Pentamethylcyclopentadienylmethyltitanium Silsesquioxanes and Their Zwitterionic Complexes with Tris(pentafluorophenyl)borane

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Received August 21, 2009

Reaction of $[(\eta^5-C_5Me_5)TiMe_3]$ with $[(c-C_5H_9)_7Si_8O_{12}(OH)]$ (SIPOSS) or $[(c-C_5H_9)_7Si_7O_9-$ (OSiMe₃)(OH)₂)] (DIPOSS') affords stoichiometrically the half-sandwich titanium-disiloxy-methyl complexes $[(\eta^5 - C_5Me_5)](c - C_5H_9)_7Si_8O_{12}O_2TiMe]$ (1) and $[(\eta^5 - C_5Me_5)](c - C_5H_9)_7Si_7O_9(OSiMe_3)$ -O₃ TiMe] (2), respectively. Compound 2 consists of the two stereoisomers possessing the (η^5 -C₅Me₅) ligand and OSiMe₃ group in syn- (2a) and anti-position (2b). The more abundant $2a (2a/2b \approx 2:1)$ was isolated by fractional crystallization. Compounds 1 and 2a reacted rapidly with $B(C_6F_5)_3$ to give zwitterionic complexes $[(\eta^5-C_5Me_5)\{(c-C_5H_9)_7Si_8O_{12}O\}_2Ti]^{(+)}[(\mu-Me)B(C_6F_5)_3]^{(-)}$ (3) and syn- $[(\eta^5-C_5Me_5)\{(c-C_5H_9)_7Si_7O_9(OSiMe_3)O_2\}Ti]^{(+)}[(\mu-Me)B(C_6F_5)_3]^{(-)}$ (4a), respectively. Infrared spectra proved that 3 and 4a were thermally stable in the solid state, and the structure of 4a was determined by X-ray single-crystal analysis. In contrast, ¹H, ¹³C, and ¹⁹F NMR spectra of **3** in toluene C_7D_8 revealed that it was completely dissociated into initial components at 25 °C; however, the features of 3 were dominating already at -35 °C. On the other hand, 4a was dissociated only slightly at 25 °C. Stable ionic complexes 7 and 8 were prepared by reacting $[PhNHMe_2]^+[B(C_6F_5)_4]^-$ with 1 and 2, respectively. Both 7 and 8 contained the molecule PhNMe₂ coordinated to the titanium cation, and 8 consisted of the syn- and anti-isomers 8a and 8b in abundances found for 2a/2b. Analogous reaction of 1 and 2 with $[Ph_3C]^+[B(C_6F_5)_4]^-$ afforded impure ionic complexes 9 and 10. When dissolved in the presence of PhNMe₂, the amine coordinated to the titanium cations, thus reproducing complexes 7 and 8a/8b, identified by ¹H NMR spectra. All compounds 1-10 were inactive in polymerization of styrene to syndiotactic polymer. A low activity was achieved by adding of 2 equiv of AlMe₃ to 3 or **4**.

Introduction

Polyhedral oligomeric silsesquioxanes (POSS) containing monosilanol, e.g., $[(c-C_5H_9)_7Si_8O_{12}(OH)]$ (SIPOSS), disilanol, e.g., *endo*- $[(c-C_5H_9)_8Si_8O_{11}(OH)_2]$ (DIPOSS), and trisilanol functionalities, e.g., $[(c-C_5H_9)_7Si_7O_9(OH)_3]$ (TRIPOSS)¹ have been used to mimic the behavior of silica surface hydroxyl groups acting as an anchor for homogeneous catalysts. Compared with the silica surface where a singlesite catalyst is difficult to obtain due to a variety of Si-O-H groups acting in isolated or cooperative modes,² the POSS

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silanols offer the opportunity to study the stability and catalytic properties of well-defined single-site catalytic centers with the siloxy environment that occurs in silicaanchored catalytic species.³ The use of POSS silanols for the preparation of metal silanolates was reviewed,⁴ and among early transition metal (Ti, Zr, Hf) POSS silanolates⁵

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numerous representatives were investigated as catalyst precursors for polymerization of olefins.⁶

Activation of the half-sandwich precursors with $B(C_6F_5)_3$ has been investigated in detail by R. Duchateau et al.^{6a,c} in an effort to address the thermal stability of cationic catalytic species grafted on a silica surface. The catalyst precursors of the type $Cp'Ti(OR')(CH_2Ph)_2$ were generated from $Cp'Ti(CH_2Ph)_3$ $(Cp' = 1,3-C_5H_3(SiMe_3)_2)$ and silanols (R'OH = SIPOSS or Ph₃SiOH), and the relation between the acidity of the silanols and the stability of ionic products arising from interaction of $Cp'Ti(OR')(CH_2Ph)_2$ with $B(C_6F_5)_3$ was studied. The pK_a measurements and DFT calculations of deprotonation energies showed that Ph₃SiOH is significantly less Brønsted acidic than SIPOSS, and correspondingly, ¹⁹F NMR investigation established that the equilibrium (eq 1) is shifted more to the product side for the less electron-withdrawing OSiPh₃ ligand.

$$Cp'Ti(OR')(CH_2Ph)_2 + B(C_6F_5)_3$$

$$\rightleftharpoons [Cp'Ti(OR')(CH_2Ph)]^{(+)}[(CH_2Ph)B(C_6F_5)_3]^{(-)}$$
(1)

Ethene and 1-hexene polymerization tests revealed that both systems afforded atactic poly-1-hexene with a narrow distribution of molecular weight (D = 2.0), pointing to a single-site catalytic center, and the system with OSiPh₃ was twice as active as that with the SIPOSS anion in polymerization of ethene, apparently in accord with a higher concentration of ionic catalytic species in equilibrium 1.^{6c}

Investigations of half-sandwich titanium systems Cp'Ti- $(OR')Me_2/B(C_6F_5)_3$ containing other organic siloxy or alkoxy ligands OR' revealed that their thermal stability is generally rather low. A recent study of the system for $Cp' = \eta^5 - C_5 Me_5$ (Cp*) and $OR' = OSi^i Pr_3$ proved that zwitterionic complexes $[Cp*Ti(OSi^{i}Pr_{3})(Me)]^{(+)}[MeB(C_{6}-F_{5})_{3}]^{(-)}$ were formed and were observable in solution for several days.⁷ The systems for $Cp' = \eta^5 - C_5 H_5 (Cp)$ and OR' =OC₆H₃Me₂-2,6 or similar ligands generated zwitterionic complexes $[CpTi(OR')(Me)]^{(+)}[MeB(C_6F_5)_3]^{(-)};$ however, these were unstable in solution even at -20 °C, decomposing in two concurrent ways while eliminating HC₆F₅ and MeB- $(C_6F_5)_2$.⁸ The system for $Cp' = Cp^*$ and $OR' = OSi(CH_2CH_2-$ SiMePh₂)₃ also generated the zwitterionic [Cp*Ti(OR')-(Me)]⁽⁺⁾[MeB(C₆F₅)₃]⁽⁻⁾ complex in solution, which decomposed at room temperature with $t_{1/2} \approx 48$ h to give two decomposition products, the same as in the preceding case.⁹

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Similar decomposition reactions were also acting in a recently attempted synthesis of dialkoxo-bridged cyclopentadienylsiloxo titanium cationic complexes.^{7,10} Surprisingly, the lowest stability for complexes of this type was noticed for the expected $[Cp*Ti(O'Bu)(Me)]^{(+)}[MeB(C_6F_5)_3]^{(-)}$ complex, which decomposed immediately after mixing its precursors.¹¹ The complete elimination of isobutene however indicated a different decomposition pathway.¹²

In the absence of the OR' ligand, the [Cp*TiMe₃]/ $[B(C_6F_5)_3]$ system formed a highly active catalyst for either polymerization of ethene to a high molecular weight polymer or styrene to syndiotactic polystyrene (syn-PS) when its components were mixed in the presence of monomer using nonpolar solvents.^{13a} When no monomers were added, the reaction led to the formation of the anticipated zwitterionic complex $[Cp*TiMe_2]^{(+)}[MeB(C_6F_5)_3]^{(-)}$ in an NMR tube experiment at low temperature; however, this product rapidly decomposed at room temperature and was then inactive toward olefins.^{13b} Replacement of one Me group with an alkoxy group led to a decrease in catalytic activity, which was attributed to the decreased electrophilicity of the metal resulting from π -electron donation of the alkoxy oxygen lone pair to the empty d orbital on the metal.^{13c} The application of the C₆F₅ or OC₆F₅ ligands as poor π electron donor OR' moieties yielded thermally unstable zwitterionic complexes with $B(C_6F_5)_3$.^{13d} The only halfsandwich alkoxytitanium complexes of this type characterized in the solid state were the catalytically inactive zwitterionic dialkoxy complexes $[Cp*Ti(OR')_2]^{(+)}[MeB(C_6F_5)_3]^{(-)}$ where $R' = {}^{\prime}Bu^{11}$ or ${}^{\prime}Pr.^{14}$ Their X-ray crystal structures showed that the methyl carbon atom was σ -bonded to boron, and hydrogen atoms of the methyl group exerted an agostic interaction¹⁵ with the titanium atom, similarly to that known for zirconocene zwitterionic complexes.¹⁶

Recently, the effect of π -donation of the lone electron pair from oxygen into the Ti–O bond was evaluated for a series of Cp*₂Ti(III)OR derivatives using the energy of the 1a₁ \rightarrow b₂ transition in their electronic absorption spectra as an inherent measure of the effect.^{17a} The spectroscopic data revealed

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that the oxygen π -donation effect is increasing in the order of OR groups $(c-C_5H_9)_7Si_8O_{12}O$ (SIPOSS) < $(^{t}BuO)_3SiO$ < $Ph_3SiO < {}^{i}Pr_3SiO < PhO < HO < {}^{t}BuO < MeO, and DFT$ calculations showed that the effect is inversely proportional to polarity of the Ti-O bond.^{17b} This implies that POSS ligands will afford the least stable complexes in both [Cp*Ti(OR)(Me)]⁽⁺⁾[MeB(C₆F₅)₃]⁽⁻⁾ and [Cp*Ti(OR)₂)]⁽⁺⁾- $[MeB(C_6F_5)_3]^{(-)}$ series. The low thermal stability of the former complexes did not allow their isolation and investiga-tion in the solid state; $^{6-11,13}$ however, the presence of the second OR group highly increased the stability of the latter complexes for $R = {}^{t}BuO$ and ${}^{t}PrO$ ligands.^{11,14} This gives a good prospect for investigation of properties of analogous complexes with OR being a POSS ligand. Although they are expected to be catalytically inactive, their subsequent activation, e.g., by methylation with AlMe₃, should be applicable for the design of single-site cationic centers grafted on the silica surface without using methylaluminoxane.

Here we report the synthesis of the zwitterionic $[Cp^*Ti(OR)_2]^{(+)}[(\mu-Me)B(C_6F_5)_3]^{(-)}$ and similar ion-pair complexes $[Cp^*Ti(OR)_2)]^+[B(C_6F_5)_4]^-$, with OR being derived from SIPOSS or $[(c-C_5H_9)_7Si_7O_9(OSiMe_3)(OH)_2]$ (DIPO-SS'),^{1b} and activation of the zwitterionic complexes with AlMe₃ for polymerization of styrene.

Results and Discussion

Half-Sandwich Methyltitanium Complexes with Silsesquioxanes. An easy access to the titanium-monomethyl complexes $[Cp^{*}{(c-C_{5}H_{9})_{7}Si_{8}O_{12}O_{2}TiMe]}$ (1) and a mixture of *syn*- $[Cp^{*}{(c-C_{5}H_{9})_{7}Si_{7}O_{9}}(OSiMe_{3})O_{2}]TiMe]$ (2a) and *anti*- $[Cp^{*}{(c-C_{5}H_{9})_{7}Si_{7}O_{9}}(OSiMe_{3})O_{2}]TiMe]$ (2b) complexes was found in the reaction of commercial $[Cp^{*}TiMe_{3}]$ with $[(c-C_{5}H_{9})_{7}Si_{8}O_{12}(OH)]$ (SIPOSS) and $[(c-C_{5}H_{9})_{7}Si_{7}O_{9} (OSiMe_{3})(OH)_{2}]$ (DIPOSS'), respectively (Scheme 1).

The reaction proceeded in hexane in a stoichiometric way at room temperature and was indicated by evolution of methane and by slight intensification of the pale yellow color of the [Cp*TiMe₃] solution. This was surprising since the Cp'/Ti(CH₂Ph)₃ (Cp''=1,3-C₅H₃(SiMe₃)₂) did not react with more than one SIPOSS molecule.^{6c} Actually, a 5% excess of [Cp*TiMe₃] was used to ascertain the complete consumption of the POSS component because its unreacted residue was easily removed from the reaction mixture as for the most soluble component. On the other hand, the Ti-Me bond in 1 and 2 (i.e., 2a + 2b) appeared to be extremely unreactive, as it did not react with even one molar excess of the POSS reagents at 60 °C. Both 1 and 2 proved to be thermally robust, as they did not change after heating to 160 °C under vacuum. The composition of 1, 2a, and 2b was determined from ¹H, ¹³C, and ²⁹Si NMR spectra by integrals of resonances for the C₅Me₅, cyclopentyl groups of the POSS ligands, and the Ti-Me group. The NMR spectra of the crude product 2 revealed two sets of signals in the intensity ratio 2:1 attributed to 2a and 2b. Compound 2a was separated from 2b by crystallization from hexane solution, and its structure with the Cp* ligand in *syn*-position to the OSiMe₃ group was deduced from a 1D NOESY spectrum, where the irradiation of the OSiMe₃ signal at 0.28 ppm gave rise to the signal at 2.06 ppm of the η^5 -C₅Me₅ ligand. A fraction crystallizing from the ultimate mother liquor was strongly enriched in 2b (90%), showing interaction between resonances of OSiMe₃ at 0.28 ppm and TiMe at 1.16 ppm in the 1D NOESY experiment.

Compounds 1 and 2a formed transparent crystals in hexane; however, when the hexane was evaporated under vacuum or in argon, they became opaque, as they were losing the hexane of crystallization. This property hampered the X-ray single-crystal investigation because the crystals lost some hexane before they were fixed to the measuring rod. The structure of 1 was solved, confirming its formula in Scheme 1; however, the data refinement was unsuccessful. The infrared spectra of 1 and 2 were dominated by very strong absorption bands due to valence Si-O-Si vibrations of the silsesquioxane cages at $v_{max} = 1095 \text{ cm}^{-1}$, and the next intense absorption band due to the valence Si–O(Ti) vibration was displayed at 984 cm⁻¹ for **1** and at 988 cm⁻¹ for both 2a and 2b (90%). These wavenumbers are comparable with those for the Si-O(Ti) vibration in Cp*₂Ti(III)(SIPOSS)^{17b} at 1038 cm⁻¹ on one side and in Ti(IV) titanasilsesquioxanes in the range 918–970 cm^{-1 5e,18a,b} or in Ti(OSiR₃)₄ complexes close to 918 cm⁻¹.^{18c} Conformers **2a** and **2b** (90%) differed in the shape of the broad absorption band at 1095 cm^{-1} , indicating a slight difference in Si–O–Si vibrations of the silsesquioxane cages; however, the absorption bands due to the OSiMe₃ group at 840 and 753 cm⁻¹ did not differ for 2a and 2b (see Supporting Information).

Formation of Zwitterionic Complexes 3 and 4a from 1 and 2a, Respectively. Mixing of 1 or 2a in a 5% excess over the equimolar ratio with $B(C_6F_5)_3$ in toluene gave immediately an orange solution, which after solvent evaporation at 60 °C under vacuum afforded an orange solid. This was dissolved

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in hexane and purified by crystallization driven by a slow evaporation of the solvent under vacuum. Excess 1 and 2a were removed with mother liquors, and orange crystalline products 3 and 4a were washed with cold condensing hexane vapor. The orange crystals of both 3 and 4a remained transparent as long as they were wet with the solvent; however, when dried, they turned opaque due to the loss of hexane of crystallization. Therefore, the samples were thoroughly dried by overnight evacuation to 2×10^{-4} Torr at 60 °C for analytical and spectroscopic investigation, while hexane-wet crystals were submitted for X-ray single-crystal analysis. The solid-state IR-ATR spectra of solid 3 and 4a showed the absence of free $B(C_6F_5)_3$ and 1 or 2a, and the solids obtained by evaporation of the respective mother liquors showed in addition to the above spectra of 3 or 4a only very weak absorption bands of excess $1 (984 \text{ cm}^{-1})$ or 2a (988 cm^{-1}) . Hence, it could be assumed that the adducts of 1 and 2a with $B(C_6F_5)_3$ were formed quantitatively (Schemes 2 and 3). Further investigation of compounds 3 and 4a by NMR and IR methods in solution, however, revealed substantial differences in stability of the both products.

The ¹H, ¹³C, and ¹⁹F NMR spectra of **3** and **4a** in C₆D₆ or toluene C₇D₈ solutions revealed that complexes **3** and **4a** in these aromatic solvents dissociate to give equilibria 2 and 3 with equilibrium constants $K_{4a} > K_3$.

$$1 + B(C_6F_5)_3 \xrightarrow{K_3} 3 \tag{2}$$

$$\mathbf{2a} + \mathbf{B}(\mathbf{C}_{6}\mathbf{F}_{5})_{3} \xrightarrow{K_{4a}} \mathbf{4a}$$
(3)

The thermal stability of all components of the equilibria toward toluene was proved by thermal cycling of the C_7D_8 solutions of 3 and 4a in flame-sealed NMR tubes three times in the range 25-90 °C, giving reproducible spectra. The solution of 4a in C₆D₆ at 25 °C displayed ¹H NMR spectra that differed only marginally in chemical shifts from those of 2a. The presence of the zwitterionic complex was deduced from broadening of the signal for the bridging methyl group at 0.85 ppm with a half-width of ca. 6 Hz. Unfortunately, the MeB group was not detected in the ¹³C NMR spectra, which did not allow the determination of the ${}^{1}J_{CH}$ coupling constant, whose reduced value would be indicative of the pre-sence of agostic interaction.¹⁹ Stronger evidence for the presence of 4a came from ¹⁹F NMR spectra, showing a set of three new signals having a difference between the metaand *para*-fluorine resonances ($\Delta\delta(m,p-F) = 5.2$ ppm) that is typical for a cation-anion association occurring in zwitterionic complexes,^{20a} defined also as inner-sphere ion pairs (ISIP).^{20b} Both features were also previously found for zwitterionic complexes $[Cp^*Ti(OR)_2)^{(+)}[MeB(C_6F_5)_3]^{(-)}$



(R = 'Bu or 'Pr).^{11,14} In addition, the resonance in the ¹¹B NMR spectrum of **4a** at -13 ppm is indicative of the $[(\mu-Me)B(C_6F_5)_3]^{(-)}$ species.²¹ The 1D NOESY NMR experiments indicate that the *syn*-configuration of **2a** was preserved in **4a**. This was further confirmed by the X-ray crystal structure of **4a** (see below). Alerting was, however, that weak signals of free $B(C_6F_5)_3$ were also observed besides those of **4a**, indicating a slight complex dissociation. The thermally induced dissociation of **4a** in C_7D_8 was particularly well observed in the ¹⁹F NMR spectra. The overwhelming signals attributable to **4a** at 25 °C disappeared at ca. 65 °C, and only signals belonging to $B(C_6F_5)_3$ were observed above this temperature. The quantitative assessment of the spectra components was, however, rather difficult because the chemical equilibria were accompanied by varying rates of exchange processes, changing the shape and chemical shifts of resonance signals (see Supporting Information).

Contrary to **4a**, a solution of **3** in C₆D₆ at 25 °C showed no evidence for the presence of the zwitterionic complex, and only weak and broad signals belonging to **1** and B(C₆F₅)₃ were found in both ¹H and ¹⁹F NMR spectra. However, strong features of only **3** were observed at -35 °C in C₇H₈ in the ¹⁹F NMR spectra, showing a new set of signals with $\Delta\delta(m,p-F) = 4.9$ ppm. These signals broadened with increasing temperature and disappeared at 5 °C. The broad signals of B(C₆F₅)₃ were first observed at 25 °C and narrowed further with increasing temperature (to 75 °C). A practical absence of signals of both **3** and B(C₆F₅)₃ in the range

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(b) Zuccaccia, C.; Stahl, N. G.; Macchioni, A.; Chen, M.-C.; Roberts, J. A.; Marks, T. J. J. Am. Chem. Soc. 2004, 126, 1448–1464, and references therein.

⁽²¹⁾ Maggioni, D.; Beringhelli, T.; D'Alfonso, G.; Resconi, L. J. Organomet. Chem. 2005, 690, 640–646.

5-20 °C was due to extensive exchange broadening for all components of equilibrium 2.

The solid-state IR-ATR spectra of 3 and 4a were characterized by shifts and splitting of valence Si-O(Ti) vibrations from 984 cm^{-1} for 1 to 932 and 919 cm $^{-1}$ for 3 and from 988 cm $^{-1}$ for 2 to 964 and 953 cm⁻¹ in 4a. A larger shift for 3 compared to 4a reflects a higher polarity of the Si-O(Ti) bond because this silicon atom is involved in three Si-O-Si bonds, while in 4 the silicon atom takes part in only two Si-O-Si bonds and binds one rather electron-donating cyclopentyl group.^{5e,18} The kinematic and steric factors due to bonding of the DIPOSS' ligand by two Si-O(Ti) bonds should also favor higher wavenumbers for ν (Si–O(Ti)) vibrations in 4. The vibrations of the Si-O-SiMe₃ group in free DIPOSS', 2, and 4a moved only slightly and were assigned to the bands at 847 and 868 cm^{-1} for 4a. The IR spectra of 3 in hexane solution revealed its dissociation into 1 and $B(C_6F_5)_3$ with about 25% of 3 retained, as deduced from the low intensity of the bands at 919 and 932 cm^{-1} . It is apparent that some concentration of **3** was also present in the C₆D₆ solution at 25 °C according to equilibrium 2, but not observed due to large NMR line broadening. The IR spectrum of 4a in hexane did not reveal even a trace of free $B(C_6F_5)_3$, in contrast from the ¹⁹F NMR spectra in C_6D_6 or C₇D₈, which reflects a poorer solvation ability of hexane with regard to the aromatic hydrocarbons.

Crystal Structure of 4a. A simplified PLATON drawing of 4a is shown in Figure 1, and selected geometric parameters are listed in Table 1. The ligands around the titanium atom are arranged roughly in such a way that the plane defined by the Ti and B atoms and the centroid of the cyclopentadienyl ring (Cg) approximately bisects the cage of the DIPOSS' ligand. The latter is, however, distorted, as seen from its attachment to titanium with virtually equal Ti-O bonds of 1.80 Å but with the Ti–O–Si angles differing by more than 11° (see Table 1). The structure of the DIPOSS' ligand in 4a is similar to those found in free DIPOSS', its bis-(diphenylphosphino)ethane platinum complex,^{22a} chromate complex,^{22b} or various titanium complexes.^{5f} The DIPOSS' cage is formed of Si-O bonds with the lengths in the range 1.608 - 1.625(2) A, and the mouth to the cage is defined by nonbonding distances between O(1) and O(2) of 2.872(3) Å and between Si(1) and Si(5) of 5.391(1) Å. It is worthwhile to compare Ti-O, Si-O(Ti), and Ti-Cg bond lengths of 4a with those found for the Cp*Ti complex with two cyclohexylcontaining DIPOSS' ligands, $syn_syn_{-}[(\eta^5-C_5Me_5)]{(c-C_6 H_{11}_{7}Si_{7}O_{9}(OSiMe_{3})O_{2}$ { (*c*-C₆H₁₁)₇Si₇O₉(OSiMe_{3})O(OH) } Ti] (6) (Chart 1).^{5f} On the other hand, to discuss the zwitterionic bonding in 4a, its geometric data can be compared with those for $[Cp*Ti(O^{T}Bu)_{2}]^{(+)}[(\mu-Me)B(C_{6}F_{5})_{3}]^{(-)}$ (5) (Chart 1),¹¹ whose catalytic activity induced by addition of AlMe₃ will be compared with those of **3** and **4a** (see below).

The titanium-ligand bond lengths for the above compounds and the $[Cp*Ti(O'Bu)_3]$ complex²³ related to **5** are gathered in Table 2. It is surprising that replacement of the methylborate anion with the singly bonded DIPOSS' ligand causes elongation of the Ti-Cg distance by as much as 0.3 Å. On the other side, a distinctly shorter Ti-C(μ) distance in **4a**



Figure 1. PLATON drawing of $[Cp^*{(c-C_5H_9)_7Si_7O_9(OSi-Me_3)O_2}Ti]^{(+)}[(\mu-Me)B(C_6F_5)_3]^{(-)}$ (**4a**) at the 30% probability level with atom-labeling scheme. Cyclopentyl groups and hydrogen atoms except those on the (μ -Me) C(49) atom are omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) for Compound 4a

Ti-Cg ^a	2.0301(15)	Ti-C(49)	2.356(3)
Ti - O(1)	1.796(2)	Ti-O(2)	1.803(2)
Si(1) - O(1)	1.639(2)	Si(5)-O(2)	1.640(2)
Si(3)-O(12)	1.608(2)	O(12)-Si(8)	1.639(2)
B-C(49)	1.680(4)	B-C(50)	1.643(4)
B-C(56)	1.661(4)	B-C(62)	1.645(5)
Ti-H(49A)	2.24(4)	Ti-H(49B)	2.17(4)
Ti-H(49C)	2.26(4)		
Cg-Ti-O(1)	116.39(9)	Cg-Ti-O(2)	114.85(8)
Cg-Ti-C(49)	119.13(9)	O(1) - Ti - O(2)	105.87(9)
O(1)-Ti-C(49)	99.01(10)	O(2)-Ti-C(49)	98.95(10)
Ti - O(1) - Si(1)	161.35(14)	Ti-O(2)-Si(5)	145.68(13)
Ti-C(49)-B	172.9(2)	C(49) - B - C(50)	109.7(2)
C(49) - B - C(56)	107.9(2)	C(49) - B - C(62)	106.7(2)
B-C(49)-H(49A)	112.5(19)	B-C(49)-H(49B)	105.8(18)
B-C(49)-H(49C)	111.3(19)	Ti-C(49)-H(49A)	70.9(19)
Ti-C(49)-H(49B)	67.1(18)	Ti-C(49)-H(49C)	72.2(19)
"Ca donatas tha	contraid of the	C(1, 5) avalamenta dian	1 min a

^{*a*}Cg denotes the centroid of the C(1-5) cyclopentadienyl ring.

with respect to 5 can reflect a lower electron density on the titanium atom due to a lower oxygen π -donation effect.¹⁷ This effect should be enhanced for [Cp*Ti(O'Bu)₃], resulting in elongation of the Ti-Cg distance; however, the observed simultaneous elongation of the Ti-O bonds can indicate that the steric congestion at the titanium atom can take part. The bonding of $[(\mu-Me)B(C_6F_5)_3]^{(-)}$ to titanium is similar to that in 5. One of the bridging methyl group hydrogens, H(49B), embedded in the Ti-C(49)-B angle $(172.9(2)^{\circ})$ showed the shortest distance to titanium (2.17(3) Å) and the smallest Ti-C(49)-H(49B) angle of 67.1(2)°; however, all bridging methyl C-H bonds fulfill conditions for agostic bonding interaction to titanium since the d⁰ titanium atom has empty orbitals to interact with the σ -C-H bonding orbitals, the Ti-C and Ti-H distances are comparable, and the Ti-C-H angle is smaller than 100°.^{15b,c} In solution, they all contribute equally to a general electrostatic bonding interaction between the titanium and boron atoms. A similar orientation of the bridging methyl group was previously found in zirconocene complexes [Me₄C₂- $(\eta^{5}-C_{5}H_{4})_{2}ZrMe]^{(+)}[MeB(C_{6}F_{5})_{3}]^{(-)}, {}^{16a} rac-[Me_{2}Si\{\eta^{5}-C_{5}H_{2}-(2-Me-4-{}^{r}Bu)\}_{2}ZrMe]^{(+)}[MeB(C_{6}F_{5})_{3}]^{(-)}, {}^{16b} and [\{\eta^{5}-C_{5}H_{3}-(1,2-Me_{2})\}_{2}ZrMe]^{(+)}[MeB(C_{6}F_{5})_{3}]^{(-)}, {}^{16c}$

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⁽²³⁾ The crystal structure of $[(Cp^*)Ti(O^tBu)_3]$ will be published; unit cell characterization: $P2/_1c$, *a* 15.2964(3) Å, *b* 8.6293(1) Å, *c* 18.1119(4) Å, β 89.8924(11)°.





compound	Ti-O	Si-O(Ti)	Ti-Cg	$Ti-C(\mu)$	ref
6 4a 5 [Cp*Ti(O'Bu) ₃]	1.789-1.805(3) 1.796, 1.803(2) 1.766, 1.756(1) 1.785-1.806(2)	1.571-1.580(3) 1.639, 1.640(2)	2.317(5) 2.0301(15) 2.0464(7) 2.1007(12)	2.356(3) 2.436(1)	5f this work 11 23



Scheme 5



Reactions of 1 and 2 with *N*,*N*-Dimethylanilinium and Trityl Tetrakis(pentafluorophenyl)borates. Stirring of toluene solutions of **1** or **2** in a slight excess over the equimolar ratio with the low-soluble solid [PhNHMe₂]⁺[B(C₆F₅)₄]⁻ resulted in dissolution of the latter to give cleanly ionic complexes [Cp*{(c-C₅H₉)₇Si₈O₁₂O}₂Ti(κ -N-PhNMe₂)]⁺[B(C₆F₅)₄]⁻ (7) (Scheme 4) or a mixture of *syn*- and *anti*-stereoisomers [Cp*{(c-C₅H₉)₇Si₇O₉(OSiMe₃)O₂}Ti(κ -N-PhNMe₂)]⁺[B(C₆F₅)₄]⁻ (8a and 8b) (Scheme 5). The NMR probe reaction of **1** with

[PhNHMe₂]⁺[B(C₆F₅)₄]⁻ confirmed the formation of methane (0.15 ppm in the ¹H NMR spectrum) accompanied with a gradual diminishing of the Ti*Me* signal of **1** while raising a new signal for the C₅*Me*₅ group at 1.83 ppm and a broad signal at 2.71 ppm for the N*Me*₂ group of *N*,*N*-dimethylaniline coordinated to the titanium cation in **7**. The ¹H NMR spectrum of a mixture of **8a** and **8b** possessed similar characteristic features to that of **7**. The C₅*Me*₅ signal occurred at 1.81 ppm for **8a** and at 1.68 ppm for **8b** and a broad signal of

Scheme 6



 NMe_2 of the coordinated dimethylaniline at 2.55 ppm for 8a and at 2.97 ppm for 8b. In addition, the signal for the OSiMe₃ group was displayed at 0.21 ppm for 8a and at -0.18 ppm for 8b. This assignment was based on a 1D NOESY experiment, where irradiation of the C_5Me_5 signal at 1.81 ppm enhanced the $OSiMe_3$ signal at 0.21 ppm and the NMe_2 signal at 2.55 ppm. The enhancement of the latter signal also proved that *N*,*N*-dimethylaniline was coordinated to the titanium center. The N,N-dimethylaniline coordinated to cationic zirconium centers gave either a similarly broad signal or two signals for the two diastereotopic Me groups usually high-field shifted from the signal of free N,N-dimethylaniline.²⁴ The chemical shifts for NMe2 in 7, 8a, and 8b were not shifted far from that of the free ligand (δ 2.2–2.5 ppm depending on both temperature and concentration),^{24e} which would indicate that N,N-dimethylaniline was only weakly bound. However, an exhaustive evacuation of the solid complexes did not result in its loss (see below).

The reaction of $[Ph_3C]^+[B(C_6F_5)_4]^-$ with 1 to give $[Cp^*](c C_5H_9)_7Si_8O_{12}O_2Ti]^+[B(C_6F_5)_4]^-$ (9) (Scheme 6) was less unambiguous, yielding a number of minor byproducts. The NMR probe experiment showed a gradual diminution of the TiMe signal at 1.02 ppm concurrent with a rise of the signal at 2.02 ppm due to the formed Ph₃CMe.²⁵ In a region typical for the C_5Me_5 resonances (1.6–2.4 ppm) the main signal remained virtually at the same position as in 1 (2.04 ppm); however, it was somewhat decreasing in intensity while four new peaks were increasing, finally reaching only minor intensities. In a preparative experiment, a solid product was isolated and washed with hexane to remove Ph₃CMe, whose signal was nearly coincident with that of the main product. The ¹H NMR spectrum of the purified product showed, besides the absence of the TiMe group of 1, one dominant singlet signal at 2.03 ppm, which was tentatively assigned to C_5Me_5 of 9, and a minor unidentified singlet signal at 2.39 ppm. Due to uncertainty in the assignment of 9, the solid product was reacted with an excess of N,N-dimethylaniline. After removal of most of the free N,N-dimethylaniline under vacuum at 60 °C the ¹H NMR spectrum of the residue in C_6D_6 reproduced the signals obtained above for **7** in intensity corresponding to complete conversion of **9** to **7** (eq 4). In addition, the appearance of signals of

$$9 + PhNMe_2 \rightarrow 7 \tag{4}$$

free dimethylaniline with the sharp NMe_2 resonance at 2.43 ppm indicated that some amount of the amine remained entrapped in the solid 7.

A mixture of **2a** and **2b** also did not react cleanly with $[Ph_3C]^+[B(C_6F_5)_4]^-$ to give *syn-* and *anti-*[Cp*{($c-C_5H_9$)₇Si₇O₉-(OSiMe₃)O₂}Ti]⁺[B(C₆F₅)₄]⁻ (**10a** and **10b**) (Scheme 7).

The solid product after washing with hexane displayed a ¹H NMR spectrum showing a complex signal pattern for both OSi Me_3 and C₅ Me_5 protons with two dominating sets of signals at 0.19/1.83 ppm and 0.09/1.94 ppm, which were tentatively assigned to **10a** and **10b**, respectively. It is note-worthy that the signal of the SiMe₃ protons at 0.09 ppm was surprisingly broad ($\nu_{1/2} = 8.5$ Hz). This apparently indicates an intramolecular coordination of the oxygen atom of the OSiMe₃ group to the titanium atom in **10b**. This coordination bond is not, however, strong since addition of excess *N*,*N*-dimethylaniline to the above product mixture followed by its evaporation under vacuum resulted in the disappearance of the above signals for both **10a** and **10b**. Instead, the above signals for a mixture of **8a** and **8b** (eq 5) in intensities corresponding

$$10 + PhNMe_2 \rightarrow 8 \tag{5}$$

to the ratio of 2a/2b in 2 were observed in addition to minor unidentified resonances. The trace of free dimethylaniline was also observed with its NMe₂ group resonating at 2.21 ppm. None of compounds 7–10 crystallized, which precluded their effective purification and separation of *syn*and *anti*-stereoisomers 8a/8b and 10a/10b.

The solid-state IR-ATR spectra of 7-10 showed absorption bands of the $[B(C_6F_5)_4]^-$ anion, which are not sensitive to the nature of the cation. Among them the strong band at 978 cm⁻¹ falls into the range where the valence Si–O(Ti) vibrations should be sought. The band is easily recognized because its position and intensity relative to other absorption bands of the $[B(C_6F_5)_4]^-$ anion are constant. In DIPOSS' complexes it competes in intensity with the most intense broad band of Si–O–Si vibrations, and in SIPOSS compounds it is

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(c) Schrock, R. R.; Casado, A. L.; Goodman, J. T.; Liang, L.-C.; Bonitatebus, P. J., Jr.; Davis, W. M. Organometallics 2000, 19, 5325–5341. (d) Hollink, E.; Wei, P.; Stephan, D. W. Organometallics 2004, 23, 1562–1569.
(e) Wilson, P. A.; Wright, J. A.; Oganesyan, V. S.; Lancaster, S. J.; Bochmann, M. Organometallics 2008, 27, 6371–6374.

⁽²⁵⁾ Obrey, S. J.; Bott, S. G.; Barron, A. R. Organometallics 2001, 20, 5162–5170.



the second most intense band in the spectra. The Si-O(Ti) vibrations for SIPOSS compounds 7 and 9 are assigned to bands at 919/938 and 917/934 cm⁻¹, and in DIPOSS' compounds 8 and 10 to bands at 948 and 951 cm⁻¹, respectively.

Styrene Polymerization. All complexes **3**–**10** were inactive for polymerization of styrene in toluene at 50 °C, like the dialkoxy zwitterionic complexes $[Cp^*Ti(O'Bu)_2]^{(+)}[(\mu-Me)B(C_6F_5)_3]^{(-)}$ (**5**)¹¹ and $[Cp^*Ti(O'Pr)_2]^{(+)}[(\mu-Me)B(C_6-F_5)_3]^{(-)}$.¹⁴ The siloxy(alkoxy)-methyl(benzyl) zwitterionic and ionic complexes were reported to have low thermal stability;^{6a,c,7–10,13} however, it was also suggested that the zwitterionic complexes $[Cp^*Ti(OR)Me]^{(+)}[(\mu-Me)B(C_6-F_5)_3]^{(-)}$ should be active in styrene polymerization to syndiotactic polystyrene (syn-PS), and perhaps, they could be more convenient than the system made by mixing Cp^*TiMe_3 with $B(C_6F_5)_3$, which is superior in activity but very rapidly deactivated. ^{13b-d} Hence, an attempt was made to methylate the titanium center in zwitterionic complexes **3**, **4**, and **5** via metathesis reaction with AlMe₃ (eq 6). Since the above zwitterionic complexes are formed nearly

$$[Cp*Ti(OR)_{2}]^{(+)}[(\mu-Me)B(C_{6}F_{5})_{3}]^{(-)}$$

+ AlMe₃ \nvec{} [Cp*Ti(OR)Me]^{(+)}[(\mu-Me)B(C_{6}F_{5})_{3}]^{(-)}
+ AlMe_{2}(OR) (6)

immediately, the catalytic complexes were prepared in the polymerization reactor by mixing of toluene solutions of their components in styrene/toluene, addition of 1, 2, or 3 molar equiv of AlMe₃ being the last. Only addition of 2 molar equiv of AlMe₃ to 3, 4, and 5 triggered the polymerization of styrene to syn-PS, albeit with low activity (Table 3). The tert-butoxy and DIPOSS' complexes exerted virtually the same activity and produced a more than 90% syndiotactic polystyrene (syn-PS). In contrast, the SIPOSS complex showed a lower activity, and the polymer contained only 75% of syn-PS. This can be accounted for by the abovenoted dissociation of 3 in solution, which led to a decrease in concentration of the catalytic species, on one hand, and to a $B(C_6F_5)_3$ -induced cationic polymerization to give a 2-buta-none-soluble atactic PS.^{13c} The molecular weights M_w of syn-PS follow the trend of decreasing stability of the complexes in toluene solution (5 > 4 > 3), as determined by NMR methods above and in ref 11). The D values above 3.0 indicate the presence of likely two catalytic centers, which can arise from a competitive interaction of AlMe₃ with the cationic and anionic part of the zwitterionic complexes. In addition to the titanium methylation, as anticipated by eq 6,

 Table 3. Polymerization of Styrene with Complexes 3, 4, and 5

 Combined with 2 equiv of AlMe₃^a

catalyst	conver- sion (%)	syn- PS (%)	activity ^b	$M_{ m w}$	$T_{\rm m}$ (°C)	$D \left(M_{\rm w}/M_{\rm n} ight)$
3	1.8	75	368	254 600	271	3.93
4	2.5	91	520	323 750	269	3.37
5	2.6	92	528	523 400	269	3.10

^{*a*} Polymerization conditions: [Ti] 1.25×10^{-3} M, [styrene] = 2.178 M, [AlMe₃] = 2.50×10^{-3} M, toluene 6.0 mL, styrene 2.0 mL, temperature 50 °C, time 30 min. ^{*b*} Activity: kg of polymer/[mol(Ti) × mol(styrene) × h].

Table 4. Polymerization of Styrene with Complexes 1, 2, and Cp*Ti(O'Bu)₂Me Combined with MAO^a

catalyst precursor	conversion (%)	yield (g)	syn-PS (%)	activity ^b
1	35.9	0.664	98	7483
2	24.2	0.443	99	5035
Cp*Ti(O'Bu) ₂ Me	24.5	0.446	99	5104

^{*a*} Polymerization conditions: [Ti] 1.25×10^{-3} M, [styrene] = 2.178 M, [Al]/[Ti] = 250, toluene 6.0 mL, styrene 2.0 mL, temperature 50 °C, time 30 min. ^{*b*} Activity: kg of polymer/[mol(Ti) × mol(styrene) × h].

the trimethylaluminum is known to exchange methyl group-(s) with the pentafluorophenyl groups of the borane, affording products of lower Lewis acidity than that of $B(C_6F_5)_3$.²⁶ The reaction with the borane is apparently the reason for the necessity to use a molar AlMe₃/Ti ratio of 2. A low efficiency of the formation of catalytic centers was further confirmed by polymerization tests where the titanium precursors 1, 2, and Cp*Ti(O'Bu)₂Me were combined with MAO under the same experimental conditions. Activities of these systems were 1 order higher and ordered $1 > 2 \sim Cp*Ti(O'Bu)_2Me$ (see Table 4).

Investigations of the composition of the 3-5/2 AlMe₃ systems by means of NMR spectroscopy were abandoned due to an expected large variety of products, which, moreover, could not be identical with those obtained in the presence of styrene. However, some insight into the above systems was obtained from the metathesis reaction of compounds 1, 2, and Cp*Ti(O'Bu)₂Me with 2 equiv of AlMe₃, yielding various amounts of Cp*TiMe₃ and Cp*Ti(OR)Me₂ compounds as determined by ¹H and ¹³C NMR spectra.²⁷

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Surprisingly, under comparable conditions (60 °C) the largest amount (at least 32%) of Cp*TiMe₃ was obtained for **1**, somewhat less for **2** (14%), and Cp*TiMe₃ was absent for Cp*Ti(O'Bu)₂Me where Cp*Ti(O'Bu)Me₂ roughly amounted to 70% and the initial compound 30%.

The shift of equilibria 7 to the right in the order $1 > 2 \gg$ Cp*Ti(O'Bu)₂Me following from

$$Cp*Ti(OR)_{2}Me + AlMe_{3} \rightleftharpoons Cp*Ti(OR)Me_{2}$$
$$+ Al(OR)Me_{2} \rightleftharpoons Cp*TiMe_{3} + Al(OR)_{2}Me \quad (7)$$

these experiments did not respond to the above polymerization activities of the 3-5/2 AlMe₃ systems (Table 3); however, it conforms to activities found for the MAO systems (Table 4). The ease of the Ti-O(Si) bond metathesis with the Al-Me bond is apparently an important factor for accounting for the extremely high activities of some $Cp*Ti(OSiR_3)_3/$ MAO systems ([Al]/[Ti] = 500, 70 °C).²⁸ Among them the TRIPOSS complex $[Cp*Ti\{(c-C_5H_9)_7Si_7O_9(O)_3\}]$ exerted activity (6900 kg of polymer/[mol(Ti) \times mol(styrene) \times h) comparable to that of 1/MAO (Table 4). These results show that although the OSi≡ ligands do not participate in the construction of the active center, which is generally proposed to be, for example, the Cp*Ti(III)(η^2 -styrene)(η^1 -styrene) cation,²⁹ the silica-grafted half-sandwich titanocene is easily replaced with the MAO molecule(s) playing the role of silicagrafted counteranion.

From the other point of view, the silica-grafted Cp*TiCl₃/ MAO system ([Al]/[Ti]=600, 50 °C) exerted yet lower activities than those of Table 3; however, the activity increased by more than 1 order at the polymerization temperature of 110 °C,³⁰ a temperature that has never been used for homogeneous catalysts since a drop in activity was reported at temperatures above 70 °C.²⁹ This invokes the idea that an active Ti(III) cation is formed under action of styrene at high temperature, and this can be stable enough in the presence of the silicagrafted MAO counteranion. Following this, there is a good prospect for the use of Cp*TiMe3 in grafting to silica and preparation of surface catalytic complexes thereof using borane. The above observed dissociation of complex 3 in nonpolar solvents does not imply that the surface, catalytic complex $[Cp*Ti(OR)Me]^{(+)}[(\mu-Me)B(C_6F_5)_3]^{(-)}$ (R = Si from silica SiOH group) cannot be stable in the absence of solvents. Attempts to model such systems using the SIPOSS ligand are under way.

Conclusions

The zwitterionic complexes **3** and **4a** are formed easily from the half-sandwich titanium disiloxymonomethyl compounds **1** and **2a**, respectively, by adding an equimolar amount of $B(C_6F_5)_3$. The compounds are thermally stable at least to 60 °C in the solid state; however, they dissociate in solutions, releasing the initial reagents. The equilibrium constants for formation of **3** and **4a** (K_3 and K_{4a}) could not be determined from NMR data because the thermally induced concentration changes were accompanied with varying exchange rates; however, the temperature at which $K_3 \approx K_{4a}$ was found to be about 50 °C lower for 3. A higher stability of 4a with regard to 3 is in agreement with the acidity measurement for SIPOSS and DIPOSS' using an overlapping indicator method, which put DIPOSS' as being less acidic ($pK_{ip} = 9.5 \pm 0.1$) than SIPOSS ($pK_{ip} = 8.9 \pm 0.4$).^{3a} The difference in the stability of DIPOSS' and SIPOSS zwitterionic complexes was smeared out for the ion-pair complexes 7-10; however, higher frequencies of Si-O(Ti) vibrations in DIPOSS' compounds 4a, 8, and 10 compared to SIPOSS compounds 3, 7, and 9 are in qualitative agreement with $K_{4a} > K_3$. The X-ray crystal structure of 4a gave Ti-Cg and $Ti-C(\mu)$ bond lengths close to those of the di-tertbutoxy complex 5, although the latter is more stable in solution. Complexes 3, 4, and 5 were activated by addition of 2 molar equiv of AlMe₃ to catalyze the styrene polymerization to syn-PS. However, the catalysts were of low activity, as could be expected from the low stability of the boranegenerated [Cp*Ti(OR)Me]⁽⁺⁾ species in solution.^{7-10,13} Also, the generation of these species from inactive $[Cp*Ti(OR)_2]^{(+)}$ by metathesis with AlMe₃ is not efficient since AlMe₃ is known to competitively react with borate anions to give products of low Lewis acidity.²⁶ These results indicate a poor prospect for obtaining a highly active boraneactivated polymerization catalyst with the titanium atom grafted to a silica surface except that Cp*TiMe₃ is reacted with isolated Si-O-H groups to generate after addition of $B(C_6F_5)_3$ the $[Cp*Ti(OR)Me]^{(+)}[(\mu-Me)B(C_6F_5)_3]^{(-)}$ species (R = surface Si atom).

Experimental Section

General Considerations. Reactions of POSS monosilanol [(c-C₅H₉)₇Si₈O₁₂OH] (SIPOSS) and disilanol [(c-C₅H₉)₇Si₇O₉-(OSiMe₃)(OH)₂] (DIPOSS') with [Cp*TiMe₃] (1) to give products 1 and 2, respectively, and reactions of 1 and 2 with $[B(C_6F_6)_3]$ or with the solid salts $[PhNMe_2H]^+[B(C_6F_5)_4]^-$ and $[Ph_3C]^+[B(C_6F_5)_4]^-$ were carried out on a vacuum/argon line in sealed all-glass devices equipped with breakable seals. All airsensitive solid compounds were handled in a Labmaster 130 (mBraun) glovebox under purified nitrogen (concentrations of oxygen and water were lower than 2.0 ppm) to weigh the reagents, to prepare KBr pellets for IR spectra, or to fix single crystals into Lindemann glass capillaries for X-ray diffraction analysis. IR spectra were measured on a Nicolet Avatar FT IR spectrometer in the range 400-4000 cm⁻¹ and/or on a Nicolet 380 FT IR with an attenuated total reflectance (ATR) cell, equipped with a silicon crystal in the range 650-4000 cm⁻ (resolution 4 cm^{-1} , 64 scans). A special air-protected cell for the IR-ATR measurement was charged with the solid sample in a glovebag under argon. KBr pellets were measured under nitrogen in an air-protected compartment equipped with KBr windows. The IR-ATR data for neat samples were generally in qualitative agreement with those obtained from KBr pellets. The former data are presented for all compounds since they eliminate effects arising from interaction of ionic samples with the KBr matrix. Hexane solutions were filled into KBr cells (d=0.025-0.1 cm) under argon in a glovebag. ¹H (300 MHz), ¹³C (75 MHz), ²⁹Si (59.6 MHz), and ¹⁹F (282.2 MHz) NMR spectra were measured on a Varian Mercury 300 spectrometer in C_6D_6 or C₇D₈.¹¹ B NMR (160.4 MHz) spectra were acquired on a UNITY Inova 500 MHz at 273 K in C7D8. Sample tubes were filled on a vacuum line and sealed off with flame. Monitoring of reactions by NMR spectra was done using NMR sample tubes equipped with Teflon screw-caps. They were charged under argon in a glovebag. Elemental analyses were carried out on a FLASH EA1112 CHN/O automatic elemental analyzer (Thermo Scientific).

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Chemicals. The solvents hexane and toluene were dried by refluxing over LiAlH4 and stored as solutions of green dimeric titanocene $[(\mu - \eta^5: \eta^5 - C_5H_4C_5H_4)(\mu - H)_2 \{Ti(\eta^5 - C_5H_5)\}_2]^{.31}$ Commercial [Cp*TiMe₃] was purchased from Strem Chemicals, Inc., and was not further purified. It was handled and weighed under an argon atmosphere and transferred into reaction ampules on a vacuum/argon line. The monosilanol POSS [(c-C₅H₉)₇Si₇O₁₂-SiOH] (SIPOSS) and trisilanol POSS [(c-C₅H₉)₇Si₇O₉(OH)₃] (TRIPOSS) (all Aldrich) were degassed and used as such. [(c- C_5H_9)₇Si₇O₉(OSiMe₃)(OH)₂] (DIPOSS') was prepared from TRIPOSS according to the literature.^{1b} B(C₆F₅)₃ (Strem Chemicals, Inc.) was analyzed by ATR under argon for the presence of hydrolytic products (indicated by the absorption band at 1290 cm^{-1}) and purified by reacting with an estimated amount of [Cp*TiMe₃] in hexane. A brown solution was separated from a brown oily sediment, the hexane was distilled off under vacuum, and the colorless $B(C_6F_5)_3$ was obtained by sublimation of the residue at 100 °C in high vacuum. The final purity was tested using ¹⁹F NMR.³² Trityl tetrakis(pentafluorophenyl)borate, $[Ph_3C]^+[B(C_6F_5)_4]^-$, and *N*,*N*-dimethylanilinium tetrakis(pentafluorophenyl)borate, $[PhNMe_2H]^+[B(C_6F_5)_4]^-$, were purchased from Aldrich and handled as such under argon. [Cp*Ti-(O'Bu)₂Me] was obtained as described.¹¹ Styrene (Aldrich) was degassed and distilled under vacuum on solid green dimeric titanocene. The green solution did not change its color after warming to 60 °C for 30 min. The styrene was again degassed by a freezing/thawing cycle and distributed by vacuum distillation into ampules. Trimethylaluminum in toluene (1.0 M) was diluted with toluene and distributed to make 10 μ mol/2.0 mL doses. N,N-Dimethylaniline (Aldrich) was distilled under argon and degassed. The toluene solution of MAO (Aldrich) was used as such.

Preparation of $[Cp^*{(c-C_5H_9)_7Si_8O_{12}O}_2TiMe]$ (1). The reagents [Cp*TiMe₃] (0.228 g, 1.0 mmol) and SIPOSS (1.838 g, 1.96 mmol) were weighed under argon into a reaction ampule attached to an argon/vacuum line, which was cooled to -70 °C. After sealing off the filling arm, the ampule was degassed, and hexane (15 mL) was distilled onto the reaction mixture. The mixture was left to warm to room temperature under stirring while the bubbling of liberated methane was observed. After stirring for another 1 h the formed yellow solution was evaporated under vacuum to dryness, and the solid residue was dissolved in hexane. The saturated solution was cooled to -28 °C, affording transparent yellow crystals. These were separated from the mother liquor and dried by evacuating overnight at 2 \times 10⁻³ Torr to give a light yellow pseudocrystalline material. The loss of hexane of crystallization during tranfer of transparent crystals from hexane to Nujol oil and to the cooled rod of the X-ray diffractometer was apparently responsible for the poor diffraction data. These allowed solving the structure and identifying all the ligands and the Ti-Me bond, but precluded the anisotropic refinement. Yield: 1.75 g (88%).

Data for 1 are as follows. ¹H NMR (298 K, C₆D₆): 1.04 (s, 3H, Ti*Me*), 1.10–1.40 (m, 14H, C*H*, cyclopentyl), 1.40–2.18 (m, 112H, C*H*₂, cyclopentyl), 2.04 (s, 15H, C₅*Me*₅). ¹³C{¹H} NMR (298 K, C₆D₆): 11.69 (C₅*Me*₅), 22.66, 22.78 (CH, cyclopentyl), 27.50, 27.63, 27.86, 27.90 (CH₂, cyclopentyl), 54.53 (Ti*Me*), 124.24 (C₅Me₅). ²⁹Si NMR (298 K, C₆D₆): -110.8 (1Si, *Si*O₄); -66.0 (3Si); -65.9 (1Si); -65.8 (3Si). IR (ATR Si, cm⁻¹): 2947 (m), 2911 (w, sh), 2863 (m), 1451 (w), 1378 (vw), 1246 (w), 1097 (vs), 1043 (m), 1024 (m, sh), 984 (s), 917 (w), 731 (vw), 676 (vw). Anal. Calcd for C₈₁H₁₄₄O₂₆Si₁₆Ti (2031.29): C, 47.89; H, 7.14. Found: C, 47.94; H, 7.18.

Preparation of a Mixture of *syn*- and *anti*-[Cp*{($c-C_5H_9$)₇-Si₇O₉(OSiMe₃)O₂}TiMe] (2a and 2b) and Isolation of *syn*-Isomer (2a). [Cp*TiMe₃] (0.19 g, 0.83 mmol) and DIPOSS' (0.725 g, 0.76 mmol) were reacted in hexane in the same manner as described above for 1. Crystallization of a crude solid product from a saturated hexane solution (ca. 5 mL) at -28 °C afforded a yellow crystalline mixture of *syn*-2a and *anti*-2b. Composition from NMR data: 2a 66%, 2b 33%. After drying under vacuum overnight a light yellow pseudocrystalline material was obtained. Yield: 0.79 g (91%).

Data for **2** (**2a** + **2b**) are as follows. IR (ATR Si, cm⁻¹): 2948 (s), 2909 (m, sh), 2864 (m), 1449 (vw), 1249 (w), 1094 (vs, b), 1062 (s), 1042 (s, sh), 988 (s), 944 (m), 914 (m, b), 861 (w), 840 (m), 754 (w). Anal. Calcd for $C_{49}H_{90}O_{12}Si_8Ti$ (1143.82): C, 51.45; H, 7.93. Found: C, 51.49; H, 7.98.

Isolation of 2a was performed by fractional crystallization from a saturated hexane solution driven by a slow evaporation of hexane under vacuum. The first crop of crystals contained pure 2a. Drying under vacuum yielded 0.32 g (37%). The NMR data for 2b were obtained from the content of the ultimate mother liquor, consisting of 2b (90%) and 2a (10%).

Data for **2a** are as follows. ¹H NMR (298 K, C₆D₆): 0.28 (s, 9H, Si Me_3), 0.84 (s, 3H, TiMe), 1.06–1.28 (m, 7H, CH, cyclopentyl), 1.44–1.62 (m, 14H, CH₂, cyclopentyl), 1.62–1.86 (m, 28H, CH₂, cyclopentyl), 1.86–2.03 (m, 14H, CH₂, cyclopentyl), 2.06 (s, 15H, C₅ Me_5). ¹³C{¹H} NMR (298 K, C₆D₆): 2.33 (Si Me_3), 11.95 (C₅ Me_5), 23.10, 23.29, 23.93, 24.10, 25.84 (CH, cyclopentyl), 27.32, 27.47, 27.50, 27.64, 27.75, 28.07, 28.10, 28.18, 28.36, 28.54 (CH₂, cyclopentyl), 47.15 (TiMe), 123.61 (C₅Me₅). ²⁹Si (298 K, C₆D₆): -67.44 (2Si), -66.70 (2Si), -65.74 (1Si), -65.57 (1Si), -64.96 (1Si), 7.72 (1Si, SiMe₃).

Data for **2b** are as follows. ¹H NMR (298 K, C₆D₆): 0.28 (s, 9H, Si Me_3); 1.06–1.28 (m, 7H, CH, cyclopentyl), 1.16 (s, 3H, TiMe); 1.44–1.62 (m, 14H, CH₂, cyclopentyl); 1.62–1.86 (m, 28H, CH₂, cyclopentyl); 1.86–2.03 (m, 14H, CH₂, cyclopentyl); 1.93 (s, 15H, C₅ Me_5). ¹³C{¹H} NMR (298 K, C₆D₆) selected signals: 2.29 (Si Me_3); 11.67 (C₅ Me_5); 23.10, 23.20, 24.10, 24.63, 25.43 (CH, cyclopentyl); 27.3–28.6 (CH₂, cyclopentyl); 55.10 (TiMe); 122.86 (C₅Me₅). ²⁹Si NMR (298 K, C₆D₆): -67.90 (2Si); -67.25 (2Si); -66.66 (1Si); -65.67 (1Si); -64.74 (1Si); 7.78 (1Si, SiMe₃).

Preparation of [Cp*{(*c*-C₅H₉)₇Si₈O₁₂O}₂Ti]⁽⁺⁾[(μ -Me)B(C₆-F₅)₃]⁽⁻⁾ (3). Compound 1 (0.426 g, 0.21 mmol) was dissolved in 3.0 mL of toluene, and this solution was mixed with a solution of B(C₆F₅)₃ in toluene (2.0 mL of a 0.1 M solution) at room temperature. The product formation was indicated by an immediate color change from yellow to brownish-orange. All the solvent was evaporated under vacuum, and the product was dissolved in hexane (10 mL), leaving traces of brown oil. Orange crystals of **3** were obtained by a slow vacuum distillation of the solvent into an attached ampule at room temperature. The residual mother liquor (ca. 1 mL) containing excess **1** was also removed. A bright orange crystalline product was washed out with condensing hexane vapors. After drying under vacuum of 2 × 10⁻⁴ Torr at 60 °C an opaque pseudocrystalline solid was obtained. Yield: 0.41 g (80%).

Data for **3** are as follows. ¹H NMR (238 K, C_7D_8): 0.92 (br s, 3H, BMe), 1.02–1.28 (m, 14H, CH, cyclopentyl), 1.38–2.16 (m, 112H, CH₂, cyclopentyl), 1.99 (s, 15H, C_5Me_5). ¹⁹F NMR (238 K, C_7D_8): –133.0 (br s, 6F, o-F); –159.3 (br s, 3F, p-F); –164.2 (br s, 2F, m-F). IR (ATR Si, cm⁻¹): 2950 (s), 2909 (m, sh), 2864 (m), 1640 (vw), 1510 (w), 1458 (m), 1382 (vw), 1247 (w), 1101 (vs), 1006 (m), 972 (m), 932 (s), 919 (s), 798 (w), 732 (w), 670 (w), 662 (w). Anal. Calcd for $C_{99}H_{144}O_{26}Si_{16}F_{15}BTi$ (2543.30): C, 46.75; H, 5.71. Found: C, 46.70; H, 5.68.

Preparation of $[Cp^{*}{(c-C_{5}H_{9})_{7}Si_{7}O_{9}(OSiMe_{3})O_{2}}Ti]^{(+)}[(\mu-Me)B(C_{6}F_{5})_{3}]^{(-)}$ (4a). Compound 2a (0.240 g, 0.21 mmol) in 3.0 mL of toluene reacted with the solution of $B(C_{6}F_{5})_{3}$ in toluene (2.0 mL of 0.1 M solution) in the same way as for 3.

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After replacement of toluene with hexane an orange crystalline material of **4a** was obtained by crystallization from the latter. The orange crystalline material of **4a** was dried overnight at 2×10^{-4} Torr to give a light orange product. Yield: 0.27 g (82%).

Data for 4a are as follows. ¹H NMR (298 K, C_6D_6): 0.20 (s, 9H, SiMe₃); 0.85 (br s, 3H, BMe); 0.94-1.20 (m, 7H, CH, cyclopentyl), 1.40-1.76 (m, 42H, CH₂, cyclopentyl); 1.76-1.92 (m, 14H, CH_2 , cyclopentyl); 2.04 (s, 15H, C_5Me_5). ¹³C{¹H} NMR (298 K, C₆D₆): 2.26 (SiMe₃); 12.61 (C₅Me₅); 22.03, 22.91, 23.76, 25.54 (CH, cyclopentyl); 27.22, 27.30, 27.37, 27.40, 27.51, 27.66, 27.88, 27.94, 28.00, 28.43 (*C*H₂, cyclopentyl); 133.62 (*C*₅Me₅); 137.52 (d of multiplets, ${}^{1}J_{CF} \approx 255$ Hz, *m*-*C*F); 139.92 (d of multiplets, ${}^{1}J_{CF} \approx 245$ Hz, *p*-*C*F); 148.73 (d of multiplets, ${}^{1}J_{CF} \approx 235$ Hz, *o*-*C*F). 19 F NMR (298 K, C₆D₆): -133.0 (br s, 6F, o-F); -159.7 (br s, 3F, p-F); -164.9 (br s, 2F, *m*-*F*). ²⁹Si NMR (298 K, C₆D₆): -66.61 (2Si); -65.02 (1Si); -64.92 (1Si); -64.74 (1Si); -64.05 (2Si); 8.16 (1Si, SiMe₃). ¹¹B NMR (273 K, C_7D_8): -13 ($\Delta v_{1/2}$ = 46 Hz). IR (ATR Si, cm⁻¹): 2951 (m), 2912 (w, sh), 2865 (m), 1640 (w), 1511 (m), 1458 (s), 1393 (vw), 1382 (w), 1366 (vw), 1322 (vw), 1269 (w, sh), 1252 (m), 1112 (s, sh), 1085 (vs), 1061 (s, sh), 1044 (s, sh), 973 (s,sh), 964 (vs), 953 (s, sh), 909 (w, sh), 868 (s), 847 (m), 800 (w), 758 (w), 734 (w), 660 (w). Anal. Calcd for C₆₇H₉₀-O₁₂Si₈F₁₅BTi (1655.83): C, 48.60; H, 5.48. Found: C, 48.56; Н, 5.52.

Reaction of 1 with $[C_6H_5NHMe_2]^+[B(C_6F_5)_4]^-$ to Give $[Cp^*\{(c-C_5H_9)_7Si_8O_{12}O\}_2Ti(NMe_2Ph-\kappa-N)]^+[B(C_6F_5)_4]^-$ (7). A solution of 1 (0.426 g, 0.21 mmol) in 5.0 mL of toluene under argon atmosphere was added to the solid $[C_6H_5NHMe_2]^+$ - $[B(C_6F_5)_4]^-$ (0.160 g, 0.20 mmol), and the mixture was stirred for 5 h. All volatiles were distilled off under vacuum, and the orange residue was extracted repeatedly with 20 mL of hexane. Evaporation of combined extracts afforded an amorphous solid. This was rinsed with condensing hexane vapor and dried under vacuum to give a yellow powder. Yield: 0.42 g (75%).

Data for 7 are as follows. ¹H NMR (298 K, C_6D_6): 1.05–1.28 (m, 14H, CH, cyclopentyl), 1.40-2.00 (m, 56H, CH₂, cyclopentyl); 1.83 (s, 15H, C₅Me₅); 2.71 (br s, 6H, NMe₂); 7.04 (t, ${}^{3}J_{HH} =$ 7.5 Hz, 1H, CH_{para}, Ph); 7.17–7.22 (m, 2H, Ph); 7.28–7.35 (m, 2H, Ph). ${}^{13}C{}^{1}H$ NMR (298 K, C₆D₆): 12.29 (C₅Me₅); 21.94, 22.38 (CH, cyclopentyl); 27.48, 27.70, 27.91 (CH2, cyclopentyl); 50.43 (NMe2Ph); 118.22, 121.00, 130.16 (CH, NMe₂Ph); 137.01 (d of multiplets, ${}^{1}J_{CF} = 236$ Hz, m-CF); 137.14 (C₅Me₅); 138.80 (d of multiplets, ${}^{1}J_{CF} = 241$ Hz, *p*-*C*F); 146.05 (C_{ipso} , NMe₂*Ph*); 149.05 (d of multiplets, ${}^{1}J_{CF} =$ 243 Hz, *o*-*C*F). 19 F NMR (298 K, C₆D₆): -132.3 (br s, 6F, *o*-*F*); -163.4 (m, 3F, *p*-*F*); -167.1 (br s, 2F, *m*-*F*). ²⁹Si NMR (298 K, C₆D₆): -109.47 (1Si, SiO₄); -65.65 (3Si); -65.63 (1Si); -65.24 (3Si). IR (ATR Si, cm⁻¹): 2949 (m), 2912 (w, sh), 2865 (m), 1642 (vw), 1512 (m), 1462 (s), 1452 (m, sh), 1274 (w), 1245 (w), 1100 (vs, b), 1028 (w), 1005 (m, b), 978 (s), 938 (m, b), 919 (m, b), 771 (w), 754 (w), 683 (w), 661 (w). Anal. Calcd for C112H152O26-Si₁₆F₂₀NBTi (2816.51): C, 47.76; H, 5.44. Found: C, 47.72; H, 5.47.

Reaction of 1 with $[C_6H_5NHMe_2]^+[B(C_6F_5)_4]^-$ in an NMR **Tube.** A solution of 1 (0.163 g, 0.08 mmol) in 0.8 mL of C_6D_6 was added under argon atmosphere to solid $[C_6H_5NHMe_2]^+$ - $[B(C_6F_5)_4]^-$ (0.095 g, 0.12 mmol) in an NMR tube, and this was closed with a screw-tightened Teflon cap. Measurements of ¹H, ¹³C, and ¹⁹F spectra after 20 min intervals revealed the formation of the ion-pair complex $[Cp^*{(c-C_5H_9)_7Si_8O_{12}O}_2Ti-(C_6H_5NMe_2)]^+[B(C_6F_5)_4]^-$ (7) at the expense of 1. Methane evolved during the reaction, giving the ¹H NMR signal at δ_H 0.15 ppm. Consumption of 1 was complete after 90 min, while an excess of the low-soluble $[C_6H_5NHMe_2]^+[B(C_6F_5)_4]^-$ remained at the bottom of the tube and was not observed in the NMR spectra.

Reaction of 2 with $[C_6H_5NHMe_2]^+[B(C_6F_5)_4]^-$ to Give $[Cp^* {(c-C_5H_9)_7Si_7O_9(OSiMe_3)O_2}]$ Ti $(NMe_2Ph-\kappa-N)]^+[B(C_6F_5)_4]^-$ (8). A solution of 2 (a mixture of 2a and 2b) in toluene (0.2 mmol in

3.0 mL) was added to a solution of $[C_6H_5NHMe_2]^+[B(C_6F_5)_4]^-$ (0.135 g, 0.17 mmol) in 20 mL of toluene to give a yellow solution. After stirring the mixture for 1 h the solution was evaporated under vacuum. The oily residue was repeatedly extracted with 15 mL of hexane to give a yellow oil. This was rinsed with 10 mL of hexane and dried under vacuum. Yield: 0.29 g (76%).

Data for **8** are as follows. IR (ATR Si, cm⁻¹): 2951 (s), 2913 (w, sh), 2866 (m), 1641 (w), 1513 (m), 1462 (s), 1410 (vw), 1381 (w), 1276 (w), 1252 (w), 1105 (s, sh), 1083 (vs), 1058 (s), 1040 (s, sh), 978 (vs), 948 (s), 911 (m), 860 (m), 844 (m), 773 (m), 755 (m), 727 (w), 699 (w), 683 (m), 661 (m). Anal. Calcd for $C_{80}H_{98}O_{12}$ -Si₈F₂₀NBTi (1929.04): C, 49.81; H, 5.12. Found: C, 49.77; H, 5.08.

The NMR spectra were assigned to *syn-8a* and *anti-8b* on the basis of 1D NOESY experiments. The ratio **8a/8b** was close to 2:1.

Data for **8a** are as follows. ¹H NMR (298 K, C₆D₆): 0.21 (s, 9H, Si*Me*₃); 1.00–1.20 (m, 7H, C*H*, cyclopentyl); 1.42–1.77 (m, 42H, C*H*₂, cyclopentyl); 1.81 (s, 15H, C₅*Me*₅); 1.80–1.98 (m, 14H, C*H*₂, cyclopentyl); 2.55 (br s, 6H, N*Me*₂); 7.08–7.26 (m, 5H, *Ph*). ¹³C{¹H} NMR (298 K, C₆D₆): 2.10 (Si*Me*₃); 12.76 (C₅*Me*₅); 22.73, 22.79, 23.31, 23.55, 25.38 (CH, cyclopentyl); 27.00–28.50 (CH₂, cyclopentyl); 51.48 (N*Me*₂Ph); 118.18, 120.95, 130.39 (CH, NMe₂*Ph*); 135.94 (C₅Me₅); 137.06 (d of multiplets, ¹*J*_{CF}=243 Hz, *m*-CF); 138.93 (d of multiplets, ¹*J*_{CF}= 246 Hz, *p*-CF); 146.96 (C_{ipso}, NMe₂*Ph*); 149.17 (d of multiplets, ¹*J*_{CF}=242 Hz, *o*-CF). ²⁹Si{¹H} NMR (99.3 MHz, 298 K, C₆D₆): -65.89 (2Si); -65.32 (1Si); -64.76 (1Si); -64.38 (1Si); -63.77 (2Si); 8.98 (1Si, *Si*Me₃).

Data for **8b** are as follows. ¹H NMR (300 MHz, 298 K, C₆D₆): -0.18 (s, 9H, Si*Me*₃); 1.00–1.20 (m, 7H, C*H*, cyclopentyl), 1.42–1.77 (m, 42H, C*H*₂, cyclopentyl); 1.68 (s, 15H, C₅*Me*₅); 1.95–2.08 (m, 14H, C*H*₂, cyclopentyl); 2.97 (br s, 6H, N*Me*₂); 7.08–7.26 (m, 5H, *Ph*). ¹³C{¹H} NMR (75 MHz, 298 K, C₆D₆): 1.55 (Si*Me*₃); 12.23 (C₅*Me*₅); 22.63, 24.82, 25.19, remaining signals are overlapped by signals of the more abundant stereoisomer (*C*H, cyclopentyl); 27.00–28.50 (*C*H₂, cyclopentyl); 52.27 (N*Me*₂Ph); 120.86, 129.13, one signal was not found (*C*H, NMe₂*Ph*); 135.05 (C₅Me₅); 137.06 (d of multiplets, ¹*J*_{CF} = 243 Hz, *m*-CF); 138.93 (d of multiplets, ¹*J*_{CF} = 246 Hz, *p*-CF); 146.62 (*C*_{ipso}, NMe₂*Ph*); 149.17 (d of multiplets, ¹*J*_{CF} = 242 Hz, *o*-CF). ²⁹Si{¹H} NMR (99.3 MHz, 298 K, C₆D₆): -66.26 (2Si); -65.15 (1Si); -65.08 (1Si); -64.93 (2Si); -64.55 (1Si); 9.26 (1Si, *Si*Me₃).

Reaction of 1 with $[Ph_3C]^+[B(C_6F_5)_4]^-$ to Give Impure $[Cp^*{(c (C_5H_9)_7Si_8O_{12}O_{2}Ti]^+[B(C_6F_5)_4]^-$ (9). A solution of 7 (0.426 g, 0.21 mmol) in 5.0 mL of toluene was added under an argon atmosphere to solid $[Ph_3C]^+[B(C_6F_5)_4]^-$ (0.184 g, 0.20 mmol), and the mixture was stirred for 5 h. All volatiles were distilled off under vacuum, and the red-brown oily residue was extracted repeatedly with 20 mL of hexane to collect a low-soluble redbrown oil (a remaining brown oily solid residue insoluble in hexane was discarded). Evaporation of combined extracts afforded an oil, which, upon warming to ca. 40 °C, suddenly released the solvent, forming a solid foam. The foam disappeared after condensing hexane vapor on it to form an oily solid sticking to the ampule walls. The hexane extract was separated, and the residue dried under vacuum, forming a foam again. The solid product was then mechanically scraped from the walls and collected. Yield: 0.34 g (63%).

Data for **9** are as follows. ¹H NMR (298 K, C_6D_6): 1.08–1.36 (m, 14H, *CH*, cyclopentyl), 1.44–2.06 (m, 112H, *CH*₂, cyclopentyl), 2.03 (s, 15H, C_5Me_5). IR (ATR Si, cm⁻¹): 2949 (s), 2913 (w, sh), 2866 (m), 1643 (vw), 1512 (w), 1463 (s), 1275 (vw), 1246 (w), 1103 (vs), 1028 (m), 1001 (m), 978 (s), 934 (m, sh), 917 (s, b), 775 (w), 755 (w), 700 (w), 682 (w), 660 (w).

Reaction of 9 with PhNMe₂ to Give 7. Solid **9** (0.18 g) was dissolved in toluene (3.0 mL), and PhNMe₂ (0.3 mL) was added. After stirring for 30 min at ambient temperature all volatiles

were evaporated under vacuum, at 2×10^{-4} Torr and 60 °C. A dark orange solid was dissolved in C₆D₆. The ¹H and ¹⁹F NMR spectra of the product identified compound 7 to be by far the main component (>85%).

Reaction of 2 with $[Ph_3C]^+[B(C_6F_5)_4]^-$ to Give Impure $[Cp^*{(c C_5H_9$ ₇Si₇O₉(OSiMe₃)O₂{Ti}⁺[B(C₆F₅)₄]⁻ (10). A solution of 2 in toluene (0.21 mmol in 3.0 mL) was added to a suspension of solid $[Ph_3C]^+[B(C_6F_5)_4]^-$ (0.19 g, 0.20 mmol) in 10 mL of toluene, and the mixture was stirred at room temperature for 3 h to give an orange-brown solution. All volatiles were distilled off under vacuum, and the red-brown oily residue was extracted repeatedly with 20 mL of hexane to collect a red-brown oil poorly soluble in hexane (a remaining brown, oily solid residue insoluble in hexane was discarded). The hexane from combined extracts was partly evaporated under vacuum, and the mother liquor (10 mL) was separated from an orange-brown oily residue. The hexane mother liquor contained, according to IR spectra, mainly Ph3CMe. The oily residue was dried under a vacuum of 2×10^{-4} Torr, at 60 °C, to give a brown solid containing, according to ¹H NMR, mainly a mixture of isomers 10a and 10b in the ratio 2:1. The presence of minor singlet signals in the ¹H NMR spectra close to resonances for C_5Me_5 and $SiMe_3$ indicated the presence of impurities, which were not identified. Yield: 0.30 g (83%).

Data for **10** are as follows. ¹H NMR (298 K, C_6D_6) **10a**: 0.19 (s, 9H, Si Me_3), 0.94–1.14 (m, 7H, CH, cyclopentyl), 1.42–2.02 (m, 56H, CH₂, cyclopentyl), 1.83 (s, 15H, C_5Me_5). **10b**: 0.09 (br s, $\nu_{1/2}$ = 8.5 Hz, 9H, Si Me_3), 0.94–1.14 (m, 7H, CH, cyclopentyl), 1.42–2.02 m, 56H, CH₂, cyclopentyl), 1.94 (s, 15H, C_5Me_5). IR (ATR Si, cm⁻¹): 2951 (s), 2913 (w, sh), 2865 (m), 1642 (w), 1512 (m), 1463 (s), 1410 (vw), 1382 (w), 1275 (w), 1254 (w), 1114 (s, sh), 1085 (vs), 1038 (m), 978 (vs), 951 (s, b), 909 (m, sh), 860 (m, b), 774 (m), 755 (m), 727 (w), 683 (m), 661 (m).

Reaction of 10 with PhNMe₂ to Give 8. Solid **10** (0.14 g) was dissolved in toluene (3.0 mL), and *N*,*N*-dimethylaniline (0.3 mL) was added. After stirring for 30 min at ambient temperature all volatiles were evaporated under vacuum, at 2×10^{-4} Torr at 60 °C. A dark orange solid was dissolved in C₆D₆. The ¹H and ¹⁹F NMR spectra of the product revealed that a mixture of compounds **8a** and **8b** in about 2:1 abundance formed the main component (> 80%).

Styrene Polymerization. The reaction components were dosed to the evacuated reactor equipped with a magnetic stirring bar in the order styrene (2.0 mL), the titanium precursor (Cp*Ti- $(O^{t}Bu)_{2}Me$, 2, or 1, 10 μ mol in 2.0 mL of toluene), B(C₆F₅)₃ (10 µmol in 2.0 mL of toluene), and AlMe₃ (20 µmol in 2.0 mL of toluene). The polymerization mixture was cooled to about 5 °C and sealed off with a flame. The reactor was immersed into a thermostated water bath, and its contents were rapidly stirred. After 30 min the reactor was cooled to 20 °C and opened to air, and the contents were poured into ethanol (50 mL) acidified with aqueous HCl. The reactor was washed with ethanol/HCl, and washings with the solid polymer were combined with the main product part. After stirring for 1 h the polymer was filtered off, washed repeatedly with ethanol, and dried in a vacuum oven at 120 °C to constant weight. The syndiotacticity was determined by polymer extraction with boiling 2-butanone for 6 h followed by drying of the residue until constant weight. The melting temperature, T_m, was determined by DSC analysis, and $M_{\rm w}$ and $M_{\rm p}$ were determined by the GPC method. In preliminary polymerizations with MAO the above titanium precursors were activated with 1.66 mL of a toluene solution of MAO ([Al] = 1.51 M).

Reactions of 1, 2, and [Cp*Ti(O'Bu)_2Me] with 2 equiv of AlMe₃. A solution of titanium compound in toluene (50 μ mol in 1.0 mL) was mixed with a solution of AlMe₃ in toluene (100 μ mol in 1.0 mL) in a sealed ampule, and this was heated to 60 °C in a water bath for 1 h. Then all volatiles including AlMe₃ and methylaluminum *tert*-butoxides were evaporated on a vacuum line at 60 °C, then the very low-volatile products were condensed

Table 5. Crystal Data and Structure Refinement for Compound 4a

	r
empirical formula	C _{68,50} H _{93,50} BF ₁₅ O ₁₂ Si ₈ Ti
fw	1677.36
temperature	150(2) K
cryst syst, space group	triclinic, P1 (No. 2)
unit cell dimens	a 14.5433(3) Å, α 104.1142(11)°
	$b 15.8531(3) \text{ Å}, \beta 92.3741(9)^{\circ}$
	$c 19.9883(4) \text{ Å}, \gamma 113.0560(11)^{\circ}$
volume	$4063.61(14) \text{ Å}^3$
Z, calcd density	2. 1.371 Mg/m^3
absorp coeff u	0.313 mm^{-1}
F(000)	1749
cryst size	$0.5 imes 0.3 imes 0.075 \text{ mm}^3$
$\theta_{\min}; \theta_{\max}$	2.03°; 27.49°
limiting indices	$-13 \le h \le 18, -20 \le k \le 20,$
e	$-25 \le l \le 25$
reflns collected/unique	68 319/18 362
	[R(int) = 0.0433]
completeness to $\theta = 27.49$	98.6%
parameters	952
goodness-of-fit on F^2	1.042
final R indices $[I > 2\sigma(I)]$	R1 = 0.0535, wR2 = 0.1382
<i>R</i> indices (all data)	R1 = 0.1203, wR2 = 0.1624
largest diff peak and hole	$0.877 \text{ and } -0.593 \text{ e } \text{\AA}^3$

to activated charcoal cooled with liquid nitrogen. The residue (yellow solid for **2**, yellow oil for **1** or for $Cp^*Ti(O'Bu)_2Me$) was dissolved in 1.4 mL of C_6D_6 or C_7D_8 , and the solution was poured into an NMR sample tube, sealed with flame, and analyzed by ¹H and ¹³C NMR spectroscopy.

The 1/2AlMe₃ system yielded Cp*TiMe₃ (Ti*Me* $\delta_{\rm H}/\delta_{\rm C}$ 1.00/ 61.16 ppm)²⁷ and most probably Cp*Ti(SIPOSS)Me₂, with Ti*Me* $\delta_{\rm H}/\delta_{\rm C}$ 0.76/55.93 ppm, C₅*Me*₅ $\delta_{\rm H}/\delta_{\rm C}$ 1.86/11.67 ppm, and C₅Me₅ at $\delta_{\rm C}$ 123.05 ppm. Integrals for Ti*Me* resonances indicated contents of these compounds as 32% and 60%, whereas other minor signals observed using qHSQC indicated the presence of trace amounts of 1 and two other products in the total amount of 8%. In the Al*Me* resonance range -0.3 to 0.4 ppm, the characteristic signals of the Al*Me*₂ group at $\delta_{\rm H}/\delta_{\rm C}$ -0.14/-7.10 ppm for (SIPOSSAlMe₂)_n were observed³³ besides other signals at $\delta_{\rm H}/\delta_{\rm C}$ -0.29/-13.05, -0.24/-8.67, 0.17/0.50, and 0.38/0.50, which were not identified.

The 2/2AlMe₃ system afforded a wide range of products, where only signals of Cp*TiMe₃ and trace amounts of **2** were identified. The Cp*TiMe₃ content of 14% was calculated from the integral of the peak at $\delta_{\rm H}$ 1.00 ppm with respect to the sum of integrals in the TiMe range 0.58–0.92 ppm.

The Cp*Ti(O'Bu)₂Me/2AlMe₃ system afforded the following titanium compounds: Cp*Ti(O'Bu)Me₂ ($\delta_{\rm H}$ 1.44 (TiMe₂) and 1.82 (C₅Me₅) ppm in integral ratio 6:15) (70%) and Cp*Ti-(O'Bu)₂Me ($\delta_{\rm H}$ 1.30 (TiMe) and 1.94 (C₅Me₅) ppm) (30%).¹¹ The presence of Cp*TiMe₃ was observed after this system was heated to 100 °C for 1 h: Cp*TiMe₃ 5%, (Cp*Ti(O'Bu)Me₂ 81%, and Cp*Ti(O'Bu)₂Me 14%.

X-ray Crystallography. Compound **4a** was recrystallized from hexane at room temperature to give thin orange plates. These were transferred to a glovebag in a saturated hexane solution under argon, immersed in Nujol oil, and mounted onto a measuring rod of a diffractometer under a stream of cooled nitrogen. Diffraction data were collected on a Nonius KappaCCD diffractometer (Mo K α radiation, $\lambda = 0.71073$ Å) at 150(2) K and processed by the HKL program package.³⁴ The phase problem was solved by direct methods (SIR97),³⁵ followed by consecutive Fourier syntheses, and refined by

⁽³³⁾ Skowronska-Ptasinska, M. D.; Duchateau, R.; van Santen, R. A.; Yap, G. P. A. *Organometallics* **2001**, *20*, 3519–3530.

⁽³⁴⁾ Otwinowski, Z.; Minor, W. *HKL Denzo* and *Scalepack* program package by Nonius. For a reference, see: Otwinowski, Z.; Minor, W. *Methods Enzymol.* **1997**, *276*, 307–326.

⁽³⁵⁾ Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Polidori, G. J. Appl. Crystallogr. **1994**, *27*, 435–436.

full-matrix least-squares on F^2 (SHELXL-97).³⁶ Relevant crystallographic data are given in Table 5. All non-hydrogen atoms were refined anisotropically except those with partial occupancy factors. The hydrogen atoms were recalculated into idealized positions (riding model) and assigned temperature factors H_{iso} -(H) = (1.2–1.5) U_{eq} (pivot atom), except for the hydrogen atoms on bridging methyl carbon atom C(49). These were found on difference Fourier maps and refined isotropically without any restraints. Several cyclopentyl moieties were disordered into two positions with partial occupancy; the atoms involved in this disorder were refined isotropically. The solvating hexane molecule occupying the center of symmetry in the unit cell was disordered due to flexibility of its linear chain. Moreover, the low electron densities of corresponding maxima on the Fourier

(36) Sheldrick, G. M. SHELXL97, Program for Crystal Structure Refinement from Diffraction Data; University of Göttingen: Göttingen, 1997.

map indicate only the partial presence of the whole solvating molecule in the unit cell. The hexane was partly released from the crystal during its transfer on the measuring rod.

Acknowledgment. This research was supported by the Academy of Sciences of the Czech Republic (Grant No. KAN100400701) and the Ministry of Education, Youth and Sports (Project No. LC06070). I.C. thanks MSM-0021620857.

Supporting Information Available: CIF file for the structure 4a (XRAY.CIF). Supporting Information and PLATON drawing at 30% probability for structure 4a, IR (ATR-Si) spectra of 1, 3, 7, and 9 (Figure 1); 2, 4a, 8, and 10 (Figure 2), ¹H NMR spectra of reacting 1 with the solid $[C_6H_5NHMe_2]^+[B(C_6F_5)_4]^-$ to give 7, and ¹⁹F NMR spectra of 8 at 25–95 °C. This material is available free of charge via the Internet at http://pubs.acs.org.