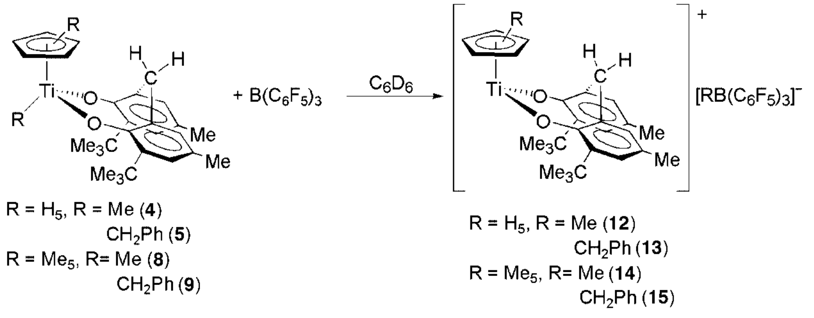
When $[CPh_3][B(C_6F_5)_4]$ is used as co-catalyst (runs 1, 5, 9 and 13) the activity is of the same order of magnitude as that obtained with MAO as co-catalyst. However, and in agreement with the results obtained in the propylene polymerisation, activation with the borane salt affords atactic PS (>92% of atactic microstructure). The similarity in the activity values found for the four alkyl complexes studied when the borane salt is used as co-catalyst is noteworthy and shows that the nature of the cyclopentadienyl ring has no influence on the activity. The addition of TIBA as scavenger in the precursor/$[CPh_3][B(C_6F_5)_4]$ systems (runs 2, 6, 10 and 14) dramatically decreased the activity. No polymerisation was found for the precursor/$[B(C_6F_5)_3]$ system (runs 4, 8, 12 and 16). The molecular weight of the PS obtained with the precursor/$[CPh_3][B(C_6F_5)_4]$ systems is very low but increases when MAO is used as co-catalyst, reaching an order of magnitude of 10^5 with the pentamethylcyclopentadienyl compounds **8** and **9**.

Reaction with Lewis Acids

In order to gain a better knowledge of the nature of the active species and the chemical behaviour of the mono(alkyl)bis(phenoxido) precatalyst systems in the α-olefin polymerisation processes, the reactions of the methyl and benzyl derivatives **4**, **5**, **8** and **9** with Lewis acids such as $B(C_6F_5)_3$ and $[CPh_3][B(C_6F_5)_4]$ were studied using a stoichiometric 1:1 Ti/B ratio and monitored by ^1H NMR spectroscopy. Likewise, the reaction of the chloromono(cyclopentadienyl) derivative **1** with trimethylaluminium was examined. All the procedures were carried out in NMR tubes fitted with Teflon valves to prevent water and oxygen entry and with C_6D_6 as reaction solvent at room temperature.

After addition of C_6D_6 to a mixture of $B(C_6F_5)_3$ and the corresponding neutral derivative **4**, **5**, **8** or **9** at room temperature in an NMR tube in a glovebox, the samples were quickly introduced into the spectrometer and the spectra recorded at 25 °C over a period of time. The reaction produces an appreciable change in the solution's colour from yellow for the methyl derivatives or orange for the benzyl compounds to dark red. After 1 h at room temperature, formation of the ionic species $[Ti(\eta^5\text{-}C_5H_5)(\eta^2\text{-}mbmp)][MeB(C_6F_5)_3]$ (**12**) and $[Ti(\eta^5\text{-}C_5H_5)(\eta^2\text{-}mbmp)][(PhCH_2)B(C_6F_5)_3]$ (**13**; Scheme 4) was detected. For the $\eta^5\text{-}C_5Me_5$ derivatives it was necessary to heat the reaction mixtures at 100 °C for 24 h to complete the reaction and to obtain the ionic compounds $[Ti(\eta^5\text{-}C_5Me_5)(\eta^2\text{-}mbmp)][MeB(C_6F_5)_3]$ (**14**) and $[Ti(\eta^5\text{-}C_5Me_5)(\eta^2\text{-}mbmp)][(PhCH_2)B(C_6F_5)_3]$ (**15**; Scheme 4). However, the reaction of **4** with an equimolecular amount of $[CPh_3][B(C_6F_5)_4]$ at room temperature in C_6D_6 gave an intractable mixture of unidentified products.

Complexes **12**–**15** are partially soluble in C_6D_6 and are stable in solution at room temperature over long periods of time (days). The ^1H NMR spectra (C_6D_6, 25 °C) show signals of equivalent *t*Bu and Me groups and two resonances for the phenyl protons of the bis(phenoxido) ligand, consistent with a C_s symmetry. The resonances of the cyclopentadienyl protons are shifted to low field with respect to the neutral precursors, as expected. The methyl group of the $[MeB(C_6F_5)_4]^-$ fragment gives signals at δ = 0.84 and 0.91 ppm for derivatives **12** and **14**, respectively, suggesting a certain interaction between the anionic and the cationic centres.[25–29] The signals of the methylene protons of the benzylborate anion $[(PhCH_2)B(C_6F_5)_4]^-$ appear at δ = 3.14 and 2.90 ppm for derivatives **13** and **15**, respectively. It is not easy to establish a limit to determine the coordination or non-coordination of the anionic and cationic centres by analysing the methylene benzylborate anion resonances. Generally, values of $\delta_{CH_2B} < 3.0$ ppm seem to indicate the existence of an anion–cation interaction for the $[(PhCH_2)B(C_6F_5)_4]^-$ anion,[10,25,30,31] although exceptions to this rule have been found.[8,32] The resonance of the C_{ipso} phenyl ring of the benzylborate anion is a good probe to determine the type of interaction with the metal centre. The ^{13}C NMR spectra (C_6D_6, 25 °C) for derivatives **13** and **15** show signals at δ = 152.5 and 160.3 ppm assignable to the C_{ipso} phenyl ring carbon atom. This indicates a certain degree of η^6-coordination of the phenyl ring of the benzylborate anion to the cationic metal centre (δ = 148.6 ppm in the free anion).[33,34] The ^{19}F NMR spectra of the cationic species **12**–**15** give $\Delta\delta(p,m\text{-}F)$ values of 3.52, 3.40, 3.41 and 5.10 ppm, respectively, indicating the existence of interactions between the ion pairs that are particularly strong for the pentamethylcyclopentadienyl ionic species **15** with the benzylborate anion.[25,35]



Scheme 4.

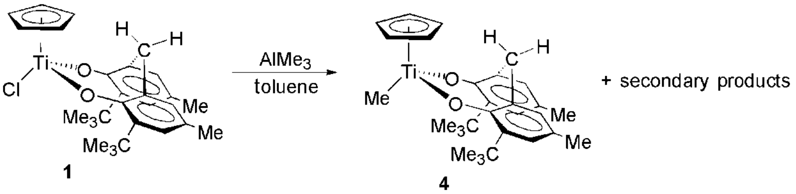
These results permit us to conclude that the Lewis acid $B(C_6F_5)_3$ reacts with the neutral complexes $[TiR'(\eta^5\text{-}C_5R_5)(\eta^2\text{-mbmp})]$ by abstraction of the alkyl group R′ to give the highly stable cationic species $[Ti(\eta^5\text{-}C_5R_5)(\eta^2\text{-mbmp})]^+$, which retains the Ti–O bonds and the bidentate bis(phenoxido) ligand bonded to the titanium centre. Formation of such a stable species exhibiting strong interactions with the anionic unit prevents coordination of the olefin and, as a consequence, these systems are inactive in propylene and styrene polymerisation. With $[CPh_3][B(C_6F_5)_4]$ we could initially assume a similar reactivity. However, the $[B(C_6F_5)_4]^-$ unit is a less coordinating anion than $[RB(C_6F_5)_4]^-$ to afford $[Ti(\eta^5\text{-}C_5R_5)(\eta^2\text{-mbmp})][B(C_6F_5)_4]$, which is active in styrene polymerisation. In the absence of olefin, these $[B(C_6F_5)_4]^-$ systems show a lack of stability, with fast and immediate decomposition observed in solution.

A new family of compounds containing only one metal–alkyl bond that are active in olefin polymerisation has been reported recently. Mechanistic pathways to explain the efficient α-olefin polymerisation of these compounds activated with boron reagents have been proposed.[36–39] In the absence of TIBA, the olefin polymerisation activity observed for complexes **4**, **5**, **8** and **9** with $[CPh_3][B(C_6F_5)_4]$ as co-catalyst can be explained by these mechanistic pathways.

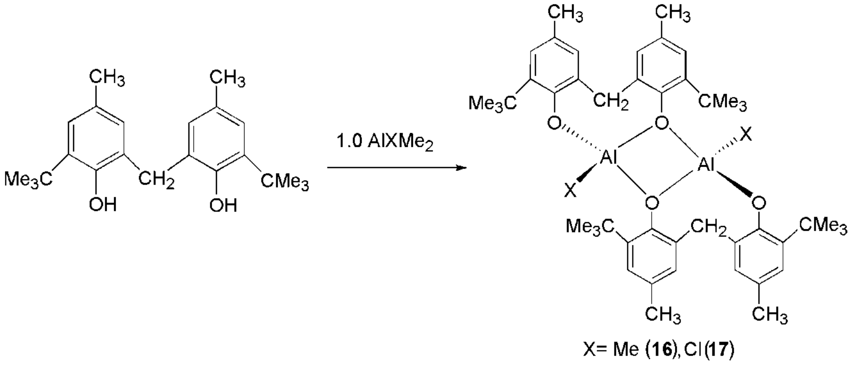
Aluminium compounds are normally used as co-catalysts (MAO) to generate the active species or as scavenger reagents (TIBA) during olefin polymerisation. The former occurs by replacement of the halo groups in the precursor with alkyl groups and then abstraction of one of these alkyl groups to give cationic alkyl species, which are considered to be the active species in the process. As our neutral species with general formula $[TiCl(\eta^5\text{-}C_5R_5)(\eta^2\text{-mbmp})]$ $[\eta^5\text{-}C_5R_5 = \eta^5\text{-}C_5H_5$ (**1**), $\eta^5\text{-}C_5Me_5$ (**2**), $\eta^5\text{-}C_5H_4SiMe_2Cl$ (**3**)$]$[11] only possess one chlorido group at the metal centre, we were motivated to investigate the reactivity of compound **1** with $AlMe_3$. Thus, a solution of the mono(chlorido) compound $[Ti(\eta^5\text{-}C_5H_5)(\eta^2\text{-mbmp})Cl]$ (**1**) was treated with 1 equiv. of $AlMe_3$ in toluene at –78 °C (Scheme 5). ^1H NMR spectroscopic analysis revealed complex **4** to be essentially the only reaction product, thereby indicating alkylation of the Ti–Cl bond and selective formation of the methyl derivative. The NMR spectra also show the presence of traces of signals assignable to secondary products containing the bis(phenoxido) ligand. The intensity of these signals increases when an excess of $AlMe_3$ is used as reagent, along with the disappearance of the signals assignable to compound **4**. Transmetallation reactions of the bis(phenoxido) ligand from titanium to aluminium could explain the formation of these secondary products.[20,40]

In an attempt to identify the nature of these secondary products, we performed the reaction of the bis(phenol) $mbmpH_2$ with $AlMe_3$ or $AlClMe_2$ in a 1:1 molar ratio in toluene at –78 °C. White solids were obtained in both cases, which were characterised by elemental analysis and NMR spectroscopy as the compounds $[AlMe(mbmp)]_2$ (**16**) and $[AlCl(mbmp)]_2$ (**17**; Scheme 6). The thf adduct monomer species [AlCl(mbmp)(thf)] obtained by reaction of $mbmpH_2$ with $AlClEt_2$ in thf has been described previously, although the dimeric species was not characterised.[41]

Complexes **16** and **17** are insoluble in aliphatic hydrocarbons (hexane, pentane), scarcely soluble in aromatic solvents and highly water-sensitive. They can be stored for months under an inert gas without decomposition. The ^1H NMR spectra (C_6D_6 and $CDCl_3$, 25 °C) show AB spin systems for the methylene protons, indicating coordination of the bis(phenoxido) ligand. The *tert*-butyl and methyl groups are not equivalent, with each appearing as two singlets. A



Scheme 5.



Scheme 6.

high-field-shifted signal assignable to equivalent Al–Me groups is also observed for complex **16**. The $^{13}C\{^1H\}$ NMR spectra show twelve signals for the phenyl rings and a pair of signals for the *tert*-butyl and methyl groups. These spectroscopic data agree with the structure proposed in Scheme 6.

Comparison of the spectroscopic data rules out the presence of complexes **16** and **17** in the final products obtained in the reaction of **1** with $AlMe_3$, although transmetallation reactions of the bis(phenoxido) ligand from titanium to aluminium could produce bis(phenoxido)aluminium derivatives of different composition.

The complexes $[TiR'(\eta^5\text{-}C_5R_5)(\eta^2\text{-mbmp})]$ have only one alkyl ligand coordinated to the metal centre. We therefore assume that in these polymerisation reactions the aluminium reagents (MAO used as co-catalyst or TIBA used as scavenger) react with these precursors through transmetallation processes of the bis(phenoxido) ligand from titanium to aluminium to generate active cationic alkyltitanium species in a Ziegler–Natta-type olefin polymerisation.

Concluding Remarks

We have described the synthesis and characterisation of mono(alkyl)mono(cyclopentadienyl)titanium complexes $[TiR'(\eta^5\text{-}C_5R_5)(\eta^2\text{-mbmp})]$ containing the bis(phenoxido) bidentate dianionic ligand 2,2′-methylenebis(6-*tert*-butyl-4-methylphenoxido) (η^2-mbmp). The μ-oxido compound $[\{Ti(\eta^5\text{-}C_5H_5)(\eta^2\text{-mbmp})\}_2(\mu\text{-O})]$ is also obtained by reaction of $[TiPh(\eta^5\text{-}C_5H_5)(\eta^2\text{-mbmp})]$ with traces of water in toluene. Density functional calculations for these complexes have provided remarkable conclusions about their structural behaviour, which have been confirmed by X-ray diffraction studies in the solid state. After activation with MAO or $[CPh_3][B(C_6F_5)_4]$, these alkylmono(cyclopentadienyl)titanium derivatives are suitable for olefin (propylene and styrene) polymerisation, while reaction with $B(C_6F_5)_3$ produces inactive species. Polypropylene containing large isotactic stereoblocks obtained by a chain-end control mechanism is produced at low temperature. The nature of the active species in the olefin polymerisation processes has been examined spectroscopically.

Experimental Section

General Considerations: All manipulations were performed under argon using Schlenk and vacuum-line techniques or in a glovebox (model HE-63). The solvents were purified by distillation under argon before use in the presence of the appropriate drying/deoxygenating agent. Deuterated solvents were stored under an inert gas over activated molecular sieves (4 Å) and degassed by several freeze-pump-thaw cycles. LiMe, MgClBz, LiPh, $mbmpH_2$ [2,2′-CH_2-bis(6-*t*Bu-4-$CH_3C_6H_2$-1-OH)], $AlMe_3$ (2.0 M hexane solution), $AlClMe_2$ (1.0 M hexane solution) were purchased (Aldrich) and used without further purification. Li_2mbmp,[3] $[B(C_6F_5)_3]$,[42] $[CPh_3][B(C_6F_5)_4]$[43] and $LiCH_2SiMe_3$[44] were prepared by known procedures. Polymerisation-grade propylene from Aldrich was purified by passage through two columns packed with activated alumina and molecular sieves (4 Å). Styrene was distilled at reduced pressure from calcium hydride and stored in the refrigerator. Methylaluminoxane (MAO, 10% solution in toluene) was purchased from WITCO GmbH. C, H and N microanalyses were performed with a Perkin–Elmer 240B and/or Heraeus CHN-O-Rapid microanalyzer. Polymer melt endotherms were determined with a Perkin–Elmer DSC-4 differential scanning calorimeter. NMR spectra, measured at 25 °C, were recorded with Varian Unity FT-300 (^1H NMR at 300 MHz, ^{13}C NMR at 75 MHz) or Unity-Plus FT-500 (^1H NMR at 500 MHz, ^{13}C NMR at 125 MHz) spectrometers, and chemical shifts (δ, ppm) are referenced to $SiMe_4$ relative to the carbon resonances (^{13}C) and the residual protons (^1H) of the solvent. ^{19}F NMR spectra were recorded with a Varian Unity FT-500 and chemical shifts (δ, ppm) are referenced to $CFCl_3$.

$[TiMe(\eta^5\text{-}C_5H_5)(\eta^2\text{-mbmp})]$ (4): A 1.5 M solution of LiMe in diethyl ether (0.30 mL, 0.45 mmol) was added at –78 °C to a solution of **1** (0.22 g, 0.45 mmol) in hexane (50 mL). The reaction mixture was slowly warmed to room temperature and stirred overnight. The solvent was completely removed and after extraction with hexane and concentration of the combined extracts, a bright yellow solid was obtained which was recrystallised from cold hexane and characterised as **4** (0.16 g, 75% yield). $C_{29}H_{38}O_2Ti$ (466.50): calcd. C 74.70, H 8.16; found C 74.57, H 8.19. ^1H NMR (300 MHz, C_6D_6, 25 °C): δ = 7.13, 7.00 (AA′ spin system, 2×2 H, Ph), 6.13 (s, 5 H, C_5H_5), 3.83, 3.43 (AB spin system, $\Delta\delta$ = 0.40 ppm, $^2J_{H,H}$ = 13.5 Hz, 2×1 H, CH_2), 2.17 (s, 6 H, CH_3Ph), 1.38 [s, 18 H, $C(CH_3)_3$], 1.31 (s, 3 H, $TiCH_3$) ppm. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.07, 6.89 (AA′ spin system, 2×2 H, Ph), 6.53 (s, 5 H, C_5H_5), 3.76, 3.40 (AB spin system, 2×1 H, CH_2), 2.25 (s, 6 H, CH_3Ph), 1.28 [s, 18 H, $C(CH_3)_3$], 1.14 (s, 3 H, $TiCH_3$) ppm. ^{13}C NMR (125 MHz, C_6D_6, 25 °C): δ = 161.6, 137.3, 136.5, 130.2, 129.3, 126.2 (all Ph), 114.98 (C_5H_5), 52.8 ($TiCH_3$), 36.0 (CH_2), 35.5 [$C(CH_3)_3$], 30.9 [$C(CH_3)_3$], 21.4 (CH_3-Ph) ppm.

$[Ti(CH_2Ph)(\eta^5\text{-}C_5H_5)(\eta^2\text{-mbmp})]$ (5): A 2.0 M solution of MgClBz in thf (0.30 mL, 0.62 mmol) was added at –78 °C to a solution of **1** (0.30 g, 0.62 mmol) in hexane (50 mL). The reaction mixture was slowly warmed to room temperature and stirred overnight and the solvent was then completely removed under vacuum. Recrystallisation from hexane gave a light orange solid which was characterised as **5** (0.23 g, 70% yield). Correct elemental analysis data could not be obtained, although satisfactory spectroscopic data were obtained. ^1H NMR (300 MHz, C_6D_6, 25 °C): δ = 7.28 (m, 5 H, CH_2Ph), 7.11, 7.01 (AA′ spin system, 2×2 H, Ph), 6.01 (s, 5 H, C_5H_5), 3.84, 3.36 (AB spin system, $\Delta\delta$ = 0.48 ppm, $^2J_{H,H}$ = 13.7 Hz, 2×1 H, CH_2), 3.24 (s, 2 H, $TiCH_2$Ph), 2.18 (s, 6 H, CH_3Ph), 1.47 [s, 18 H, $C(CH_3)_3$] ppm. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.07, 6.92 (AA′ spin system, 2×2 H, Ph), 7.30 (t, $J_{H,H}$ = 8.0 Hz, 2 H, *m*-CH_2Ph), 7.17 (d, $J_{H,H}$ = 7.9 Hz, 2 H, *o*-CH_2Ph), 7.01 (t, $J_{H,H}$ = 8.1 Hz, 1 H, *p*-CH_2Ph), 6.27 (s, 5 H, C_5H_5), 3.83, 3.38 (AB spin system, 2×1 H, CH_2), 2.99 (s, 2 H, $TiCH_2$Ph), 2.25 (s, 6 H, CH_3Ph), 1.41 [s, 18 H, $C(CH_3)_3$] ppm. ^{13}C NMR (125 MHz, C_6D_6, 25 °C): δ = 161.8, 137.1, 137.0, 130.0, 129.3, 126.4 (all Ph), 152.0 (*ipso*-CH_2Ph), 128.6 (*p*-CH_2Ph), 126.0 (*m*-CH_2Ph), 123.4 (*o*-CH_2Ph), 117.0 (C_5H_5), 77.2 ($TiCH_2$Ph), 36.1 (CH_2), 35.4 [$C(CH_3)_3$], 30.8 [$C(CH_3)_3$], 21.0 (CH_3-Ph) ppm.

$[TiPh(\eta^5\text{-}C_5H_5)(\eta^2\text{-mbmp})]$ (6a, 6b, 6c): A 1.8 M solution of LiPh in diethyl ether (0.35 mL, 0.62 mmol) was added at –78 °C to a solution of **1** (0.30 g, 0.62 mmol) in hexane (50 mL). The reaction mixture was slowly warmed to room temperature and stirred for 12 h. The resulting solution was concentrated under vacuum and a brown oily solid was obtained; spectroscopic analysis revealed a mixture of three isomers **6a**, **6b** and **6c**. Two isomers were obtained as analytically pure samples after repeated recrystallisation from toluene. $C_{34}H_{40}O_2Ti$ (528.56): calcd. C 77.29, H 7.58; found C 77.12, H 7.74. ^1H NMR (300 MHz, C_6D_6, 25 °C): **6a**: δ = 7.08, 7.00 (AA′ spin system, 2 × 2 H, Ph), 7.45, 7.02 (d, $J_{H,H}$ = 8.0 Hz, and m, 2 H + 3 H, Ph), 6.26 (s, 5 H, C_5H_5), 4.51, 3.36 (AB spin system, $\Delta\delta$ = 1.15 ppm, $^2J_{H,H}$ = 13.2 Hz, 2 × 1 H, CH_2), 2.18 (s, 6 H, $\mathit{CH_3}$Ph), 1.43 [s, 18 H, $C(CH_3)_3$] ppm; **6b**: δ = 7.19, 7.04 (AA′ spin system, 2 × 2 H, Ph), 7.61, 6.92 (d, $J_{H,H}$ = 8.0 Hz, and m, 2 H + 3 H, Ph), 6.42 (s, 5 H, C_5H_5), 3.95, 3.49 (AB spin system, 2 × 1 H, $\Delta\delta$ = 0.46 ppm, $^2J_{H,H}$ = 13.7 Hz, CH_2), 2.18 (s, 6 H, $\mathit{CH_3}$Ph), 1.20 [s, 18 H, $C(CH_3)_3$] ppm; **6c**: δ = 7.06, 6.95 (AA′ spin system, 2 × 2 H, Ph), 7.35, 7.09 (d, $J_{H,H}$ = 8.0 Hz, and m, 2 H + 3 H, Ph), 6.55 (s, 5 H, C_5H_5), 5.15, 3.02 (AB spin system, $\Delta\delta$ = 2.13 ppm, $^2J_{H,H}$ = 13.7 Hz, 2 × 1 H, CH_2), 2.07 (s, 6 H, $\mathit{CH_3}$Ph), 1.45 [s, 18 H, $C(CH_3)_3$] ppm. ^{13}C NMR (125 MHz, C_6D_6, 25 °C): **6a**: δ = 162.6, 136.9, 136.7, 133.9, 128.9, 125.6 (all Ph), 129.2 (*p-Ph*), 129.0 (*m-Ph*), 127.4 (*o-Ph*), 115.6 (C_5H_5), 35.1 (CH_2), 35.2 [$\mathit{C}(CH_3)_3$], 30.8 [$C(\mathit{CH_3})_3$], 21.1 ($\mathit{CH_3}$-Ph) ppm; **6b**, δ = 161.7, 137.0, 135.6, 129.2, 128.0, 126.8 (all Ph), 134.8 (*p-Ph*), 130.3 (*m-Ph*), 126.3 (*o-Ph*), 116.1 (C_5H_5), 35.4 (CH_2), 35.2 [$\mathit{C}(CH_3)_3$], 31.0 [$C(\mathit{CH_3})_3$], 21.1 ($\mathit{CH_3}$-Ph ppm); **6c**: δ = 161.7, 140.6, 134.8, 131.1, 126.4, 125.4 (all Ph), 134.3 (*p*-$CH_2\mathit{Ph}$), 129.7 (*m*-$CH_2\mathit{Ph}$), 127.6 (*o*-$CH_2\mathit{Ph}$), 116.5 (C_5H_5), 35.2 (CH_2), 35.1 [$\mathit{C}(CH_3)_3$], 29.9 [$C(\mathit{CH_3})_3$], 21.0 ($\mathit{CH_3}$-Ph) ppm.

[Ti(CH_2SiMe_3)(η^5-C_5H_5)(η^2-mbmp)] (7): A red solution of **1** (0.30 g, 0.62 mmol) in 40 mL of hexane was treated with a solution of $LiCH_2SiMe_3$ (0.06 g, 0.62 mmol) in diethyl ether (20 mL), at –78 °C. The reaction mixture was slowly warmed to room temperature, stirred for 12 h and the solvent completely removed. After extraction with hexane and concentration of the combined extracts, an orange microcrystalline solid was obtained, which was recrystallised from a cold mixture of toluene and hexane and characterised as **7** (0.25 g, 73% yield). $C_{32}H_{46}O_2SiTi$ (538.67): calcd. C 71.38, H 8.55; found C 71.23, H 8.34. ^1H NMR (300 MHz, C_6D_6, 25 °C): δ = 7.11, 6.98 (AA′ spin system, 2 × 2 H, Ph), 6.32 (s, 5 H, C_5H_5), 4.02, 3.34 (AB spin system, $\Delta\delta$ = 0.68 ppm, $^2J_{H,H}$ = 13.5 Hz, 2 × 1 H, CH_2), 2.17 (s, 6 H, $\mathit{CH_3}$Ph), 1.80 (s, 2 H, Ti$\mathit{CH_2}$SiMe$_3$), 1.38 [s, 18 H, $C(CH_3)_3$], 0.29 (s, 9 H, $TiCH_2Si\mathit{Me_3}$) ppm. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.04, 6.87 (AA′ spin system, 2 × 2 H, Ph), 6.57 (s, 5 H, C_5H_5), 3.98, 3.34 (AB spin system, 2 × 1 H, CH_2), 2.24 (s, 6 H, $\mathit{CH_3}$Ph), 1.58 (s, 2 H, Ti$\mathit{CH_2}$SiMe$_3$), 1.29 [s, 18 H, $C(CH_3)_3$], 0.16 (s, 9 H, $TiCH_2Si\mathit{Me_3}$) ppm. ^{13}C NMR (125 MHz, C_6D_6, 25 °C): δ = 161.9, 136.9, 136.5, 129.8, 129.1, 125.8 (all Ph), 114.5 (C_5H_5), 72.5 (Ti$\mathit{C}H_2SiMe_3$), 35.7 (CH_2), 35.3 [$\mathit{C}(CH_3)_3$], 30.7 [$C(\mathit{CH_3})_3$], 21.0 ($\mathit{CH_3}$-Ph), 3.2 ($TiCH_2Si\mathit{Me_3}$) ppm.

[TiMe(η^5-C_5Me_5)(η^2-mbmp)] (8): A 1.5 M solution of LiMe in diethyl ether (0.36 mL, 0.54 mmol) was added to a solution of **2** (0.30 g, 0.54 mmol) in hexane (60 mL) at –78 °C. The reaction mixture was slowly warmed to room temperature and stirred for 6 h. After filtration, the resulting bright yellow solution was concentrated to dryness. A bright yellow solid was obtained, which was recrystallised from cold hexane and characterised as **8** (0.22 g, 77% yield). $C_{34}H_{48}TiO_2$ (536.63): calcd. C 76.14, H 8.96; found C 76.07, H 8.91. ^1H NMR (300 MHz, C_6D_6, 25 °C): δ = 7.13, 7.00 (AA′ spin system, 2 × 2 H, Ph), 3.88, 3.47 (AB spin system, $\Delta\delta$ = 0.41 ppm, $^2J_{H,H}$ = 13.4 Hz, 2 × 1 H, CH_2), 2.16 (s, 6 H, $\mathit{CH_3}$Ph), 1.92 (s, 15 H, C_5Me_5), 1.39 [s, 18 H, $C(CH_3)_3$], 1.10 (s, 3 H, $TiCH_3$) ppm. ^{13}C NMR (125 MHz, C_6D_6, 25 °C): δ = 160.1, 137.1, 134.9, 129.2, 128.7, 123.6 (all Ph), 126.2 ($\mathit{C_5}Me_5$), 54.8 ($TiCH_3$), 35.1 (CH_2), 35.0 [$\mathit{C}(CH_3)_3$], 30.8 [$C(\mathit{CH_3})_3$], 21.0 ($\mathit{CH_3}$-Ph), 11.9 ($C_5\mathit{Me_5}$) ppm.

[Ti(CH_2Ph)(η^5-C_5Me_5)(η^2-mbmp)] (9): A 2.0 M solution of MgClBz in thf (0.50 mL, 1.00 mmol) was added to a solution of **2** (0.56 g, 1.00 mmol) in hexane (60 mL) at –78 °C. The reaction mixture was slowly warmed to room temperature and stirred overnight. After filtration, the solvent was completely removed from the resulting orange solution. Recrystallisation from hexane gave a light orange solid, which was again recrystallised from cold hexane and characterised as **9** (0.39 g, 63% yield). $C_{40}H_{52}O_2Ti$ (612.72): calcd. C 78.43, H 8.50; found C 78.31, H 8.77. ^1H NMR (300 MHz, C_6D_6, 25 °C): δ = 7.02, 7.00 (AA′ spin system, 2 × 2 H, Ph), 7.00 (m, 5 H, $CH_2\mathit{Ph}$), 3.75, 3.44 (AB spin system, $\Delta\delta$ = 0.31 ppm, $^2J_{H,H}$ = 13.7 Hz, 2 × 1 H, CH_2), 2.91 (s, 2 H, Ti$\mathit{CH_2}$Ph), 2.17 (s, 6 H, $\mathit{CH_3}$Ph), 1.89 (s, 15 H, C_5Me_5), 1.34 [s, 18 H, $C(CH_3)_3$] ppm. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.03–6.95 (m, 4 H and 5 H, Ph and $CH_2\mathit{Ph}$), 3.64, 3.39 (AB spin system, 2 × 1 H, CH_2), 2.77 (s, 2 H, Ti$\mathit{CH_2}$Ph), 2.24 (s, 6 H, $\mathit{CH_3}$Ph), 1.97 (s, 15 H, C_5Me_5), 1.24 [s, 18 H, $C(CH_3)_3$] ppm. ^{13}C NMR (125 MHz, C_6D_6, 25 °C): δ = 160.4, 137.1, 135.1, 129.5, 128.9, 126.6 (all Ph), 148.4 (*ipso*-$CH_2\mathit{Ph}$), 129.4 (*p*-$CH_2\mathit{Ph}$), 124.7 (*m*-$CH_2\mathit{Ph}$), 123.6 (*o*-$CH_2\mathit{Ph}$), 127.8 ($\mathit{C_5}Me_5$), 76.7 (Ti$\mathit{C}H_2$Ph), 35.4 (CH_2), 35.3 [$\mathit{C}(CH_3)_3$], 31.3 [$C(\mathit{CH_3})_3$], 21.0 ($\mathit{CH_3}$-Ph), 12.0 ($C_5\mathit{Me_5}$) ppm.

[Ti(CH_2SiMe_3)(η^5-C_5Me_5)(η^2-mbmp)] (10a, 10b): A red solution of **2** (0.52 g, 0.93 mmol) in 50 mL of hexane was treated, at –78 °C, with a solution of $LiCH_2SiMe_3$ (0.09 g, 0.95 mmol) in 20 mL of diethyl ether. The reaction mixture was warmed to room temperature, stirred for 12 h and the solvent was completely removed. After extraction with hexane and concentration of the combined extracts, an orange microcrystalline solid was obtained, which was recrystallised from cold hexane and characterised as **10a** (0.34 g, 60%) containing a small amount of isomer **10b**. $C_{37}H_{56}O_2SiTi$ (608.81): calcd. C 73.03, H 9.21; found C 72.91, H 9.16. ^1H NMR (300 MHz, C_6D_6, 25 °C): **10a**: δ = 7.11, 7.04 (AA′ spin system, 2 × 2 H, Ph), 3.66, 3.38 (AB spin system, $\Delta\delta$ = 0.28 ppm, $^2J_{H,H}$ = 13.4 Hz, 2 × 1 H, CH_2), 2.17 (s, 6 H, $\mathit{CH_3}$Ph), 1.93 (s, 15 H, C_5Me_5), 1.49 [s, 18 H, $C(CH_3)_3$], 1.16 (s, 2 H, Ti$\mathit{CH_2}$SiMe$_3$), 0.18 (s, 9 H, $TiCH_2Si\mathit{Me_3}$) ppm; **10b**: δ = 7.04, 6.96 (AA′ spin system, 2 × 2 H, Ph), 4.08, 3.40 (AB spin system, $\Delta\delta$ = 0.68 ppm, $^2J_{H,H}$ = 13.4 Hz, 2 × 1 H, CH_2), 2.11 (s, 6 H, $\mathit{CH_3}$Ph), 2.02 (s, 15 H, C_5Me_5), 1.47 (s, 2 H, Ti$\mathit{CH_2}$SiMe$_3$), 1.44 [s, 18 H, $C(CH_3)_3$], –0.007 (s, 9 H, $TiCH_2Si\mathit{Me_3}$) ppm. ^{13}C NMR (125 MHz, C_6D_6, 25 °C): **10a**: δ = 160.8, 136.6, 134.8, 129.0, 128.3, 124.2 (all Ph), 126.6 ($\mathit{C_5}Me_5$), 67.9 (Ti$\mathit{C}H_2SiMe_3$), 35.4 (CH_2), 35.7 [$\mathit{C}(CH_3)_3$], 32.3 [$C(\mathit{CH_3})_3$], 21.1 ($\mathit{CH_3}$-Ph), 12.5 (C_5Me_5), 4.4 ($TiCH_2Si\mathit{Me_3}$) ppm. The small amount of **10b** in the sample did not allow its ^{13}C NMR signals to be assigned accurately.

[{Ti(η^5-C_5H_5)(η^2-mbmp)}$_2$(μ-O)] (11): Distilled water (6.8 µL, 0.38 mmol) was added at room temperature to a solution of **6** (0.20 g, 0.38 mmol) in toluene (20 mL). The solvent was completely removed to give a red solid, which was recrystallised from diethyl ether to afford **11** as a crystalline solid. $C_{56}H_{70}O_5Ti_2$ (918.91): calcd. C 73.22, H 7.67; found C 73.20, H 7.49. ^1H NMR (300 MHz, C_6D_6, 25 °C): δ = 7.10, 7.02, 6.83 (two AA′ spin systems, 1 H, 2 × 1 H, 1 H, Ph), 6.56 (s, 10 H, C_5H_5), 4.24, 3.24 (AB spin system, $\Delta\delta$ = 1.00 ppm, $^2J_{H,H}$ = 13.6 Hz, 2 × 2 H, CH_2), 2.21, 2.18 (s, 2 × 6 H, $\mathit{CH_3}$Ph), 1.69, 0.94 [s, 2 × 18 H, $C(CH_3)_3$] ppm. ^{13}C NMR (125 MHz, C_6D_6, 25 °C): δ = 164.1, 163.3, 136.9, 136.6, 136.4, 133.0, 130.6, 129.8, 128.9, 128.5, 125.7, 125.2 (all Ph), 116.4 (C_5H_5), 34.8 (CH_2), 35.3, 35.1 [2 × $\mathit{C}(CH_3)_3$], 31.9, 30.0 [2 × $C(\mathit{CH_3})_3$], 21.1, 21.0 (2 × $\mathit{CH_3}$-Ph) ppm.

[Ti(η^5-C_5H_5)(η^2-mbmp)][MeB(C_6F_5)$_3$] (12): C_6D_6 was added to a mixture of **4** (0.018 g, 0.04 mmol) and $B(C_6F_5)_3$ (0.019 g, 0.04 mmol) at room temperature in an NMR tube fitted with a Teflon valve inside a glovebox. The NMR tube was quickly introduced into the NMR equipment and the spectra were recorded at room temperature. The formation of **12** was deduced spectroscopically. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ = 7.03, 6.94 (AA′ spin system, 2×2 H, Ph), 6.33 (s, 5 H, C_5H_5), 4.05, 3,36 (AB spin system, 2×1 H, $\Delta\delta$ = 0.69 ppm, CH_2), 2.12 (s, 6 H, CH_3Ph), 1.43 [s, 18 H, $C(CH_3)_3$], 0.84 (br. s, 3 H, BCH_3) ppm. ^{13}C NMR (125 MHz, C_6D_6, 25 °C): δ = 163.6, 137.4, 136.6, 131.2, 129.1, 126.2 (all Ph), 149.8, 147.8, 138.2, 136.5 (all C_6F_5), 118.2 (C_5H_5), 35.5 (CH_2), 35.4 [$C(CH_3)_3$], 31.2 [$C(CH_3)_3$], 21.1 (CH_3-Ph), 10.5 (BCH_3) ppm. ^{19}F NMR (300 MHz, C_6D_6, 25 °C): δ = –136.5, –160.0, –163.5 ppm.

[Ti(η^5-C_5H_5)(η^2-mbmp)][(CH_2Ph)B(C_6F_5)$_3$] (13): The same procedure described for **12**, using a mixture of **5** (0.020 g, 0.04 mmol) and B(C_6F_5)$_3$ (0.019 g, 0.04 mmol), resulted in the formation of **13**. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ = 7.03, 6.94 (AA′ spin system, 2×2 H, Ph), 6.50, 6.41, 6.26 (o, m, *p*-CH_2Ph), 6.33 (s, 5 H, C_5H_5), 4.05, 3.36 (AB spin system, 2×1 H, $\Delta\delta$ = 0.69 ppm, CH_2), 2.12 (s, 6 H, CH_3Ph), 1.43 [s, 18 H, $C(CH_3)_3$], 3.14 (br. s, 2 H, BCH_2Ph) ppm. ^{13}C NMR (125 MHz, C_6D_6, 25 °C): δ = 163.6, 137.4, 136.6, 131.2, 129.1, 126.2 (all Ph), 149.8, 147.8, 138.6, 136.4 (all C_6F_5), 152.5 (C_{ipso}-CH_2Ph), 129.4, 127.4, 122.3 (*o*-, *m*-, *p*-CH_2Ph), 118.2 (C_5H_5), 38.2 (BCH_2Ph), 35.5 (CH_2), 35.4 [$C(CH_3)_3$], 31.2 [$C(CH_3)_3$], 21.1 (CH_3-Ph) ppm. ^{19}F NMR (300 MHz, C_6D_6, 25 °C): δ = –132.7, –161.1, –164.5 ppm.

[Ti(η^5-C_5Me_5)(η^2-mbmp)][MeB(C_6F_5)$_3$] (14): The same procedure described for **12**, using a mixture of **8** (0.021 g, 0.04 mmol) and B(C_6F_5)$_3$ (0.019 g, 0.04 mmol), resulted in the formation of **14**. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ = 7.04, 6.96 (AA′ spin system, 2×2 H, Ph), 3.98, 3.40 (AB spin system, 2×1 H, $\Delta\delta$ = 0.58 ppm, CH_2), 2.11 (s, 6 H, CH_3Ph), 2.02 (s, 15 H, C_5Me_5), 1.45 [s, 18 H, $C(CH_3)_3$], 0.91 (br. s, 3 H, BCH_3) ppm. ^{13}C NMR (125 MHz, C_6D_6, 25 °C): δ = 161.4, 137.6, 134.8, 130.4, 129.4, 126.6 (all Ph), 149.6, 147.8, 138.6, 136.5 (all C_6F_5), 128.3 (C_5Me_5), 35.1 (CH_2), 35.4 [$C(CH_3)_3$], 31.5 [$C(CH_3)_3$], 21.1 (CH_3-Ph), 13.1 (C_5Me_5), 10.5 (BCH_3) ppm. ^{19}F NMR (300 MHz, C_6D_6, 25 °C): δ = –136.1, –160.5, –163.9 ppm.

[Ti(η^5-C_5Me_5)(η^2-mbmp)][(CH_2Ph)B(C_6F_5)$_3$] (15): The same procedure described for **12**, using a mixture of **9** (0.024 g, 0.04 mmol) and B(C_6F_5)$_3$ (0.019 g, 0.04 mmol), resulted in the formation of **15**. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ = 7.04, 6.96 (AA′ spin system, 2×2 H, Ph), 7.10–6.70 (*o*-, *m*-, *p*-CH_2Ph), 3.96, 3.40 (AB spin system, 2×1 H, $\Delta\delta$ = 0.56 ppm, CH_2), 2.10 (s, 6 H, CH_3Ph), 2.02 (s, 15 H, C_5Me_5), 1.45 [s, 18 H, $C(CH_3)_3$], 2.90 (br. s, 2 H, BCH_2Ph) ppm. ^{13}C NMR (125 MHz, C_6D_6, 25 °C): δ = 161.5, 137.6, 134.8, 130.5, 129.5, 126.6 (all Ph), 150.4, 147.2, 139.0, 135.6 (all C_6F_5), 160.3 (C_{ipso}-CH_2Ph), 128.6 (C_5Me_5), 37.3 (BCH_2Ph), 35.1 (CH_2), 35.4 [$C(CH_3)_3$], 31.5 [$C(CH_3)_3$], 21.1 (CH_3-Ph), 13.1 (C_5Me_5) ppm; signals of *o*-, *m*-, *p*-CH_2Ph not found. ^{19}F NMR (300 MHz, C_6D_6, 25 °C): δ = –135.0, –159.5, –164.6 ppm.

[AlMe(mbmp)]$_2$ (16): $AlMe_3$ (0.3 mL of a 2.0 M solution in hexane, 0.59 mmol) was added to a solution of mbmpH_2 (0.2 g, 0.59 mmol) in 25 mL of toluene at room temperature. After a few minutes, a white solid appeared and the reaction mixture was stirred for 5 h. The solution was filtered and the white solid was washed twice with hexane and characterised as **16** (0.29 g, 65% yield). $C_{48}H_{66}Al_2O_4$ (761.02): calcd. C 75.80, H 8.68; found C 75.67, H 8.90. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ = 7.41, 7.21, 7.04, 6.88 (AA′ spin systems, 4×2 H, Ph), 4.70, 3.69 (AB spin system, 2×2 H, $\Delta\delta$ = 1.01 ppm, CH_2), 2.32, 1.83 (s, 2×6 H, CH_3Ph), 1.40, 1.37 [s, 2×18 H, $C(CH_3)_3$], 0.15 (s, 6 H, $AlCH_3$) ppm. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.07, 7.03, 6.98, 6.95 (AA′ spin systems, 4×2 H, Ph), 4.33, 3.53 (AB spin system, $\Delta\delta$ = 0.80 ppm, $^2J_{H,H}$ = 13.7 Hz, 2×2 H, CH_2), 2.30, 2.22 (s, 2×6 H, CH_3Ph), 1.36, 1.21 [s, 2×18 H, $C(CH_3)_3$], –0.33 (s, 6 H, $AlCH_3$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 151.2, 144.3, 140.9, 137.7, 134.4, 132.7, 130.6, 130.5, 127.8, 127.4, 127.1, 126.3 (all Ph), 35.0 (CH_2), 36.1, 34.5 [$C(CH_3)_3$], 31.8, 29.7 [$C(CH_3)_3$], 21.1, 21.0 (CH_3-Ph), 14.2 ($AlCH_3$) ppm.

[AlCl(mbmp)]$_2$ (17): $AlClMe_2$ (0.9 mL of a 1.0 M solution in hexane, 0.88 mmol) was added to a solution of mbmpH_2 (0.3 g, 0.88 mmol) in 25 mL of toluene at room temperature. After a few minutes, a white solid appeared and the reaction mixture was stirred for 3 h. The solution was filtered and the white solid was washed twice with hexane and toluene and characterised as **17** (0.37 g, 53% yield). $C_{46}H_{60}Al_2Cl_2O_4$ (801.85): calcd. C 68.90, H 7.54; found C 68.83, H 7.49. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ = 7.41, 7.18, 7.05, 6.88 (AA′ spin systems, 4×2 H, Ph), 4.83, 3.90 (AB spin system, 2×2 H, $\Delta\delta$ = 0.93 ppm, CH_2), 2.27, 1.79 (s, 2×6 H, CH_3Ph), 1.44, 1.43 [s, 2×18 H, $C(CH_3)_3$] ppm. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.09, 7.05, 7.02, 6.97 (AA′ spin systems, 4×2 H, Ph), 4.35, 3.68 (AB sin systems, $\Delta\delta$ = 0.67 ppm, $^2J_{H,H}$ = 14.6 Hz, 2×2 H, CH_2), 2.31, 2.22 (s, 2×6 H, CH_3Ph), 1.40, 1.23 [s, 2×18 H, $C(CH_3)_3$] ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 149.9, 140.8, 138.5, 135.9, 132.8, 131.0, 130.2, 129.1, 128.9, 128.2, 128.0, 126.7 (all Ph), 35.2 (CH_2), 36.1, 34.5 [$C(CH_3)_3$], 32.3, 29.8 [$C(CH_3)_3$], 21.1, 21.0 (CH_3-Ph) ppm.

Polymerisation of Propylene: A 250-mL Büchi reactor equipped with a mechanical stirrer was first evacuated and then charged with dried scavenger (MAO) and toluene (150 mL). A 10-mL pressure tube was charged with the titanium complex solution in toluene (4 mL). The reactor was purged three times with the monomer by pressurizing and venting. The monomer was then equilibrated with the toluene in the reactor for 30 min at the polymerisation temperature and pressure (kept constant at 1 atm over the run) with constant stirring. In the runs in which liquid propylene was used, the reactor was first equilibrated at 0 °C with constant stirring and then fed with the monomer. The reaction was initiated by injecting the solution containing the catalytic system under argon pressure. After the desired reaction time, the reactor was vented and the polymer was precipitated into 10% HCl in methanol, washed with clean methanol and dried in a vacuum oven at 60 °C to constant weight.

Polymerisation of Styrene: A 100-mL glass pressure bottle with magnetic stirrer was vented and charged with toluene, MAO and 5 mL of the monomer. The mixture was then equilibrated at the polymerisation temperature with constant stirring and the reaction was initiated by injecting the solution of the catalyst in toluene (4 mL). After the desired reaction time, the reactor was vented and the polymer was precipitated into 10% HCl in methanol, washed with clean methanol and dried in a vacuum oven at 40 °C to constant weight. The polymer was extracted with refluxing thf for 5 h and dried again to constant weight in order to determine the sPS portion of the polymer obtained.

Polymer Analyses: Molecular weights were determined by high-temperature gel permeation chromatography using propylene and polystyrene as GPC calibration standards and 1,2,4-trichlorobenzene as eluent. The glass transition temperature and melting temperature were determined at a heating rate of 20 °C min^{-1}. ^{1}H and ^{13}C NMR measurements were performed at 363 K in [D_2]1,1,2,2-tetrachloroethane and referenced using the solvent peaks. The areas of the nine peaks in the methyl region determined from spectral integrations in polypropylene samples were used to characterise the sample microstructure. Analyses of the polymer properties were performed at the University of Ulm (Germany), Inorganic Chemistry II Department.

Single-Crystal X-ray Structure Determination of Compounds 8, 9 and 11·0.75 C_6H_{14}: Crystal data and details of the structure deter-

Table 7. Crystallographic data for compounds **8**, **9** and **11**·0.75 C_6H_{14}.

	8	**9**	**11**·0.75 C_6H_{14}
Empirical formula	$C_{34}H_{48}O_2Ti$	$C_{40}H_{52}O_2Ti$	$C_{121}H_{161}O_{10}Ti_4$
Formula mass	536.59	612.69	1967.10
Colour/habit	orange/fragment	orange/fragment	orange/fragment
Crystal dimensions [mm]	0.20 × 0.36 × 0.61	0.15 × 0.33 × 0.64	0.23 × 0.36 × 0.56
Crystal system	monoclinic	monoclinic	triclinic
Space group	$P2_1/n$ (no. 14)	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)
a [Å]	11.0192(1)	11.2375(1)	11.5443(1)
b [Å]	16.2903(1)	17.6831(1)	14.4543(1)
c [Å]	18.7555(2)	17.9601(1)	18.1492(2)
α [°]	90	90	98.6156(3)
β [°]	90.1907(4)	105.4970(4)	106.9058(4)
γ [°]	90	90	91.9242(4)
V [Å^3]	3366.71(5)	3439.17(4)	2855.35(5)
Z	4	4	1
T [K]	153	173	123
$D_{calcd.}$ [g cm^{-3}]	1.059	1.183	1.144
μ [mm^{-1}]	0.279	0.281	0.324
$F(000)$	1160	1320	1055
θ range [°]	2.48–25.35	1.65–25.32	1.85–25.38
Index ranges (h, k, l)	±13, ±19, ±22	±13, ±21, ±21	±13, ±17, ±21
No. of refections collected	80030	62663	59488
No. of independent reflections/R_{int}	6157/0.044	6249/0.034	10449/0.042
No. of obsd reflections [$I > 2\sigma(I)$]	4990	5495	8948
No. of data/restraints/parameters	6157/0/348	6249/0/405	10449/0/920
$R1/wR2$ [$I > 2\sigma(I)$][a]	0.0400/0.1202	0.0458/0.1258	0.0431/0.1129
$R1/wR2$ (all data)[a]	0.0510/0.1248	0.0521/0.1307	0.0522/0.1205
GOF (on F^2)[a]	1.118	1.032	1.027
Largest difference peak/hole [e Å^{-3}]	+0.43/–0.36	+0.44/–0.35	+0.52/–0.57

[a] $R1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$; $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $GOF = \{\Sigma[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$.

mination are presented in Table 7. Suitable single crystals for the X-ray diffraction study were grown from hexane in all cases. A clear orange fragment was stored under perfluorinated ether, transferred into a Lindemann capillary, fixed, and sealed. Preliminary examination and data collection were carried out with an area detecting system (Nonius, MACH3, κ-CCD) at the window of a rotating anode (Nonius, FR591) with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). The unit-cell parameters were obtained by full-matrix least-squares refinement of 6411 (6477, 10431) reflections. Data collection was performed at 153 (173, 123) K (Oxford Cryosystems) in the range 2.48°< θ < 25.35° (1.65°< θ < 25.32°, 1.85°< θ < 25.38°) for a total of nine (nine, seven) data sets in rotation scan mode with $\Delta\varphi/\Delta\omega$ = 1.0° (1.0°, 1.0°). A total of 80030 (62663, 59488) intensities were integrated. Raw data were corrected for Lorentz, polarisation, and, arising from the scaling procedure, latent decay and absorption effects. After merging [R_{int} = 0.044 (0.034, 0.042)] a total of 6157 (6249, 10449) (all data) and 4990 (5495, 8948) [$I > 2\sigma(I)$] reflections remained and all these data were used in the subsequent refinement. The structures were solved by a combination of direct methods and difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic displacement parameters. For **8** and **9**, all hydrogen atoms were placed in ideal positions (riding model). For **11**·0.75 C_6H_{14}, all hydrogen atoms located at the titanium complex were found in the difference map calculated from the model containing all non-hydrogen atoms. The hydrogen positions were refined with individual isotropic displacement parameters. All hydrogen positions located at the disordered hexane solvent molecule were placed in calculated positions (riding model). Full-matrix least-squares refinements with 348 (405, 920) parameters were carried out by minimizing $\Sigma w(F_o^2 - F_c^2)^2$ with the SHELXL-97 weighting scheme and stopped at shift/err < 0.001 (0.001, 0.001). The final residual electron density maps showed no remarkable features. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from the International Tables for Crystallography. All calculations were performed with an Intel Pentium II PC, with the STRUX-V system, including the programs PLATON, SIR92 and SHELXL-97.[45–50] In **8**, a problem with an unresolvable solvent molecule was resolved with the PLATON[49] *Calc Squeeze* procedure. For **9**, a disorder [0.821(4):0.179(4)] of the cyclopentadienyl ring was clearly resolved. For **11**·0.75 C_6H_{14}, the solvent molecule appeared to be disordered over three positions (3:2:1) with an overall occupancy factor of 0.75. CCDC-631035 (**8**), -631036 (**9**) and -631037 (**11**·0.75 C_6H_{14}) 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 footnote on the first page of this article): ^{13}C NMR spectra for the PP sample obtained in run 2 and run 6 (Table 5).

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