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Monocyclopentadienyl and *ansa*-Monocyclopentadienylalkoxo Complexes of Titanium Containing the 2,2′-Methylenebis(6-*tert*-butyl-4-methylphenoxo) Ligand. Synthesis, Characterization, and Polymerization Catalyst Behavior. Molecular Structure of Ti(η^5-C_5H_5)(η^2-MBMP)Cl, Ti(η^5-C_5Me_5)(η^2-MBMP)Cl, and Ti(η^5-$C_5H_4SiMe_2$-η^1-MBMP)Cl_2

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The dialkoxo titanium complexes TiCp′(η^2-MBMP)Cl [Cp′ = η^5-C_5H_5 (**1**); η^5-C_5Me_5 (**2**)] have been prepared in good yields by reaction of Li_2(MBMP) with the corresponding monocyclopentadienyltrichloro titanium derivative. In a similar reaction the addition of 1 equiv of Li_2(MBMP) to Ti(η^5-$C_5H_4SiMe_2Cl$)Cl_3 generates the analogous titanium compound Ti(η^5-$C_5H_4SiMe_2Cl$)(η^2-MBMP)Cl (**3**), while the *ansa*-cyclopentadienylalkoxo complex Ti(η^5-C_5H_4-$SiMe_2$-η^1-MBMP)Cl_2 (**4**) is formed when $MBMPH_2$ is treated with Ti(η^5-$C_5H_4SiMe_2Cl$)Cl_3 in the presence of NEt_3 in 1:1:2 molar ratio. Compounds **1**, **2** and **4** have been characterized by single-crystal X-ray crystallography. DFT calculations were performed in order to elucidate the energies and geometries for these compounds. Upon addition of methylaluminoxane (MAO), the bisphenoxo complexes are active in the polymerization of α-olefins.

Introduction

In recent years, one of the achievements in transition organometallic chemistry has been the development of Ziegler−Natta catalysis for the polymerization of ethylene and α-olefins. Monocyclopentadienyl titanium derivatives of the type $TiCp'X_nL_{3-n}$ (Cp′ = substituted or unsubstituted cyclopentadienyl ring) have shown remarkable catalytic activities when used as catalysts for these α-olefin polymerization reactions.[1−4] It is now well accepted that the Ziegler−Natta catalyst precursors (cyclopentadienyl or non-cyclopentadienyl group 4 metal derivatives) must have two or more halide or alkyl coordinated groups. In the presence of a cocatalyst one of these groups is abstracted to form an activated cationic species in which the olefin is coordinated and inserted in the remaining metal−alkyl bond. The well-known cyclopentadienyl mono-amido[5−7] or bis-amido[8]

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derivatives are precatalyst examples containing only a single such group and are also of potential interest in the context of single-site olefin polymerization catalysis.

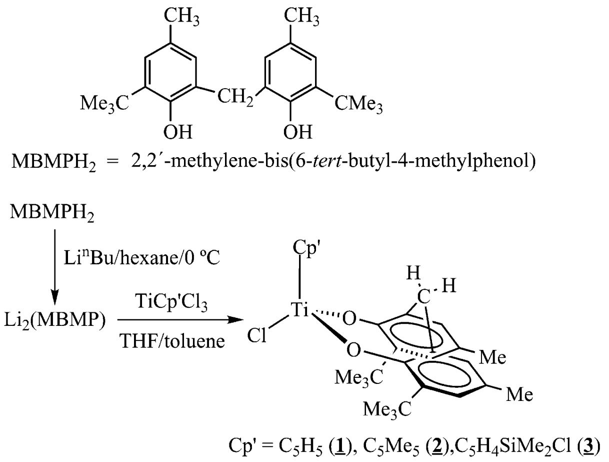
Metal alkoxo derivatives are used as catalyst in a wide range of homogeneous reactions. Alkoxo (or phenoxo) ligands stabilize early transition metal elements in high oxidation states.[9,10] As an aryloxo ligand example, it has been found that chelate phenoxo molecules of the type 2,2′-X-bis(4-methyl-6-*tert*-butylphenoxo) (X = CH_2,[11] CH_2-CH_2,[12] S,[13,14] Te[15]) can act as dianionic ligands coordinated to group 4 transition metals. When the titanium and zirconium alkoxo compounds are combined with MAO, they become highly active catalysts in the α-olefin polymerization.[16−19]

As part of our investigations aimed at elucidating the effect of metal environment on the reactivity of complexes of this type, we have synthesized a new class of monochloro titanium systems containing one dialkoxobidentate ligand, 2,2′-methylenebis(4-methyl-6-*tert*-butylphenoxo) = MBMP, and one cyclopentadienyl ring. Here we report the synthesis of the monocyclopentadienyl dialkoxo monochloro Ti(η^5-C_5H_5)(η^2-MBMP)Cl, Ti(η^5-C_5Me_5)(η^2-MBMP)Cl and Ti(η^5-$C_5H_4SiMe_2Cl$)(η^2-MBMP)Cl compounds and the *ansa*-cyclopentadienylalkoxo dichloro Ti(η^5-$C_5H_4SiMe_2$-η^1-MBMP)Cl_2 derivative, as well as their catalytic application in α-olefin polymerizations. The X-ray molecular structures of Ti(η^5-C_5H_5)(η^2-MBMP)Cl, Ti(η^5-C_5Me_5)(η^2-MBMP)Cl, and Ti(η^5-$C_5H_4SiMe_2$-η^1-MBMP)Cl_2 complexes were determined by diffraction methods, and calculations using the density functional theoretical (DFT) method were carried out.

Results and Discussion

Synthesis of Complexes. Addition of 1 equiv of Li_2(MBMP)[10] in THF solution to TiCp′Cl_3 in hexane, at −78 °C, affords the TiCp′(η^2-MBMP)Cl (Cp′ = η^5-C_5H_5 (**1**); η^5-C_5Me_5 (**2**)) compounds containing the bidentate dianionic η^2-MBMP ligand. Compounds **1** and **2** were isolated as red microcrystalline solids in about 90% yield (Scheme 1). Compound **1** has been previously synthesized by reaction of Na_2(MBMP) with Ti(η^5-C_5H_5)Cl_3 and obtained in lower yields (63%).[11] In a similar reaction the addition of 1 equiv of Li_2(MBMP) to Ti(η^5-$C_5H_4SiMe_2Cl$)Cl_3 in hexane, at low temperature, gives the monocyclopentadienyl η^2-MBMP derivative Ti(η^5-$C_5H_4SiMe_2Cl$)(η^2-MBMP)Cl (**3**), while the reaction of Ti(η^5-$C_5H_4SiMe_2Cl$)Cl_3 with $MBMPH_2$ in the presence of NEt_3 in 1:1:2 molar ratio in hexane, at −78 °C, produces a mixture of **3** and the cyclopentadienylalkoxo complex Ti(η^5-$C_5H_4SiMe_2$-η^1-MBMP)Cl_2 (**4**) (Scheme 2). Compound **4** was obtained as an analytically pure substance after recrystallization, as it is less soluble in hexane than **3**. Linked cyclopentadienylamido complexes of group 4 transition metals have attracted recent interest, as they provide an important class of compounds with applications as polymerization catalyst,[6c] while only a few linked cyclopentadienylalkoxo complexes of these metals have been reported.[20]

Scheme 1



Compounds **1**−**4** are soluble in chlorinated solvents (chloroform and dichloromethane) as well as in aromatic (benzene, toluene) and aliphatic hydrocarbons (pentane and hexane). They were characterized by elemental analysis and NMR spectroscopy and can be stored for months under an inert atmosphere without decomposition. They also remain air stable for some weeks in the solid state. The analytical composition exactly fits the proposed formulation. The molecular structures of **1**, **2**, and **4** were determined by X-ray diffraction methods.

The NMR spectra (C_6D_6 and $CDCl_3$, room temperature) for the complexes **1**−**3** show patterns for the MBMP fragment similar to those described for compounds containing the same diphenoxo ligand. The ^1H NMR resonances of the methylene bridge indicate the formation of the metallacyclic ring and are very sensitive to changes in the coordination sphere of the metal center. The two CH_2 protons appear as a singlet in the free phenol, but when the dioxotitanacycle is formed in compounds **1**−**3**, they give rise to a pair of doublets. Both equivalent *tert*-butyl groups and the two methyl substituents on the phenyl rings appear as singlets between δ 1.44−1.38 and 2.11−2.12 in C_6D_6, respec-

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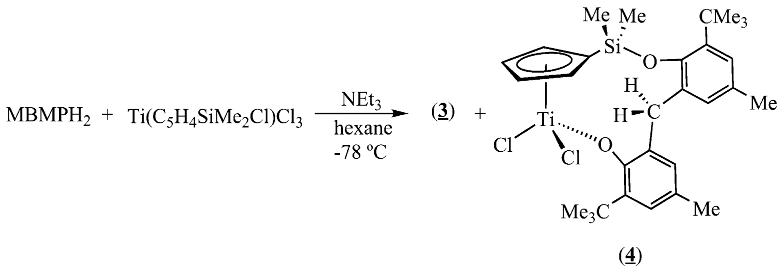
Scheme 2



tively. The protons at positions 3 and 5 on the phenyl ring appear as two doublets with a coupling constant of $^4J_{HH}$ = 1.83 Hz. Singlets are observed for the cyclopentadienyl and the methylcyclopentadienyl ring protons in the expected region of the spectra for compounds **1** and **2**, while the ^{1}H NMR spectrum of compound **3** exhibits one AA′BB′ spin system for the cyclopentadienyl ring protons and one singlet assignable to the methyl groups bonded to silicon. For all of these compounds, structural features similar to those described from ^{1}H 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.

The bidentate MBMP ligand can adapt its interaction with the metal center to changes in the metallic atom environment. This ligand forms a very stable eight-membered metallacycle and contains a methylene bridge in which the hydrogen atoms are very influenced by the other ligands coordinated to the metal. The ^{1}H chemical shifts for the methylene protons vary considerably depending on the nature of the other ligands coordinated to the titanium atom, although their relationship with these structural factors is not yet fully defined. The value of the chemical shift difference between the two methylene protons of the diphenoxo ligand, obtained from ^{1}H NMR spectra, was initially considered an effective probe to elucidate the metallacycle conformation adopted by the MBMP ligand in the metal coordination sphere.[11] It also has been proposed that this characteristic spectroscopic parameter is very sensitive to the electronegativity of the ligands coordinated to the metal center.[21] From literature, comparing the crystallographic data of Ti(MBMP)Cl_2 and $ZrCp_2$(MBMP) with their NMR behavior, it is assumed that the *boat* conformation of the titanium compound (in the solid state) produces a 0.34 ppm separation between the methylene proton doublets, while the *chair* conformation of the cyclopentadienyl zirconium derivative exhibits, in solution, two doublets separated by 1.07 ppm.[11] The two doublets are separated by 0.75[11] and 0.68 ppm in compounds **1** and **2**, and both exhibit a *boat* conformation in the solid state as evidenced by their X-ray diffraction studies (see X-ray study).

The ^{1}H NMR spectrum of **4** shows two singlets for nonequivalent *tert*-butyl groups, two singlets for nonequivalent methyl groups, and four signals assignable to the phenyl protons of the dialkoxo ligand. However, only one singlet for the methylene CH_2 protons, one AA′BB′ spin system for the C_5H_4 ring protons, and one signal for the SiMe_2 resonances are observed in the spectrum, suggesting a molecular structure that must have a time-averaged mirror plane of symmetry.

The asymmetric solid state structure of **4** (see X-ray study) contrasts with the C_s symmetry observed in solution at room temperature and suggests that this compound exhibits dynamic behavior in solution involving a flipping process in the silicon−titanium bridge with interconversion of the two otherwise nonequivalent methylene protons and $SiMe_2$ methyl groups, generating an AA′BB′ spin system for the cyclopentadienyl ring protons. A Gibbs activation energy $\Delta G^\ddagger$ of 9.6 kcal/mol at 203 K in the coalescence temperature calculated for the mutual exchange of methylene proton resonances (AB spin system) was obtained for this process in complex **4**. A fluxional process of the nine-membered titanacycle ring in Ti(EBMP)X_2 [EBMP = 2,2′-CH_2CH_2-bis(4-methyl-6-*tert*-butylphenoxo)], equivalent to an enantiomerization similar to that observed in organic heterocyclic compounds, has been described as an inversion of the ring.[12] Fluxional behavior in cyclopentadienylamido titanium derivatives, involving interconversion between two enantiomeric conformations of a seven-membered Cp−Si−N−C−C−N−Ti metallacycle, has also been detected.[22]

Study of the Molecular Structure. Theoretical and Conformational Studies and Crystal Structure of Ti(η^5-C_5H_5)(η^2-MBMP)Cl (1), Ti(η^5-C_5Me_5)(η^2-MBMP)Cl (2), and Ti(η^5-$C_5H_4SiMe_2$-η^1-MBMP)Cl_2 (4). Considering the bonding character of the diphenoxo ligand, as well as the two other additional but distinct ligands coordinated to the metal center, a priori we propose for the TiCp′(η^2-MBMP)Cl 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).

The HF method with B3LYP hybrid exchange−correlation energy functional[23] implemented in the Gaussian suite of programs[24] using a 3-21g* basis set was performed in order to explore the potential energy surface (PES) and locate the minima involved in those

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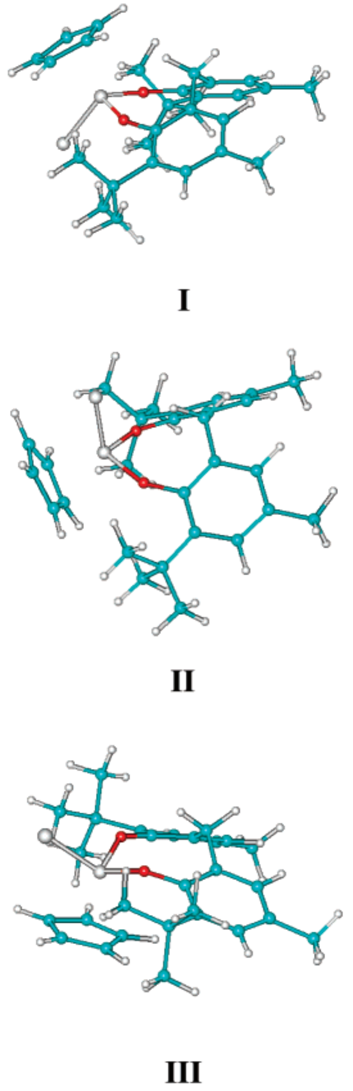
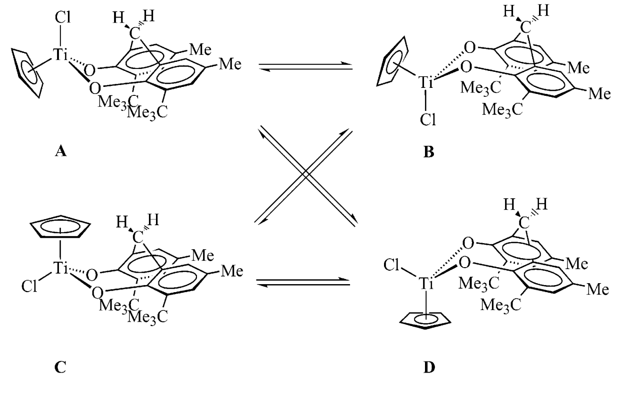


Figure 1. Optimized structures for the TiCp′(η^2-MBMP)-Cl complexes.

Scheme 3



processes. All of the structures were optimized at this level of theory, to study the character of the found stationary points. An analysis of the approximate Hessian confirms all these points to be minima in the PES.

In our search, three different conformers were found (Figure 1). The most stable conformer (**I**) has an intermediate geometry between a *boat* and a *chair* conformation (intermediate between **C** and **B** in Scheme 3, slightly nearer to the *boat* than to the *chair*), with the Cp ligand close to the methylene bridge between phenyl groups. The Ti−O bond distance is short (1.78 Å), and a high valence angle (C−O−Ti) value of 154° was found. A high degree of planarity in the C−O−Ti−O−C core with a value for the dihedral angle (Figure 2) defined by the O−Ti−O and O−C−C−O planes of 11.6° was calculated for this conformer. This dihedral angle differs depending on the nature of the X group bridging the two phenoxo fragments. When X = S (with coordination to the metal center) for sulfur-diphenoxo compounds (SBMP derivatives) values near 50° are observed, while for X = CH_2 (no coordination to metal center) (MBMP derivatives) the corresponding angle has a value of 2°.[13a]

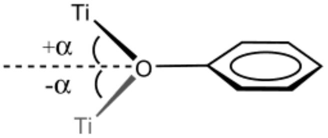


Figure 2. Lateral view of the dihedral angle defined by the Ti−O−C(Ph) unit.

Table 1. Energetics and Boltzmann Populations for the Calculated Isomers

isomer	energy[a] B3Lyp/3-21g*	relative energy[b]	Boltzmann equilibrium population[c]
I	−2535.54061420	0	98.5
II	−2535.53665739	2.5	1.5
III	−2535.52139667	12.1	0.0

[a] Absolute energy of the optimized geometries in hartrees. [b] Energy in kcal/mol relative to the most stable conformer (**I**). [c] Percent populations of the different conformers at 298 K following a distribution of the energies according to Boltzman's distribution law for a system in equilibrium.

The second calculated conformer (**II** in Figure 1 corresponding to a disposition near the form **A** in Scheme 3) has the same arrangement as conformer **I**, but the Cp and Cl ligands are interchanged between them. The same pattern in the bond between oxygen atoms and titanium is maintained with only slight differences (the values for the Ti−O bond distance and the bond angle C−O−Ti are 1.79 Å and 153°, respectively). These calculations suggest for conformers **I** and **II** a clear degree of multiple bond in the Ti−O link close to sp hybridization.

The third conformer (**III** in Figure 1 corresponding to a disposition near form **D** in Scheme 3) exhibits different behavior from **I** and **II**, resulting from its geometrical structure. It presents a closer sp^2 oxygen angle (C−O−Ti = 142°) and a larger Ti−O bond distance (1.81 Å).

The absolute and the relative formation energies and the relative number of molecules, on the grounds of Boltzmann's equilibrium distribution at 298 K of these three conformers, are listed in Table 1.

As a result of the calculations, two conformers related through the ring inversion process could be expected. Conformer **III**, in which the oxygen atoms move toward sp^2 hybridization, was the most unstable through Ti−O bond weakening, raising the energy 12 kcal/mol over the most stable conformer. An activation barrier of $\Delta G^{\ddagger}$(6 °C) = 13.9 kcal mol^{-1} for the ring inversion was determined for compound Si(MBMP)Me_2 from the coalescence of the two SiMe resonances in the NMR

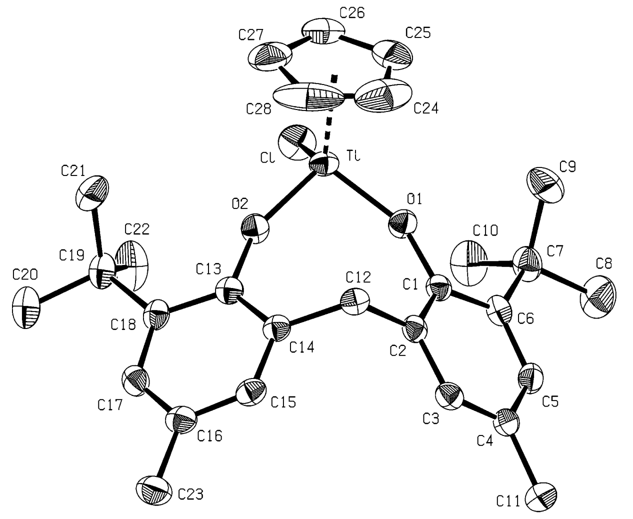


Figure 3. ORTEP[52] representation of complex **1** in the solid state. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

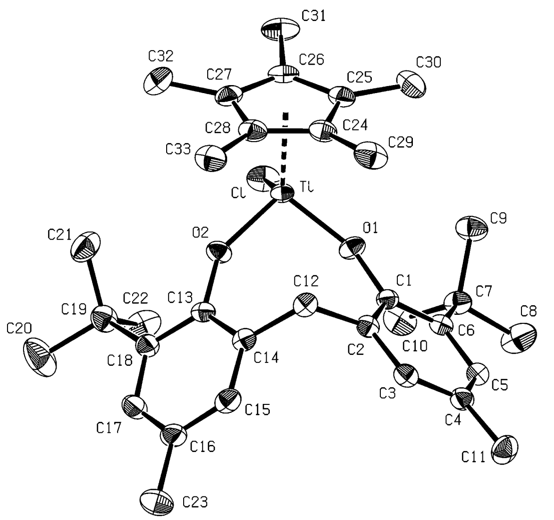


Figure 4. ORTEP[52] representation of complex **2** in the solid state. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

spectrum,[25] and conformational exchange between the *boat* and *chair* conformations was observed for the metoxo derivative Ti(MBMP)(OMe)$_2$ at room temperature[21] and for M(MBMP)(NMe)$_2$ (M = Ti, Zr) at 125 °C.[10]

To establish and to confirm the structural details of the molecular geometry in the solid state for this type of compounds, crystal X-ray structure analyses of **1**, **2**, and **4** were carried out. Single crystals of **1** and **2** obtained by slow recrystallization from hexane solution were of good enough quality to be analyzed by X-ray diffraction. Preliminary crystallographic studies of **1** have been described,[11] although further discussions of the results have not been found in the literature. The structure of **1** shows that this complex has a *boat* structure similar to Ti(MBMP)Cl$_2$ with the Cp in a pseudoaxial position. The Ti–O bond distances in **1** are longer than those found in the dichloro compound, suggesting less π-metal–oxygen interaction.[11] Complex **1** was structurally characterized for comparison with **2**, and only selected bond distances and angles are given in brackets along with a structural discussion of compound **2**.

The crystal structures of **1** and **2** are shown in Figures 3 and 4, respectively. Table 2 summarizes selected bond distances and angles.

Table 2. Selected Bond Distances (Å) and Angles (deg) for 1, 2, and 4

	1	**2**	**4**
Ti–Cl(1)	2.2891(6)	2.2946(4)	2.2671(6)
Ti- -Cl2			2.2454(5)
Ti–O1	1.7864(13)	1.8099(10)	1.7829(12)
Ti–O2	1.7952(13)	1.8159(10)	
Ti–C24	2.328(4)	2.372(2)	2.342(2)
Ti–C25	2.380(2)	2.399(2)	2.330(2)
Ti–C26	2.405(2)	2.427(2)	2.345(2)
Ti–C27	2.384(2)	2.390(2)	2.373(2)
Ti–C28	2.334(3)	2.369(2)	2.386(2)
Ti···Cg[a])	2.052	2.063	2.027
O1–C1	1.368(2)	1.364(2)	1.370(2)
O2–C13	1.367(2)	1.360(2)	1.386(2)
Si–O2			1.644(1)
Cl(1)–Ti–O1	103.61(5)	101.72(3)	103.91(4)
Cl(1)–Ti–O2	103.48(5)	101.85(3)	
Cl(1)–Ti–Cg	111.69	112.71	112.92
Cl(1)–Ti–Cl2			100.06(2)
Cl2–Ti–O1			104.68(4)
Cl2–Ti–Cg			115.74
O1–Ti–O2	99.47(6)	98.61(5)	
O1–Ti–Cg	117.19	120.58	117.47
O2–Ti–Cg	119.29	118.41	
Ti–O1–C1	155.25(12)	152.53(9)	154.49(11)
Ti–O2–C13	152.43(11)	148.45(9)	
Si–O2–C13			131.72(11)

[a] Cg denotes the centroid of the cyclopentadienyl ligand.

As can be seen from the structural data, the titanium core of **1** is nearly identical to **2**. The compounds are monomeric, similar to other titanium complexes bearing this methylene-bridged bisphenoxo ligand[11,21] and in contrast to the halo-bridged dinuclear structure formed in compounds with tellurium-,[15] sulfinyl-,[26a] and disulfide-linked bisphenoxo ligands.[26b] The coordination geometry around the titanium atom is a pseudo three-legged piano stool, as expected for complexes of the type TiCpL$_3$.[27] 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.[3a,15,19] The metal–oxygen bond lengths in **2** [**1**], Ti–O1 1.8099(10) Å [1.7864(13) Å] and Ti–O2 1.8159(10) Å [1.7952(13) Å], correlate with the wider bond angle at the O1 oxygen atom (C–O1–Ti), 152.53(9)° [155.25(12)°], compared with the angle at the O2 atom (C–O2–Ti), 148.45(9)° [152.43(11)°], and are in the expected range for titanium complexes with a linked bisphenoxo ligand where the oxygen atoms are (σ+π) donors.[10,12] These Ti–O bond distances are significantly longer than the average Ti–O bond distances found for the non-cyclopentadienyl compound, for which a Ti–O bond order >2 has been proposed.[11,12] Replacing one chlorine by a better metal-donor cyclopentadienyl ligand increases the Ti–O bond length, reducing the corresponding bond order.[15,18] The value of the bite angle of the bisphenoxo ligand O1–Ti–O2 is 98.61(5)° [99.47(6)°], slightly smaller than those observed for

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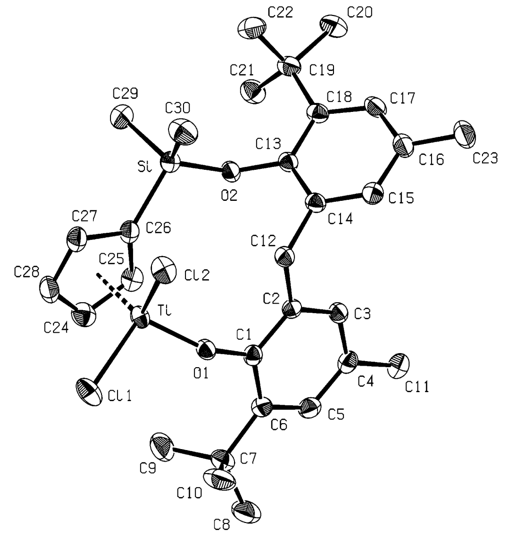

Figure 5. ORTEP[52] representation of complex **4** in the solid state. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

other complexes containing the MBMP ligand[10,11,28] and other monocyclopentadienyl nonchelating bisphenoxo titanium complexes[1c] and significantly smaller than that found in the analogous compound with the tellurium bridge [Ti(C_5Me_5)(TeBMP)Cl] (122.5(2)°).[15] The distortion of the chelate ligand is probably due to the steric hindrance of the pentamethylcyclopentadienyl ligand. The methyl groups disturb the protons of the methylene bridge, which is located far away from the Cp*, inducing a narrowing in the O−Ti−O angle. The dihedral angle between the two phenyl rings is 107.69(4)° [119.14(5)°] (this difference of about 12° can be attributed to the difference Cp/Cp*), more opened than other values found in the literature.[10,15,17,19,28]

The dihedral angle between the planes defined by Ti, O1, O2 and O1, O2, C1, C13 has a value of 13.7(1)° [11.1(1)°] (Figure 2), similar to that described for methylene-bridged diphenoxo compounds but significantly longer than that found in sulfur-bridged diphenoxo derivatives.[13a]

These observed structural parameters correlate well with the calculated value for the most stable conformer (**I**) deduced by DFT calculations.

The titanium−chlorine bond length is 2.2946(4) Å [2.2891(6) Å], significantly longer than those found in Ti(MBMP)Cl_2 [2.215(2) and 2.206(2) Å],[11] while it is shorter than the value of 2.343(2) and 2.318(1) Å observed for Ti(C_5Me_5)(TeBMP)Cl[15] and TiCp(SBMP)-Cl,[19] respectively.

The structure of complex **4** was confirmed by a single-crystal X-ray diffraction study. Figure 5 shows an ORTEP view of the structure along with the atom-labeling scheme. Selected bond distances and bond angles with their standard deviations are listed in Table 2.

The structure consists of discrete monomeric units with a pseudo three-legged piano stool coordination geometry around the titanium atom similar to that found for complexes of the type $TiCpCl_3$.[27] The Cg−Ti−O1 angle, where Cg represents the centroid of the C_5H_4 ring, at 117.47° is significantly larger than the corresponding angle in the constrained *ansa*-monocyclopentadienylsilylamido complexes [Ti{(η^5-$C_5R_4SiMe_2$-η-NR′}-Cl_2].[29] This result suggests that increasing the length of the Cp−Ti spacer leaves a less open metal center, which is also reflected in the Cl1−Ti−Cl2 angle value of 100.06(2)°, which is in the normal range observed for unconstrained monocyclopentadienylamido derivatives.[30] The titanium−chlorine bond lengths are 2.2454(5) and 2.2671(6) Å, slightly shorter than the values found for compounds **1** and **2** and in the range of dichloro monocyclopentadienyl derivatives.[30]

If the centroid of the cyclopentadienyl ring is considered as a single coordination site, the central core of **4** appears as a 10-membered (Cg−Si−O−C_5−O−Ti) metallacycle. The linkage (seven members "O−C_5−O") between the cyclopentadienyl and the titanium atom adopts a helical conformation around the Cg−Ti bond, in a disposition similar to that found for analogous bidentate cyclopentadienylamido titanium derivatives.[22]

The C−C distances in the cyclopentadienyl ring [1.393(3)−1.434(3) Å] and the Ti−Cg(centroid) distance 2.027 Å are similar to those shown for a series of unconstrained complexes.[30] These features reflect that the length of the backbone leaves sufficient flexibility in the system to retain the η^5-bonding character to the C_5H_4 ring. Within the bisphenoxo bridge ligand the angles and distances seem completely normal and correspond well to those in complex **2**, exerting little steric constraint. These structural results lead to the conclusion that the length and flexibility of the chain provide considerable "freedom", more akin to unlinked monocyclopentadienyl complexes than to cyclopentadienylsiylalkoxo or cyclopentadienylsiylamido constrained geometry complexes.

The short Ti−O1 bond distance, 1.7829(12) Å, suggests a partial pπ−dπ bonding between Ti and the alkoxo ligand with a value of the Ti−O1−C1 angle of 154.49(11)°. Similar values have been reported for other linked cyclopentadienylalkoxy complexes.[20] The strain-free chelated ligand allows optimal overlap between the oxygen pπ and the vacant titanium dπ orbitals, increasing the Ti−O double-bond character with respect to the "constrained geometry" systems. The Ti−O and Ti−Cg linkage distances and the Ti−O−C bond angle are similar to those of the nonlinked cyclopentadienylalkoxo titanium derivatives.[31]

The silicon atom is almost located in the Cp plane, with a distance to this plane of 0.425(3) Å away from the metal center, as expected for a Si−C(sp^2) bond. In "constrained geometry" compounds in which the chelating ligand is short, the Si atom is displaced toward the metal center (0.85−0.95 Å).[32] In contrast, for cyclopentadienylamido compounds with longer linkages (four members) between the cyclopentadienyl and the amido functions the silicon atom is slightly located out of the Cp plane, away from the metal center.[22]

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Table 3. Polymerization of Propylene with TiCp′(η^2-MBMP)Cl/MAO

run	catalyst[a]	time (min)	yield (mg)	activity (kg of PP/mol Ti·h)	10^{-4} M_w	M_w/M_n	T_g (°C)	T_m (°C)	ΔH (J/g)
1	**1**[b]	60							
2	**1**[c]	120	399	7.4	3.2	1.76	−9.7	93	5.6
3	**1**[d]	45	45	1.5			−8.0	80	6.9
4	**1**[e]	45	3.8	0.1					
5	**1**[c]	10	87	18	2.7	1.95	−10.7	56	1.9
6	**2**[b]	120	50	0.9					
7	**2**[c]	120	40	0.7	74	4.55			
8	**3**[b]	120							
9	**3**[c]	120	233	4.3	48	3.88			

[a] 27 μmol of catalyst. [b] Propylene gas (5 atm), 30 °C. [c] Propylene liquid (40 mL), 0 °C. [d] Propylene liquid (15 mL), −40 °C. [e] Propylene liquid (7 mL), −78 °C.

Table 4. Pentand Distributions for PP Obtained with TiCp′(η^2-MBMP)Cl/MAO[e]

run	catalyst	mmmm	mmmr	rmmr	mmrr	mrmm + rrmr	mrmr	rrrr	rrrm	mrrm
2	**1**[b]	22.61	20.18	4.22	8.39	25.65	9.31	1.50	4.84	3.30
3	**1**[c]	51.63	19.22	1.56	3.90	19.92	2.90		0.43	0.80
5	**1**[d]	21.55	19.30	4.23	8.25	26.0	11.02	1.56	5.05	3.04
6	**2**[a]	6.79	8.22	3.93	11.90	23.73	13.81	9.18	17.39	5.04
7	**2**[b]	6.81	8.14	3.25	9.34	23.87	13.53	11.05	18.39	5.60
9	**3**[b]	24.98	14.92	2.93	17.28	13.76	5.12	5.12	8.13	7.76

[a] Propylene gas (5 atm), 30 °C. [b] Propylene liquid (40 mL), 0 °C, 120 min. [c] Propylene liquid (15 mL), −40 °C. [d] Propylene liquid (40 mL), 0 °C, 10 min. [e] From ^{13}C NMR spectra, % related to 100%.

The Si−O2 distance [1.644(1) Å] is similar to that found in siloxanes (mean value 1.63 Å[33]), indicating an important degree of double-bond character in the Si−O bond. The value of the Si−O2−C13 angle is 131.72(11)°.

Olefin Polymerization. Using methylalumoxane (MAO) as cocatalyst, complexes **1**−**3** were studied as α-olefin polymerization catalysts under various conditions.

Propylene polymerization was investigated using 150 mL total volume of toluene with 27 μmol of catalyst, with a 1000 Al/Ti molar ratio at different temperatures and monomer pressures (results are summarized in Table 3). Traces of polymer or no polymerization was found when the reaction was carried out at 30 °C with 5 atm of the monomer (runs 1, 6, 8). However, polymer was found at 0 °C using liquid propylene (runs 2, 5, 7, 9). Decomposition of the catalytic system in the presence of the monomer at high temperatures could be a possible explanation of this behavior. The activity (kg of PP/mol of Ti·h) at 0 °C and 120 min for **1**/MAO (7.4) is higher than for **3**/MAO (4.3), with lower activity observed for **2**/MAO (0.7), which is almost inactive. This result indicates the activity is highly influenced by the nature of the cyclopentadienyl substituents and the order of activity is comparable to that reported for other monoalkoxo complexes[1d,34] and lower than that found for complexes containing the dialkoxo chelate ligand 2,2′-S-bis(4-methyl-6-*tert*-butylphenoxo).[10]

Polymerization runs at 0 °C resulted in the formation of PP with increasing M_w ($3 \times 10^4 - 7 \times 10^5$) in the order **1** < **3** < **2**.[35,36] The relatively low molecular weight found for compounds **1**−**3** can be explained by the presence of the ^{t}Bu groups in the dialkoxo ligand. Bulky substituents in 2,6 positions of the phenoxo ligands stabilize the active species, leading to higher activities but also promote chain transfer to the aluminum and the end of the polymerization process to give low molecular weights.

Complex **2** produces atactic PP (runs 6, 7; Table 4), while complexes **1** and **3** generate isotactic PP with an isotacticity of [mmmm] = 21−52% (runs 2, 3, 5, 9), lower than those found for C_2-symmetric indenyl-based metallocenes, which typically produce highly isotactic PP.[37] In the ^{13}C NMR spectra of the polymer obtained with the system **1**/MAO at 0 and −40 °C the inspection of the methyl [mmmr] ($\delta \sim 20.3$) and [mrmm] ($\delta \sim 19.6$) pentads reveals that the stereoregulation is caused by chain-end control (mmmr:mrmm ≈ 1:1).[38] Of note is the near or total absence of the rr-centered pentads, the intensity of which is greatly reduced as the temperature falls. The converse occurs with the isotacticity of the polymers, resulting in an increase in isotacticity as the temperature is reduced. The normalized methyl pentand distribution for the sample obtained at −40 °C is well reproduced in terms of CE statistics, for a best-fit value of the probability of m diad formation Pm = 0.84.

The results obtained at different temperatures and the microstructures of the polymers obtained with **1** and **3** resemble those reported by Ewen[39] for PP obtained with the achiral metallocene $TiCp_2Ph_2$. Similar results have been published by Erker[40] for PP obtained with achiral nonbridged zirconocenes or with dicyclopentadienyl zirconium compounds containing an asymmetric

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Table 5. End Group Analysis for PP Obtained with TiCp′(η^2-MBMP)Cl/MAO[e]

run	catalyst	10^{-4} M_w	vinyl (%)[a]	vinylidene (%)[a]	2-butenyl (%)[a]
2	**1**[b]	3.2	39.26	42.54	18.20
3	**1**[c]	*f*		97.98	2.02
5	**1**[d]	2.7	44.47	40.24	15.29
6	**2**[a]	*f*	43.79	28.96	27.25
7	**2**[b]	74	54.44	27.11	18.44
9	**3**[b]		64.51	22.07	13.52

[a] Propylene gas (5 atm), 30 °C. [b] Propylene liquid (40 mL), 0 °C, 120 min. [c] Propylene liquid (15 mL), −40 °C. [d] Propylene liquid (40 mL), 0 °C, 10 min. [e] From ^{1}H NMR spectra, % refereed to 100%. [f] Not enough for analysis.

carbon in the substituent of the cyclopentadienyl rings in which the intrinsic chirality is not transferred effectively at long distances. However, these factors are very unusual for monocyclopentadienyl compounds.[39]

The olefinic region (see Table 5) of the ^{1}H NMR spectra of these polymers shows resonances attributable to vinylidene $CH_2{=}C(CH_3)P$ end groups (δ 4.65 ppm, s; δ 4.58 ppm, s), suggesting the main chain transfer processes involve β-hydrogen elimination to the metal or to a coordinated monomer unit from a 1,2 finally inserted propene unit. The spectrum for the sample obtained with **1**/MAO at −40 °C contains no other signals corresponding to end groups (run 3). However, in the spectra of samples obtained at higher temperature, resonances assignable to other kinds of end group are observed. The olefinic region of the ^{1}H NMR spectrum of the sample formed at 0 °C shows resonances attributable to vinyl (δ 4.91 ppm, m; δ 4.87 ppm, m), vinylidene (δ 4.65 ppm, s; δ 4.58 ppm, s), and 2-butenyl (δ ∼5.32) end groups. The presence of 2-butenyl end groups indicates a β-hydride elimination after a 2,1-insertion. The vinyl groups may be formed via β-methyl elimination following a 1,2-insertion or, following a 2,1-(mis)insertion, via β-hydride elimination from the methyl group. The β-methyl elimination may lead to the formation of isobutyl end groups by 1,2-insertion of monomer into the formed Ti−Me bond. Indicative resonances at δ ∼22−25 in the ^{13}C NMR for their methyl and methine resonances could not be observed, although this process could occur to a significant extent and their ^{13}C resonances may be too complex to distinguish their signals from baseline noise.[37] Consequently any conclusion about the nature of the vinyl end groups or whether they derive from 1,2- or 2,1-insertions is not made.[37]

This spectroscopic analysis permits us to conclude that the PP polymer obtained at low temperature contains large isotactic stereoblocks obtained by a chain-end control mechanism with a clear shortening of these isotactic blocks as the temperature is raised (by 2,1-enchainments), increasing the atactic character of the corresponding polymer.

The PP polymer samples obtained with compound **1** (runs 2, 3; Table 3) present a glass transition temperature at −9.7 and −8.0 °C with a melting point temperature of 93 and 80 °C and an enthalpy of $\Delta H = 5.6$ and 6.9 J/g. The values observed for the polymer obtained after 10 min of polymerization time (run 5, Table 3) are $T_g = -10.7$ °C, $T_m = 56$ °C, and $\Delta H = 1.9$ J/g. The conventional isotactic PP shows characteristic values of $T_g = 272$ K,[41] $T_m \cong 112$ °C,[42] and an enthalpy for the α-form of $\Delta H = 163.3$ J/g.[43] A glass transition temperature below 0 °C and a great endotherm around 80 °C are characteristic of an isotactic stereoblock PP[43] and indicate the presence of a crystallinity phase with a melting point lower than the isotactic PP. It can be viewed as a micelle model in which small crystallites act as physical cross-links. The calculated enthalpic content of 26.1 J/g for this polymer gives a degree of crystallinity near 16%;[43] thus for the polymers produced with our catalyst this value should be lower, as they all present an enthalpy around 6.0 J/g.

Styrene polymerization was studied using 40 mL total volume of toluene and 5 mL of monomer, and the results are summarized in Table 6. The activity (g of PS/(mol of Ti·h)) for **3**/MAO (8.0×10^6) was higher than for the system **1**/MAO (1.3×10^6), and a low activity for **2**/MAO (3.6×10^4) was found (runs 13, 8, 12; Table 6), indicating that the cyclopentadienyl ligands exert a strong influence on the activity of the catalyst. The polymerization of styrene with **3** exhibits a much higher activity, and the reaction must be stopped after 2 min, as at this stage the mass transfer problem became considerable. Runs 2−4 show the influence of the Al/Ti ratio in the activity, and the highest activity is exhibited for an Al/Ti = 1000 ratio. The activity versus temperature has also been investigated (runs 5−8), and as expected, the activity is higher as the temperature is increased. After the polymers were precipitated in acidified MeOH, they were extracted into boiling THF and >95% syndiotactic polystyrene was obtained, as evidenced by NMR spectroscopic analysis. The polymers had a high molecular weight, $\sim 5 \times 10^4$. Complexes containing similar ancillary dialkoxo ligands with different bridges between the aromatic rings have been reported to produce analogous results in activity and polymer weight of syndiotactic PS.[44]

Complexes **1** and **2** were investigated as catalysts to polymerize isoprene in the presence of excess MAO, using 40 mL total volume of toluene, 2×10^{-5} mol of catalyst, and 5 mL of monomer. The results are summarized in Table 7. Runs 1−6 show the influence of temperature in the activity, and runs 6−10 show dependence on the Al/Ti ratio. The highest activity is obtained for an Al/Ti = 1000 ratio at 40 °C for complex **1**, while compound **2** is inactive (run 11).

The precatalyst complexes **1**−**3** have only one chloro ligand. We assume that the cocatalyst MAO reacts with **1**−**3** in an initial pathway with methyl-halide exchange to afford a Ti−Me derivative, while in a subsequent reaction one of the Ti−O bonds should be cleaved by the $AlMe_3$ contained as a component in the cocatalyst MAO to generate active cationic alkyl species in a Ziegler−Natta olefin polymerization model.[45]

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Table 6. Polymerization Studies of Styrene with TiCp′(η^2-MBMP)Cl/MAO

run	catalyst	temp (°C)	time (min)	Al/Ti molar ratio	yield (g)	activity (kg of PS/mol Ti·h)	NMR	10^{-4} M_w	M_w/M_n
1	$CpTiCl_3$ [a]	50	45	1000	3.102	210	synd.		
2	**1**[b]	40	45	200	0.010	2.7	synd.	*c*	*c*
3	**1**[b]	40	45	500	0.177	47	synd.	7.7	2.76
4	**1**[b]	40	45	1000	0.258	69	synd.	7.9	2.04
5	**1**[b]	−78	45	1000	0.015	4.0	atac.	*c*	*c*
6	**1**[b]	0	45	1000	0.017	4.5	atac.	*c*	*c*
7	**1**[b]	30	45	1000	0.023	6.1	synd.	*c*	*c*
8	**1**[a]	50	10	1000	4.517	1300	synd.	2.4	3.73
9	**1**[a]	50	30	1000	4.259	420	synd.	1.8	2.78
10	**1**[a]	50	45	1000	1.500	100	synd.	*c*	*c*
11	**2**[b]	50	30	420	0.881	35	synd.	10.0	2.13
12	**2**[a]	50	45	1000	0.543	36	synd.	9.3	2.15
13	**3**[a]	50	2	1000	5.364	8000	synd.	4.5	3.85

[a] 2×10^{-5} mol of catalyst. [b] 5×10^{-6} mol of catalyst. [c] Not enough for analysis.

Table 7. Polymerization Studies of Isoprene with TiCp′(η^2-MBMP)Cl/MAO

run	catalyst[a]	temp (°C)	time (min)	Al/Ti molar ratio	yield (g)	activity (kg of PI/mol Ti·h)
1	**1**	0	5	1000	0.220	130
2	**1**	30	5	1000	1.148	690
3	**1**	40	5	1000	1.466	880
4	**1**	50	20	1000	1.521	230
5	**1**	60	20	1000	3.003	450
6	**1**	75	20	1000	3.201	480
7	**1**	40	20	750	0.560	84
8	**1**	40	20	500	1.360	200
9	**1**	40	20	250	0.102	15
10	**1**	40	30	0		
11	**2**	40	30	1000		

[a] 2×10^{-5} mol of catalyst.

Concluding Remarks

In this contribution we describe the synthesis and characterization of monocylopentadienyl titanium complexes TiCp′(η^2-MBMP)Cl containing the diphenoxo bidentate dianionic 2,2′-CH_2-bis(4-methyl-6-*tert*-butylphenoxo) ligand (η^2-MBMP) and the *ansa*-cyclopentadienylalkoxo Ti(η^5-$C_5H_4SiMe_2$-η^1-MBMP)Cl_2 compound with the diphenoxo ligand bridging the titanium and the silicon atoms. DFT theoretical calculations developed for these complexes provide remarkable conclusions about their structural behavior as confirmed from X-ray diffraction studies in the solid state. After activation with methylaluminoxane these monocyclopentadienyl titanium derivatives are suited for olefin (propylene, styrene, and isoprene) polymerization. Polypropylene containing large isotactic stereoblocks obtained by a chain-end control mechanism is produced at low temperature, increasing the atactic character with a clear shortening of the isotactic blocks as the temperature is raised.

Experimental Section

General Considerations. All manipulations were performed under argon using Schlenk and high-vacuum line techniques or in a glovebox, model HE-63. The solvents were purified by distillation under argon before use by employing the appropriate drying/deoxygenated agent. Deuterated solvents were stored over activated 4 Å molecular sieves and degassed by several freeze−thaw cycles. 2,2′-CH_2-bis(6-${}^tBu$-4-CH_3-C_6H_2-1-OH) (Aldrich) was commercially obtained and used without further purification. Li_2[2,2′-CH_2-bis(6-${}^tBu$-4-CH_3-C_6H_2-1-O)],[10] Ti(η^5-C_5H_5)Cl_3,[46] Ti(η^5-C_5Me_5)Cl_3,[47] and Ti(η^5-$C_5H_4SiMe_2Cl$)Cl_3[20b] were prepared by known procedures. Polymerization grade propylene from Aldrich was purified by passage through two columns packed with activated alumina and 4 Å molecular sieves. Styrene and isoprene were distilled at reduced pressure over 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 on a Perkin-Elmer 240B and/or Heraeus CHN-O-Rapid microanalyzer. A Perkin-Elmer DSC-4 thermoanalytic instrument was used to obtain DSC melting endotherms. NMR spectra, measured at 25 °C, were recorded on Varian Unity FT-300 (${}^1H$ NMR at 300 MHz, ${}^{13}C$ NMR at 75 MHz) or FT-500 (${}^1H$ NMR at 500 MHz, ${}^{13}C$ NMR at 125 MHz) spectrometers, and chemical shifts are referenced to $SiMe_4$ via the carbon resonances (${}^{13}C$) and the residual protons (${}^1H$) in the solvent.

Synthesis of Ti(η^5-C_5H_5)(η^2-MBMP)Cl (1). A THF solution (60 mL) of 2.40 g (6.81 mmol) of Li_2[2,2′-CH_2-bis(6-${}^tBu$-4-CH_3-C_6H_2-1-O)] was added drop by drop to a solution of Ti(η^5-C_5H_5)Cl_3 (1.50 g, 6.81 mmol) in toluene (100 mL) at −78 °C over 2 h. The cooling bath was removed, and the reaction mixture was slowly warmed to room temperature and stirred over 12 h. The reaction color changed from yellow to red in just 2−3 h. The solvent was evaporated under vacuum, and the resulting residue was extracted into hexane (50 mL). After filtration, the solution was concentrated to 10 mL and cooled to −30 °C overnight to give compound **1** as a red solid (recrystallization from cold hexane) (2.97 g, 90% yield). Anal. Calcd for $C_{28}H_{35}TiO_2Cl$: C, 69.09; H, 7.20. Found: C, 68.95; H, 7.55. ${}^1H$ NMR (300 MHz, C_6D_6, 25 °C): δ 7.04, 6.94 (AA′ spin system, 2 × 2H, Ph); 6.31 (s, 5H, C_5H_5); 4.10, 3.35 (AB spin system, 2 × 1H, $J_{H-H} = 13.73$ Hz, CH_2); 2.12 (s, 6H, CH_3-Ph); 1.43 [s, 18H, $C(CH_3)_3$]. ${}^1H$ NMR (300 MHz, $CDCl_3$, 25 °C): δ 7.03, 6.88 (AA′ spin system, 2 × 2H, Ph); 6.80 (s, 5H, C_5H_5); 4.17, 3.45 (AB spin system, 2 × 1H, $J_{H-H} = 13.72$ Hz, CH_2); 2.25 (s, 6H, CH_3Ph); 1.31 [s, 18H, $C(CH_3)_3$]. ${}^{13}C$ NMR (125 MHz, C_6D_6, 25 °C): δ 163.33, 137.57, 136.32, 131.22, 128.93, 126.16 (Ph); 118.25 (C_5H_5); 35.39 (CH_2); 35.26 [$C(CH_3)_3$]; 30.98 [$C(CH_3)_3$]; 21.06 (CH_3−Ph).

Synthesis of Ti(η^5-C_5Me_5)(η^2-MBMP)Cl (2). A THF solution (100 mL) of 5.35 g (15.2 mmol) of Li_2[2,2′-CH_2-bis(6-${}^tBu$-4-CH_3-C_6H_2-1-O)] was added drop by drop to a solution of Ti(η^5-C_5Me_5)Cl_3 (4.40 g, 15.20 mmol) in toluene (100 mL) at −78 °C over 2 h. The cooling bath was removed, and the reaction mixture was slowly warmed to room temperature and stirred over 12 h. The solvent was evaporated under vacuum, and the resulting residue was extracted into hexane (50 mL). After filtration, the solution was concentrated to 10 mL and cooled

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Table 8. Summary of Crystallographic Data for Complexes 1, 2, and 4

	1	**2**	**4**
chem formula	$C_{28}H_{35}ClO_2Ti$	$C_{33}H_{45}ClO_2Ti$	$C_{30}H_{40}Cl_2O_2SiTi$
fw	486.88	557.01	579.48
color/shape	red/plate	red/fragment	orange/ plate
cryst size (mm)	0.08 × 0.15 × 0.25	0.41 × 0.46 × 0.48	0.10 × 0.18 × 0.25
cryst syst	triclinic	monoclinic	triclinic
space group	$P\bar{1}$ (No. 2)	$P2_1$ (No. 4)	$P\bar{1}$ (No. 2)
a (Å)	9.5862(1)	9.8601(1)	9.4753(1)
b (Å)	10.5852(1)	14.2854(1)	13.0141(1)
c (Å)	14.0202(2)	11.1054(1)	13.3054(1)
α (deg)	107.7476(5)	90	68.8672(4)
β (deg)	91.8804(6)	102.2686(5)	77.3656(4)
γ (deg)	106.0438(5)	90	75.9529(4)
V (Å^3)	1291.48(3)	1528.53(2)	1468.92(2)
Z	2	2	2
T (K)	153	173	173
ρ_{calcd} (g cm^{-3})	1.252	1.210	1.310
μ (mm^{-1})	0.456	0.394	0.539
F_{000}	516	596	612
θ range (deg)	2.54−25.34	2.11−25.36	1.71−25.33
data collected (h,k,l)	±11, ±12, ±16	±11, ±17, ±13	±11, ±15, ±16
no. of reflns collected	26 713	26 554	24 992
no. of indep reflns/R_{int}	4716 (all)/0.036	5581 (all)/0.034	5364 (all)/0.032
no. of obsd reflns ($I > 2\sigma(I)$)	4043 (obsd)	5465 (obsd)	4828 (obsd)
no. of params refined	429	514	485
R1 (obsd/all)	0.0329/0.0418	0.0220/0.0228	0.0291/0.0338
wR2 (obsd/all)	0.0805/0.0859	0.0575/0.0579	0.0776/0.0809
GOF (obsd/all)	1.034/1.034	1.036/1.036	1.037/1.037
max./min. $\Delta\rho$ (e Å^{-3})	+0.24/−0.25	+0.14/−0.15	+0.36/−0.24

to −30 °C overnight to give compound **2** as a red solid (recrystallization from cold hexane) (7.15 g, 85% yield). Anal. Calcd for $C_{33}H_{45}TiClO_2$: C, 71.18; H, 8.09. Found: C, 70.75; H, 8.18. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ 7.04, 6.96 (AA′ spin system, 2 × 2H, Ph); 4.08, 3.39 (AB spin system, 2 × 1H, J_{H-H} = 13.20 Hz, CH_2); 2.11 (s, 6H, CH_3Ph); 2.02 (s, 15H, C_5Me_5); 1.44 [s, 18H, $C(CH_3)_3$]. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 6.98, 6.87 (AA′ spin system, 2 × 2H, Ph); 3.97, 3.40 (AB spin system, 2 × 1H, J_{H-H} = 13.20 Hz, CH_2); 2.22 (s, 6H, CH_3Ph); 2.20 (s, 15H, C_5Me_5); 1.29 [s, 18H, $C(CH_3)_3$]. ^{13}C NMR (125 MHz, C_6D_6, 25 °C): δ 161.19, 137.71, 134.62, 130.34, 129.03, 126.50 (Ph); 128.46 (C_5Me$_5$); 35.23 [$C(CH_3)_3$]; 34.68 (CH_2); 31.19 [$C(CH_3)_3$]; 21.01 (CH_3−Ph); 12.59 (C_5Me_5).

Synthesis of Ti(η^5-$C_5H_4SiMe_2Cl$)(η^2-MBMP)Cl (3). A THF solution (20 mL) of 0.56 g (1.60 mmol) of Li_2[2,2′-CH_2-bis(6-^{t}Bu-4-$CH_3C_6H_2$-1-O)] was added to a solution of Ti(η^5-$C_5H_4SiMe_2Cl$)Cl_3 (0.50 g, 1.60 mmol) in toluene (50 mL) at room temperature. The reaction color immediately changed from yellow to red, and the reaction mixture was stirred over 12 h. The solvent was evaporated under vacuum, and the resulting residue was extracted into hexane. After filtration, the solution was concentrated to 5 mL and cooled to −30 °C overnight to give compound **3** as a red solid (recrystallization from cold hexane) (0.75 g, 81% yield). Anal. Calcd for $C_{30}H_{40}TiSiO_2Cl_2$: C, 62.17; H, 6.97. Found: C, 62.37; H, 7.21. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ 7.01, 6.93 (AA′ spin system, 2 × 2H, Ph); 6.58, 6.33 (dd, 2 × 2H, $C_5H_4SiMe_2Cl$); 4.10, 3.35 (AB spin system, 2 × 1H, J_{H-H} = 13.54 Hz, CH_2); 2.11 (s, 6H, CH_3Ph); 1.38 [s, 18H, $C(CH_3)_3$]; 0.82 (s, 6H, $C_5H_4SiMe_2Cl$). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 7.02, 6.89 (AA′ spin system, 2 × 2H, Ph); 6.87−6.89 (m, 4H, $C_5H_4SiMe_2Cl$); 4.15, 3.40 (AB spin system, 2 × 1H, J_{H-H} = 13.55 Hz, CH_2); 2.25 (s, 6H, CH_3Ph); 1.30 [s, 18H, $C(CH_3)_3$]; 0.88 (s, 6H, $C_5H_4SiMe_2Cl$). ^{13}C NMR (125 MHz, C_6D_6, 25 °C): δ 163.56, 137.44, 136.47, 131.54, 128.92, 126.19 (Ph); 129.77 (ipso-$C_5H_4SiMe_2Cl$); 123.35, 120.86 ($C_5H_4SiMe_2Cl$); 35.44 (CH_2); 35.37 [$C(CH_3)_3$]; 31.02 [$C(CH_3)_3$]; 21.04 (CH_3−Ph); 2.52 ($C_5H_4SiMe_2Cl$).

Synthesis of Ti(η^5-$C_5H_4SiMe_2$-η^1-MBMP)Cl_2 (4). A solution of $MBMPH_2$ (0.33 g, 0.96 mmol) and NEt_3 (0.26 mL, 1.92 mmol) in hexane (30 mL) was added to a solution of Ti(η^5-$C_5H_4SiMe_2Cl$)Cl_3 (0.30 g, 0.96 mmol) in 50 mL of hexane at −78 °C. The reaction mixture was slowly warmed to room temperature and stirred over 12 h. The solvent was evaporated under vacuum to give a mixture of **3** and **4**. Compound **4** could be obtained as an analytically pure substance by recrystallization from hexane utilizing its lower solubility. Anal. Calcd for $C_{30}H_{40}TiSiO_2Cl_2$: C, 62.17; H, 6.97. Found: C, 62.09; H, 6.97. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ 7.19, 6.98, 6.66, 6.48 (ABCD spin system, 4 × 1H, Ph); 6.48, 6.41 (dd, 2 × 2H, C_5H_4-$SiMe_2$); 4.10 (br s, 2H, CH_2); 2.17, 1.89 (s, 2 × 3H, CH_3Ph); 1.52, 1.41 [s, 2 × 9H, $C(CH_3)_3$]; 0.36 (s, 6H, $C_5H_4SiMe_2$). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 7.10, 6.91, 6.81, 6.17 (ABCD spin system, 4 × 1H, Ph); 6.98, 6.87 (dd, 2 × 2H, $C_5H_4SiMe_2$); 3.88 (br s, 2H, CH_2); 2.31, 2.15 (s, 2 × 3H, CH_3Ph); 1.40, 1.38 [s, 2 × 9H, $C(CH_3)_3$]; 0.43 (s, 6H, $C_5H_4SiMe_2$). ^{13}C NMR (125 MHz, C_6D_6, 25 °C): δ 166.40, 150.11, 140.72, 137.18, 137.00, 137.47, 132.79, 131.96, 131.26, 129.62, 127.49, 127.00 (Ph); 125.38 (ipso-$C_5H_4SiMe_2$); 125.89, 125.19 ($C_5H_4SiMe_2$); 35.15 (CH_2); 35.02, 34.86 [$C(CH_3)_3$]; 30.84, 30.64 [$C(CH_3)_3$]; 21.24, 20.91 (CH_3−Ph); 1.30 ($C_5H_4SiMe_2$).

Polymerization Procedure. Polymerization runs were carried out by following the general procedure.

Polymerization of Propylene. A 250 mL Büchi reactor equipped with a mechanical stirrer was first evacuated and then charged with dried scavenger methylaluminoxane (MAO) and toluene (150 mL). A 10 mL pressure tube was charged with the titanium complex in a toluene solution previously preactivated (2 min) with 1 mL of MAO. The reactor was purged with the monomer three times by pressurizing and venting. The monomer was then equilibrated with the toluene in the reactor for 30 min at the polymerization 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 was reached 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.

Polymerization of Styrene and Isoprene. A 100 mL glass pressure bottle with magnetic stirring was vented and charged with toluene, MAO, and 5 mL of the monomer. The mixture was then equilibrated at the polymerization temperature with constant stirring, and the reaction was initiated by injecting the solution of the catalyst previously preactivated (2 min) with the cocatalyst MAO. After the desired reaction time was reached 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 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}H and ^{13}C NMR measurements were performed at 363 K in 1,1,2,2-tetrachloroethane-d_2 referenced using the solvent peak. The areas of the nine peaks in the methyl region determined from spectral integrations were used to characterize the sample microstructure.

X-ray Crystallography for Compounds 1, 2, and 4. Crystals suitable for diffraction experiments were selected, coated with perfluorinated ether, and fixed in a capillary. Preliminary examination and data collection were carried out on a Nonius Kappa-CCD device at the window of a rotating anode X-ray generator and graphite-monochromated Mo Kα radiation (λ = 0.71073 Å), controlled by the COLLECT software package.[48] A total of 470 (826/798) collected images were processed using Denzo. Absorption and/or decay effects were corrected during the scaling procedure.[49] The structures were solved by direct methods[50] and refined with standard difference Fourier techniques.[51] All non-hydrogen atoms of the asymmetric unit were refined with anisotropic thermal displacement parameters. All hydrogen atoms were found in the difference Fourier maps and refined freely with individual isotropic thermal displacement parameters. Full-matrix least-squares refinements were carried out by minimizing $\sum w(F_o^2 - F_c^2)^2$ with the SHELXL-97 weighting scheme and stopped at maximum shift/err < 0.001. The right enantiomer for **2** is proofed by Flack's parameter $\epsilon = -0.02(1)$. For details see Table 8. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-206871 (**1**), CCDC-206869 (**2**), and CCDC-206870 (**4**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033, e-mail: deposit@ccdc.cam.ac.uk).

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Supporting Information Available: Tables of crystal and data collection parameters, atomic coordinates, bond lengths, bond angles, and thermal displacement parameters for **1**, **2**, and **4**, and a file with details of the DFT calculations with optimized geometries and final energies with corrections for exchange and correlation factors. This material is available free of charge via the Internet at http://pubs.acs.org.

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