

SYNTHESIS AND STRUCTURE OF PERMETHYLCYCLOPENTADIENYL-TITANIUM DIISOPROPOXIDE ZWITTERIONIC COMPLEX

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Half-sandwich pentamethylcyclopentadienyltitanium chloroisopropoxides [Ti(η^5 -C₅Me₅)-Ti(O*i*-Pr)_{*n*}Cl_{3-*n*}] (*n* = 1 (**1**) or 2 (**2**)) and methylisopropoxides [Ti(η^5 -C₅Me₅)-Ti(O*i*-Pr)_{*n*}Me_{3-*n*}] (*n* = 1 (**3**) or 2 (**4**)) were prepared and characterized by spectroscopic methods, and compound **1** by single crystal X-ray diffraction analysis. Compounds **3** and **4** were reacted with an equimolar quantity of B(C₆F₅)₃, however, only compound **4** afforded a crystalline product of limited stability at ambient temperature. Its single crystal X-ray diffraction analysis revealed that it is the zwitterionic complex [(η^5 -C₅Me₅)-Ti(O*i*-Pr)₂]⁺[(μ -Me)B(C₆F₅)₃]⁻ (**5**) and its crystal structure is very similar to the recently reported *tert*-butoxy complex [(η^5 -C₅Me₅)-Ti(O*t*-Bu)₂]⁺[(μ -Me)B(C₆F₅)₃]⁻ (**6**). The ¹H, ¹³C, and ¹⁹F NMR spectra in C₆D₆ solution also showed the features analogous to those of **6**. 1D NOESY experiments proved a close through space interaction of irradiated C₅Me₅ or OCHMe₂ protons with the bridging Ti...Me-B group. The NMR data indicate the inner sphere ion pair structure of **5** in C₆D₆, like for **6**. The crystal structure geometry of the C-H bonds of the Ti...Me-B group fulfils conditions for their agostic interaction with the titanium centre. Although structurally similar to **6**, compound **5** is less thermally stable apparently due to a lower bulkiness of O*i*-Pr group compared to that of O*t*-Bu group.

Keywords: Titanium; Half-sandwich; Titanium isopropoxide; Tris(pentafluorophenyl)borane; Zwitterionic complex; Cationic titanium complex; NMR spectra; Crystal structure.

The most commonly used catalysts for polymerization of styrene to syndiotactic polystyrene are based on a combination of various half-sandwich titanium trihalides or alkoxides with methylalumoxane (MAO)¹. The systems are convenient for industrial application², however, due to poorly defined

MAO they do not allow the detail investigation of the catalytic center³. Successful investigation of single site polymerization catalysts based on early transition metal metallocene dialkyls – tris(pentafluorophenyl)borane⁴ raised the wave of interest in analogous half-sandwich catalysts. The catalysts formed from $[(\eta^5\text{-C}_5\text{Me}_5)\text{TiMe}_3]$ and $[\text{B}(\text{C}_6\text{F}_5)_3]$, where the formation of an ionic pair $[(\eta^5\text{-C}_5\text{Me}_5)\text{TiMe}_2]^+[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$ was anticipated, appeared to be highly active for polymerization of ethene to a high-molecular polymer, and styrene to syn-PS or atactic polystyrene (a-PS) in dependence on the solvent nature^{5a}. Whereas the formation of syn-PS in aromatic solvents was compatible with stereo-directed polymerization on ion-pair single-site catalysts, the polymerization to a-PS proceeding in polar solvents like CH_2Cl_2 or $1,2\text{-C}_2\text{H}_4\text{Cl}_2$ pointed to a free carbocationic catalysis^{5b}. The high activity of the single-site systems was, however, conditioned by the presence of the monomer when the catalyst components were reacting. Mixing of the catalyst components in the absence of olefins resulted in marginal polymerization activity. Indeed, NMR tube experiments with mixing the components at low temperature gave evidence for the formation of the $[(\eta^5\text{-C}_5\text{Me}_5)\text{-TiMe}_2]^+[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$ complex and its rapid decomposition at room temperature⁶. Modification of the titanium component by introduction of an alkoxy or aryloxy group instead of one or two methyls gave generally less active catalysts because of decreased electrophilicity of the metal due to a π -electron donation of the alkoxy oxygen lone electron pairs to the empty d-orbitals^{7a}. An attempt to suppress this π -electron donation by using perfluoroaryl or perfluoroaryloxy ligands resulted in identification of cationic complexes $[(\eta^5\text{-C}_5\text{Me}_5)\text{TiMeR}]^+[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$ where $\text{R} = \text{C}_6\text{F}_5$ or OC_6F_5 at low temperature by NMR spectra. Unfortunately, the complexes could not be isolated because of their low thermal stability. The compound made from $[(\eta^5\text{-C}_5\text{Me}_5)\text{TiMe}(\text{OC}_6\text{F}_5)_2]$ at $-50\text{ }^\circ\text{C}$ in CD_2Cl_2 was according to NMR spectra the ion pair $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ti}(\text{OC}_6\text{F}_5)_2]^+[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$ showing a free borate anion. However, the compound dissociated at only $-10\text{ }^\circ\text{C}$ to initial components^{7b}. Another catalyst precursor, the trialkylsiloxy complex $[(\eta^5\text{-C}_5\text{Me}_5)\text{TiMe}_2\text{OSiR}_3]$, where $\text{R} = 2\text{-(diphenylmethylsilyl)ethane-1-yl}$, gave rise to a cationic complex which had the half-life time of 2 days⁸. We have recently succeeded to prepare extremely thermally stable cationic complex $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ti}(\text{Ot-Bu})_2]^+[(\mu\text{-Me})\text{B}(\text{C}_6\text{F}_5)_3]^-$ (**6**) (Chart 1) from $[(\eta^5\text{-C}_5\text{Me}_5)\text{TiMe}(\text{Ot-Bu})_2]$ and $[\text{B}(\text{C}_6\text{F}_5)_3]$, however, the complex was no catalyst for ethene or styrene polymerization⁹.

Here we extend our studies to the synthesis of half-sandwich complexes $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ti}(\text{O}i\text{-Pr})\text{Me}_2]$ (**3**) and $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ti}(\text{O}i\text{-Pr})_2\text{Me}]$ (**4**), and the

formation of well-defined zwitterionic complex $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ti}(\text{O}i\text{-Pr})_2]^+ [(\mu\text{-Me})\text{B}(\text{C}_6\text{F}_5)_3]^-$ (**5**) from **4** and $[\text{B}(\text{C}_6\text{F}_5)_3]$.

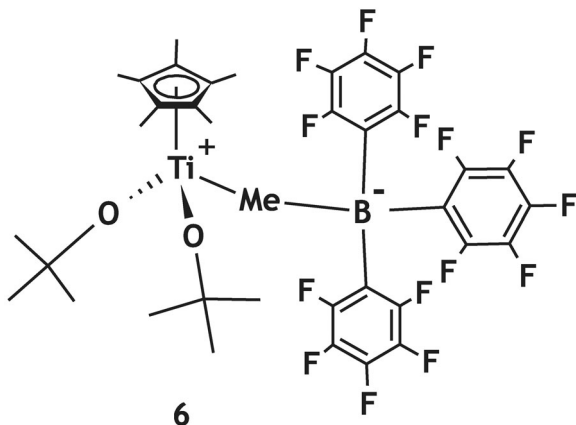
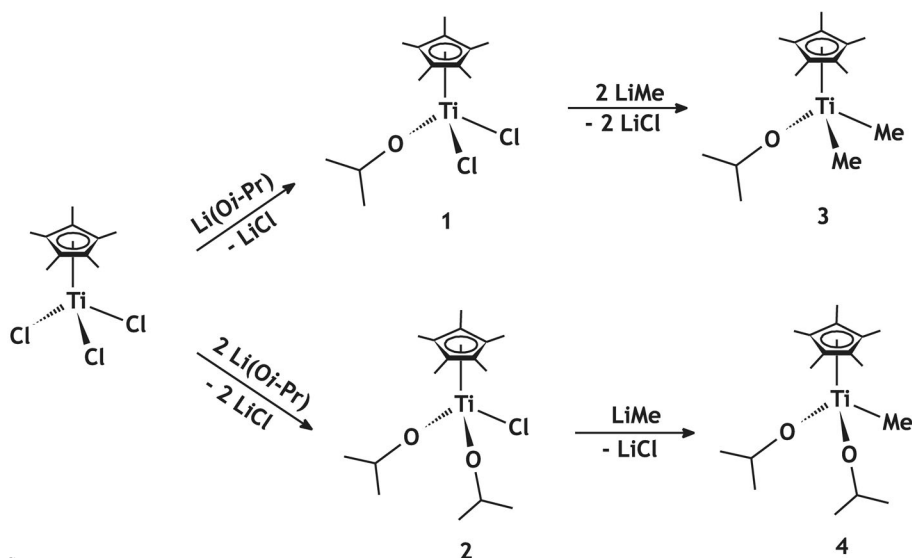


CHART 1

RESULTS AND DISCUSSION

The precursors for the formation of titanium half-sandwich cationic complexes $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ti}(\text{O}i\text{-Pr})\text{Me}_2]$ (**3**) and $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ti}(\text{O}i\text{-Pr})_2\text{Me}]$ (**4**) were obtained from commercial $[(\eta^5\text{-C}_5\text{Me}_5)\text{TiCl}_3]$ in two steps according to Scheme 1. Addition of one equivalent of $\text{Li}(\text{O}i\text{-Pr})$ in hexane afforded the solid $[(\eta^5\text{-C}_5\text{Me}_5)\text{TiCl}_2(\text{O}i\text{-Pr})]$ (**1**) and two equivalents the oily $[(\eta^5\text{-C}_5\text{Me}_5)\text{-TiCl}(\text{O}i\text{-Pr})_2]$ (**2**). Compound **1** was purified by crystallization from hexane and compound **2** by vacuum distillation. Compounds **1** and **2** were reacted with two or one equivalents of LiMe in diethyl ether to give yellowish oils of **3** and **4**. These were purified by vacuum distillation. All compounds were characterized by ^1H and ^{13}C NMR and IR spectra, and compound **1** by single-crystal X-ray diffraction analysis (see below). The ^1H and ^{13}C NMR spectra for **1**–**4** are gathered in Table I. For pairs of compounds **1/2** the most profound shifts to lower magnetic field are observed for δ_{C} of the cyclopentadienyl sp^2 carbons C_5Me_5 and the tertiary carbon of isopropoxy group OCHMe_2 as a result of an decreased electrophilicity of the central metal due to the replacement of Cl with *Oi-Pr*. For pair of compounds **3/4** δ_{C} of TiMe carbon atom indicates that the *Oi-Pr* group is a stronger electron donor than the Me group.

Addition of one equivalent of $[\text{B}(\text{C}_6\text{F}_5)_3]$ to **4** in toluene afforded a bright orange solution of the zwitterionic complex $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ti}(\text{O}i\text{-Pr})_2]^+ [(\mu\text{-Me})\text{B}(\text{C}_6\text{F}_5)_3]^-$.



$[(\mu\text{-Me})\text{B}(\text{C}_6\text{F}_5)_3]^-$ (**5**) as virtually the only product (Eq. (1)). Orange plates of **5** were obtained by cooling the toluene solution to $-18\text{ }^\circ\text{C}$ for one week. The crystalline **5** was stable at $-18\text{ }^\circ\text{C}$, however, it decomposed after several days at room temperature. Therefore, the crystals for X-ray diffraction analysis, infrared and ^1H , ^{13}C and ^{19}F NMR spectra were warmed to ambient temperature for necessarily not more than 2 h. The solution of **5** in C_6D_6 when kept in dark was stable for one week, and after a month only ca. 20% of it decomposed. The ^1H , ^{13}C and ^{19}F NMR spectra of **5** were very similar to those of complex $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ti}(\text{O}t\text{-Bu})_2]^+[(\mu\text{-Me})\text{B}(\text{C}_6\text{F}_5)_3]^-$ (**6**) (see Table I)⁹.

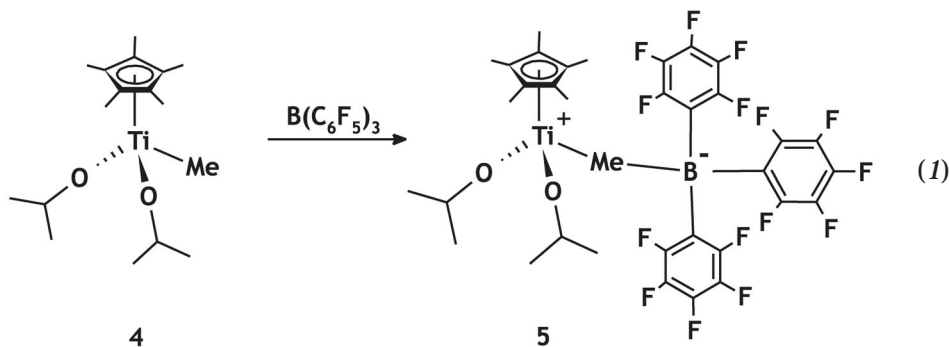


TABLE I
 ^1H and ^{13}C NMR spectra of precursors **1–4** and zwitterionic complexes **5** and **6** (δ , ppm)

Compd.	^1H NMR				^{13}C NMR				
	OCHMe ₂	C ₅ Me ₅	OCHMe ₂	TiMe	C ₅ Me ₅	OCHMe ₂	OCHMe ₂	C ₅ Me ₅	TiMe
1	1.18	1.95	4.68	–	12.61	24.87	82.53	130.44	–
2	1.15, 1.16 ^a	1.99	4.72	–	11.91	25.76, 25.8 ^a	78.30	125.18	–
3	1.32	1.81	4.68	0.42	11.44	26.50	76.25	120.70	47.83
4	1.18	1.92	4.60	0.52	11.35	26.56, 26.70 ^a	75.29	119.78	37.70
5	0.83	1.59	4.48	0.53 ^b	11.43	25.13	82.48	130.29	b
6	1.01 ^c	1.63	–	0.45 ^b	12.2	31.6 ^c	90.2 ^c	130.7	b

^a Methyl groups in isopropoxy groups are nonequivalent. ^b Ti...Me-B group (δ_{C} not observed). ^c The data concerns OCMe₃ group.

A broad signal in ^1H NMR spectrum of **5** observed at 0.53 ppm can be assigned to a bridging $\text{Ti}\cdots\text{Me}-\text{B}$ moiety, similarly to **6**. However, the corresponding δ_{C} resonance of the $\text{Ti}\cdots\text{Me}-\text{B}$ moiety was not observable in either of these zwitterionic complexes⁹. This assignment for **5** was supported by 1D NOESY experiments using irradiation of C_5Me_5 or OCHMe_2 protons. The both of them showed a close through space interaction with the $\text{Ti}\cdots\text{Me}-\text{B}$ group similarly as for **6**. Moreover, the ^{19}F NMR spectrum of **5** displayed the difference between the *meta*- and *para*-fluorine resonance $\Delta\delta(m,p\text{-F}) = 4.9$ ppm, only marginally different from the value of $\Delta\delta(m,p\text{-F}) = 5.00$ ppm found for **6** (ref.⁹). These values are indicative for a strong cation-anion association¹⁰ featuring a model of inner sphere ion pair (ISIP)¹¹.

The EI-MS spectrum of **5** occurred only at 270 °C showing free $[\text{B}(\text{C}_6\text{F}_5)_3]$ and the C_5Me_5 ion and their fragment ions. The infrared spectrum of **5** confirmed the presence of both titanium and boron components, however, it is too complex to identify features belonging to the bridging $\text{Ti}\cdots\text{Me}-\text{B}$ group. Thus, the most valuable information on the structure of **5** was obtained from X-ray single crystal analysis (see below). Compound **5** in saturated toluene solution did not catalyze the polymerization of styrene at 50 °C.

Addition of one equivalent of $[\text{B}(\text{C}_6\text{F}_5)_3]$ to **3** in toluene resulted in the formation of a further untreatable brown oil, apparently a decomposition product of a transiently formed cationic titanium complex.

Crystal Structure of Compound **1**

The asymmetrical molecule of **1** is crystallizing in monoclinic space group $P2_1/c$. The PLATON drawing of **1** is shown in Fig. 1, important molecular parameters are listed in Table II. Large anisotropic thermal parameters for carbon atoms of the pentamethylcyclopentadienyl ligand (see Fig. 1) indicate some rotational mobility of the ligand with very little intra- and/or intermolecular steric interactions. The effect of isopropoxy group can be recognized from comparison of molecular parameters of **1** with those of cyclopentadienyltitanium trichloro compounds. In the absence of crystal structure of $[(\eta^5\text{-C}_5\text{Me}_5)\text{TiCl}_3]$, the crystal data are known for the closest compounds $[(\eta^5\text{-C}_5\text{Me}_4\text{Et})\text{TiCl}_3]$ (**7**)¹², $[(\eta^5\text{-C}_5\text{Me}_4\text{H})\text{TiCl}_3]$ (**8**)¹³, $[(\eta^5\text{-C}_5\text{Me}_4\text{-}(\text{CH}_2)_3\text{CH}=\text{CH}_2)\text{TiCl}_3]$ (**9**)¹⁴ or $[(\eta^5\text{-C}_5\text{Me}_4\text{-}t\text{-Bu})\text{TiCl}_3]$ (**10**)¹⁵. The isopropoxy complex **1** does not differ from these compounds in the Ti-Cg (Cg - centroid of the cyclopentadienyl ring) distance, however, the Ti-Cl bonds in **1** are longer by ca. 0.03 Å. The piano stool configuration of **1** is distorted, showing a larger Cg-Ti-O angle ($118.41(14)^\circ$) compared to the Cg-Ti-Cl

TABLE II
Selected bond lengths (in Å) and bond angles (in °) for compound **1**

Bond distances			
Ti-Cg ^a	2.035(3)	Ti-O	1.738(3)
Ti-Cl(1)	2.2738(14)	Ti-Cl(2)	2.2761(14)
Ti-C(1)	2.381(5)	Ti-C(2)	2.365(5)
Ti-C(3)	2.322(4)	Ti-C(4)	2.327(4)
Ti-C(5)	2.358(5)	C _{ring} -C _{ring} (Cp)	1.362–1.416(9)
C _{ring} -C _{Me}	1.496–1.514(9)	O-C(11)	1.407(6)
C(11)-C(12)	1.439(9)	C(11)-C(13)	1.444(9)
Bond angles			
Cg-Ti-O	118.41(14)	Cg-Ti-Cl(1)	114.43(9)
Cg-Ti-Cl(2)	114.81(9)	Cl(1)-Ti-Cl(2)	101.60(7)
O-Ti-Cl(1)	103.81(9)	O-Ti-Cl(2)	102.11(12)
Ti-O-C(11)	168.4(4)	C(12)-C(11)-C(13)	117.3(6)

^a Cg denotes the centroid of C(1–5) cyclopentadienyl ring.

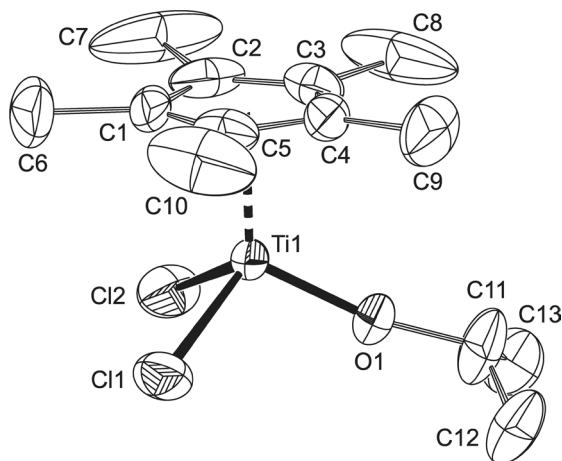


FIG. 1
PLATON drawing of compound **1** at the 30% probability level with atom labeling scheme. Hydrogens are omitted for clarity

angles ($114.43(9)^\circ$ and $114.81(9)^\circ$). This distortion was found to be even larger in the similar $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ti}(\text{O}-2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)\text{Cl}_2]$ phenoxy compound showing the $\text{C}_g\text{-Ti-O}$ angle 120.5° and $\text{C}_g\text{-Ti-Cl}$ angles 111.1 and 116.1° . The steric bulkiness of the phenoxy ligand, or its electron attractive effect, accounts for a longer Ti-O bond distance ($1.772(3)$ Å), a shorter O-C length ($1.367(5)$ Å), and a larger Ti-O-C angle ($173.0(3)^\circ$, ref.¹⁶) (cf. data for **1** in Table II). The geometric parameters for the isopropoxytitanium group in **1** fall into the range of data found for terminal isopropoxy groups on the surface of the cluster $[\text{Ti}_3(\mu_3\text{-O})(\mu\text{-OOCPh}_3)_2(\mu\text{-O}i\text{-Pr})_3(\text{O}i\text{-Pr})_5]$ ¹⁷.

Crystal Structure of Compound **5**

The molecule of **5** (Fig. 2) is in most respects an analogue of the first thermally stable half-sandwich titanium complex **6**, however, geometric parameters of **5** (Table III) deviate in many cases from those of **6**⁹. Since the precision of structural parameter determination in both compounds is similar

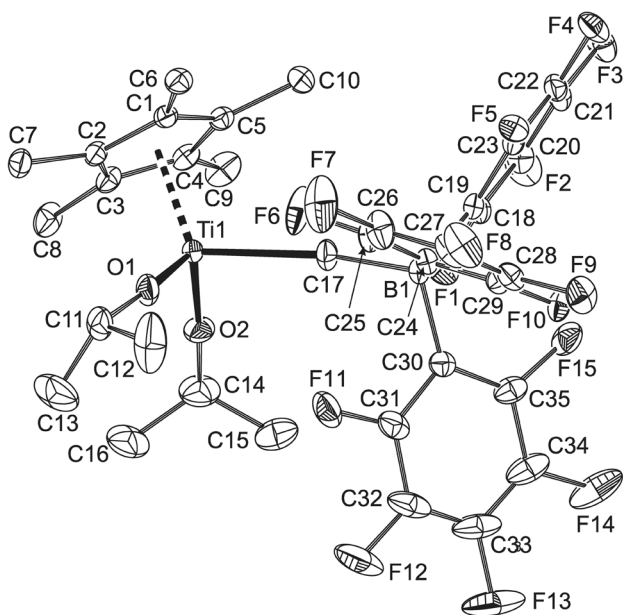


FIG. 2

PLATON drawing of compound **5** at the 30% probability level with atom labeling scheme. Hydrogens are omitted for clarity

(**6**: $R = 0.0361$, **5**: $R = 0.0437$) the comparison of geometric parameters is reliable. Replacement of *tert*-butoxy groups in **6** with isopropoxy groups resulted in discernible shortening of the Ti–Cg distance (2.0296(10) versus 2.0464(7) Å) and Ti–C(17) bond length (2.400(2) versus 2.436(1) Å) whereas the Ti–O bond lengths differed only negligibly. The methyl carbon atoms

TABLE III
Selected bond lengths (in Å) and bond angles (in °) for compound **5**

Bond distances			
Ti–Cg ^a	2.0296(10)	Ti–C(1)	2.3598(18)
Ti–C(2)	2.3289(18)	Ti–C(3)	2.3357(19)
Ti–C(4)	2.390(2)	Ti–C(5)	2.3964(19)
C _{ring} –C _{ring} (Cp)	1.416–1.431(3)	C _{ring} –C _{Me}	1.496–1.504(3)
Ti–O(1)	1.7567(15)	Ti–O(2)	1.7604(15)
Ti–C(17)	2.400(2)	B–C(17)	1.668(3)
B–C(18)	1.649(3)	B–C(24)	1.646(3)
B–C(30)	1.655(3)	O(1)–C(11)	1.426(3)
O(2)–C(4)	1.404(3)	C–F(range) ^b	1.337–1.355(3)
C–C _{Me} (O ⁱ Pr)	1.489–1.506(4)	C–C(Ph) ^b	1.363–1.389(3)
C(17)–H(range)	0.98–1.02(3)	Ti–H(17A)	2.30(2)
Ti–H(17B)	2.19(3)	Ti–H(17C)	2.41(2)
Bond angles			
Cg–Ti–O(1)	118.51(6)	Cg–Ti–O(2)	117.21(7)
Cg–Ti–C(11)	115.31(6)	O(1)–Ti–O(2)	106.57(8)
O(1)–Ti–C(17)	98.08(7)	O(2)–Ti–C(17)	97.68(8)
Ti–O(1)–C(11)	170.53(15)	Ti–O(2)–C(14)	176.56(18)
Ti–C(17)–B	172.05(16)	C(17)–B–C(18)	104.92(15)
C(17)–B–C(24)	111.88(16)	C(17)–B–C(30)	108.27(16)
C(18)–B–C(24)	112.32(15)	C(18)–B–C(30)	113.46(15)
C(24)–B–C(30)	106.04(15)	B–C(17)–H(17A)	106.0(14)
B–C(17)–H(17B)	107.7(14)	B–C(17)–H(17C)	108.8(14)
Ti–C(17)–H(17A)	72.0(14)	Ti–C(17)–H(17B)	66.1(16)
Ti–C(17)–H(17C)	78.8(14)		

^a Cg denotes the centroid of C(1–5) cyclopentadienyl ring. ^b Range of values for all the three C₆F₅ groups.

of the $\eta^5\text{-C}_5\text{Me}_5$ ligand were placed close to the least-squares plane of the cyclopentadienyl ring except C(10) showing the deviation of 0.123(4) Å apparently due to the close contact with one of the pentafluorophenyl groups (Fig. 2), the effect also observed for **6**. The isopropoxytitanium moieties are less bent at the oxygen atom than *tert*-butoxytitanium ones (average 173.5(2)° versus 168.0(1)°)⁹ which should indicate a larger oxygen π -donation into the Ti–O bond¹⁸, and the concerned O–C bonds are discernibly shorter (by average 0.025 Å)⁹. However, both the parameters can be affected by a higher steric congestion in the *tert*-butoxy complex **6**. The B–C(17) bond length is only slightly shorter than in **6** (1.668(3) Å versus 1.679(2) Å) and the angles B–C(17)–H on average do not differ. The bridging Ti...Me–B bonding shows a slightly larger Ti–C(17)–B angle (172.05(16)° versus 169.0(1)°. The nature of this bonding is to be a combination of electrostatic attraction with agostic bonding interaction of C–H bonds of the sp^3 -hybridized methyl carbon with the titanium atom. Although it could not be proved by NMR method because a broad signal for the borate methyl group did not allow us to determine the $^1J_{\text{CH}}$ coupling constants whose reduced value would be indicative for the presence of agostic interaction^{19,20a} the necessary chemical and steric conditions for its occurrence are fulfilled. The d^0 titanium atom has empty orbitals to interact with the $\sigma\text{-C-H}$ bonding orbital, the Ti–C and Ti–H distances are comparable, and angles Ti–C–H are smaller than 100° (ref.²⁰). A similar orientation of the bridging methyl group in zirconocene contact ion pairs $[\text{Me}_4\text{C}_2(\eta^5\text{-C}_5\text{H}_4)_2\text{ZrMe}]^+\text{MeB}(\text{C}_6\text{F}_5)_3^-$ (ref.^{21a}), *rac*- $[\text{Me}_2\text{Si}\{\eta^5\text{-C}_5\text{H}_2(2\text{-Me-4-}t\text{-Bu})\}_2\text{ZrMe}]^+[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$ (ref.^{21b}), and $[\{\eta^5\text{-C}_5\text{H}_3(1,2\text{-Me}_2)\}_2\text{ZrMe}]^+[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$ (ref.^{21c}) was previously found, the Zr–C and Zr–H distances to the bridging borate methyl being longer just due to a larger covalent radius of Zr with respect to Ti.

Conclusions

Zwitterionic isopropoxy complex **5** showed a lower thermal stability than the *tert*-butoxy complex **6** in spite of the fact that its important bonds were found shorter in the solid state. The lower stability of **5** is to be sought in a lower steric congestion due to the replacement of *tert*-butoxy with isopropoxy groups and/or in the presence of reactive hydrogen atoms in the isopropoxy groups. Both complexes **5** and **6** do not catalyze the polymerization of olefins apparently due to the lack of free Ti–C bond moiety.

EXPERIMENTAL

General Comments and Methods

Reactions leading to permethylocyclopentadienyltitanium methylisopropoxides **3** and **4** were carried out under nitrogen or argon atmosphere. Further purification of the products by vacuum distillation and/or crystallization was performed in all-sealed vacuum systems using magnetically breakable seals. The synthesis and isolation of cationic complexes was performed in vacuum systems only. Crystals of **1** and **5** for EI-MS measurements and melting point determinations were placed into glass capillaries in a glovebox Labmaster 130 (mBraun) under purified nitrogen (concentrations of oxygen and water were lower than 2.0 ppm). ^1H (299.98 MHz), ^{13}C (75.44 MHz), and ^{19}F (282.22 MHz) NMR spectra were recorded on a Varian Mercury 300 spectrometer at 298 K if not noticed otherwise. Chemical shifts (δ , ppm) are given relative to the solvent signal (C_6D_6 : δ_{H} 7.15, δ_{C} 128.00). EI-MS spectra were obtained on a VG-7070E mass spectrometer at 70 eV. Crystalline or liquid samples in sealed capillaries were opened and inserted into the direct inlet under argon. The spectra are represented by the peaks of relative abundance higher than 7% and by important peaks of lower intensity. Samples of **1** and **5** in KBr pellets were prepared in a glovebox Labmaster 130 (mBraun) and their IR spectra were recorded in an air-protecting cuvette on a Nicolet Avatar FT-IR spectrometer in the range of 400–4000 cm^{-1} . IR ATR spectra were measured on a Nicolet 380 FT-IR spectrometer using a silicon crystal under argon. The EI-MS samples of **1** and **2** were completely evaporated without changing the fragmentation pattern; this proves the uniformity of the compounds. Furthermore, crystal structures of **1** and **5** were determined by X-ray diffraction analysis.

Chemicals

Solvents tetrahydrofuran (THF), hexane, methyl *tert*-butyl ether (MTBE) and toluene were dried by refluxing over LiAlH_4 and stored as solutions of dimeric titanocene $[(\mu-\eta^5:\eta^5\text{-C}_{10}\text{H}_8)-(\mu\text{-H})_2\{\text{Ti}(\eta^5\text{-C}_5\text{H}_5)_2\}]_2$ (ref.²²). Methylolithium (LiMe) 1.6 M in diethyl ether (Aldrich) and isopropoxyolithium ($\text{Li}(\text{O}i\text{-Pr})$) 1.0 M in hexanes (Aldrich) were dosed by syringe under argon. $[(\eta^5\text{-C}_5\text{Me}_5)\text{TiCl}_3]$ was purchased from Strem Chemicals and used as such. $\text{B}(\text{C}_6\text{F}_5)_3$ (Strem Chemicals) was analyzed by IR spectroscopy (ATR method) for purity, and only pure samples were used for the generation of zwitterionic complexes.

Synthesis of $[(\eta^5\text{-C}_5\text{Me}_5)\text{TiCl}_2(\text{O}i\text{-Pr})]$ (**1**)

$[(\eta^5\text{-C}_5\text{Me}_5)\text{TiCl}_3]$ (2.26 g, 7.8 mmol) was dissolved in THF (40 ml), and 1.0 M solution of $\text{Li}(\text{O}i\text{-Pr})$ in hexanes (7.9 ml, 7.9 mmol) was slowly added under stirring and cooling with ice bath. After stirring at room temperature for another 2 h all volatiles were evaporated in vacuum and the residue was extracted with hexane. Orange crystals of **1** were obtained by slow distillation of the solvent at room temperature. Yield of **1** was 2.0 g (85%). M.p. 115 °C. ^1H NMR (C_6D_6): 1.18 (d, $^3J_{\text{HH}} = 6.1$, 6 H, CHMe_2); 1.95 (s, 15 H, C_5Me_5); 4.68 (septuplet, $^3J_{\text{HH}} = 6.1$, 1 H, CHMe_2). ^{13}C $\{^1\text{H}\}$ NMR (C_6D_6): 12.61 (C_5Me_5); 24.87 (CHMe_2); 82.53 (CHMe_2); 130.44 (C_5Me_5). EI-MS (direct inlet), m/z (%): 314 (9), 312 (M^{+} ; 12), 235 (7), 297 ($[\text{M} - \text{Me}]^+$; 7), 276 ($[\text{M} - \text{HCl}]^+$; 11), 256 (9), 255 (14), 254 ($[\text{M} - \text{C}_3\text{H}_6\text{O}]^+$; 45), 253 (30), 252 ($[\text{M} - \text{C}_3\text{H}_8\text{O}]^+$; 44), 251 (8), 236 (11), 235 (7), 234 ($[\text{M} - \text{Cl} - \text{C}_3\text{H}_7]^+$; 21), 219 (8), 218 (14), 217 ($[\text{M} - \text{HCl} - \text{C}_3\text{H}_7\text{O}]^+$; 16), 216 (10), 215 (6), 213 (9), 136 (9), 135 ($[\text{C}_5\text{Me}_5]^+$; 100),

120 (10), 119 (33), 105 (15), 91 (13). IR (KBr): 2981 (s), 2971 (s, sh), 2922 (s), 2888 (m, sh), 2865 (m), 1493 (m, sh), 1484 (m), 1460 (m, sh), 1445 (m), 1431 (m), 1379 (s), 1365 (m), 1330 (m), 1261 (w), 1168 (m), 1132 (s, sh), 1113 (vs), 1072 (w), 1016 (vs), 864 (m), 805 (w), 761 (m), 610 (m), 452 (s), 409 (m).

Synthesis of $[(\eta^5\text{-C}_5\text{Me}_5)\text{TiCl}(\text{O}i\text{-Pr})_2]$ (**2**)

Compound **2** was prepared analogously to **1** from $[(\eta^5\text{-C}_5\text{Me}_5)\text{TiCl}_3]$ (2.08 g, 7.15 mmol) and 1.0 M solution of Li(O*i*-Pr) in hexanes (14.3 ml, 14.3 mmol). At variance, the reaction mixture was stirred at room temperature for 20 h to run the reaction to completion. After distillation off the volatiles at 30 °C, the residue was separated from LiCl by extraction with hexane. Then, the hexane was evaporated and the product distilled in vacuum at 90 °C (0.1 torr). Yield of yellow oil of **2** was 1.5 g (65%). ^1H NMR (C_6D_6): 1.15, 1.16 ($2 \times \text{d}$, $2 \times {}^3J_{\text{HH}} = 6.0$, 2×6 H, CHMe₂); 1.99 (s, 15 H, C₅Me₅); 4.72 (septuplet, ${}^3J_{\text{HH}} = 6.0$, 2 H, CHMe₂). ^{13}C $\{^1\text{H}\}$ NMR (C_6D_6): 11.91 (C₅Me₅); 25.76, 25.83 (MeCHMe); 78.30 (MeCHMe); 125.18 (C₅Me₅). EI-MS (direct inlet), m/z (%): 338 (13), 337 (9), 336 (M⁺; 32), 301 [M - Cl]⁺; 11), 279 (20), 278 (45), 277 (65), 276 ([M - C₃H₈O]⁺; 100), 275 (21), 274 (9), 242 ([M - Cl - C₃H₇O]⁺; 10), 240 (7), 237 (11), 236 (13), 235 ([M - C₃H₆ - C₃H₇O]⁺; 38), 234 (19), 220 (39), 219 (27), 218 ([M - 2 C₃H₇O]⁺; 72), 217 (31), 216 (18), 215 (8), 213 (11), 200 (8), 199 (14), 198 (7), 195 (8), 135 ([C₅Me₅]⁺; 41), 120 (10), 119 (26), 105 (16), 91 (12). IR (KBr): 2969 (vs), 2929 (s, sh), 2917 (s), 2862 (s), 1489 (m), 1461 (s, sh), 1447 (s), 1437 (s, sh), 1376 (s), 1361 (s), 1329 (s), 1260 (vw), 1228 (vw), 1164 (vs), 1128 (vs), 1116 (s, sh), 1070 (m), 1020 (vs), 988 (vs), 848 (s), 804 (w), 748 (w), 668 (vw), 639 (m), 616 (s, sh), 598 (s), 549 (vw), 456 (s), 422 (s).

Synthesis of $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ti}(\text{O}i\text{-Pr})\text{Me}_2]$ (**3**)

A 1.6 M solution of LiMe in diethyl ether (4.2 ml, 6.64 mmol) was slowly (within 2 h) added to an ice-cooled solution of **1** (1.04 g, 3.32 mmol) in diethyl ether (25 ml) under vigorous stirring. After stirring at room temperature for another 2 h, the solvents were distilled off under a decreased pressure, and the residue was extracted with hexane. After evaporation of hexane in vacuum, an oily product was distilled in dynamic vacuum (10⁻² torr) at 40 °C. The product was further fractionated in vacuum, collecting the middle fraction until its IR spectrum remained constant. Yield of yellow oil of **3** was 0.65 g (72%). ^1H NMR (C_6D_6): 0.42 (s, 6 H, TiMe); 1.32 (d, ${}^3J_{\text{HH}} = 6.0$, 6 H, CHMe₂); 1.81 (s, 15 H, C₅Me₅); 4.68 (septuplet, ${}^3J_{\text{HH}} = 6.0$, 1 H, CHMe₂). ^{13}C $\{^1\text{H}\}$ NMR (C_6D_6): 11.44 (C₅Me₅); 26.50 (CHMe₂); 47.83 (TiMe); 76.25 (CHMe₂); 120.70 (C₅Me₅). IR (KBr): 2968 (vs), 2945 (s, sh), 2920 (vs), 2865 (vs), 2761 (w), 1493 (vw), 1461 (w), 1446 (m), 1434 (m), 1397 (m), 1376 (s), 1360 (m), 1331 (m), 1163 (vs), 1144 (vs), 1129 (s, sh), 1110 (m, sh), 1066 (w), 1026 (vs), 855 (m), 794 (s), 644 (m), 622 (w), 563 (m), 520 (s), 453 (m).

Synthesis of $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ti}(\text{O}i\text{-Pr})_2\text{Me}]$ (**4**)

Compound **4** was prepared from **2** in a procedure analogous to synthesis of **3** from **1**. A larger scale one pot synthesis without isolation of **2** is feasible, as follows. A 1.0 M solution of Li(O*i*-Pr) in hexanes (15.2 ml, 15.2 mmol) was slowly added under stirring to an ice-cooled solution of $[(\eta^5\text{-C}_5\text{Me}_5)\text{TiCl}_3]$ (2.19 g, 7.57 mmol) in 25 ml of THF. After stirring at room temperature for 1 h, the reaction mixture was cooled to -20 °C and 1.6 M LiMe in

diethyl ether (4.8 ml, 7.6 mmol) was slowly added. After stirring at room temperature for another 2 h, the solvents were distilled off under a decreased pressure, and the residue was extracted with hexane. After evaporation of hexane in vacuum, an oily product was distilled in dynamic vacuum (10^{-2} torr) at 70 °C. Yield of yellow oil of **4** was 2.0 g (84%). ^1H NMR (C_6D_6): 0.52 (s, 3 H, TiMe); 1.18 (d, $^3J_{\text{HH}} = 5.7$, 12 H, CHMe_2); 1.92 (s, 15 H, C_5Me_5); 4.60 (septuplet, $^3J_{\text{HH}} = 5.7$, 2 H, CHMe_2). ^{13}C (^1H) NMR (C_6D_6): 11.35 (C_5Me_5); 26.56, 26.70 (CHMe_2); 37.70 (TiMe); 75.29 (CHMe_2); 119.78 (C_5Me_5). IR (KBr): 2967 (vs), 2929 (vs, sh), 2915 (vs), 2875 (s, sh), 2858 (vs), 2724 (w), 2616 (m), 1493 (w), 1461 (m, sh), 1447 (s), 1433 (m, sh), 1405 (m), 1375 (s), 1359 (s), 1331 (s), 1166 (vs), 1148 (vs), 1127 (vs), 1067 (w), 1022 (vs), 990 (vs, sh), 850 (s), 804 (w), 781 (w, br), 638 (s, sh), 621 (s), 586 (s), 569 (s, sh), 522 (m, sh), 504 (s), 458 (s). IR (ATR Si): 2965 (s), 2928 (s, sh), 2913 (s), 2876 (s, sh), 2857 (s), 2723 (w), 2615 (m), 1495 (w), 1461 (m, sh), 1446 (s), 1432 (m, sh), 1406 (w), 1374 (s), 1359 (s), 1330 (s), 1164 (vs), 1147 (vs, sh), 1123 (vs), 1069 (w), 1017 (vs), 989 (vs, sh), 848 (vs), 772 (w, br), 637 (s, sh), 619 (vs), 585 (s), 569 (s, sh), 504 (vs), 455 (vs).

Preparation of $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ti}(i\text{-PrO})_2]^+[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$ (**5**)

A solution of **4** (0.32 g, 1.02 mmol) in toluene (15 ml) was mixed with a solution of $\text{B}(\text{C}_6\text{F}_5)_3$ in 20 ml of toluene at room temperature and the mixture was stirred for 2 h. Then the solvent was evaporated under vacuum till the final volume of 15 ml, and the solution was left to crystallize at -18 °C. Orange crystalline material was separated from the mother liquor, and dried in vacuo. Bright orange crystals were obtained by recrystallization from hexane. Yield of **5** was 0.62 g (74%). ^1H NMR (C_6D_6): 0.53 (br s, 3 H, MeB); 0.83 (d, $^3J_{\text{HH}} = 5.7$, 12 H, CHMe_2); 1.59 (s, 15 H, C_5Me_5); 4.48 (septuplet, $^3J_{\text{HH}} = 5.7$, 2 H, CHMe_2). ^{13}C (^1H) NMR (75 MHz, 298 K, C_6D_6): 11.43 (C_5Me_5); 25.13 (CHMe_2); 82.48 (CHMe_2); 130.29 (C_5Me_5); 137.64 (d of multiplets, $^1J_{\text{CF}} = 242$, *m*-CF); 139.49 (d of multiplets, $^1J_{\text{CF}} = 243$, *p*-CF); 148.97 (d of multiplets, $^1J_{\text{CF}} = 232$, *o*-CF); BCH_3 and BC_{ipso} were not observed. ^{19}F (C_6D_6): -133.20 (m, 6 F, *o*-F); -160.55 (br s, 3 F, *p*-F); -165.46 (br s, 6 F, *m*-F). EI-MS (270 °C), *m/z* (relative abundance, %): 828 (M^{+} ; not observed), 512 ($[\text{B}(\text{C}_6\text{F}_5)_3]^{+}$; 12), 364 ($[\text{BF}(\text{C}_6\text{F}_5)_2]^{+}$; 15), 216 ($[\text{BF}_2\text{C}_6\text{F}_5]^{+}$; 13), 197 (9), 136 (33), 135 ($[\text{C}_5\text{Me}_5]^{+}$; 100), 134 (28), 133 (18), 121 (30), 119 (54). IR (ATR, Si crystal): 2977 (m), 2930 (w), 2914 (w, sh), 2873 (w), 2808 (vw), 2622 (vw), 1643 (m), 1598 (vw), 1515 (m), 1459 (vs), 1447 (vs, sh), 1390 (m, sh), 1382 (m), 1365 (m), 1332 (m), 1276 (m), 1267 (m, sh), 1161 (m), 1122 (s, sh), 1099 (vs), 1081 (s, sh), 1016 (vs, sh), 1008 (vs), 972 (vs), 961 (vs), 923 (w), 906 (m), 885 (m), 857 (m), 802 (s), 769 (w), 761 (m), 746 (m), 736 (w), 670 (m), 654 (m), 617 (m), 602 (m), 591 (m), 571 (w), 503 (vw), 460 (m).

Crystal Structure Analysis of **1** and **5**

Yellow prism of **1** and orange prism of **5** were mounted into Lindemann glass capillaries in a glovebox under purified nitrogen and sealed by a wax. Diffraction data were collected on a Nonius KappaCCD diffractometer and analyzed by the *HKL* program package²³. The structure was solved by direct methods (SIR92)²⁴, and refined by full-matrix least-squares on F^2 (SHELXL97)²⁵. Relevant crystallographic data are given in Table IV. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were fixed and refined in their theoretical positions except those residing at the bridging methyl C(17) atom of compound **5**. These were identified on difference electron density maps and refined with isotropic thermal motion parameters. Crystallographic data, details of their collection and the structure refinement

are given in Table IV. CCDC 682752 (for **1**) and CCDC 685627 (for **5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

TABLE IV
Crystal and structure refinement data for compounds **1** and **5**

Parameter	1	5
Formula	C ₁₃ H ₂₂ Cl ₂ O ₂ Ti	C ₃₅ H ₃₂ BF ₁₅ O ₂ Ti
Molecular weight	313.11	828.32
Space group	monoclinic <i>P2</i> ₁ / <i>c</i>	triclinic <i>P</i> -1
<i>a</i> , Å	12.0927(4)	10.9055(2)
<i>b</i> , Å	8.9339(5)	11.9721(4)
<i>c</i> , Å	15.4052(7)	14.8984(4)
α , °	90	80.9882(13)
β , °	102.504(3)	82.3290(15)
γ , °	90	72.2904(15)
<i>V</i> , Å ³ ; <i>Z</i>	1624.82(13); 4	1822.48(8); 2
<i>D</i> _{calcd} , g cm ⁻³	1.280	1.509
μ , mm ⁻¹	0.840	0.343
Color and habit	yellow prism	orange prism
Crystal size, mm ³	0.68 × 0.55 × 0.40	0.61 × 0.63 × 0.40
<i>T</i> , K	293(2)	150(2)
<i>F</i> (000)	656	840
θ_{\min} ; θ_{\max} , °	2.71; 27.48	1.39; 27.57
Range of <i>hkl</i>	-15/15; -10/10; -19/19	-14/13; -15/15; -19/19
No. measured diffrns	12495	34071
No. unique diffrns	3712	8375
No. observed diffrns ^a	3712	8375
No. of parameters	162	508
<i>R</i> (<i>F</i>); <i>wR</i> (<i>F</i> ²) obsd. diffrns	0.0728; 0.1929	0.0437; 0.1109
<i>R</i> (<i>F</i>); <i>wR</i> (<i>F</i> ²) all data	0.0975; 0.2149	0.0587; 0.1218
GOOF (<i>F</i> ²), all data	1.045	1.042
Max. and min. residual density, e Å ⁻³	0.754; -0.567	1.077; -0.535

^a Diffractions with $I_o > 2\sigma(I_o)$.

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