Monocyclopentadienyl Chloro Bisphenoxo $Ti(\eta^5\text{-}C_5H_4SiMe_2Cl)(\eta^2\text{-MBMP})Cl$ Derivative: Ti−Cl, Ti−O, and Si−Cl Reactivity. Crystal Structure of $Ti(\eta^5\text{-}C_5H_4SiMe_3)(\eta^2\text{-MBMP})Cl$ and $Ti(\eta^5\text{-}C_5H_4SiMe_2\text{-}\eta^1\text{-MBMP})(CH_2Ph)_2$

Marta González-Maupoey and Tomás Cuenca*

Departamento de Química Inorgánica, Universidad de Alcalá, Campus Universitario,
28871 Alcalá de Henares, Spain

Eberhardt Herdtweck

Lehrstuhl für Anorganische Chemie, Technische Universität München, Lichtenberstrasse 4,
D-85747 Garching bei München, Germany

Received April 28, 2006

The monocyclopentadienyl η^2-bisphenoxo chloro compound $Ti(\eta^5\text{-}C_5H_4SiMe_3)(\eta^2\text{-MBMP})Cl$ (**3**), containing the bidentate dianionic η^2-MBMP ligand coordinated to the titanium center, has been prepared in good yield by reaction of 1 equiv of $Li_2(MBMP)$ with $Ti(\eta^5\text{-}C_5H_4SiMe_3)Cl_3$ in hexane, at −78 °C. The compound $Ti(\eta^5\text{-}C_5H_4SiMe_2Cl)(\eta^2\text{-MBMP})Cl$ (**1**) reacts with alkylating reagents MgClR [R = Me, CH_2Ph] or LiMe, in hexane or toluene, at low or room temperature, to afford the monocyclopentadienyl η^2-bisphenoxo derivatives $Ti(\eta^5\text{-}C_5H_4SiMe_2X)(\eta^2\text{-MBMP})R$ [R = Me, X = Cl (**4**); R = X = Me (**5**); R = CH_2Ph, X = Cl (**6**); R = X = CH_2Ph (**7**)] or the *ansa*-monocyclopentadienylphenoxo dibenzyl complex $Ti(\eta^5\text{-}C_5H_4SiMe_2\text{-}\eta^1\text{-MBMP})(CH_2Ph)_2$ (**8**), depending on the reaction conditions. *ansa*-Monocyclopentadienylphenoxo dialkyl complexes $Ti(\eta^5\text{-}C_5H_4SiMe_2\text{-}\eta^1\text{-MBMP})R_2$ [R = CH_2Ph (**8**), Me (**9**)] can be alternatively synthesized by treatment of $Ti(\eta^5\text{-}C_5H_4SiMe_2\text{-}\eta^1\text{-MBMP})Cl_2$ (**2**) with 2 equiv of MgCl(CH_2Ph) or MgClMe. Compounds **3** and **8** have been characterized by single-crystal X-ray crystallography. Upon addition of methylaluminoxane, these bisphenoxo complexes are active in the polymerization of ethylene and styrene.

Introduction

Alkoxo (or aryloxo) ligands stabilize early transition metal elements in high oxidation states,[1−3] and the resulting derivatives are used as catalysts in a wide range of homogeneous reactions. Alkyl−alkoxo (or alkyl−aryloxo) derivatives of group 4 transition metals are highly sensitive to air moisture and to light, making their synthesis very difficult.[4] Titanium and zirconium alkoxo (or aryloxo) derivatives, combined with methylaluminoxane or boron reagents, as cocatalysts, exhibit high activity as catalysts in α-olefin polymerization processes.[5−12]

Examples of aryloxo ligands include chelate alkoxo[13,14] and phenoxo molecules of the type 2,2′-X-bis(4-methyl-6-*tert*-butylphenoxo) (X = CH_2,[15] CH_2CH_2,[16−18] S,[19] Te[20]), which can act as dianionic ligands coordinated to group 4 transition metals. As part of our investigations aimed at elucidating the effect of the metal environment on the reactivity of complexes of this type, we have synthesized and described a series of monochloro titanium systems containing the bisphenoxo bidentate ligand

---

* Corresponding author. Tel: 34918854655. Fax: 34 918854683. E-mail: tomas.cuenca@uah.es.

[1] Bradley, D. C.; Mehrotra, R. C.; Gaur, D. P. *Metal Alkoxides*; Academic Press: New York, 1978.

[2] Bradley, D. C.; Mehrotra, R. C.; Rothwell, I. P.; Singh, A. *Alkoxo and Aryloxo Derivatives of Metals*; Academic Press: San Diego, CA, 2002.

[3] Chisholm, M. H.; Huang, J. H.; Huffman, J. C.; Streib, W. E.; Tiedtke, D. *Polyhedron* **1997**, *16*, 2941−2949.

[4] Mishra, S.; Singh, A. *Trans. Met. Chem.* **2005**, *30*, 163−169.

[5] Sernetz, F. G.; Mülhaupt, R.; Fokken, S.; Okuda, J. *Macromolecules* **1997**, *30*, 1562−1569.

[6] Miyatake, T.; Mizunuma, K.; Seki, Y.; Kakugo, M. *Makromol. Chem.-Rapid Commun.* **1989**, *10*, 349−352.

[7] Miyatake, T.; Mizunuma, K.; Kakugo, M. *Makromol. Chem.-Macromol. Symp.* **1993**, *66*, 203−214.

[8] van der Linden, A.; Schaverien, C. J.; Meijboom, N.; Ganter, C.; Orpen, A. G. *J. Am. Chem. Soc.* **1995**, *117*, 3008−3021.

[9] Chen, Y. X.; Fu, P. F.; Stern, C. L.; Marks, T. J. *Organometallics* **1997**, *16*, 5958−5963.

[10] Amor, F.; Fokken, S.; Kleinhenn, T.; Spaniol, T. P.; Okuda, J. *J. Organomet. Chem.* **2001**, *621*, 3−9.

[11] Chan, M. C. W.; Tam, K. H.; Zhu, N. Y.; Chiu, P.; Matsui, S. *Organometallics* **2006**, *25*, 785−792.

[12] Phomphrai, K.; Fenwick, A. E.; Sharma, S.; Fanwick, P. E.; Caruthers, J. M.; Delgass, W. N.; Abu-Omar, M. M.; Rothwell, I. P. *Organometallics* **2006**, *25*, 214−220.

[13] Lavanant, L.; Silvestru, A.; Faucheux, A.; Toupet, L.; Jordan, R. F.; Carpentier, J. F. *Organometallics* **2005**, *24*, 5604−5619.

[14] Lavanant, L.; Toupet, L.; Lehmann, C. W.; Carpentier, J. F. *Organometallics* **2005**, *24*, 5620−5633.

[15] Floriani, C.; Corazza, F.; Lesueur, W.; Chiesi-Villa, A.; Guastini, C. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 66−67.

[16] Fokken, S.; Spaniol, T. P.; Okuda, J.; Sernetz, F. G.; Mulhaupt, R. *Organometallics* **1997**, *16*, 4240−4242.

[17] Anthis, J. W.; Larsen, A. O.; White, P. S.; Gagne, M. R. *J. Organomet. Chem.* **2003**, *688*, 121−124.

[18] Anthis, J. W.; Filippov, I.; Wigley, D. E. *Inorg. Chem.* **2004**, *43*, 716−724.

[19] Porri, L.; Ripa, A.; Colombo, P.; Miano, E.; Capelli, S.; Meille, S. V. *J. Organomet. Chem.* **1996**, *514*, 213−217.

[20] Nakayama, Y.; Watanabe, K.; Ueyama, N.; Nakamura, A.; Harada, A.; Okuda, J. *Organometallics* **2000**, *19*, 2498−2503.

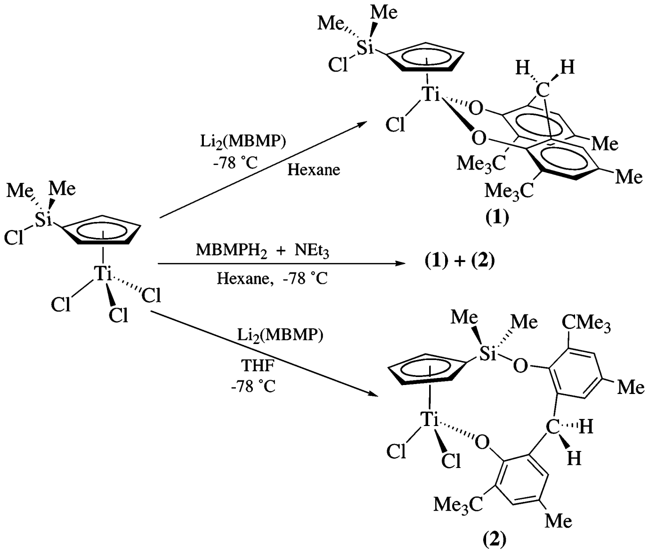
10.1021/om060368q CCC: \$33.50

2,2′-methylene-bis(4-methyl-6-*tert*-butylphenoxo) (MBMP) combined with the cyclopentadienyl ring.[21] Related monocyclopentadienyl titanium derivatives of the type $TiCp'L_nL'_{3-n}$ (Cp′ = substituted or unsubstituted cyclopentadienyl ring; L, L′ = anionic donor ligands)[22] have shown remarkable catalytic activities when used as catalysts for α-olefin polymerization reactions.[23−31]

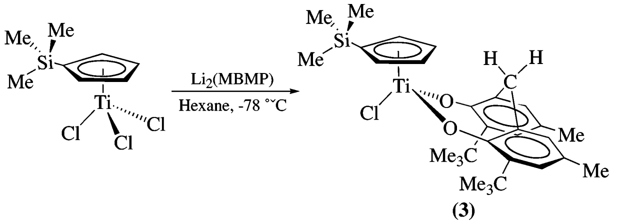
Here we report the reactions of Ti(η^5-$C_5H_4SiMe_2Cl$)(η^2-MBMP)Cl with alkylating reagents to afford monocyclopentadienyl η^2-bisphenoxo Ti(η^5-$C_5H_4SiMe_2Cl$)(η^2-MBMP)R and Ti(η^5-$C_5H_4SiMe_2R$)(η^2-MBMP)R derivatives or *ansa*-monocyclopentadienylphenoxo dialkyl Ti(η^5-$C_5H_4SiMe_2$-η^1-MBMP)-R_2 complexes depending on the reaction conditions and their catalytic application in α-olefin polymerization. The reactivity studies reveal that the Ti−Cl, Si−Cl, and Ti−O bonds exhibit different chemical behavior depending on the temperature, solvent, and alkylating reagent used. The complexes obtained have been characterized by analytical and spectroscopic methods, and the X-ray molecular structures of Ti(η^5-$C_5H_4SiMe_3$)-(η^2-MBMP)Cl and Ti(η^5-$C_5H_4SiMe_2$-η^1-MBMP)($CH_2Ph)_2$ complexes have been determined by diffraction methods.

Linked cyclopentadienylamido complexes of titanium and zirconium have attracted recent interest, as they provide an important class of compounds with applications as polymerization catalysts.[32] The well-known[33−36] cyclopentadienyl monoamido[32,37,38] or bis-amido[39] derivatives are precatalyst examples containing only a single metal−halo or metal−alkyl bond and are of potential interest in the context of single-site olefin polymerization catalysis. Nevertheless, a few linked cyclopentadienylphenoxo[22,40−42] and indenylphenoxo[43] complexes of these metals have been reported. The synthesis and characterization of new derivatives of formula Ti(η^5-$C_5H_4SiMe_2$-η^1-MBMP)R_2 represents a significant contribution to the dearth of this type of complex described in the literature.

Scheme 1



Scheme 2



Results and Discussion

Synthesis of Complexes. In a previous paper[21] we reported the addition of 1 equiv of Li_2(MBMP) to Ti(η^5-$C_5H_4SiMe_2Cl$)-Cl_3 in hexane, at low temperature, to give the monocyclopentadienyl η^2-MBMP derivative Ti(η^5-$C_5H_4SiMe_2Cl$)(η^2-MBMP)-Cl (**1**), 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 **1** and the cyclopentadienylphenoxo complex Ti(η^5-$C_5H_4SiMe_2$-η^1-MBMP)Cl_2 (**2**). Complex **2** can also be obtained, as an analytically pure substance, by reaction of Li_2(MBMP) with Ti(η^5-$C_5H_4SiMe_2$-Cl)Cl_3 in polar solvents (THF), at low temperature, after recrystallization, as a compound less soluble in hexane than **1** (Scheme 1).

Following the detailed procedure reported for **1**, addition of 1 equiv of Li_2(MBMP) to Ti(η^5-$C_5H_4SiMe_3$)Cl_3 in hexane at −78 °C affords the monocyclopentadienyl chloro bisphenoxo compound Ti(η^5-$C_5H_4SiMe_3$)(η^2-MBMP)Cl (**3**) containing the bidentate dianionic η^2-MBMP ligand coordinated to the titanium center, isolated as a red product in 88% yield (Scheme 2).

Complex **1** offers the opportunity to study and compare the different reactivity of the two types of chloro atoms (Ti−Cl and Si−Cl) contained in the compound, with alkylating reagents.

---

[21] González-Maupoey, M.; Cuenca, T.; Frutos, L. M.; Castaño, O.; Herdtweck, E. *Organometallics* **2003**, *22*, 2694−2704.

[22] Cuenca, T. In *Comprehensive Organometallic Chemsitry III*; Mingos, M. P., Crabtree, R. H., Eds.; Bochmann, M., Vol. Ed.; Elsevier: London, 2006; Vol. 4, Chapter 5.

[23] Nomura, K.; Naga, N.; Miki, M.; Yanagi, K.; Imai, A. *Organometallics* **1998**, *17*, 2152−2154.

[24] Nomura, K.; Komatsu, T.; Imanishi, Y. *Macromolecules* **2000**, *33*, 8122−8124.

[25] Stephan, D. W.; Stewart, J. C.; Guerin, F.; Spence, R. E. v. H.; Xu, W.; Harrison, D. G. *Organometallics* **1999**, *18*, 1116−1118.

[26] Firth, A. V.; Stewart, J. C.; Hoskin, A. J.; Stephan, D. W. *J. Organomet. Chem.* **1999**, *591*, 185−193.

[27] Doherty, S.; Errington, R. J.; Jarvis, A. P.; Collins, S.; Clegg, W.; Elsegood, M. R. J. *Organometallics* **1998**, *17*, 3408−3410.

[28] Doherty, S.; Errington, R. J.; Housley, N.; Ridland, J.; Clegg, W.; Elsegood, M. R. J. *Organometallics* **1999**, *18*, 1018−1029.

[29] Fokken, S.; Spaniol, T. P.; Kang, H. C.; Massa, W.; Okuda, J. *Organometallics* **1996**, *15*, 5069−5072.

[30] Kim, Y.; Hong, E.; Lee, M. H.; Kim, J.; Han, Y.; Do, Y. *Organometallics* **1999**, *18*, 36−39.

[31] Kim, Y.; Han, Y.; Do, Y. *J. Organomet. Chem.* **2001**, *634*, 19−24.

[32] McKnight, A. L.; Waymouth, R. M. *Chem. Rev.* **1998**, *98*, 2587−2598.

[33] Stevens, J. C.; Timmers, F. J.; Wilson, D. R.; Schmidt, G. F.; Nickias, P. N.; Rosen, R. K.; Knight, G. W.; Lai, S. (Dow) Eur. Patent Appl. EP 416,815, 1991 (*Chem. Abstr.* **1991**, *115*, 93163).

[34] Canich, J. A. M. (Exxon) Eur. Patent Appl. EP 420,436, 1991 (*Chem. Abstr.* **1991**, *115*, 184145).

[35] Panell, R. B.; Canich, J. A. M.; Hlatky, G. G. (Exxon) PCT Int. Appl. WO 94/00500, 1994.

[36] Nickias, P. N.; McAdon, M. H.; Patton, J. T. (Dow) PCT Int. Appl. WO 97/15583, 1997.

[37] Piers, W. E.; Shapiro, P. J.; Bunel, E. E.; Bercaw, J. E. *Synlett* **1990**, 74−84.

[38] Jin, J. Z.; Wilson, D. R.; Chen, E. Y. X. *Chem. Commun.* **2002**, 708−709.

[39] Cano, J.; Royo, P.; Lanfranchi, M.; Pellinghelli, M. A.; Tiripicchio, A. *Angew. Chem., Int. Ed.* **2001**, *40*, 2495−2497.

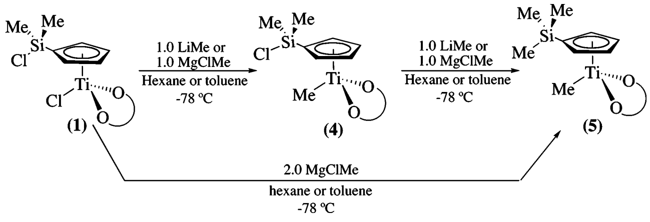
[40] Turner, L. E.; Thorn, M. G.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **2004**, *23*, 1576−1593.

[41] Rau, A.; Schmitz, S.; Luft, G. *J. Organomet. Chem.* **2000**, *608*, 71−75.

[42] Zhang, Y. T.; Wang, J. H.; Mu, Y.; Shi, Z.; Lu, C. S.; Zhang, Y. R.; Qiao, L. J.; Feng, S. H. *Organometallics* **2003**, *22*, 3877−3883.

[43] Zhang, Y. T.; Mu, Y.; Lu, C. S.; Li, G. H.; Xu, J. S.; Zhang, Y. R.; Zhu, D. S.; Feng, S. H. *Organometallics* **2004**, *23*, 540−546.

Scheme 3

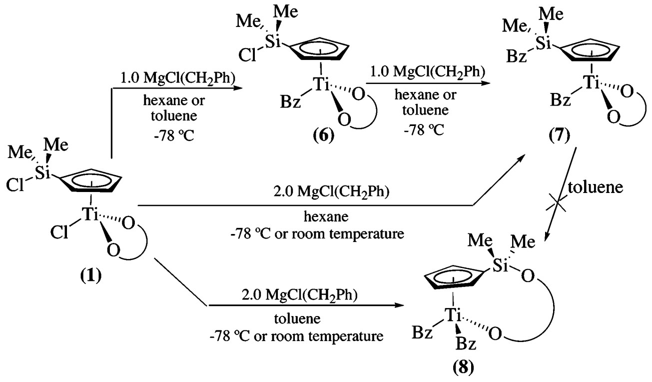


When **1** is treated with 1 or 2 equiv of MgClR [R = Me, CH_2-Ph] or LiMe, different types of alkyl derivatives are obtained. The formation of monocyclopentadienyl η^2-bisphenoxo derivatives Ti(η^5-$C_5H_4SiMe_2X$)(η^2-MBMP)R [R = Me, X = Cl (**4**); R = X = Me (**5**); R = CH_2Ph, X = Cl (**6**); R = X = CH_2Ph (**7**)] or the *ansa*-monocyclopentadienylphenoxo dibenzyl complex Ti(η^5-$C_5H_4SiMe_2$-η^1-MBMP)$(CH_2Ph)_2$ (**8**) is observed depending on the reaction conditions. Compound **8** can also be synthesized by reaction of complex **2** with $MgCl(CH_2Ph)$. Similar reaction of **2** with MgClMe affords the *ansa*-monocyclopentadienylphenoxo dimethyl derivative Ti(η^5-$C_5H_4SiMe_2$-η^1-MBMP)Me_2 (**9**).

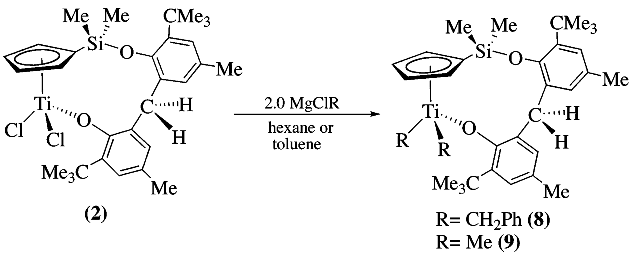
Addition of 1 equiv of LiMe or MgClMe to a solution of **1** in hexane or toluene at low temperature (−78 °C) produces a change of color from red to dark yellow. Analysis of the resulting product indicates that the monoalkylation in the Ti−Cl bond takes place, leaving the Si−Cl bond unreacted, and the chlorodimethylsilyl−cyclopentadienyl monomethyl η^2-bisphenoxo derivative **4** is obtained in 56% yield. The reaction of complex **4** with one additional equivalent of LiMe or MgClMe, in hexane or toluene at −78 °C, proceeds with the alkylation of the Si−Cl bond, affording the trimethylsilyl−cyclopentadienyl monomethyl η^2-bisphenoxo compound **5** in high yield (Scheme 3). Compound **5** can also be prepared by treatment of 2 equiv of LiMe or MgClMe with **1**, in hexane or toluene at −78 °C. Complexes **4** and **5** are considered as monocyclopentadienyl bisphenoxo monoalkyl derivatives, maintaining the η^2-coordination of the bisphenoxo ligand to the titanium center. Analogous behavior has been observed in our research group in the study of complexes bearing the chlorodimethylsilyl−cyclopentadienyl ligand,[44,45] indicating that in compound **1** and related derivatives the Ti−Cl bond reacts selectively toward the Si−Cl in the presence of alkylating reagents.

Similarly, the addition of 1 equiv of $MgCl(CH_2Ph)$ to a solution of **1** in hexane or toluene at low temperature (−78 °C) selectively results in the alkylation of the Ti−Cl bond with formation of the chlorodimethylsilyl−cyclopentadienyl monobenzyl bisphenoxo complex **6** in 65% yield, which further reacts with 1 equiv of $MgCl(CH_2Ph)$ in either hexane or toluene to give the benzyldimethylsilyl−cyclopentadienyl derivative **7** in 58% yield. The remaining Si−Cl has been alkylated, and the bisphenoxo ligand maintains the η^2-coordination to the titanium center (Scheme 4). Derivative **7** can also be obtained as a pure substance, by addition of 2 equiv of $MgCl(CH_2Ph)$ to a solution of **1** in hexane at −78 °C. The same result is obtained when this reaction is carried out in hexane at room temperature. However, the addition of 2 equiv of $MgCl(CH_2Ph)$ to a solution of **1** in toluene (room temperature or −78 °C) leads to the *ansa*-cyclopentadienylphenoxo dibenzyl derivative **8**, indicating that structural reorganization of the bisphenoxo ligand has occurred, now adopting a bridge disposition between the titanium and silicon atoms (Scheme 4). It is noteworthy that complex **7** dissolved in toluene (room temperature or −78 °C) does not evolve into complex **8** even after several days, suggesting that the reorganization of the bisphenoxo ligand must occur during the alkylating reaction in toluene in the presence of 2 equiv of $MgCl(CH_2Ph)$ and does not proceed after the Si−benzyl bond is formed.

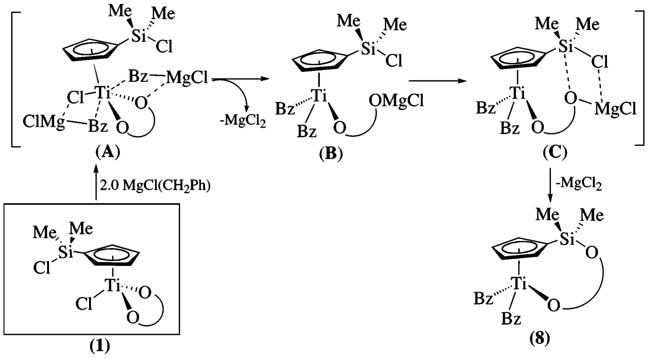
Scheme 4



Scheme 5



Scheme 6



The reaction of **2** with 2 equiv of MgClR (R = Me, CH_2Ph), in hexane or toluene and independent of the reaction temperature conditions, gives the *ansa*-cyclopentadienylphenoxo dialkyl derivatives **8** (72% yield) and **9** (65% yield), respectively (Scheme 5). In contrast to complex **8**, compound **9** cannot be prepared by reaction of complex **1** with the appropriate alkylating reagent in any reaction conditions.

On the basis of these results, we propose that the addition of 2 equiv of $MgCl(CH_2Ph)$ all at once to a solution of the chlorodimethylsilyl−cyclopentadienyl η^2-bisphenoxo chloro titanium complex **1** in a polar solvents (THF or toluene) allows the interaction of this alkylating reagent with the Ti−Cl and Ti−O bonds, leaving the Si−Cl bond unaltered, with the formation of the intermediate species **A** (Scheme 6). After the alkylation reactions of both Ti−Cl and Ti−O bonds are complete, the elimination of $MgCl_2$ and the unit "−OMgCl" produces the intermediate species **B**. The previously chelating

---

(44) Ciruelos, S.; Cuenca, T.; Gómez-Sal, P.; Manzanero, A.; Royo, P. *Organometallics* **1995**, *14*, 177−185.

(45) Ciruelo, G.; Cuenca, T.; Gómez, R.; Gómez-Sal, P.; Martin, A.; Rodríguez, G.; Royo, P. *J. Organomet. Chem.* **1997**, *547*, 287−296.

nature of the bisphenoxo ligand favors the presence in the surroundings of the unit "−OMgCl", which can approach and interact with the remaining Si−Cl bond. This interaction forms the intermediate species **C**, allowing the alkylation of the Si−Cl bond to afford the final product **8** with elimination of $MgCl_2$. The formation of the new Si−O bond should be favored in polar solvents due to the ionic nature of the oxygen−magnesium interaction, which could explain the structural reorganization in the synthesis of **8** when toluene is used as solvent in the reaction. Similarly, the formation of compound **2** is favored in THF solvent.[21] When the reaction is carried out by progressive addition of $MgCl(CH_2Ph)$ in a polar or nonpolar solvent, the first equivalent of alkylating reagent selectively produces the alkylation of the Ti−Cl bond with formation of the chlorodimethylsilyl−cyclopentadienyl monobenzyl bisphenoxo derivative **6**. The presence of the titanium−alkyl bond modifies the electronic properties of the titanium center in this compound compared with the analogous situation in the corresponding chloro compound **1**. Subsequently, the addition of the second equivalent of $MgCl(CH_2Ph)$ selectively proceeds with the alkylation of the Si−Cl bond, leaving the Ti−O bond unreacted and generating complex **7**. Nevertheless, for the methylation reaction, the observed results suggest a higher stability for the Ti−O bonds of the bisphenoxo ligand with respect to the Ti−Cl and Si−Cl bond in any reaction conditions, preventing reorganization of the bisphenoxo group and indicating that the reactivity of the chlorodimethylsilyl−cyclopentadienyl η^2-bisphenoxo chloro titanium complex **1** is also dependent on the nature of the alkylating reagent.

Compounds **3**−**7** are soluble in chlorinated solvents (chloroform and dichloromethane) and aromatic (benzene, toluene) and aliphatic hydrocarbons (pentane and hexane). Complex **3** remains air-stable for some weeks in the solid state, but the alkyl derivatives are more readily hydrolyzed, although they can be stored for months under an inert atmosphere without decomposition. Complexes **8** and **9** are partially soluble in toluene and chlorinated solvents (chloroform and dichloromethane) but insoluble in hexane, and they exhibit higher stability than alkyl complexes **4**−**7**. All of these compounds were characterized by elemental analysis and NMR spectroscopy. The analytical composition exactly fits the proposed formulation. The molecular structures of **3** and **8** were determined by X-ray diffraction methods.

The NMR spectra (C_6D_6 and $CDCl_3$, room temperature) for complexes **3**−**7** show patterns of signals for the MBMP fragment similar to those described for compounds containing the same bisphenoxo ligand. The two CH_2 protons in the ^1H NMR spectra appear as a pair of doublets, found with chemical shift difference values of 0.89 ppm (C_6D_6) (0.82 ppm, $CDCl_3$) for the chloro derivative **3** or an average of 0.48 ppm (0.39−0.56 ppm, C_6D_6; 0.46 ppm, $CDCl_3$) for the alkyl derivatives **4**−**7**. Both equivalent *tert*-butyl groups and the two methyl substituents on the phenyl rings appear as singlets in the expected region of the spectra. The protons at positions 3 and 5 on the phenyl ring appear as AA′ spin systems with $^4J_{HH}$ coupling constant values of ca. 1.80 Hz. The protons on the cyclopentadienyl ring display an AA′BB′ spin system, and a singlet is observed for the methyl groups bonded to the silicon atom. These spectroscopic data are consistent with C_s molecular symmetry. The alkyl ligands bonded to the titanium center show the expected resonances in the ^1H NMR spectra, one singlet for the methyl ligand and one singlet for the methylene protons for the CH_2Ph group. Structural features similar to those described from ^1H NMR spectroscopy can be deduced from the $^{13}C\{^1H\}$ NMR spectra (C_6D_6, room temperature). Alkyl substituents in the silicon atom show the same patterns of signals shifted upfield with respect to the resonances assigned to the titanium−alkyl groups.

The NMR spectra (C_6D_6 and $CDCl_3$, room temperature) for complexes **8** and **9** show more complicated patterns of resonances for the MBMP fragment. The two phenyl rings of the bisphenoxo ligand are not equivalent, giving two signals for the *tert*-butyl groups and two singlets for the two methyl substituents on the phenyl rings. Four resonances for the protons on the phenyl rings are also observed, while the protons of the methylene bridge appear as a broad signal. The cyclopentadienyl protons display an AA′BB′ spin system, and only one singlet is observed for the equivalent methyl groups bonded to the silicon atom. The same spectroscopic features can also be deduced from the $^{13}C\{^1H\}$ NMR data (C_6D_6, room temperature). These spectroscopic data support the presence of a mirror plane in the molecular structure containing the titanium center, the methylene bridge carbon, and the silicon atom, bisecting the RTiR and MeSiMe angles and dividing the cyclopentadienyl ring into two equivalent fragments. As discussed in the next paragraph, the structure symmetry in the solid state of complexes **8** and **9** contrasts with the C_s symmetry observed in solution at room temperature. This fact suggests dynamic behavior in solution through a flipping process at the silicon−titanium bridge with interconversion of the two methylene protons, making these two protons and the two methyl groups bonded to the silicon atom equivalent and generating an AA′BB′ spin system for the cyclopentadienyl ring protons. For this process we have obtained Gibbs activation enthalpy values ($\Delta G^{\#}$) of 9.6, 8.9, and 9.6 kcal/mol at 203, 178, and 193 K for **8** and **9** derivatives and the previously reported complex **2**,[21] respectively. A similar fluxional process of the nine-membered metallacycle in the TiX_2(EBMP) [EBMP = 2,2′-CH_2CH_2-bis(4-methyl-6-*tert*-butylphenoxo)] has been described as a ring inversion, equivalent to an enantiomerization similar to that observed in heterocyclic organic compounds.[16] Fluxional behavior in cyclopentadienyl-amido derivatives of titanium has also been detected, which involves an interconversion between two enantiomeric conformations of a seven-membered metallacycle Cp−Si−N−C−C−N−Ti.[46]

Preliminary studies on ethylene and styrene polymerization activation for the *ansa*-monocyclopentadienylphenoxo dihalo and dialkyl derivatives **2**, **8**, and **9** in the presence of methylaluminoxane (MAO) were carried out in toluene at different temperatures and reaction times (Table 1). In the ethylene polymerization, the exchange of chloro by an alkyl ligand produces a decreae in observed activities, while the three compounds exhibit similar activity in the polymerization of styrene. The catalytic activity is sensitive to temperature, increasing the polymerization activity at relatively high temperatures (50−60 °C). It is noteworthy that the ethylene polymerization activity of **2** decreases significantly from 50 °C to 90 °C, while the opposite happens for **9**. Bulky monocyclopentadienyl−aryloxo derivatives such as $Ti(\eta^5\text{-}C_5R_5)(OC_6H_3\text{-}Pr^i{}_2\text{-}2,6)Cl_2$ (R = H, Me) have been shown to be active in ethylene polymerization.[23] The properties of the Cp-phenoxo dichloro titanium complex $Ti(C_5H_4CMe_2\text{-}2\text{-}C_6H_4O)Cl_2$ in the presence of MAO or the system $AlBu_3/[Me_2PhNH]^+[B(C_6F_5)_4]$ as cocatalysts for the polymerization of ethylene at high pressures have been studied. The higher activities are obtained with the Ti/MAO system.[40]

---

(46) Jiménez, G.; Rodríguez, E.; Gómez-Sal, P.; Royo, P.; Cuenca, T.; Galakhov, M. *Organometallics* **2001**, *20*, 2459−2467.

Table 1. Polymerization of Ethylene and Styrene with 2, 8, and 9

run	catalyst^a	time (min)	temperature (°C)	yield (g)	activity (kg of polymer/mol Ti·h)
Polymerization of Ethylene (1 atm)					
1	**2**	30	40	1.32	132
2	**2**	30	50	1.70	170
3	**2**	30	90	1.48	148
4	**8**	30	40	traces^b	
5	**8**	30	50	0.01	1.5
6	**8**	30	90	0.02	2.6
7	**9**	30	40	0.02	2.5
8	**9**	30	50	0.25	25
9	**9**	30	90	0.44	44
Polymerization of Styrene (5 mL)					
10	**2**	15	40	0.75	150
11	**2**	15	50	2.62	523
12	**2**	15	60	2.63	526
13	**8**	10	40	1.33	398
14	**8**	10	50	2.77	831
15	**8**	10	60	2.26	679
16	**9**	10	40	0.20	58
17	**9**	10	50	0.37	111
18	**9**	10	60	1.47	442

[a] 20 μmol of catalyst, cocatalyst: MAO (Al/Ti= 1000); 40 mL of toluene. [b] Not enough for analysis.

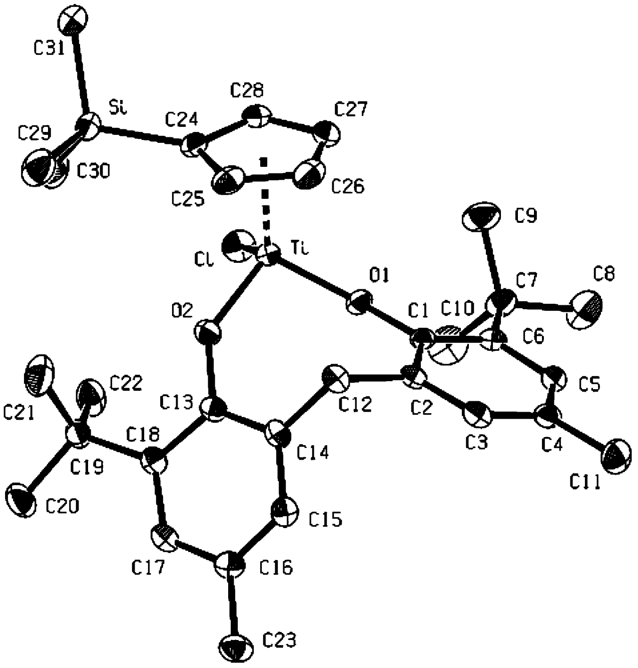


Figure 1. ORTEP style plot of compound **3** in the solid state. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for 3 and 8

3		8	
Ti−O1	1.792(1)	Ti−O1	1.817(2)
Ti−O2	1.822(1)	Ti−C31	2.126(3)
Ti−Cl	2.2891(5)	Ti−C38	2.133(3)
O1−C1	1.367(2)	O1−C1	1.373(3)
O2−C13	1.378(2)	O2−C13	1.383(3)
Ti−C24	2.405(2)	Ti−C24	2.386(3)
Ti−C25	2.362(2)	Ti−C25	2.354(3)
Ti−C26	2.361(2)	Ti−C26	2.359(3)
Ti−C27	2.398(2)	Ti−C27	2.373(3)
Ti−C28	2.408(2)	Ti−C28	2.381(3)
Ti−Cg^a	2.063	Ti−Cg^a	2.047
Si−C24	1.881(2)	Si−C24	1.874(3)
		Si−O2	1.653(2)
Cl−Ti−O1	99.31(4)	C38−Ti−O1	97.94(9)
Cl−Ti−O2	104.47(4)	C38−Ti−C31	100.1(1)
Cl−Ti−Cg^a	113.3	C38−Ti−Cg^a	112.2
O1−Ti−O2	100.52(5)	O1−Ti−C31	103.7(1)
O1−Ti−Cg^a	118.4	O1−Ti−Cg^a	126.0
O2−Ti−Cg^a	118.2	C31−Ti−Cg^a	113.2
Ti−O1−C1	154.8(1)	Ti−O1−C1	158.1(2)
Ti−O2−C13	139.8(1)	Ti−C31−C32	128.6(2)
		Ti−C38−C39	127.7(2)
C2−C12−C14	115.2(1)	C2−C12−C14	118.7(2)
C24−Si−C29	106.2(1)	C24−Si−C29	104.8(1)
C24−Si−C30	111.6(1)	C24−Si−C30	111.9(1)
C24−Si−C31	108.4(1)	C24−Si−O2	108.3(1)
C29−Si−C30	112.6(1)	C29−Si−C30	110.0(1)

[a] Cg denotes the cyclopentadienyl centroid.

Crystal Structure of Ti(η^5-$C_5H_4SiMe_3$)(η^2-MBMP)Cl (3) and Ti(η^5-$C_5H_4SiMe_2$-η^1-MBMP)(CH_2Ph)$_2$ (8). To confirm structural details of the molecular geometry in the solid state for this type of compound, crystal X-ray structure analyses of **3** and **8** were carried out. Single crystals of both complexes obtained by slow recrystallization from toluene solution were of good enough quality to be analyzed by X-ray diffraction.

The crystal structure of **3** is shown in Figure 1, and Table 2 summarizes selected bond distances and angles. The MBMP ligand adopts a puckered chelate disposition with the typical *boat* conformation in the solid state and with the methylene bridge pointing toward the cyclopentadienyl ring.[9,10,20,29] This disposition confirms the preferred structure for this type of complex as deduced by theoretical studies for the chloro derivatives.[21]

The coordination geometry around the titanium atom is a pseudo-three-legged piano stool, as expected for complexes of the type $TiCpL_3$.[47] The metal−oxygen bond lengths [av 1.807 Å] are in the expected range for titanium complexes containing the η^2-bisphenoxo ligand with (σ+π) donor oxygen atoms.[3,16] The Ti−Cl bond distance is longer than the values found in $TiCl_2$(MBMP) [2.215(2) and 2.206(2) Å][15] but similar to that found in analogous related structures for cyclopentadienyl chloro derivatives [2.2891(6) Å for Ti(η^5-C_5H_5)(η^2-MBMP)Cl and 2.2946(4) Å for Ti(η^5-C_5Me_5)(η^2-MBMP)Cl].[21] Compared with the structures of Ti(η^5-C_5R_5)(η^2-MBMP)Cl (R = H, Me), the structure of compound **3** is essentially equivalent but showing some small differences. The O1−Ti−O2 angle in **3** is more open, and it exhibits a slight distortion of the Ti−O−O cycle. The Ti−O2 bond distance [1.822(1) Å] is longer than Ti−O1 [1.792(1) Å], while the related complexes Ti(η^5-C_5R_5)(η^2-MBMP)Cl (R = H, Me) show very similar values. This asymmetric disposition is also reflected in the two different Ti−O−C angles, Ti−O2−C13 [139.8(1)°] being closer than Ti−O1−C1 [154.8(1)°].

The $SiMe_3$ substituent on the cyclopentadienyl ligand is placed vertical to the plane formed by the chloro atom, the methylene bridge carbon, the metal center, and the centroid of the cyclopentadienyl ligand, to avoid steric repulsion with the methylene bridge group. This reduction in steric hindrance implies that the distortion of the metallacycle, which prevents the steric repulsion between the $SiMe_3$ group and the *tert*-butyl substituent, produces an increase in the stability of the molecule.

Figure 2 shows an ORTEP view of the structure of complex **8** along with the atom-labeling scheme. Selected bond distances and bond angles with their standard deviations are listed in Table

---

[47] Rogers, R. D.; Benning, M. M.; Kurihara, L. K.; Moriarty, K. J.; Rausch, M. D. *J. Organomet. Chem.* **1985**, *293*, 51−60.

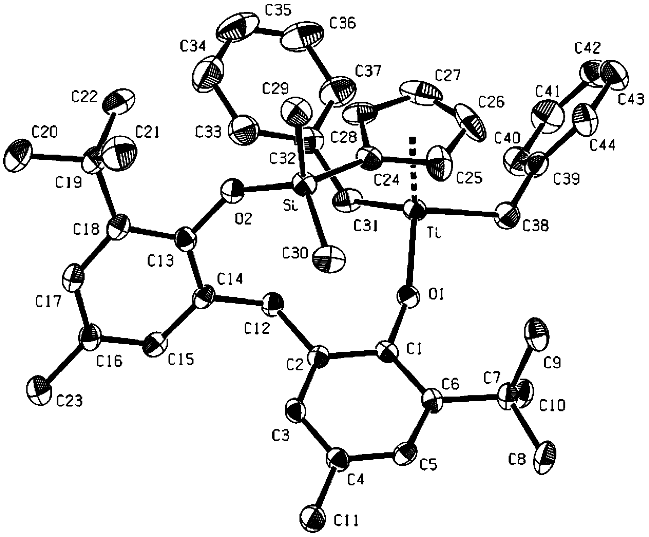


Figure 2. ORTEP style plot of compound **8** in the solid state. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

2. The structure is similar to that reported for the chloro complex[21] and consists of discrete monomeric units with a pseudo-three-legged piano stool coordination geometry around the titanium atom. The titanium coordination is described as pseudotetrahedral. The Ti−C(ring) distances are consistent with an η^5-coordination. The Cg−Ti−O1 angle, where Cg represents the centroid of the C$_5$H$_4$ ring, at 126.0°, is significantly larger than the corresponding angle in the constrained *ansa*-monocyclopentadienylsilylamido complexes [Ti(η^5-C$_5$R$_4$SiMe$_2$-η-NR′)-Cl$_2$],[2] suggesting that increasing the length of the Cp−Ti spacer leaves a less open metal center. The titanium−carbon bond lengths (av 2.1295 Å) and the Ti−C(31)−C(32) (128.6(2)°) and Ti−C(38)−C(39) (127.7(2)°) correspond to normal benzyl dispositions.

If the centroid of the cyclopentadienyl ring is considered as a single coordination site, the central core of **8** 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 cyclopentadienyl−amido titanium derivatives.[22]

The short Ti−O1 bond distance of 1.817(2) Å suggests partial pπ−dπ bonding between Ti and the phenoxo ligand with a value of the Ti−O1−C1 angle of 158.1(2)°. Similar values have been reported for other linked cyclopentadienyl−alkoxo 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 cyclopentadienyl alkoxo titanium derivatives.[31]

The Si−O2 distance [1.653(2) 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.

Concluding Remarks

The results described in this contribution allow us to provide remarkable conclusions concerning the chemical behavior of the chlorodimethylsilyl−cyclopentadienyl η^2-bisphenoxo chloro titanium derivative Ti(η^5-C$_5$H$_4$SiMe$_2$Cl)(η^2-MBMP)Cl (**1**) in alkylating reactions. The nature of the final product depends on the solvent, temperature, and type of alkylating reagent used, with different reactivity of the Ti−Cl, Si−Cl, or Ti−O bonds contained in the compound. The alkylation reaction with 2 equiv of LiMe or MgClMe proceeds with selective reactivity of the Ti−Cl bond, followed by alkylation of the Si−Cl bond, leaving the Ti−O bond unaltered, to give monocyclopentadienyl η^2-bisphenoxo derivatives Ti(η^5-C$_5$H$_4$SiMe$_2$X)(η^2-MBMP)R. When 2 equiv of MgCl(CH$_2$Ph) are used and the reaction undergoes progressive addition of the alkylating reagent, the products of the reaction are similar to those obtained with the methyl alkylating reagent, indicating that first the Ti−Cl bond and then the Si−Cl bond are alkylated, while leaving the Ti−O bond unreacted. However, the direct reaction with 2 equiv of MgCl-(CH$_2$Ph) in toluene causes a reorganization of the bisphenoxo bonding ligand to afford the *ansa*-monocyclopentadienylphenoxo dibenzyl derivative Ti(η^5-C$_5$H$_4$SiMe$_2$-η^1-MBMP)(CH$_2$Ph)$_2$. Analogous *ansa*-monocyclopentadienylphenoxo dialkyl derivatives Ti(η^5-C$_5$H$_4$SiMe$_2$-η^1-MBMP)R$_2$ can be prepared by treatment of Ti(η^5-C$_5$H$_4$SiMe$_2$-η^1-MBMP)Cl$_2$ with 2 equiv of MgCl(CH$_2$Ph) or MgClMe.

Experimental Section

General Considerations. All manipulations were performed under argon using Schlenk and high-vacuum line techniques or in a glovebox VAC, model HE-63. The solvents were purified by distillation under argon before use by employing the appropriate drying/deoxygenating agent. Deuterated solvents were stored over activated 4 Å molecular sieves and degassed by several freeze−thaw cycles. LiMe, MgClMe, MgCl(CH$_2$Ph), and 2,2′-CH$_2$-bis(6-^{t}Bu-4-CH$_3$-C$_6$H$_2$-1-OH) (Aldrich) were commercially obtained and used without further purification. Li$_2$[2,2′-CH$_2$-bis(6-^{t}Bu-4-CH$_3$-C$_6$H$_2$-1-O)][21] was prepared by known procedures. Polymerization grade ethylene from Aldrich was purified by passage through two columns packed with activated alumina and 4 Å molecular sieves. Styrene was distilled at reduced pressure over calcium hydride and stored in the refrigerator in the dark. Methylaluminoxane (MAO) 10% solution in toluene was purchased from WITCO GmbH. C, H, and N microanalyses were performed on a Perkin-Elmer. NMR spectra, measured at 25 °C, were recorded on Varian Unity FT-300 (^{1}H NMR at 300 MHz, ^{13}C NMR at 75 MHz) or Unity-Plus FT-500 (^{1}H NMR at 500 MHz, ^{13}C NMR at 125 MHz) spectrometers, and chemical shifts (δ, ppm) are referenced to SiMe$_4$ via the carbon resonances (^{13}C) and the residual protons (^{1}H) of the solvent.

Synthesis of Ti(η^5-C$_5$H$_4$SiMe$_3$)(η^2-MBMP)Cl (3). Li$_2$(MBMP) (0.43 g, 1.23 mmol) in THF (20 mL) was added to a solution of 0.36 g (1.23 mmol) of Ti(η^5-C$_5$H$_4$SiMe$_3$)(η^2-MBMP)Cl$_3$ in hexane (50 mL) at room temperature. The reaction mixture was slowly warmed to room temperature and stirred for 5 h. The solvent was then completely removed. After extraction into hexane a red solid was obtained, which was recrystallized from cold hexane and characterized as **3** (0.60 g, 88% yield). Anal. Calcd for C$_{31}$H$_{43}$-TiSiO$_2$Cl: C, 66.62; H, 7.70. Found: C, 66.41; H, 7.48. ^{1}H NMR (300 MHz, C$_6$D$_6$, 25 °C): δ 7.03, 6.95 (AA′ spin system, 2 × 2H, Ph); 6.59, 6.46 (AA′BB′ spin system, 2 × 2H, C$_5$*H*$_4$SiMe$_3$); 4.26, 3.37 (AB spin system, 2 × 1H, $\Delta\delta = 0.89$ ppm, $^2J_{H-H} = 13.0$ Hz, CH$_2$); 2.13 (s, 6H, *CH*$_3$Ph); 1.44 [s, 18H, C(CH$_3$)$_3$]; 0.39 (s, 9H, C$_5$H$_4$Si*Me*$_3$). ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C): δ 7.00, 6.87 (AA′ spin system, 2 × 2H, Ph); 6.86, 6.80 (AA′BB′ spin system, 2 × 2H, C$_5$*H*$_4$SiMe$_3$); 4.22, 3.40 (AB spin system, 2 × 1H, $\Delta\delta =$ 0.82 ppm, $^2J_{H-H} = 12.9$ Hz, CH$_2$); 2.24 (s, 6H, *CH*$_3$Ph); 1.30 [s, 18H, C(CH$_3$)$_3$]; 0.34 (s, 9H, C$_5$H$_4$Si*Me*$_3$). ^{13}C NMR (125 MHz, C$_6$D$_6$, 25 °C): δ 163.4, 137.4, 136.1, 131.2, 128.9, 126.2 (Ph); 134.5 (*ipso*-*C*$_5$H$_4$SiMe$_3$); 123.9, 121.0 (*C*$_5$H$_4$SiMe$_3$); 35.8 (CH$_2$); 35.8 [*C*(CH$_3$)$_3$]; 31.5 [C(*C*H$_3$)$_3$]; 21.5 (*C*H$_3$-Ph); 0.2 (C$_5$H$_4$Si*Me*$_3$).

Synthesis of Ti(η^5-C$_5$H$_4$SiMe$_2$Cl)(η^2-MBMP)Me (4). A 3.0 M solution of MgClMe (0.29 mL, 0.86 mmol) in THF was added to a solution of Ti(η^5-C$_5$H$_4$SiMe$_2$Cl)(η^2-MBMP)Cl (0.50 g, 0.86

mmol) in hexane (70 mL) at −78 °C. The reaction mixture was slowly warmed to room temperature and stirred for 6 h. The solvent was completely removed and the resulting solid extracted into hexane. After concentrating the solution, a yellow powder was obtained, which was recrystallized from cold hexane and characterized as **4** (0.27 g, 56% yield). Anal. Calcd for $C_{31}H_{43}TiSiO_2Cl$: C, 66.54; H, 7.69. Found: C, 66.47; H, 7.82. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ 7.09, 6.99 (AA′ spin system, 2 × 2H, Ph); 6.39 (m, 4H, $C_5\mathit{H}_4SiMe_2Cl$); 3.82, 3.43 (AB spin system, 2 × 1H, $\Delta\delta = 0.39$ ppm, $^{2}J_{H-H} = 13.6$ Hz, CH_2); 2.14 (s, 6H, $\mathit{CH_3}$Ph); 1.37 [s, 18H, $C(CH_3)_3$]; 1.35 (s, 3H, Ti-CH_3); 0.48 (s, 6H, $C_5H_4Si\mathit{Me}_2Cl$). ^{13}C NMR (125 MHz, C_6D_6, 25 °C): δ 161.2, 136.8, 136.1, 130.3, 129.0, 126.1 (Ph); 121.3 (*ipso*-$\mathit{C}_5H_4SiMe_2Cl$); 119.9, 119.6 ($\mathit{C}_5H_4SiMe_2Cl$); 54.4 (Ti-CH_3); 36.2 (CH_2); 35.3 [$\mathit{C}(CH_3)_3$]; 30.9 [$C(\mathit{CH}_3)_3$]; 21.2 (CH_3-Ph); 2.9 ($C_5H_4Si\mathit{Me}_2Cl$).

Synthesis of Ti(η^5-$C_5H_4SiMe_3$)(η^2-MBMP)Me (5). Following the procedure described for **4** using 0.57 mL (1.72 mmol) of a 3.0 M solution of MgClMe in THF and 0.50 g (0.86 mmol) of Ti(η^5-$C_5H_4SiMe_2Cl$)(η^2-MBMP)Cl in hexane (70 mL), a bright yellow solid was obtained, which was characterized as **5** (0.29 g, 63% yield). Anal. Calcd for $C_{32}H_{46}TiSiO_2$: C, 71.35; H, 8.61. Found: C, 71.14; H, 8.40. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ 7.12, 7.00 (AA′ spin system, 2 × 2H, Ph); 6.50, 6.33 (AA′BB′ spin system, 2 × 2H, $C_5\mathit{H}_4SiMe_3$); 3.89, 3.44 (AB spin system, 2 × 1H, $\Delta\delta = 0.45$ ppm, $^{2}J_{H-H} = 13.7$ Hz, CH_2); 2.15 (s, 6H, CH_3Ph); 1.40 [s, 18H, $C(CH_3)_3$]; 1.36 (s, 3H, Ti−CH_3); 0.20 (s, 9H, $C_5H_4Si\mathit{Me}_3$). ^{13}C NMR (125 MHz, C_6D_6, 25 °C): δ 161.2, 136.8, 135.9, 130.0, 129.0, 126.0 (Ph); 126.0 (*ipso*-$\mathit{C}_5H_4SiMe_3$); 120.0, 119.5 ($\mathit{C}_5H_4SiMe_3$); 53.5 (Ti-CH_3); 36.1 (CH_2); 35.2 [$\mathit{C}(CH_3)_3$]; 30.8 [$C(\mathit{CH}_3)_3$]; 21.2 (CH_3-Ph); −0.17 ($C_5H_4Si\mathit{Me}_3$).

Synthesis of Ti(η^5-$C_5H_4SiMe_2Cl$)(η^2-MBMP)(CH_2Ph) (6). Following the procedure described for **4** using 0.26 mL (0.50 mmol) of a 2.0 M solution of MgCl(CH_2Ph) in THF and 0.30 g (0.50 mmol) of Ti(η^5-$C_5H_4SiMe_2Cl$)(η^2-MBMP)Cl in hexane (70 mL), a light brown powder was obtained, which was characterized as **6** (0.21 g, 65% yield). Anal. Calcd for $C_{37}H_{47}TiSiO_2Cl$: C, 70.00; H, 7.41. Found: C, 69.80; H, 7.23. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ 7.31 (m, 5H, $CH_2\mathit{Ph}$); 7.06, 6.99 (AA′ spin system, 2 × 2H, Ph); 6.43, 6.26 (AA′BB′ spin system, 2 × 2H, $C_5\mathit{H}_4SiMe_2Cl$); 3.88, 3.38 (AB spin system, 2 × 1H, $\Delta\delta = 0.50$ ppm, $^{2}J_{H-H} = 13.6$ Hz, CH_2); 3.31 (s, 2H, Ti-CH_2Ph); 2.14 (s, 6H, CH_3Ph); 1.45 [s, 18H, $C(CH_3)_3$]; 0.42 (s, 6H, $C_5H_4Si\mathit{Me}_2Cl$). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 7.34 (m, 5H, $CH_2\mathit{Ph}$); 7.07, 6.96 (AA′ spin system, 2 × 2H, Ph); 6.47, 6.40 (AA′BB′ spin system, 2 × 2H, $C_5\mathit{H}_4SiMe_2Cl$); 3.86, 3.40 (AB spin system, 2 × 1H, $\Delta\delta = 0.46$ ppm, $^{2}J_{H-H} = 13.4$ Hz, CH_2); 3.05 (s, 2H, Ti-CH_2Ph); 2.30 (s, 6H, CH_3Ph); 1.45 [s, 18H, $C(CH_3)_3$]; 0.16 (s, 6H, $C_5H_4Si\mathit{Me}_2Cl$). ^{13}C NMR (125 MHz, C_6D_6, 25 °C): δ 161.4, 136.9, 136.6, 129.1, 128.5, 126.6 (Ph); 151.8 (*ipso*-$CH_2\mathit{Ph}$); 130.1 (*p*-$CH_2\mathit{Ph}$); 126.2 (*m*-$CH_2\mathit{Ph}$); 123.5 (*o*-$CH_2\mathit{Ph}$); 123.5 (*ipso*-$\mathit{C}_5H_4SiMe_2Cl$), 123.1, 122.3 ($\mathit{C}_5H_4SiMe_2Cl$); 78.4 (Ti-$\mathit{C}H_2$Ph); 37.1 (CH_2); 35.8 [$\mathit{C}(CH_3)_3$]; 31.3 [$C(\mathit{CH}_3)_3$]; 21.5 (CH_3-Ph); −0.01 ($C_5H_4Si\mathit{Me}_2Cl$).

Synthesis of Ti(η^5-$C_5H_4SiMe_2(CH_2Ph)$)(η^2-MBMP)(CH_2Ph) (7). Following the procedure described for **4** using 0.52 mL (1.00 mmol) of a 2.0 M solution of MgCl(CH_2Ph) in THF and 0.30 g (0.50 mmol) of Ti(η^5-$C_5H_4SiMe_2Cl$)(η^2-MBMP)Cl in hexane (50 mL), a dark brown powder was obtained, which was characterized as **7** (0.20 g, 58% yield). Anal. Calcd for $C_{44}H_{54}TiSiO_2Cl$: C, 76.38; H, 7.87. Found: C, 76.10; H, 7.50. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ 7.34−7.00 (m, 10H, $CH_2\mathit{Ph}$); 7.10, 7.00 (AA′ spin system, 2 × 2H, Ph); 6.35 (m, 4H, $C_5\mathit{H}_4SiMe_2Bz$); 3.97, 3.41 (AB spin system, 2 × 1H, $\Delta\delta = 0.56$ ppm, $^{2}J_{H-H} = 13.7$ Hz, CH_2); 3.31 (s, 2H, Ti-CH_2Ph); 2.07 (s, 2H, SiCH_2Ph); 2.15 (s, 6H, CH_3Ph); 1.48 [s, 18H, $C(CH_3)_3$]; 0.14 (s, 6H, $C_5H_4Si\mathit{Me}_2Bz$). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 7.30−6.90 (m, 10H, $CH_2\mathit{Ph}$); 7.02, 6.91 (AA′ spin system, 2 × 2H, Ph); 6.42, 6.35 (m, 4H, $C_5\mathit{H}_4SiMe_2Bz$); 3.81, 3.35 (AB spin system, 2 × 1H, $\Delta\delta = 0.46$ ppm, $^{2}J_{H-H} = 13.7$ Hz, CH_2); 3.00 (s, 2H, Ti-CH_2Ph); 2.34 (s, 2H, SiCH_2Ph); 2.25 (s, 6H, CH_3Ph); 1.40 [s, 18H, $C(CH_3)_3$]; 0.11 (s, 6H, $C_5H_4Si\mathit{Me}_2(CH_2Ph)$). ^{13}C NMR (125 MHz, C_6D_6, 25 °C): δ 161.4, 151.8, 141.9, 136.9, 136.6, 130.1, 129.1, 128.8, 128.5, 128.2, 127.8, 127.4, 126.6, 126.2 (aromatic); 123.5 (*ipso*-$\mathit{C}_5H_4SiMe_2(CH_2Ph)$); 123.1, 122.3 ($\mathit{C}_5H_4SiMe_2(CH_2Ph)$); 78.4 (Ti-$\mathit{C}H_2$Ph); 38.5 (Si-$\mathit{C}H_2$Ph); 37.1 ($CH_2$); 35.8 [$\mathit{C}(CH_3)_3$]; 31.3 [$C(\mathit{CH}_3)_3$]; 21.5 ($\mathit{CH}_3$-Ph); −0.02 ($C_5H_4Si\mathit{Me}_2(CH_2Ph)$).

Synthesis of Ti(η^5-$C_5H_4SiMe_2$-η^1-MBMP)(CH_2Ph)$_2$ (8). A 2.0 M solution of MgCl(CH_2Ph) (0.34 mL, 0.69 mmol) in THF was added to a solution of Ti(η^5-$C_5H_4SiMe_2$-η^1-MBMP)Cl_2 (0.20 g, 0.34 mmol) in toluene (50 mL) at −78 °C, followed by stirring overnight. After warming to room temperature, the solvent was completely removed and the solid obtained extracted into hexane. Concentrating the resulting solution gave a solid, which was recrystallized from cold hexane and characterized as **8** (0.17 g, 72% yield). Anal. Calcd for $C_{44}H_{54}TiSiO_2$: C, 76.54; H, 7.83. Found: C, 76.43; H, 7.64. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ 7.20−6.90 (m, 14H, aromatic); 6.37, 6.00 (AA′BB′ spin system, 2 × 2H, $C_5\mathit{H}_4SiMe_2$); 3.85 (br s, 2H, CH_2); 3.08, 2.77 (2 × 2H, Ti-CH_2Ph); 2.22, 2.04 (s, 2 × 3H, CH_3Ph); 1.58, 1.38 [s, 2 × 9H, $C(CH_3)_3$]; 0.13 (s, 6H, $C_5H_4Si\mathit{Me}_2$). ^{1}H NMR (300 MHz, CD_2Cl_2, 25 °C): δ 7.15 (m, 4H, *m*-$CH_2\mathit{Ph}$), 6.89 (m, 2H, *p*-$CH_2\mathit{Ph}$), 6.85 (m, 4H, *o*-$CH_2\mathit{Ph}$); 7.06, 7.02, 6.54, 6.38 (two AA′ spin systems, 4 × 1H, Ph); 6.38, 6.25 (AA′BB′ spin system, 2 × 2H, $C_5\mathit{H}_4SiMe_2$); 3.71 (br s, 2H, CH_2); 2.98, 2.55 (2 × 2H, Ti-CH_2Ph); 2.32, 2.21 (s, 2 × 3H, CH_3Ph); 1.51, 1.37 [s, 2 × 9H, $C(CH_3)_3$]; 0.13 (s, 6H, $C_5H_4Si\mathit{Me}_2$). ^{13}C NMR (125 MHz, C_6D_6, 25 °C): δ 162.3, 150.0, 140.3, 137.0, 132.4, 131.5, 130.9, 130.5, 128.9, 127.0, 125.7, 121.7 (Ph); 151.2, 128.6, 128.3, 126.5 (Ti-$CH_2\mathit{Ph}$); 124.2, 123.0 ($\mathit{C}_5H_4SiMe_2$); 88.4 (Ti-CH_2-Ph); 33.7 (CH_2); 35.3, 35.0 [$\mathit{C}(CH_3)_3$]; 30.5 [$C(\mathit{CH}_3)_3$]; 21.4, 21.2 (CH_3-Ph); 2.2 ($C_5H_4Si\mathit{Me}_2$).

Synthesis of Ti(η^5-$C_5H_4SiMe_2$-η^1-MBMP)Me_2 (9). Following the procedure described for **8** using 0.34 mL (1.03 mmol) of a 3.0 M solution of MgClMe in THF and 0.30 g (0.52 mmol) of Ti(η^5-$C_5H_4SiMe_2$-η^1-MBMP)Cl_2 in hexane (50 mL), a bright yellow solid was obtained, which was recrystallized from cold toluene and characterized as **9** (0.18 g, 65% yield). Anal. Calcd for $C_{32}H_{46}TiSiO_2$: C, 71.35; H, 8.61. Found: C, 69.33; H, 8.49. The isolated yellow solid consisted mainly of **9**, but it contained some unremovable amount of $MgCl_2$, which prevented us from obtaining correct elemental analysis, though satisfactory spectroscopy data were obtained. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ 7.15, 7.10, 6.85, 6.79 (two AA′ spin systems, 4 × 1H, Ph); 6.51, 6.08 (AA′BB′ spin system, 2 × 2H, $C_5\mathit{H}_4SiMe_2$); 3.73 (br s, 2H, CH_2); 2.17, 2.05 (s, 2 × 3H, CH_3Ph); 1.61, 1.43 [s, 2 × 9H, $C(CH_3)_3$]; 1.03 (s, 6H, Ti-CH_3); 0.25 (s, 6H, $C_5H_4Si\mathit{Me}_2$). ^{13}C NMR (125 MHz, C_6D_6, 25 °C): δ 162.0, 150.2, 140.2, 136.7, 132.1, 131.1, 130.4, 129.3, 127.9, 126.9, 125.6 (Ph); 126.0 (*ipso*-$\mathit{C}_5H_4SiMe_2$); 119.9, 118.7 ($\mathit{C}_5H_4SiMe_2$); 57.6 (Ti-CH_3); 33.8 (CH_2); 35.3, 35.0 [$\mathit{C}(CH_3)_3$]; 30.7, 30.4 [$C(\mathit{CH}_3)_3$]; 21.4, 21.1 (CH_3-Ph); 2.3 ($C_5H_4Si\mathit{Me}_2$).

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

Table 3. Crystallographic Data for Compounds 3 and 8

	3	**8**
formula	$C_{31}H_{43}ClO_2SiTi$	$C_{44}H_{54}O_2SiTi$
fw	559.06	690.83
color/habit	red/plate	red/fragment
cryst dimens, mm^3	0.21 × 0.48 × 0.61	0.06 × 0.18 × 0.28
cryst syst	monoclinic	orthorhombic
space group	$P2_1/n$ (no. 14)	*Pbca* (no. 61)
a, Å	12.7806(1)	16.2785(2)
b, Å	14.2076(1)	16.9519(2)
c, Å	17.5955(1)	27.6714(5)
β, deg	108.0383(3)	90
V, Å^3	3037.98(4)	7635.96(19)
Z	4	8
T, K	173	173
D_{calcd}, g cm^{-3}	1.222	1.202
μ, mm^{-1}	0.434	0.291
F(000)	1192	2960
θ range, deg	1.88−25.36	1.88−25.34
index ranges (*h*, *k*, *l*)	±15, ±17, ±21	±19, ±20, ±33
no. of rflns collected	67 571	39 965
no. of indep rflns/R_{int}	5560/0.049	6928/0.062
no. of obsd rflns ($I > 2\sigma(I)$)	4819	5822
no. of data/restraints/params	5560/0/497	6928/0/443
R1/wR2 ($I > 2\sigma(I)$)^a	0.0306/0.0739	0.0610/0.1089
R1/wR2 (all data)^a	0.0388/0.0773	0.0783/0.1146
GOF (on F^2)^a	1.035	1.204
largest diff peak and hole, e Å^{-3}	+0.27/−0.30	+0.47/−0.37

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

Polymerization of styrene: 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.

Single-Crystal X-ray Structure Determination of Compounds 3 and 8. Crystal data and details of the structure determination are presented in Table 3. Suitable single crystals for the X-ray diffraction study were grown from toluene. A clear red plate (red fragment) was stored under perfluorinated ether, transferred in a Lindemann capillary, fixed, and sealed. Preliminary examination and data collection were carried out on an area detecting system (NONIUS, MACH3, κ-CCD) at the window of a rotating anode (NONIUS, FR591) and graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The unit cell parameters were obtained by full-matrix least-squares refinement of 5816 (7311) reflections. Data collection were performed at 173 (173) K (Oxford Cryosystems) within a θ-range of $1.88° < \theta < 25.36°$ ($1.88° < \theta < 25.34°$). Each was measured with eight (three) data sets in rotation scan modus with $\Delta\varphi/\Delta\omega = 1.0°$ ($\Delta\omega = 0.5°$). A total number of 67 571 (39 965) intensities were integrated. Raw data were corrected for Lorentz, polarization, and, arising from the scaling procedure, latent decay and absorption effects. After merging [$R_{\text{int}} = 0.049$ (0.062)] a sum of 5560 (6928) (all data) and 4819 (5822) [$I > 2\sigma(I)$], respectively, remained and all data were used. 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 **3**, all hydrogen atom positions 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. For **8**, all hydrogen atoms were placed in ideal positions (riding model). Full-matrix least-squares refinements with 497 (443) parameters were carried out by minimizing $\sum w(F_o^2 - F_c^2)^2$ with the SHELXL-97 weighting scheme and stopped at shift/err < 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 *International Tables for Crystallography*. All calculations were performed on an Intel Pentium II PC, with the STRUX-V system, including the programs PLATON, SIR92, and SHELXL-97.[48−53] For **8**, the overall quality of the study suffers from the tiny crystal and its poor scattering power. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication. 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).

Acknowledgment. Financial support for this research by DGICYT (Project MAT2004-02614), CAM (Project S-0505-PPQ/0328-02), and European Commission (Contract No. HPRN-CT2000-00004) is gratefully acknowledged. M.G.-M. acknowledges Comunidad de Madrid (CAM) for the award of a Fellowship.

Supporting Information Available: Tables of crystal and data collection parameters, atomic coordinates, bond lengths, bond angles, and thermal displacement parameters for **3** and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM060368Q

---

(48) *Data Collection Software for Nonius k-CCD Devices*; Delft, The Netherlands, 2001.

(49) Otwinowski, Z.; Minor, W. *Methods Enzymol.* **1997**, *276*, 307ff.

(50) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Camalli, M. SIR92. *J. Appl. Crystallogr.* **1994**, *27*, 435−436.

(51) *International Tables for Crystallography*; Wilson, A. J. C., Ed.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1992; Vol. C, Tables 6.1.1.4, 4.2.6.8, and 4.2.4.2.

(52) Spek, A. L. *PLATON*, A Multipurpose Crystallographic Tool; Utrecht University: Utrecht, The Netherlands, 2001.

(53) Sheldrick, G. M. *SHELXL-97*; Universität Göttingen: Göttingen, Germany, 1998.