Mono- and Dinuclear Cyclopentadienylsiloxo Titanium Complexes: Synthesis, Reactivity, and Catalytic Polymerization Applications

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Hydrolysis of the (dichloromethylsilyl)cyclopentadienyl titanium compound [Ti(η^5-$C_5Me_4SiMeCl_2$)Cl_3] gave the metallasiloxane dinuclear complex [$(TiCl_2)_2$(μ-{(η^5-$C_5Me_4SiMeO)_2$(μ-O)})] (**1a**). Addition of 4 equiv of RMgCl (R = Me, Bz) to **1a** afforded the corresponding tetraalkyl dititanium derivatives [$(TiR_2)_2$(μ-{(η^5-$C_5Me_4SiMeO)_2$(μ-O)})] (R = Me **1b**, Bz **1c**). The benzyl compound **1c** reacted with $E(C_6F_5)_3$ (E = B, Al) and $[Ph_3C][B(C_6F_5)_4]$ to give the bridged dititanium compounds [$(TiBz)_2$(μ-{(η^5-$C_5Me_4SiMeO)_2$(μ-O)})(μ-X)][Q] (Q = $BzB(C_6F_5)_3$; X = Br, **2Br**; Cl, **2Cl**; F, **2F**; Q = $BzAl(C_6F_5)_3$; X = Cl, **3Cl**; Q = $B(C_6F_5)_4$; X = Bz, **4Bz**; Cl, **4Cl**) by benzyl abstraction and further reaction with the corresponding halogenated solvents. The addition of excess $B(C_6F_5)_3$ to **1c** gave the bis(zwitterionic) benzyl intermediate [(TiBz{η^6-$PhCH_2B(C_6F_5)_3$})$_2$(μ-{(η^5-$C_5Me_4SiMeO)_2$(μ-O)})] (**6**), which evolved into the bis(zwitterionic) fulvene derivative [(Ti{η^6-$PhCH_2B(C_6F_5)_3$})$_2$(μ-{(η^5-C_5Me_3(η^1-CH_2)$SiMeO)_2$(μ-O)})] (**5**). Related mononuclear siloxo compounds [$TiCp^*R_2(OSi\textit{i}Pr_3)$] (Cp* = η^5-C_5Me_5; R = Cl, **7a**; Me, **7b**) were obtained from the reaction of [$TiCp^*R_3$] (R = Cl, Me) with $HOSi\textit{i}Pr_3$. Compound **7b** reacted with $E(C_6F_5)_3$ (E = B, Al) in C_6D_6, affording the thermally stable ion-paired derivatives [$TiCp^*Me(OSi\textit{i}Pr_3)\{MeE(C_6F_5)_3\}$] (E = B, **8B**; Al, **8Al**). The chloro dinuclear **1a** and mononuclear **7a** complexes were tested as ethylene polymerization catalysts and the alkyl complexes **1b**, **1c**, and **7b** as methylmethacrylate polymerization catalysts.

Introduction

The cooperative effect between two metal atoms has been shown to induce important modifications in polymerization behavior with respect to related mononuclear systems where the metal atoms are far enough from each other. It has been reported that several types of bimetallic group 4 metal compounds produced a significant increase in the content of branches in ethylene polymerization, and also a significantly enhanced α-olefin incorporation was observed in ethylene−α-olefin copolymerization processes.[1−13] Conversely, methylmethacrylate polymerization may follow a dinuclear mechanism, and thus, the employment of bimetallic systems can be of interest to modify the polymer's properties.[14,15]

One of the most efficient methods used to bring two metal centers in close proximity generates covalent bridges between two monometallic compounds to give dinuclear systems. Functionalization of cyclopentadienyl rings with chlorosilyl groups has been a particularly useful procedure to synthesize dinuclear compounds through hydrolysis of the Si−Cl bonds. Depending on the metal atom and its environment, two types of dinuclear derivatives have been isolated, one with Si−O−Si oxo bridges for Nb,[16−18] Mo,[19] and W[19] and other with Si−O−M bridges for group 4 metals[20−23] and Nb.[17,18] Related dinuclear compounds containing Si−O−Si bridges have also been described

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by introducing a biscyclopentadienyl ligand linked by Si−O−Si moieties for Ti,[24,25] Zr,[25] and Hf.[25]

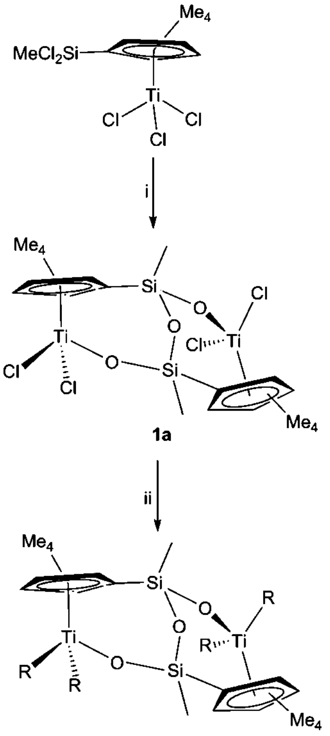
Continuing with our interest in chlorosilylcyclopentadienyl complexes,[16,18,26−31] we describe in this work the use of the $[Ti(C_5Me_4SiMeCl_2)Cl_3]$[28] derivative with a $SiCl_2$ moiety in the cyclopentadienyl ring as the starting material to generate dinuclear compounds with both types of Si−O−Si and Si−O−Ti bridges by a hydrolysis reaction. Complexes containing these types of bridges can be useful as models for titania-silica materials, as it facilitates the study of the active Ti centers with well-defined and soluble monomeric compounds.[32−39]

The reactivity of the new dinuclear compounds with different molar ratios of Lewis acids has been explored with the aim of studying the influence of the dinuclear system in the activation of each titanium atom. We have also compared the behavior of the dinuclear compounds with related mononuclear siloxo derivatives. Finally, comparative studies related to ethylene and methylmethacrylate polymerization processes were carried out with both dinuclear and mononuclear compounds.

Results and Discussion

Neutral Dinuclear Compounds. Hydrolysis of the dichlorosilyl-functionalized cyclopentadienyl mononuclear compound $[Ti(C_5Me_4SiMeCl_2)Cl_3]$[28] in ethyl ether solution afforded the dinuclear siloxo complex $[(TiCl_2)_2(\mu\text{-}\{(\eta^5\text{-}C_5Me_4SiMeO)_2(\mu\text{-}O)\})]$ (**1a**) in high yield (Scheme 1). Formation of the dinuclear compound with η^5-C_5Me_4SiMeO bridges between the metal atoms follows the behavior reported previously for the hydrolysis of related monochlorosilyl-functionalized cyclopentadienyl derivatives.[16−18] However, simultaneous hydrolysis of the second Si−Cl bond in the starting product gave rise to the formation of an additional Si−O−Si bridge. Compound **1** showed remarkable stability to possible further hydrolysis processes. Although compound **1** contains two diastereogenic Si atoms, the intrinsically diastereoselective formation of the Si−O−Si bridge is responsible for the generation of only one diastereoisomer of C_2 symmetry, consistent with the ^1H and ^{13}C NMR spectra observed for the resulting reaction product. Thus, both cyclopentadienyl η^5-C_5Me_4Si ligands were equivalent, presenting an ABCD system, and also only one resonance was observed for both equivalent Si-Me groups.

Scheme 1[a]



R = Me **1b**, R =Bz **1c**

[a] (i) H_2O, Et_2O, 120 °C, 24 h; (ii) RMgCl (R = Me, Bz), Et_2O.

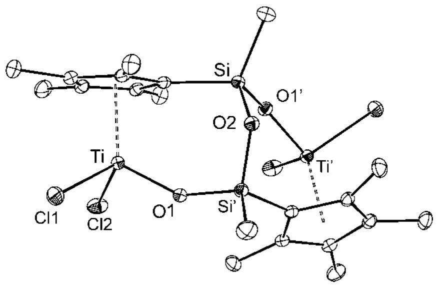


Figure 1. ORTEP plot of the molecular structure of $[(TiCl_2)_2(\mu\text{-}\{(\eta^5\text{-}C_5Me_4SiMeO)_2(\mu\text{-}O)\})]$ (**1a**) in the solid state. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. Symmetry code ′ = 1−*x*, *y*, 0.5−*z*.

The molecular structure of **1a** is illustrated in Figure 1, and selected bond lengths and angles are listed in Table 1. It consists of a dinuclear molecule formed by two $[TiCl_2(\mu\text{-}\{\eta^5\text{-}C_5Me_4SiMeO\})]$ units in which the oxygen atoms link both metal fragments through a pair of Si−O−Ti bridges. The molecule is located on a crystallographic 2-fold axis that bisects the Si−O2−Si′ angle. Furthermore, one additional oxygen atom also links both silicon atoms through a Si−O−Si bridge. The presence of this Si−O−Si bridge causes a slight elongation of the Ti−O bond and a reduction of ca. 10° for the Si−O−Ti angle compared with related Si−O−Ti bridges in the dinuclear compounds $[(TiCl_2)_2(\mu\text{-}\{\eta^5\text{-}C_5R_4SiMe_2O\}_2)]$ (R = H,[20] **A**; Me,[23] **B**). A similar reduction was observed in the structure of $[(TiMe_2)_2(\mu\text{-}\{\eta^5\text{-}C_5Me_4SiMe_2O\}_2)(\mu\text{-}CH_2)]$[41] (**C**), with one additional bridge between the titanium atoms. However, the Ti−Ti

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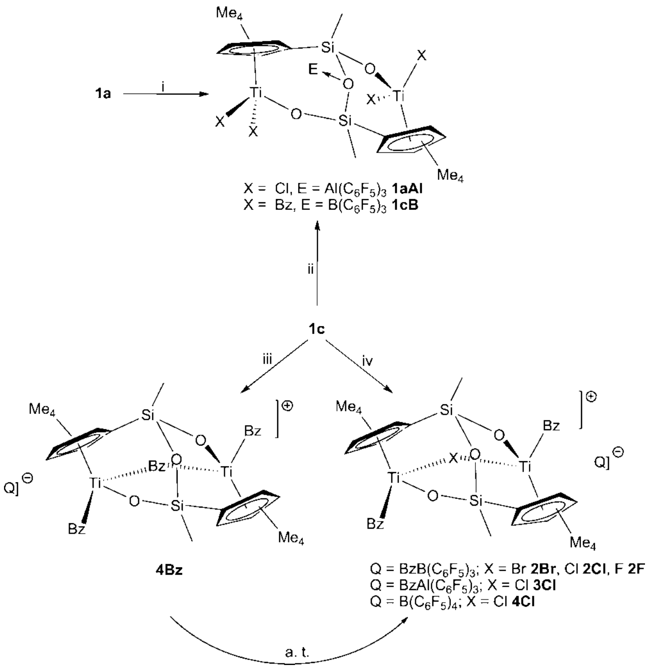
Table 1. Selected Bond Distances (Å) and Angles (deg) for Compounds 1a, $[(TiCl_2)_2(\mu\text{-}\{\eta^5\text{-}C_5R_4SiMe_2O\}_2)]$ (R = H, A;[20] Me, B[23]), and $[(TiMe_2)_2(\mu\text{-}\{\eta^5\text{-}C_5Me_4SiMe_2O\}_2)(\mu\text{-}CH_2)]$[41] (C)

complex	Ti−O1	Si−O1	Si−O2	Ti···Cp	Ti···Ti′	Ti−O1−Si	Si−O−Si′	Si···Si
1a	1.803(1)	1.643(1)	1.640(1)	2.038	5.193	147.96(9)	120.2(1)	2.845
A	1.767(19)	1.653(1)		2.026	5.255	160.2(1)		4.700
B	1.771(4)	1.650(4)		2.031	5.099	159.8(2)		4.829
C	1.827(1)	1.640(1)		2.058	3.371	150.09(7)		4.535

Scheme 2[a]



[a] (i) $Al(C_6F_5)_3$; (ii) $B(C_6F_5)_3$, −70 °C, CD_2Cl_2; (iii) $Ph_3C[B(C_6F_5)_4]$, −70 °C, CD_2Cl_2; (iv) $E(C_6F_5)_3$ (E = B, Al), CD_2Cl_2 or XC_6D_5.

distance, over 5 Å in **1a**, is similar to that found in complexes **A** and **B**, whereas a clear approach of both titanium atoms to ca. 3 Å was observed for compound **C**. In contrast, both silicon atoms are clearly closer in compound **1a** due to the presence of the oxo bridge. As a consequence of the Si−O−Si and Ti−CH_2−Ti bridges in **1a** and **C**, respectively, the angle formed by the planes containing both cyclopentadienyl rings is close to 30°, whereas both rings are parallel in **A** and **B**. A lower π-bonding contribution in the Ti−O and/or Si−O bonds of the Ti−O−Si bridging system would be consistent with the closer angle observed for **1a** with respect to complexes **A** and **B**.

Alkylation of compound **1a** with RMgCl (R = Me, Bz) provided the corresponding tetraalkyl complexes $[(TiR_2)_2(\mu\text{-}\{(\eta^5\text{-}C_5Me_4SiMeO)_2(\mu\text{-}O)\})]$ (R = Me, **1b**; Bz, **1c**) (Scheme 1), which were sensitive to light and decomposed slowly at ambient temperature. The NMR spectra of these complexes presented a similar pattern to that observed for **1a**, with two new sets of resonances corresponding to the new diastereotopic alkyl groups bound to each titanium atom.

Cationic Dinuclear Compounds. The tetrachloro compound **1a** reacted with $Al(C_6F_5)_3$, but not with $B(C_6F_5)_3$, to give the neutral oxo-alane adduct $[(TiCl_2)_2(\mu\text{-}\{(\eta^5\text{-}C_5Me_4SiMeO)_2(\mu\text{-}O\cdot Al(C_6F_5)_3)\})]$ (**1aAl**), which was unaltered at ambient temperature (Scheme 2). In contrast, reactions of the tetramethyl derivative **1b** with different Lewis acids ($E(C_6F_5)_3$ (E = B, Al), $[Ph_3C][B(C_6F_5)_4]$) unfortunately failed to give any characterized compound even at low temperature, whereas more easily identifiable compounds were observed when similar reactions were carried out using the tetrabenzyl derivative **1c**. In this last case, the result was dependent on the reaction conditions, temperature, solvent, and Lewis acid molar amount.

Reaction of **1c** with $B(C_6F_5)_3$ in CD_2Cl_2 at −70 °C gave the neutral oxo-borane adduct $[(TiBz_2)_2(\mu\text{-}\{(\eta^5\text{-}C_5Me_4SiMeO)_2(\mu\text{-}O\cdot B(C_6F_5)_3)\})]$ (**1cB**) as the main product (Scheme 2). Monitoring of this solution while the temperature was increased showed the slow transformation of **1cB** into the chloro-bridged compound $[(TiBz)_2(\mu\text{-}\{(\eta^5\text{-}C_5Me_4SiMeO)_2(\mu\text{-}O)\})(\mu\text{-}Cl)][BzB(C_6F_5)_3]$ (**2Cl**), which was the only product at 25 °C. It may be reasonably expected that this transformation occurred by reaction with the chlorinated solvent of the intermediate benzyl bridged cation $[(TiBz)_2(\mu\text{-}\{(\eta^5\text{-}C_5Me_4SiMeO)_2(\mu\text{-}O)\})(\mu\text{-}Bz)]^+$. This putative tribenzyl intermediate derivative was identified by NMR spectroscopy as $[(TiBz)_2(\mu\text{-}\{(\eta^5\text{-}C_5Me_4SiMeO)_2(\mu\text{-}O)\})(\mu\text{-}Bz)][B(C_6F_5)_4]$ (**4Bz**) in the reaction of **1c** with $[Ph_3C][B(C_6F_5)_4]$ in CD_2Cl_2 at −70 °C (Scheme 2), which also showed the evolution of $\mathbf{4B}^+$ to $[(TiBz)_2(\mu\text{-}\{(\eta^5\text{-}C_5Me_4SiMeO)_2(\mu\text{-}O)\})(\mu\text{-}Cl)]^+$ ($\mathbf{4Cl}^+$) at higher temperature.

The same reaction of **1c** with $B(C_6F_5)_3$ in C_6D_6 gave a brownish insoluble oil, which after dissolution in halogenated solvents gave the related halide-bridged cationic compounds $[(TiBz)_2(\mu\text{-}\{(\eta^5\text{-}C_5Me_4SiMeO)_2(\mu\text{-}O)\})(\mu\text{-}X)]^+$ (X = Br, $\mathbf{2Br}^+$ (BrC_6D_5); Cl, $\mathbf{2Cl}^+$ (ClC_6D_5 or CD_2Cl_2); F, $\mathbf{2F}^+$ (FC_6D_5)) (Scheme 2), which were characterized by NMR spectroscopy. These cationic compounds were also formed when the reaction of **1c** with $B(C_6F_5)_3$ was carried out directly in the halogenated solvents. The transformation was immediate when CD_2Cl_2 was used as solvent, whereas slower reactions were observed for the other deuterated halobenzenes according to the following sequence: FC_6D_5 (2 h) > BrC_6D_5 (24 h) > ClC_6D_5 (48 h). The reaction rate is consistent with the X−C energy bond for BrC_6D_5 and ClC_6D_5. However, the surprisingly faster activation of the stronger C−F bond could be justified by the favored formation of a thermodynamically more stable fluoride bridge, as a consequence of its smaller size, which allows better overlapping of the orbitals involved in the bridge formation.

When $Al(C_6F_5)_3$ and $[Ph_3C][B(C_6F_5)_4]$ were employed as Lewis acids, the analogous ionic compounds $[(TiBz)_2(\mu\text{-}\{(\eta^5\text{-}C_5Me_4SiMeO)_2(\mu\text{-}O)\})(\mu\text{-}Cl)][Q]$ (Q = $BzAl(C_6F_5)_3$, **3Cl**; $B(C_6F_5)_4$, **4Cl**) were obtained. Generation of toluene and 1,2-diphenylethane in all of these reactions suggests that the benzyl−halide exchange proceeded via homolytic bond cleavage.[42] Compounds **2**−**4** were stable in XC_6D_5 solutions, but in CD_2Cl_2 evolved to give the neutral chloride derivative **1a** as the only final product.

The ^1H and ^{13}C NMR spectra of the oxo-borane adduct **1cB** showed resonances very close to the starting compound **1c**, the most significant difference being observed in the ^{19}F NMR spectrum, which showed resonances corresponding to a tetracoordinated boron atom.[43−46]

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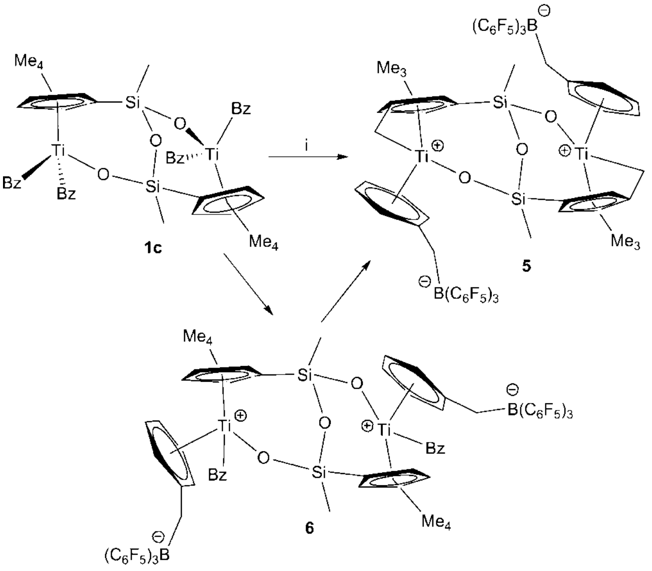
The cationic complexes $\mathbf{2}^+-\mathbf{4}^+$, in addition to the two stereogenic Si centers, present two additional stereogenic Ti atoms. However, the formation of these cationic compounds was also diastereoselective, as evidenced by the NMR spectra that showed resonances for only one diastereoisomer of C_2 symmetry, which corresponds with the formation of the halide bridge opposite the Si−O−Si bridge. Hence, an ABCD spin system similar to that discussed for complexes **1** was observed in their NMR spectra for the C_5Me_4Si substituent. The ^1H NMR spectra also showed two doublets for the diastereotopic Ti-CH_2 protons. The benzyl group attached to the titanium atoms was η^2-coordinated, in accordance with the value observed for the coupling constant J_{C-H} about 147 Hz.[47−50] The ^{19}F NMR spectra of the ionic derivatives **2X** demonstrated that no ion-pair interaction is present, in line with a $\Delta\delta(F_p - F_m)$ of 2.8 ppm.[51] Furthermore, the ^{19}F NMR spectrum of $\mathbf{2F}^+$ showed a broad resonance at negative values (δ −77.0) corresponding to the Ti−F−Ti bridge.[52,53]

In contrast, compound $\mathbf{4Bz}^+$ has the same NMR pattern as those observed for related halogen-bridged compounds $\mathbf{2}^+-\mathbf{4}^+$, with an additional broad resonance in the ^1H NMR at δ 1.87 corresponding to the CH_2 group bridging both titanium atoms. The terminal benzyl groups were η^1-coordinated, in accordance with the value observed for the coupling constant $^1J_{C-H}$ about 127 Hz. In this case, we did not observe exchange between both types of bridging and terminal benzyl ligands[54] because the presence of the Si−O−Si bridge prevents such a rearrangement.

The behavior described here for compound **1c** parallels that observed for the related dinuclear titanium compound $[(TiBz_2)_2(\mu\text{-}\{\eta^5\text{-}C_5H_4SiMe_2O\}_2)]$, for which the benzyl-bridged intermediate was unstable in aromatic solvents, decomposing to give unidentified paramagnetic species.[54] The substitution of the benzyl by a halide bridge occurring in halogenated solvents is clearly favored by the π-donating ability of this substituent, which increases the electron density, reducing their positive charge.[54−56] Cationic dinuclear group 4 complexes with halide bridges have also been formed by rearrangement of mononuclear cationic derivatives in halogenated solvents.[53,57,58]

The dinuclear nature of compound **1c** could be helpful to synthesize dinuclear dicationic derivatives by abstraction of one benzyl substituent from each titanium atom. This goal was successfully achieved by stirring **1c** with excess $B(C_6F_5)_3$ in toluene or benzene to give an insoluble oil after 3 days at 20 °C. Solutions of this oil obtained in halogenated solvents were used to characterize the reaction product as a mixture of the bis-zwitterionic fulvene derivative $[(Ti\{\eta^6\text{-}PhCH_2B(C_6F_5)_3\})_2(\mu\text{-}\{(\eta^5\text{-}C_5Me_3(\eta^1\text{-}CH_2)SiMeO)_2(\mu\text{-}O)\})]$ (**5**) as the major product (>65%) (Scheme 3) and of the monocationic halogen-bridged compound $\mathbf{2X}^+$. Unfortunately, longer reaction times did not improve the yield of **5**, nor did higher amounts of $B(C_6F_5)_3$, with only decomposition of the starting materials occurring. Compound **5** has each titanium atom stabilized by η^6-C_6H_5 coordination of the benzylborate anion. Such an interaction is of prime importance[59−61] because only decomposition, rather than formation of the dinuclear compound, could be observed when 2 equiv of the noncoordinating anion salt $[Ph_3C][B(C_6F_5)_4]$ was employed. It is remarkable that compound **5** contains two fulvene ligands, which were formed by hydrogen abstraction from a cyclopentadienyl-methyl group by both benzyl ligands bound to the titanium atoms on the proposed monobenzyl intermediate $[(TiBz\{\eta^6\text{-}PhCH_2B(C_6F_5)_3\})_2(\mu\text{-}\{(\eta^5\text{-}C_5Me_4SiMeO)_2\text{-}(\mu\text{-}O)\})]$ (**6**).

Scheme 3[a]



[a] (i) >2 $B(C_6F_5)_3$, − MeC_6H_5; toluene or BrC_6D_5.

When the same type of reaction was carried out in CD_2Cl_2, only the monocationic derivative $\mathbf{2Cl}^+$ was formed, as the substitution of the benzyl bridge in the intermediate complex $\mathbf{2Bz}^+$ was faster than abstraction of a second benzyl ligand. However, the use of XC_6D_5 (X = Br, Cl) as solvents also allowed the formation of **5**, although a higher proportion of the respective monocationic derivatives $\mathbf{2X}^+$ was observed compared with the products of reactions in toluene or benzene. It is also important to note that monocations $\mathbf{2X}^+$ did not react with excess $B(C_6F_5)_3$ or $[Ph_3C][B(C_6F_5)_4]$.

The NMR spectra of compound **5** correspond to a C_2 symmetry complex and confirm the presence of only three methyl substituents at the cyclopentadienyl ring. The main features of its ^1H NMR spectrum are the two doublets for the diastereotopic fulvene CH_2 moiety and the multiplets corre-

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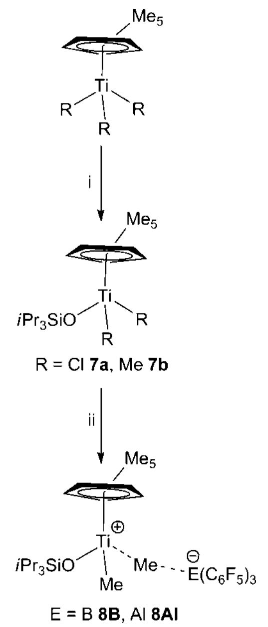
Scheme 4[a]



[a] (i) $HOSiiPr_3$; (ii) $E(C_6F_5)_3$ (E = B, Al).

sponding to the η^6-C_6H_5 fragment, which are high-field shifted with respect to the noncoordinated phenyl rings.[47,62,63] The resonance observed in the ^{13}C NMR spectroscopy at δ 87.6 for the fulvene CH_2 and the coupling constant $^1J_{C-H}$ confirm the presence of this activated methylene group.[64-67] The ^{19}F NMR spectrum shows a $\Delta\delta(F_p - F_m)$ over 4 ppm, which is consistent with the presence of an ion-pair interaction.

The nonfulvene intermediate **6** was detected by NMR spectroscopy as a minor product in the mixture obtained by reaction of **1c** with excess $B(C_6F_5)_3$ in BrC_6D_5, together with compounds **2Br** and **5**, confirming that abstraction of the benzyl ligand occurred before activation of the methyl group. The ^1H NMR spectrum of compound **6** showed four resonances of the η^5-C_5Me_4 ring, two doublets for the diastereotopic CH_2-Ti protons, and a broad signal for the CH_2-B protons, consistent with a C_2 symmetry compound.

Mononuclear Compounds. The mononuclear siloxo derivatives $[TiCp^*R_2(OSi\textit{i}Pr_3)]$ (R = Cl, **7a**; Me, **7b**) were isolated as referential model compounds for the dinuclear siloxo-bridged complexes described above. These compounds were obtained in good yields by alcoholysis of the Ti−Cl and Ti−Me bonds[32] of $[TiCp^*R_3]$ (R = Cl, Me) when treated with $HOSi\textit{i}Pr_3$ (Scheme 4) at 100 °C for 7 days for **7a** and at 25 °C for 2 h for **7b**, respectively.

The mononuclear siloxo derivative **7b** reacted with the Lewis acids $E(C_6F_5)_3$ (E = B, Al) to give the ion-paired compounds $[TiCp^*Me(OSi\textit{i}Pr_3)(MeE(C_6F_5)_3)]$ (E = B, **8B**; Al, **8Al**) (Scheme 4), which were soluble in C_6D_6. The methyl group bridging the titanium and E atoms was observed in the ^1H NMR spectra at δ 0.49 for **8B** and at δ 0.08 for **8Al**. The ^{19}F NMR spectrum of **8B** shows a value of $\Delta\delta(F_p - F_m)$ over 4 ppm, consistent with the presence of an ion-pair interaction.[51] These siloxo zwitterionic methyl compounds **8** were stable for several days,[68] contrasting with the decomposition observed when the methyl compound **1b** was reacted with $E(C_6F_5)_3$ and also with the instability observed for analogous aryloxo derivatives.[69] Apparently, this stability difference among the mononuclear siloxo and aryloxo complexes could be related to the higher π-donor ability of the oxygen atom in the siloxo substituent than in the aryloxo ligand,[70-72] although the related alkoxo derivative $[TiCp^*Me_2(O\textit{t}Bu)]$ was unstable upon addition of $B(C_6F_5)_3$ probably by activation of the *t*Bu group.[73,74]

Table 2. Ethylene Polymerization with Complexes 1a and 7a[a]

run	complex	cocat.	yield (g)	A^c	$10^5\ M_w{}^d$	$M_w/M_n{}^d$	T_m (°C)^e
1	**1a**	MAO (sol)^b	traces				
2	**1a**	dry-MAO	traces				
3	**7a**	MAO (sol)^b	8.3	664	4.63	2.58	136.0
4	**7a**	dry-MAO	11.7	936	12.84	2.09	141.9

[a] Polymerization conditions: P(ethylene) = 5 bar, T = 50 °C, solvent = toluene (200 mL), t = 30 min, [**1a**] = 2.5 μmol, [**7a**] = 5 μmol, Al/Ti = 500. [b] MAO in solution 1.5 M in toluene. [c] Activity = g PE/(mmol compd·bar·h). [d] Determined by GPC in trichlorobenzene at 140 °C vs polystyrene standards. [e] Determined by DSC measurement.

Ethylene Polymerization. The dinuclear $[(TiCl_2)_2(\mu\text{-}\{(\eta^5\text{-}C_5Me_4SiMeO)_2(\mu\text{-}O)\})]$ (**1a**) and mononuclear $[TiCp^*Cl_2(OSi\textit{i}Pr_3)]$ (**7a**) dichloro complexes were studied as ethylene polymerization catalysts in the presence of MAO and dry MAO (Al/Ti = 500, 5 bar, 50 °C). The dinuclear compound **1a** showed negligible activity under these conditions (runs 1 and 2). The steric characteristics of this bimetallic compound and its tendency to form bridges between the titanium atoms decrease the electronic and coordinative deficiency of the active species, making monomer incorporation and chain growth more difficult. A similar result was observed with a imido-bridged dititanium compound,[7] contrasting with the activity reported for dinuclear compounds with longer chains that keep the metal centers separate.[1-6,8-13]

Conversely, the mononuclear siloxo compound **7a** exhibited high activity, giving HDPE with a narrow polydispersity (runs 3 and 4). When dry MAO was employed as cocatalyst (run 4), the activity, polydispersity, and M_w were improved to give high molecular weight PE (HMWPE) with low branching, in accordance with the T_m value and the polydispersity values corresponding to single-site catalysts. These results are similar to those reported for aryloxo derivatives $[TiCp^*Cl_2(OAr)]$ reported by Nomura et al.[75,76]

MMA Polymerization. The neutral dinuclear $[(TiR_2)_2(\mu\text{-}\{(\eta^5\text{-}C_5Me_4SiMeO)_2(\mu\text{-}O)\})]$ (R = Me, **1b**; Bz, **1c**) and mononuclear $[TiCp^*Me_2(OSi\textit{i}Pr_3)]$ (**7b**) compounds were studied as catalysts for MMA polymerization in the presence of the Lewis acids $E(C_6F_5)_3$ (E = B, Al). As we have described above, total transformation of **1c** by abstraction of two benzyl ligands into

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Table 3. Polymerization of MMA[a] with Complexes 1b, 1c, and 7b with E(C_6F_5)$_3$ (E = B, Al)

run	complex	E	*t* (min)	yield (%)	10^4 M_n calc[b]	10^4 M_n (g/mol)[c]	M_w/M_n[c]	[mm] (%)[d]	[mr] (%)[d]	[rr] (%)[d]
1	**1b**	B	5	70	0.12	6.40	1.20	5	25	70
2[e]	**1b**	B	30	70	0.12	1.81	1.03	5	33	62
3[f]	**1b**	B	30	60	0.09	13.50	1.42	4	25	71
4	**1b**	Al	30	20	0.03	8.54	1.83	8	30	62
5	**1c**	B or Al	60	0						
6	**1c**	B	180	34	0.05	6.90	1.31	12	28	60
7	**1c**	Al	180	25	0.03	16.11	1.30	5	23	72
8	**7b**	B	30	60	0.04	1.51	1.01	9	28	63
9	**7b**	Al	60	0						
10[g]	**7b**	B	30	10	n.d.	n.d.	n.d.	8	29	63

[a] Polymerization conditions: dinuclear complexes [**1b**] = [**1c**] = 0.06 mmol and [E(C_6F_5)$_3$] = 0.06 mmol premixed in toluene (2 mL), then MMA (1 mL, [MMA]:[dinuclear complex] = 155, 25 °C; mononuclear complex [**7b**] = 0.12 mmol and [E(C_6F_5)$_3$] = 0.12 mmol premixed in toluene (2 mL), then MMA (1 mL, [MMA]:[**7b**] = 78), 25 °C. [b] M_n calc values = conv × [MMA]/*n*[Ti] × 100.81 g mol^{-1} (*n* = number of Ti atoms per molecule; fw MMA = 100.81). [c] Determined by GPC in THF vs polystyrene standard. [d] Determined by ^1H NMR in $CDCl_3$. [e] 5 mL of toluene. [f] *T* (°C) = −20 °C. [g] [**7b**] = 0.12 mmol and [B(C_6F_5)$_3$] = 0.06 mmol.

a dinuclear dicationic compound was not achieved even in the presence of excess E(C_6F_5)$_3$ and after several days of reaction at ambient temperature. However, to avoid possible interference from dicationic compounds, MMA polymerization studies were carried out using a dinuclear compound/cocatalyst molar ratio of 1:1. For the mononuclear compound **7b** we have used the double molar amounts with regard to dinuclear **1b** or **1c**, aiming to introduce to the solution an equal number of metal centers in each experiment and then to compare the behavior of the dinuclear and mononuclear systems.

MMA polymerization with the dinuclear **1b**/B(C_6F_5)$_3$ system was fast at ambient temperature, giving a slurry after 5 min (run 1). The experiment was then run with a larger amount of solvent to help stirring (run 2). The PMMA obtained in both cases was 70% syndiotactic, but with narrow polydispersity (PDI) for the more diluted polymerization (1.03). The experiment was repeated at −20 °C, giving a lower yield after 30 min (run 3), although the PMMA had a higher molecular weight and a higher polydispersity. When Al(C_6F_5)$_3$ was used as cocatalyst (run 4), both the yield and the syndiotacticity were lower, while the polydispersity was as high as 1.83. Conversely, polymerization with the benzyl system **1c**/E(C_6F_5)$_3$ (runs 5−7) required longer times as a consequence of the bulk and kinetic requirements of the benzyl ligand. In this case, the syndiotacticity was higher for Al(C_6F_5)$_3$ than for B(C_6F_5)$_3$, and the PMMA obtained was of high molecular weight for Al(C_6F_5)$_3$, although again the yield was lower.

MMA polymerization with the mononuclear **7b**/E(C_6F_5)$_3$ systems showed the same tendency with regard to E, giving a moderate yield for B(C_6F_5)$_3$ (run 8) but negligible activity for Al(C_6F_5)$_3$ (run 9). However, the yield and syndiotacticity for the system **7b**/B(C_6F_5)$_3$ (run 8) were lower than those observed for **1b**, although the polydispersity was as narrow as that observed for **1b** in run 2.

An experiment with half of the molecular amount of B(C_6F_5)$_3$ (run 10), corresponding to a Ti:B molar ratio of 2:1, as in the dinuclear system, gave a rather poor yield of PMMA. The difference observed in the behavior of MMA polymerization with **1b** and with **7b** when a Ti:B molar ratio of 2:1 was employed could be related to the different bimetallic pathway followed by the dinuclear compound[15] instead of the monometallic mechanism exhibited by the mononuclear derivative **7b**,[5,14,77−80] although further kinetic studies are required to assess the mechanism of this process.

Conclusions

Hydrolysis of both Si−Cl bonds of complex [Ti(η^5-$C_5Me_4SiMeCl_2$)Cl_3] generated the dinuclear derivative [($TiCl_2$)$_2$(μ-{(η^5-C_5Me_4SiMeO)$_2$(μ-O)})] (**1a**) with two siloxo η^5-C_5Me_4SiMeO units linking both Ti atoms and one oxo bridge linking both Si atoms. Alkylation of **1a** with RMgCl (R = Me, Bz) afforded the dialkyl derivatives [(TiR_2)$_2$(μ-{(η^5-C_5Me_4SiMeO)$_2$(μ-O)})] (R = Me, **1b**; Bz, **1c**). The dimethyl compound **1b** was unstable in the presence of the Lewis acids. However, the dibenzyl complex **1c** generated monocationic complexes with bridging halogen [($TiBz$)$_2$(μ-{(η^5-C_5Me_4SiMeO)$_2$(μ-O)})(μ-X)]$^+$ (X = Br, Cl, F) by reaction with E(C_6F_5)$_3$ (E = B, Al) and [Ph_3C][B(C_6F_5)$_4$] in halogenated solvents, as a consequence of the activation of the highly reactive benzyl bridge in the cationic compound [($TiBz$)$_2$(μ-{(η^5-C_5Me_4SiMeO)$_2$(μ-O)})(μ-Bz)]$^+$. Abstraction of one Ti−Bz bond of each Ti atom of **1c** was partially possible using excess B(C_6F_5)$_3$ in aromatic solvents or BrC_6D_5 to give a bis-zwitterionic compound, [(TiBz{η^6-$PhCH_2B$(C_6F_5)$_3$})$_2$(μ-{(η^5-C_5Me_4SiMeO)$_2$(μ-O)})], which was further transformed by activation of one C−H bond of a η^5-C_5Me_4 methyl group of both Ti fragments to give the bis-zwitterionic bisfulvene derivative [(Ti{η^6-$PhCH_2B$(C_6F_5)$_3$})$_2$(μ-{(η^5-C_5Me_3(η^1-CH_2)SiMeO)$_2$(μ-O)})]. The stabilization of these zwitterionic compounds was derived from η^6-phenyl coordination of the anion generated. These results showed that the close proximity of the two metal centers hindered the formation of dicationic compounds, due to the easy formation of a halogen bridge between the metal atoms or to the instability of the resulting dicationic compound.

The mononuclear siloxo compounds [TiCp*R_2(OSi*i*Pr_3)] (Cp* = C_5Me_5; R = Cl, **7a**; Me, **7b**) were synthesized by reaction of [TiCp*R_3] (R = Cl, Me) with HOSi*i*Pr_3. In contrast with the dinuclear methyl compound **1b**, **7b** gave the stable zwitterionic compounds [TiCp*Me(OSi*i*Pr_3)(MeE(C_6F_5)$_3$)] when reacted with the Lewis acids E(C_6F_5)$_3$ (E = B, Al). This stability stems from the presence of the siloxo group, compared with the instability previously described for similar alkoxo and aryloxo derivatives.

The chloro compounds **1a** and **7a** were studied as catalysts for ethylene polymerization with MAO and dry MAO as cocatalysts. Only traces of PE were obtained in the case of **1a**, whereas **7a** showed high activity. The lack of activity of compound **1a** may be due to the difficult activation of both Ti atoms of the dinuclear system, which would generate less active centers, and also to the easy formation of bridges between these two Ti atoms as a consequence of their proximity, which would make the insertion and chain-growing reaction difficult.

The methyl derivatives **1b** and **7b** polymerized MMA when activated with B(C_6F_5)$_3$, although the yield and degree of syndiotacticity of the PMMA obtained was higher with **1b**. When Al(C_6F_5)$_3$ was used as cocatalyst, the yield was clearly lower. Furthermore, the benzyl derivative **1c** also showed low activity, probably as a consequence of the lower reactivity of the Ti−benzyl versus the Ti−Me bond. Finally, the PDI of the

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PMMA obtained with both the dinuclear **1b** and mononuclear **7b** complexes showed features of living polymerization.

Two different polymerization pathways are proposed for the dinuclear and mononuclear compounds. For the first, coordination of free MMA and chain growth proceed alternatively on each Ti atom, whereas for the second, both processes occur at the same Ti atom. This last assertion was confirmed by the low yield of PMMA obtained when polymerization was attempted with a Ti:B molar ratio of 2:1.

Experimental Section

General Considerations. All manipulations were carried out under an argon atmosphere, and solvents were purified from appropriate drying agents. NMR spectra were recorded at 400.13 (^{1}H), 376.70 (^{19}F), and 100.60 (^{13}C) MHz on a Bruker AV400. Chemical shifts (δ) are given in ppm. ^{1}H and ^{13}C resonances were measured relative to solvent peaks considering TMS = 0 ppm, while ^{19}F resonance were measured relative to external $CFCl_3$. Assignment of resonances was made from HSQC and HMBC NMR experiments. Elemental analyses were performed on a Perkin-Elmer 240C. Distilled water was deoxygenated prior to its use and stored under argon. *i*Pr_3SiOH was purchased from Aldrich, degassed, and stored under Ar with molecular sieves. Compounds [Ti($C_5Me_4SiMeCl_2$)Cl_3],[28] [TiCp*R_3] (R = Cl,[81] Me[82]), $B(C_6F_5)_3$,[83] 0.5(toluene)·$Al(C_6F_5)_3$,[84] and $[Ph_3C][B(C_6F_5)_4]$[85] were prepared by literature methods. Ethylene (AGA polymer grade) was passed over columns with supported copper scavenger (BASF R3-11) and molecular sieves (4 Å) before being passed to the reactor. MMA was purchased from Aldrich, dried over CaH_2 overnight, and distilled under vacuum. The purified monomer was stored at −30 °C.

[($TiCl_2$)$_2$(μ-{(η^5-C_5Me_4SiMeO)$_2$(μ-O)})] (1a). A solution of [Ti(η^5-$C_5Me_4SiMeCl_2$)Cl_3] (2.00 g, 5.12 mmol) in diethyl ether (50 mL) was treated with 2 equiv of deoxygenated water (0.19 mL, 10.24 mmol) at room temperature. The reaction mixture was heated at 135 °C for 20 h. The volatiles were then removed under vacuum, and the remaining solid was washed with hexane (2 × 30 mL) to give **1a** as an orange solid (1.41 g, 90%). ^{1}H NMR ($CDCl_3$): 0.47 (s, 6 H, Si*Me*), 2.34 (s, 6 H, C_5*Me_4*), 2.35 (s, 6 H, C_5*Me_4*), 2.37 (s, 6 H, C_5*Me_4*), 2.38 (s, 6 H, C_5*Me_4*). ^{13}C NMR ($CDCl_3$): −1.7 (Si*Me*), 13.1, 13.7, 15.6 and 16.1 (C_5*Me_4*), 119.5, 139.1, 139.4, 141.7, and 144.8 (*C_5*Me_4). Anal. Calc for $C_{20}H_{30}O_3Si_2Ti_2Cl_4$ (612.16): C, 39.24; H, 4.94. Found: C, 39.21; H, 5.11.

[($TiMe_2$)$_2$(μ-{(η^5-C_5Me_4SiMeO)$_2$(μ-O)})] (1b). MeMgCl (3 M, 0.86 mL, 2.58 mmol) was injected into a solution of **1a** (0.38 g, 0.62 mmol) in diethyl ether (50 mL) at −78 °C. The reaction mixture was warmed to room temperature and stirred overnight. The volatiles were removed under vacuum to yield a yellow residue, which was extracted into hexane (2 × 25 mL). The volume was concentrated to ca. 20 mL and cooled to −35 °C, yielding **1b** as a yellow solid (0.19 g, 58%). ^{1}H NMR (C_6D_6): 0.44 (s, 6 H, Si*Me*), 0.67 (s, 12 H, *Me*-Ti), 1.88 (s, 6 H, C_5*Me_4*), 1.97 (s, 6 H, C_5*Me_4*), 1.99 (s, 6 H, C_5*Me_4*), 2.39 (s, 6 H, C_5*Me_4*). ^{13}C NMR (C_6D_6): −0.2 (Si*Me*), 12.0, 12.1, 13.7, and 14.3 (C_5*Me_4*), 54.7 and 56.6 (*Me*-Ti), 112.0, 127.3, 129.8, 130.4, and 132.9 (*C_5*Me_4). Anal. Calc for $C_{24}H_{42}O_3Si_2Ti_2$ (529.6): C, 54.34; H, 7.98. Found: C, 54.07; H, 7.96.

[($TiBz_2$)$_2$(μ-{(η^5-C_5Me_4SiMeO)$_2$(μ-O)})] (1c). A suspension of **1a** (2.00 g, 3.27 mmol) in diethyl ether (50 mL) at −78 °C was treated with 4 equiv of a THF solution of BzMgCl (2 M, 6.55 mL, 13.10 mmol). The reaction mixture was warmed to room temperature and stirred overnight in the absence of light. Hexane (20 mL) was then added, and the solution was filtered. The red residue was extracted again into a mixture of diethyl ether/hexane (40 mL/20 mL). The volatiles were evaporated, and the remaining solid was washed with 10 mL of hexane to isolate **1c** as a red solid (2.31 g, 85%). ^{1}H NMR (C_6D_6): 0.38 (s, 6 H, Si*Me*), 1.56 (s, 6 H, C_5*Me_4*), 1.79 (s, 6 H, C_5*Me_4*), 1.87 (s, 6 H, C_5*Me_4*), 2.06 (d, 2 H, ^2J = 9 Hz, PhC*H_2*-Ti), 2.20 (d, 2 H, ^2J = 9 Hz, PhC*H_2*-Ti), 2.24 (d, 2 H, ^2J = 9 Hz, PhC*H_2*-Ti), 2.28 (s, 6 H, C_5*Me_4*), 3.05 (d, 2 H, ^2J = 9 Hz, PhC*H_2*-Ti), 6.81−7.20 (m, 20 H, C_6*H_5*). ^{13}C NMR (C_6D_6): 0.0 (Si*Me*), 11.4, 12.1, 13.8 and 14.0 (C_5*Me_4*), 86.5 and 86.9 (Ph*C*H_2-Ti, J_{CH} = 125 Hz), 122.8, 123.1, 126.8, 127.9, 128.2, 128.5, 148.8 (Ci), and 150.4 (Ci) (*C_6*H_5), 113.4, 131.8, 132.8, 133.9, and 134.2 (*C_5*Me_4). Anal. Calc for $C_{48}H_{58}O_3Si_2Ti_2$ (833.6): C, 69.09; H, 6.95. Found: C, 69.37; H, 7.15.

[($TiCl_2$)$_2$(μ-{(η^5-C_5Me_4SiMeO)$_2$(μ-O·$Al(C_6F_5)_3$)})] (1a-Al). [($TiCl_2$)$_2$(μ-{(η^5-C_5Me_4SiMeO)$_2$(μ-O)})] (**1a**) (0.100 g, 0.16 mmol) and 0.5(toluene)·$Al(C_6F_5)_3$ (0.093 g, 0.16 mmol) were stirred in toluene (5 mL) for 5 min. The volatiles were removed under vacuum, leaving a red solid, which was washed with hexane (2 × 2 mL) to give **1a-Al** (0.180 g, 85%). ^{1}H NMR (C_6D_6): 0.29 (s, 6 H, Si*Me*), 1.93 (s, 6 H, C_5*Me_4*), 1.95 (s, 6 H, C_5*Me_4*), 1.99 (s, 6 H, C_5*Me_4*), 2.20 (s, 6 H, C_5*Me_4*). ^{13}C NMR (C_6D_6): −2.2 (Si*Me*), 13.0, 13.4, 15.2, and 16.3 (C_5*Me_4*), 120.7, 141.8, 141.9, 143.9, and 147.6 (*C_5*Me_4), 137.5, 142.3, and 150.5 (m, *C_6F_5*). ^{19}F NMR (C_6D_6): −120.4 (o-C_6*F_5*), −150.5 (p-C_6*F_5*), −160.1 (m-C_6*F_5*). Anal. Calc for $C_{38}H_{30}O_3Si_2Ti_2Cl_4AlF_{15}$ (1139.68): C, 40.01; H, 2.63. Found: C, 40.85; H, 2.58.

[($TiBz_2$)$_2$(μ-{(η^5-C_5Me_4SiMeO)$_2$(μ-O·$B(C_6F_5)_3$)})] (1c-B). A 0.5 mL sample of CD_2Cl_2 previously cooled at −78 °C was added to a mixture of **1c** (0.030 g, 0.03 mmol) and $B(C_6F_5)_3$ (0.018 g, 0.03 mmol) in a NMR tube cooled at −78 °C. NMR spectroscopy run after 5 min at −70 °C showed the formation of **1c-B** as a unique product. ^{1}H NMR (CD_2Cl_2): 0.15 (s, 6 H, Si*Me*), 1.66 (s, 6 H, C_5*Me_4*), 1.78 (s, 6 H, C_5*Me_4*), 1.84 (d, 4 H, ^2J = 9 Hz, PhC*H_2*-Ti), 1.99 (d, 2 H, ^2J = 9 Hz, PhC*H_2*-Ti), 2.14 (s, 6 H, C_5*Me_4*), 2.15 (s, 6 H, C_5*Me_4*), 2.40 (d, 2 H, ^2J = 9 Hz, PhC*H_2*-Ti), 6.75−7.20 (m, 20 H, C_6*H_5*). ^{19}F NMR (CD_2Cl_2): −127.7 (*o*-C_6*F_5*), −156.3 (*p*-C_6*F_5*), −163.2 (*m*-C_6*F_5*).

[($TiBz$)$_2$(μ-Cl)(μ-{(η^5-C_5Me_4SiMeO)$_2$(μ-O)})][$BzB(C_6F_5)_3$] (2Cl). A solution of **1c** (0.100 g, 0.11 mmol) and $B(C_6F_5)_3$ (0.061 g, 0.11 mmol) in CH_2Cl_2 (3 mL) was stirred for 5 min. The volatiles were removed under vacuum, leaving an oil, which was washed with hexane (2 × 2 mL) to give **2Cl** as a brownish oil (0.120 g, 85%). ^{1}H NMR (CD_2Cl_2): 0.38 (s, 6 H, Si*Me*), 1.70 (s, 6 H, C_5*Me_4*), 1.96 (s, 6 H, C_5*Me_4*), 2.14 (s, 6 H, C_5*Me_4*), 2.52 (s, 6 H, C_5*Me_4*), 2.83 (bs, 2 H, PhC*H_2*-B), 2.85 (d, 2 H, ^2J = 8 Hz, PhC*H_2*-Ti), 3.56 (d, 2 H, ^2J = 8 Hz, PhC*H_2*-Ti), 6.56−7.36 (m, 15 H, C_6*H_5*). ^{13}C NMR (CD_2Cl_2): −1.0 (*SiMe*), 12.8, 13.7, 16.3, and 16.7 (C_5*Me_4*), Ph*CH_2*-B was not observed, 85.9 (Ph*C*H_2-Ti, J_{CH} = 147 Hz), 122.5, 127.0, 128.9, 131.7, 133.3, and 135.7 (*C_6*H_5), 117.9, 130.1, 132.8, 137.9, and 139.5 (*C_5*Me_4), 135.7, 137.8, and 149.5 (m, *C_6F_5*), 137.1 (*Ph*CH_2-Ti, *C_i*), 149.9 (*Ph*CH_2-B, *C_i*). ^{19}F NMR (CD_2Cl_2): −129.6 (*o*-C_6*F_5*), −163.3 (*p*-C_6*F_5*), −166.1 (*m*-C_6*F_5*). Anal. Calc for $C_{59}H_{51}BF_{15}O_3Si_2Ti_2Cl$ (1290.1): C, 54.89; H, 3.95. Found: C, 54.41; H, 3.80.

[($TiBz$)$_2$(μ-X)(μ-{(η^5-C_5Me_4SiMeO)$_2$(μ-O)})][Q] (Q = $BzB(C_6F_5)_3$; X = Br, 2Br; F, 2F; Q = $BzAl(C_6F_5)_3$; X = Cl, 3Cl; Q = $B(C_6F_5)_4$; X = Cl, 4Cl). [($TiBz_2$)$_2$(μ-{(η^5-C_5Me_4SiMeO)$_2$(μ-O)})] (**1c**) (0.030 g, 0.03 mmol) and the required cocatalyst in 1:1 molar ratio ($B(C_6F_5)_3$ 0.018 g, 0.03 mmol; 0.5(toluene)·$Al(C_6F_5)_3$ 0.020 g, 0.03 mmol; $[Ph_3C][B(C_6F_5)_4]$ 0.033 g, 0.03 mmol) were loaded into a NMR tube, and 0.5 mL of the corresponding solvent

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was added (BrC_6D_5 for **2Br**, FC_6D_5 for **2F**, CD_2Cl_2 for **3Cl** and **4Cl**). Each sample was then shaken vigorously, and the reaction was monitored by NMR spectroscopy at 25 °C, showing the formation of **2Br** after 24 h, **2F** after 2 h, and **3Cl** and **4Cl** immediately.

Data for 2Br. ^{1}H NMR (BrC_6D_5): 0.17 (s, 6 H, Si*Me*), 1.36 (s, 6 H, C_5Me_4), 1.55 (s, 6 H, C_5Me_4), 1.76 (s, 6 H, C_5Me_4), 1.99 (s, 6 H, C_5Me_4), 2.48 (d, 2 H, ^{2}J = 8 Hz, $PhCH_2$-Ti), 3.02 (d, 2 H, ^{2}J = 8 Hz, $PhCH_2$-Ti), 3.25 (bs, 2 H, $PhCH_2$-B), 6.56−7.36 (m, 15 H, C_6H_5). ^{13}C NMR (BrC_6D_5): −2.3 (Si*Me*), 10.6, 12.8, 14.7, and 15.8 (C_5Me_4), 30.1 ($PhCH_2$-B), 85.6 ($PhCH_2$-Ti, J_{CH} = 148 Hz), 121.3, 125.6, 127.6, 130.0, 131.13, and 134.5 (C_6H_5), 115.6, 132.8, 135.2, 137.2, and 138.0 (C_5Me_4), 135.7, 137.8, and 149.5 (m, C_6F_5), 137.5 ($PhCH_2$-Ti, C_i), 147.7 ($PhCH_2$-B, C_i). ^{19} NMR (BrC_6D_5): −129.1 (*o*-C_6F_5), −162.8 (*p*-C_6F_5), −165.5 (*m*-C_6F_5).

Data for 2F. ^{1}H NMR (FC_6D_5): 0.19 (s, 6 H, Si*Me*), 1.40 (s, 6 H, C_5Me_4), 1.47 (s, 6 H, C_5Me_4), 1.82 (s, 6 H, C_5Me_4), 2.03 (s, 6 H, C_5Me_4), 2.43 (d, 2 H, ^{2}J = 9 Hz, $PhCH_2$-Ti), 3.14 (d, 2 H, ^{2}J = 9 Hz, $PhCH_2$-Ti), 3.28 (bs, 2 H, $PhCH_2$-B), 6.12−7.15 (m, 15 H, C_6H_5). ^{13}C NMR (FC_6D_5): −3.0 (Si*Me*), 10.4, 11.3, 14.2, and 14.7 (C_5Me_4), 84.5 ($PhCH_2$-Ti, J_{CH} = 148 Hz), 121.5, 125.9, 128.2, 128.5, 131.1, and 134.2 (C_6H_5), 116.4, 130.1, 135.4, 137.0, and 138.0 (C_5Me_4), 135.7, 137.8, and 149.5 (m, C_6F_5), 137.5 ($PhCH_2$-Ti, C_i), 148.9 ($PhCH_2$-B, C_i), $PhCH_2$-B was not observed. ^{19}F NMR (FC_6D_5): −93.8 (Ti-*F*-Ti), −130.2 (*o*-C_6F_5), −164.2 (*p*-C_6F_5), −167.0 (*m*-C_6F_5).

Data for 3Cl. ^{1}H NMR (CD_2Cl_2): 0.38 (s, 6 H, Si*Me*), 1.70 (s, 6 H, C_5Me_4), 1.96 (s, 6 H, C_5Me_4), 2.14 (s, 6 H, C_5Me_4), 2.52 (s, 6 H, C_5Me_4), 2.85 (d, 2 H, ^{2}J = 8 Hz, $PhCH_2$-Ti), 3.20 (bs, 2 H, $PhCH_2$-Al), 3.56 (d, 2 H, ^{2}J = 8 Hz, $PhCH_2$-Ti), 6.56−7.36 (m, 15 H, C_6H_5). ^{13}C NMR (CD_2Cl_2): −1.0 (Si*Me*), 12.8, 13.7, 16.3, and 16.7 (C_5Me_4), 29.0 ($PhCH_2$-Al), 85.9 ($PhCH_2$-Ti, J_{CH} = 147 Hz), 122.5, 127.0, 128.9, 131.7, 133.3, and 135.7 (C_6H_5), 117.9, 130.1, 132.8, 137.9, and 139.5 (C_5Me_4), 135.7, 137.8, and 149.5 (m, C_6F_5), 137.1 ($PhCH_2$-Ti, C_i), 149.9 ($PhCH_2$-Al, C_i). ^{19}F NMR (CD_2Cl_2): −118.6 (*o*-C_6F_5), −156.6 (*p*-C_6F_5), −162.0 (*m*-C_6F_5).

Data for 4Cl. ^{1}H NMR (CD_2Cl_2): 0.38 (s, 6 H, Si*Me*), 1.70 (s, 6 H, C_5Me_4), 1.96 (s, 6 H, C_5Me_4), 2.14 (s, 6 H, C_5Me_4), 2.52 (s, 6 H, C_5Me_4), 2.85 (d, 2 H, ^{2}J = 8 Hz, $PhCH_2$-Ti), 3.56 (d, 2 H, ^{2}J = 8 Hz, $PhCH_2$-Ti), 6.56−7.36 (m, 15 H, C_6H_5). ^{13}C NMR (CD_2Cl_2): −1.0 (Si*Me*), 12.8, 13.7, 16.3, and 16.7 (C_5Me_4), 85.9 ($PhCH_2$-Ti, J_{CH} = 147 Hz), 122.5, 127.0, 128.9, 131.7, 133.3, and 135.7 (C_6H_5), 117.9, 130.1, 132.8, 137.9, and 139.5 (C_5Me_4), 136.8, 139.7, and 149.4 (m, C_6F_5), 137.1 ($PhCH_2$-Ti, C_i). ^{19}F NMR (CD_2Cl_2): −133.5 (*o*-C_6F_5), −162.5 (*p*-C_6F_5), −166.4 (*m*-C_6F_5).

$[(TiBz)_2(\mu\text{-}Bz)(\mu\text{-}\{(\eta^5\text{-}C_5Me_4SiMeO)_2(\mu\text{-}O)\})][B(C_6F_5)_4]$ (4Bz). A 0.5 mL sample of CD_2Cl_2 previously cooled at −78 °C was added to a mixture of **1c** (0.030 g, 0.03 mmol) and $[Ph_3C][B(C_6F_5)_4]$ (0.033 g, 0.03 mmol) in a NMR tube cooled at −78 °C. The NMR spectra were run at −70 °C, showing the formation of **4Bz** as the only product. ^{1}H NMR (CD_2Cl_2): 0.12 (s, 6 H, Si*Me*), 1.65 (s, 6 H, C_5Me_4), 1.76 (s, 6 H, C_5Me_4), 2.10 (s, 6 H, C_5Me_4), 2.11 (s, 6 H, C_5Me_4), 1.87 (m, 2 H, $TiCH_2Ti$), 1.98 (d, 2 H, ^{2}J = 8 Hz, $PhCH_2$-Ti), 2.40 (d, 2 H, ^{2}J = 8 Hz, $PhCH_2$-Ti), 6.56−7.36 (m, 15 H, C_6H_5). ^{13}C NMR (CD_2Cl_2): −4.5 (Si*Me*), 7.6, 8.5, 8.7, and 9.7 (C_5Me_4), 81.7 ($TiCH_2Ti$, J_{CH} = 128 Hz), 81.4 ($PhCH_2$-Ti, J_{CH} = 127 Hz), 120.1−140.3 (C_6H_5, C_6F_5, C_5Me_4). ^{19}F NMR (CD_2Cl_2): −133.5 (*o*-C_6F_5), −162.5 (*p*-C_6F_5), −166.4 (*m*-C_6F_5).

$[(Ti\{\eta^6\text{-}PhCH_2B(C_6F_5)_3\})_2(\mu\text{-}\{(\eta^5\text{-}C_5Me_3(\eta^1\text{-}CH_2)SiMeO)_2(\mu\text{-}O)\})]$ (5). Method A: A solution of **1c** (0.030 g, 0.03 mmol) and excess of $B(C_6F_5)_3$ (0.073 g, 0.15 mmol) were stirred in toluene (3 mL) for three days at ambient temperature. The solution was filtered, and the remaining oil was washed with hexane (2 × 2 mL) to give a mixture of compounds **5** and **2Br** in 5.5:1 molar ratio. Method B: Compounds **1c** (0.030 g, 0.03 mmol) and $B(C_6F_5)_3$ (0.055 g, 0.10 mmol) were mixed in 0.5 mL of BrC_6D_5 in a NMR tube. The reaction was monitored by NMR spectroscopy, which showed the formation of a mixture of **5** and **2Br** in ca. 3:1 molar ratio after three days at ambient temperature.

Data for 5. ^{1}H NMR (BrC_6D_5): 0.07 (s, 6 H, Si*Me*), 0.92 (s, 6H, C_5Me_3), 1.21 (s, 6H, C_5Me_3), 1.73 (s, 6H, C_5Me_3), 2.39 (d, 2 H, $C_5Me_3CH_2$-Ti, ^{2}J = 2.4 Hz), 2.80 (d, 2 H, $C_5Me_3CH_2$-Ti, ^{2}J = 2.4 Hz), 2.83 (bs, 4 H, $PhCH_2$-B), 4.82 (t, 2 H, *p*-$PhCH_2$-B), 5.73 (t, 2 H, *m*-$PhCH_2$-B), 5.89 (t, 2 H, *m*-$PhCH_2$-B), 6.87 (d, 2 H, *o*-$PhCH_2$-B), 7.32 (d, 2 H, *o*-$PhCH_2$-B). ^{13}C NMR (BrC_6D_5): −0.8 (Si*Me*), 11.2, 12.2, and 13.6 (C_5Me_3), 87.6 ($C_5Me_3CH_2$-Ti, J_{CH} = 160 Hz), 119.8, 121.4, 123.6, 129.9, 131.4, and 162.8 (C_i) ($PhCH_2$-B), 118.0, 136.4, 137.3, 138.4, and 140.0 (C_5Me_3), 135.7, 137.8, and 149.5 (m, C_6F_5), $PhCH_2$-B was not observed. ^{19}F NMR (BrC_6D_5): −129.1 (*o*-C_6F_5), −159.2 (*p*-C_6F_5), −163.2 (*m*-C_6F_5).

$[(TiBz\{\eta^6\text{-}PhCH_2B(C_6F_5)_3\})_2(\mu\text{-}\{(\eta^5\text{-}C_5Me_4SiMeO)_2(\mu\text{-}O)\})]$ (6). Compound **1c** (0.030 g, 0.03 mmol) and 3 equiv of $B(C_6F_5)_3$ (0.055 g, 0.10 mmol) were mixed in 0.5 mL of BrC_6D_5 in a NMR tube. The reaction was monitored by NMR spectroscopy at room temperature, and formation of **6** was detected after 30 min as a minor product together with **5** and **2Br** in a mixture of compounds. After three days, total transformation of **6** into **5** was observed. Data for **6**: ^{1}H NMR (BrC_6D_5): −0.50 (s, 6 H, Si*Me*), 1.29 (s, 6 H, C_5Me_4), 1.71 (s, 6 H, C_5Me_4), 1.92 (s, 6 H, C_5Me_4), 2.33 (s, 6 H, C_5Me_4), 2.40 (d, 2 H, ^{2}J = 8 Hz, $PhCH_2$-Ti), 3.45 (d, 2 H, ^{2}J = 8 Hz, $PhCH_2$-Ti), 3.10 (bs, 4 H, $PhCH_2$-B), 5.20 (m, 2 H, *p*-$PhCH_2$−B), 5.41 (m, 2 H, *m*-$PhCH_2$-B), 6.80 (m, 2 H, *m*-$PhCH_2$-B), 6.88 (m, 2 H, *o*-$PhCH_2$-B), 7.10 (m, 2 H, *o*-$PhCH_2$-B). ^{13}C NMR (BrC_6D_5): 89.3 ($PhCH_2$-Ti). ^{19}F NMR (BrC_6D_5): −129.1 (*o*-C_6F_5), −159.2 (*p*-C_6F_5), −163.2 (*m*-C_6F_5).

$[TiCp^*Cl_2(OSi\textit{i}Pr_3)]$ (7a). A solution of $[TiCp^*Cl_3]$ (0.525 g, 1.81 mmol) and $\textit{i}Pr_3SiOH$ (0.475 g, 2.71 mmol) in toluene (30 mL) was refluxed for seven days. The solvent was completely removed to give a red solid, which was washed with 20 mL of hexane to afford **7a** (0.61 g, 80%). ^{1}H NMR ($CDCl_3$): 1.10 (m, 21 H, Me_2CH and Me_2CH), 2.21 (s, 15 H, C_5Me_5). ^{13}C NMR ($CDCl_3$): 13.2 (C_5Me_5), 13.8 (Me_2CH), 18.0 (Me_2CH), 131.9 (C_5Me_5). Anal. Calc for $C_{19}H_{36}OSiTiCl_2$ (426.78): C, 53.42; H, 8.43. Found: C, 53.21; H, 8.22.

$[TiCp^*Me_2(OSi\textit{i}Pr_3)]$ (7b). A toluene solution (10 mL) of $\textit{i}Pr_3SiOH$ (0.585 g, 3.29 mmol) was added dropwise to a toluene solution (20 mL) of $[TiCp^*Me_3]$ (0.750 g, 3.29 mmol) at −78 °C. The cooling bath was removed, and the reaction mixture was allowed to warm to ambient temperature and further stirred for 2 h. The solution was filtered and the volatiles were removed to yield **7b** as a yellowish oil (1.01 g, 80%). ^{1}H NMR (C_6D_6): 0.55 (*Me*-Ti), 1.24 (m, 21 H, Me_2CH and Me_2CH), 1.81 (s, 15 H, C_5Me_5). ^{13}C NMR (C_6D_6): 11.7 (C_5Me_5), 14.3 (Me_2CH), 18.5 (Me_2CH), 52.5 (*Me*-Ti), 121.8 (C_5Me_5). Anal. Calc for $C_{21}H_{42}OSiTi$ (385.88): C, 65.30; H, 10.88. Found: C, 65.01; H, 10.94.

$[TiCp^*Me(OSi\textit{i}Pr_3)\{MeE(C_6F_5)_3\}]$ (E = B, 8B; Al, 8Al). Compounds **7b** (0.100 g, 0.25 mmol) and $E(C_6F_5)_3$ ($B(C_6F_5)_3$ 0.128 g, 0.25 mmol; $Al(C_6F_5)_3$ 0.143 g, 0.25 mmol) were stirred in toluene (5 mL) for 5 min. The volatiles were removed under vacuum and the oil was washed with hexane (4 mL) to give **8B** (0.190 g, 85%) and **8Al** (0.194 g, 85%) as yellowish oils.

Data for 8B. ^{1}H NMR (C_6D_6): 0.49 (bs, 3 H, *Me*-B), 0.77 (m, 3 H, Me_2CH), 0.83 (d, 9 H, J = 7 Hz, Me_2CH), 0.91 (d, 9 H, J = 7 Hz, Me_2CH), 1.43 (s, 3 H, *Me*-Ti), 1.53 (s, 15 H, C_5Me_5). ^{13}C NMR (C_6D_6): 11.9 (C_5Me_5), 14.3 (Me_2CH), 18.4 (Me_2CH), 30.1 (*Me*-B), 73.3 (*Me*-Ti), 131.5 (C_5Me_5), 137.2 (C_6F_5), 148.6 (C_6F_5). ^{19}F NMR (C_6D_6): −133.1 (*o*-C_6F_5), −159.2 (*p*-C_6F_5), −164.3 (*m*-C_6F_5). Anal. Calc for $C_{39}H_{42}OSiTiBF_{15}$ (897.88): C, 52.12; H, 4.67. Found: C, 52.04; H, 4.56.

Data for 8Al. ^{1}H NMR (C_6D_6): 0.08 (bs, 3 H, *Me*-Al), 0.90 (m, 21 H, *Me$_2$*CH and Me$_2$C*H*), 1.20 (s, 3 H, *Me*-Ti), 1.56 (s, 15 H, C_5Me_5). ^{13}C NMR (C_6D_6): 11.8 (C_5Me_5), 14.3 (Me$_2$*C*H), 18.4 (*Me$_2$*CH), 71.3 (*Me*-Ti), *Me*-Al was not observed, 131.5 (*C$_5$*Me$_5$), 137.2 (C_6F_5), 142.3 (C_6F_5), 150.6 (C_6F_5). ^{19}F NMR (C_6D_6): −122.4 (*o*-C_6F_5), −153.7 (*p*-C_6F_5), −161.5 (*m*-C_6F_5). Anal. Calc for $C_{39}H_{42}OSiTiAlF_{15}$ (914.12): C, 51.19; H, 4.59. Found: C, 50.85; H, 4.51.

Polymerization of Ethylene with Dinuclear Complex 1a. Separate solutions of the mononuclear complex **1a** (2.5 μmol) and MAO (10% Al, 2.5 mmol) or dry MAO (2.5 mmol), in ca. Al/Ti = 500 molar ratio, in toluene (10 mL) were prepared in a glovebox. The catalytic ethylene polymerization reactions were performed in a stainless steel 1 L autoclave (Medimex) in semibatch mode (ethylene was added by replenishing flow to keep the pressure constant). The reactor was temperature- and pressure-controlled and equipped with separated toluene, catalyst, and cocatalyst injection systems. In a typical experiment, the autoclave was evacuated and heated for 1 h at 125 °C prior to use. The reactor was then brought to the desired temperature with stirring at 600 rpm and charged with 200 mL of toluene. After pressurizing with ethylene to reach 5 bar total pressure the autoclave was equilibrated for 5 min. Subsequently, the solution of MAO was injected into the reactor (using a pneumatically operated injector), and the reaction was started by injecting the **1a** solution. The reactor was stirred for 30 min and then vented. The residual MAO was destroyed by addition of 20 mL of ethanol. Polymeric product was collected, stirred in acidified ethanol overnight, and rinsed with ethanol on a glass frit. The polymer was initially dried in air and then in vacuo at 80 °C. GPC analyses of the polyethylenes were performed on a Polymer Laboratories Ltd. (PL-GPC210) chromatograph using 1,2,4-trichlorobenzene (TCB) as the mobile phase at 150 °C and using polystyrene references (full specs: column 4 PL-Gel Mixed A, Triple Detector RI + visco + LS, 90 °C). The DSC was measured on a TA Instruments DSC 2920, using a heat/cool/heat sequence employing 10 °C/min, between 20 and 160 °C.

Polymerization of Ethylene with Mononuclear Complex 7a. Polymerization was carried out as described above except for the use of a toluene solution of **7a** (5 μmol) and 2.5 mmolar equiv of MAO (Al/Ti = 500) with the aim of introducing an equal number of metal centers into the solution in each experiment.

Polymerization of MMA with Complexes 1b and 1c. In a typical procedure, complex **1b** or **1c** (0.06 mmol) and $E(C_6F_5)_3$ (0.08 mmol) were mixed in a flask inside the glovebox and stirred with 2 mL of toluene for 2 min. MMA was then quickly added. After the measured time interval, the flask was removed from the glovebox and quenched by adding 5 mL of MeOH/HCl diluted. The quenched mixture was precipitated into 150 mL of methanol, stirred overnight, filtered, and washed with methanol. The polymer collected was dissolved in acetone, precipitated in methanol at 0 °C, filtered, and dried in a vacuum oven at 80 °C. A ^{1}H NMR ($CDCl_3$) spectrum of the polymer was obtained to determine its tacticity and compared with literature. Gel permeation chromatography (GPC) analyses of polymer samples were carried out in THF as solvent at 25 °C (Waters GPCV-2000) at Alcalá University.

Polymerization of MMA with Mononuclear Complex 5b. Polymerization was carried out as described above except for the use of a toluene solution of **5b** (0.12 mmol) and $E(C_6F_5)_3$ (0.14 mmol) with the aim of introducing an equal number of metal centers into the solution in each experiment.

Single-Crystal X-ray Structure Determination of Compound 1a. Crystal data and details of the structure determination are presented in Table 4. Suitable single crystals for the X-ray diffraction study were grown from hexane. A clear orange fragment was stored under perfluorinated ether, transferred into a Lindemann capillary, fixed, and sealed. Preliminary examination and data collection[86] 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 (λ = 0.71073 Å). The unit cell parameters were obtained by full-matrix least-squares refinement of 2657 reflections. Data collection were performed at 173 K (Oxford Cryosystems) within a θ-range of 2.78° < θ < 25.36°. The crystal was measured with eight data sets in rotation scan modus with $\Delta\varphi/\Delta\omega = 1.0°$. A total number of 27 893 intensities were integrated. Raw data were corrected for Lorentz, polarization, and, arising from the scaling procedure, latent decay and absorption effects. After merging (R_{int} = 0.034) a sum of 2477 (all data) and 2254 [$I > 2\sigma(I)$] data, respectively, remained, and all data were used. The structure was solved by a combination of direct methods and difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were found and refined with individual isotropic displacement parameters. Full-matrix least-squares refinements with 201 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. 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*.[87] All calculations were performed on an Intel Pentium 4 PC, with the STRUX-V system, including the programs PLATON,[88] SIR92,[89] and SHELXL-97.[90,91] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-702723 (**1a**). Copies of the data can be

Table 4. Crystallographic Data for $[(TiCl_2)_2(\mu\text{-}\{(\eta^5\text{-}C_5Me_4SiMeO)_2(\mu\text{-}O)\})]$ (1a)

formula	$C_{20}H_{30}Cl_4O_3Si_2Ti_2$
fw	612.16
color/habit	orange/fragment
cryst dimens (mm^3)	0.08 × 0.13 × 0.25
cryst syst	monoclinic
space group	*C*2/*c* (no. 15)
a, Å	15.4858(1)
b, Å	8.3884(1)
c, Å	21.9165(2)
β, deg	108.6914(4)
V, Å^3	2696.82(4)
Z	4
T, K	173
D_{calcd}, g cm^{-3}	1.508
μ, mm^{-1}	1.097
F(000)	1256
θ range, deg	2.78−25.36
index ranges (*h*, *k*, *l*)	±18, ± 10, ± 26
no. of rflns collected	27 893
no. of indep rflns/R_{int}	2477/0.034
no. of obsd rflns ($I > 2\sigma(I)$)	2254
no. of data/restraints/params	2477/0/201
R1/wR2 ($I > 2\sigma(I)$)[a]	0.0252/0.0628
R1/wR2 (all data)[a]	0.0294/0.0650
GOF (on F^2)[a]	1.061
largest diff peak and hole (e Å^{-3})	+0.33/−0.25

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

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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: Crystallographic data for **1a** and selected NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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