

# The first thermally stable half-sandwich titanium zwitterionic complex

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## Abstract

Thermally stable zwitterionic complex  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ti}(\text{O}t\text{-Bu})_2]^{(\delta+)}\text{[(}\mu\text{-Me)B(C}_6\text{F}_5)_3]^{(\delta-)}$  (**5**) was formed by mixing equimolar quantities of  $[(\eta^5\text{-C}_5\text{Me}_5)\text{TiMe}(\text{O}t\text{-Bu})_2]$  and  $[\text{B(C}_6\text{F}_5)_3]$ . The compound was recrystallized from hot toluene and has been stable so far for 1 year at ambient temperature in the solid state and in toluene solution. The <sup>1</sup>H, <sup>19</sup>F and 1D NOESY NMR spectra in C<sub>6</sub>D<sub>6</sub> solution proved the inner sphere ion pair structure of **5**. The X-ray crystal structure of **5** revealed that the bridging methyl group is σ-bonded to boron, and all its C–H bonds fulfil criteria for agostic bonding interaction with the titanium atom. In contrast to the stable solution in C<sub>6</sub>D<sub>6</sub> compound **5** decomposed in CD<sub>2</sub>Cl<sub>2</sub> solvent within hours at room temperature.

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**Keywords:** Half-sandwich titanocenes; Zwitterionic complex; NMR spectra; Crystal structure

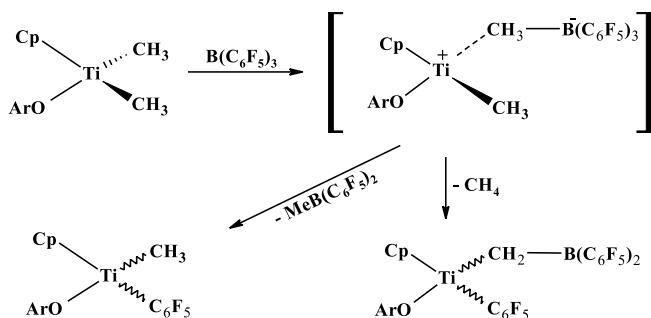
## 1. Introduction

Various half-sandwich titanium trihalides have been used in combination with methylalumoxane (MAO) as catalysts for effective polymerization of styrene to syndiotactic polystyrene (syn-PS), however, the molecular structure of catalysts is difficult to investigate [1]. Successful investigations of single site polymerization catalysts based on early transition metal metallocene dialkyls/tris(pentafluorophenyl)borane [2] 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  $[\text{B(C}_6\text{F}_5)_3]$ , where the formation of an ion pair  $[(\eta^5\text{-C}_5\text{Me}_5)\text{TiMe}_2]^+[\text{MeB(C}_6\text{F}_5)_3]^-$  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 [3a]. Whereas the formation of syn-PS in aromatic solvents was compatible with stereodirected poly-

merization on ion-pair single-site catalysts, the polymerization to a-PS proceeding in polar solvents like CH<sub>2</sub>Cl<sub>2</sub> or 1,2-C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub> pointed to a free carbocationic catalysis. This suggestion was corroborated by easy polymerization of α-methylstyrene [3b], vinyl ethers [3c], *N*-vinylcarbazole or isobutene [3d], the monomers which are known to polymerize under action of carbocationic initiators [3e]. 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 negligible polymerization activity. Indeed, NMR tube experiments with mixing the components at low temperature gave evidence for the formation of the  $[(\eta^5\text{-C}_5\text{Me}_5)\text{TiMe}_2]^+[\text{MeB(C}_6\text{F}_5)_3]^-$  complex and its rapid decomposition at room temperature [4]. 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 [5a]. An attempt to suppress this π-electron donation by using perfluoroaryl or

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Cp =  $\eta^5\text{-C}_5\text{H}_5$ , ArO = substituted phenoxide

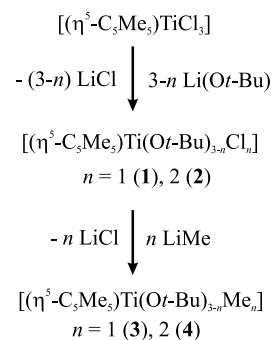
Scheme 1. Decomposition pathways for half-sandwich aryloxo zwitterionic complexes (taken from Ref. [6]).

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  $\text{OC}_6\text{F}_5$  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  $-50^\circ\text{C}$  in  $\text{CD}_2\text{Cl}_2$  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. Unfortunately, the compound dissociated at only  $-10^\circ\text{C}$  to initial components [5b]. A number of compounds  $[(\eta^5\text{-C}_5\text{H}_5)\text{TiMe}_2\text{OR}]$  where R is the phenyl group 2,6-disubstituted with bulky substituents (like phenyl, 1-naphthyl, *t*-Bu, *i*-Pr, Me) were used for the formation of cationic complexes with  $[\text{B}(\text{C}_6\text{F}_5)_3]$ . The NMR spectra gave evidence for the presence of ion-pair dissociation and the Ti–Me/Ti–Me–B exchange process, both at low temperatures. At ambient temperature, two decomposition processes of the cationic complex were recognized depending on the nature of substituents at the aryloxy ligand. In one, elimination of methane afforded neutral  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ti}(\text{OAr})(\text{C}_6\text{F}_5)\{\text{CH}_2\text{B}(\text{C}_6\text{F}_5)_2\}]$ , in the other elimination of bis(pentafluorophenyl)methylboron gave  $[(\eta^5\text{-C}_5\text{H}_5)\text{TiMe}(\text{OAr})(\text{C}_6\text{F}_5)]$  (Scheme 1) [6]. Another catalyst precursor, the trialkylsiloxy complex  $[(\eta^5\text{-C}_5\text{Me}_5)\text{TiMe}_2\text{O-SiR}_3]$ , where R = 2-(diphenylmethylsilyl)ethane-1-yl, gave rise to the cationic complex which had the half-life time of 2 days, and decomposed in  $\text{C}_6\text{D}_6$  via both ways of Scheme 1 simultaneously [7].

Here we report the synthesis of half-sandwich complexes  $[(\eta^5\text{-C}_5\text{Me}_5)\text{TiMe}(\text{O}t\text{-Bu})_2]$  (3) and  $[(\eta^5\text{-C}_5\text{Me}_5)\text{TiMe}_2(\text{O}t\text{-Bu})]$  (4), and the formation of thermally stable cationic complex  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ti}(\text{O}t\text{-Bu})_2][(\mu\text{-Me})\text{B}(\text{C}_6\text{F}_5)_3]$  (5) from 3 and  $[\text{B}(\text{C}_6\text{F}_5)_3]$ .

## 2. Results and discussion

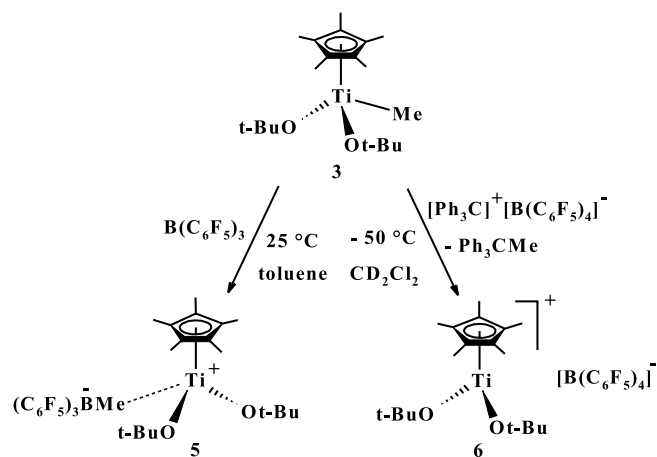
The precursors for the formation of cationic complexes  $[(\eta^5\text{-C}_5\text{Me}_5)\text{TiMe}(\text{O}t\text{-Bu})_2]$  (3) and  $[(\eta^5\text{-C}_5\text{Me}_5)\text{TiMe}_2(\text{O}t\text{-Bu})]$  (4) were obtained from commercial  $[(\eta^5\text{-C}_5\text{Me}_5)\text{TiCl}_3]$  in two steps according to Scheme 2. Addition of stoichiometric amounts of Li(*Ot*-Bu) in hexane afforded oily



Scheme 2. Synthesis of half-sandwich titanium(IV) complexes 1–4.

$[(\eta^5\text{-C}_5\text{Me}_5)\text{TiCl}(\text{O}t\text{-Bu})_2]$  (1) or solid  $[(\eta^5\text{-C}_5\text{Me}_5)\text{TiCl}_2(\text{O}t\text{-Bu})]$  (2) which were purified by vacuum distillation and crystallization from hexane, respectively. Compounds 1 and 2 were reacted with one or two equivalents of LiMe in toluene, respectively, to give yellowish oils of 3 and 4. Both the compounds were purified by vacuum distillation, and characterized by  $^1\text{H}$  and  $^{13}\text{C}$  NMR and IR spectra.

Addition of one equivalent of  $[\text{B}(\text{C}_6\text{F}_5)_3]$  to 3 in toluene resulted in the formation of new zwitterionic complex  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ti}(\text{O}t\text{-Bu})_2][(\mu\text{-Me})\text{B}(\text{C}_6\text{F}_5)_3]$  (5) as virtually the only product (Scheme 3). The thermally robust 5 was recrystallized from hot toluene to give orange plate crystals suitable for X-ray single crystal structure analysis (see below). Its stability in solution, however, strongly depended upon the solvent nature. Whereas in  $\text{C}_6\text{D}_6$  or toluene it remained stable for so far one year, in  $\text{CD}_2\text{Cl}_2$  it decomposed within hours at room temperature. The  $^1\text{H}$  NMR spectrum of 5 in  $\text{C}_6\text{D}_6$  displayed in addition to signals belonging to  $\text{C}_5\text{Me}_5$  and  $\text{OCMe}_3$  at 1.63 and 1.01, respectively, a broad signal at 0.45 ppm with halfwidth about 20 Hz. A remarkable high-field chemical shift of this signal in comparison with the unassociated  $[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$  anion in aromatic solvents (1.2–1.4 ppm) [8] indicates that compound 5 forms a contact ion-pair containing bridging  $\text{Ti}\cdots\text{Me}-\text{B}$  moiety. In order to support this suggestion



Scheme 3. Formation of complexes 5 and 6.

1D NOESY experiments were carried out with irradiation of  $C_5Me_5$  or  $OCMe_3$  protons. The both of them showed a close through space interaction with the MeB group. Moreover, the  $^{19}F$  NMR spectrum of **5** displayed the difference between the *meta* and *para* fluorine resonances  $\Delta\delta(m,p-F) = 5.0$  ppm, the value indicative for a strong cation–anion association [8a]. All these features allow us to assign **5** to an inner sphere ion pair (ISIP) [8d].

The fresh  $CD_2Cl_2$  solution of **5** showed the similar  $^1H$  NMR spectrum with downfield shifted  $C_5Me_5$  and  $OCMe_3$  signals at 2.13 and 1.35 ppm, respectively, and slightly upfield shifted MeB resonance at 0.39 ppm. Within an hour, however, a new set of resonances at 2.19, 1.41, and 0.41 ppm arose changing into a tangle of signals after several days. It can be suggested that the new set of distinct signals belonged to aggregated polynuclear species which were proposed to facilitate undesired side reactions [9]. The formation of polynuclear species was apparently due to an easier ion-pair separation in the more polar  $CD_2Cl_2$  solvent [10].

The EI-MS spectrum of **5** occurred only at 280 °C showing free  $[B(C_6F_5)_3]$  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  $Ti \cdots Me-B$  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 ethene at atmospheric pressure.

Mixing of equimolar quantities of **3** with  $[Ph_3C][B(C_6F_5)_4]$  in toluene at ambient temperature did not afford any isolable product due to decomposition of the expected solvent-separated ion pair  $[(\eta^5-C_5Me_5)Ti(Ot-Bu)_2][B(C_6F_5)_4]$  (**6**). The latter was observed when the above components were mixed in  $CD_2Cl_2$  at  $-50$  °C (Scheme 3).  $^1H$  NMR spectrum of **6** displayed the  $C_5Me_5$  and  $OCMe_3$  signals at 2.06 and 1.35 ppm, respectively, only slightly downfield shifted from resonances of **3**. The  $^{19}F$  NMR spectrum showed  $\Delta\delta(m,p-F) = 3.9$  ppm, typical for the uncoordinated  $[B(C_6F_5)_4]^-$  anion [11].

Addition of one equivalent of  $[B(C_6F_5)_3]$  to **4** in hexane solutions at ambient temperature led to an extensive gas evolution, and NMR spectra of the resulting product in  $C_6D_6$  indicated a complete loss of *tert*-butoxyl groups. Recently, elimination of isobutene from the  $[Cp_2Zr(Ot-Bu)]^+$  cation resulting in the formation of poly(isobutene) and  $[Cp_2Zr(\mu-OH)]_2^{2+}$  has been well-evidenced by NMR spectra and X-ray crystallography [11]. In the present system a mixture of titanium products was generated where individual components were not identified.

### 2.1. X-ray crystal structure of **5**

The PLATON drawing of **5** is shown in Fig. 1, and important molecular parameters are listed in Table 1. The titanium atom is pseudotetrahedrally coordinated by the  $\eta^5-C_5Me_5$

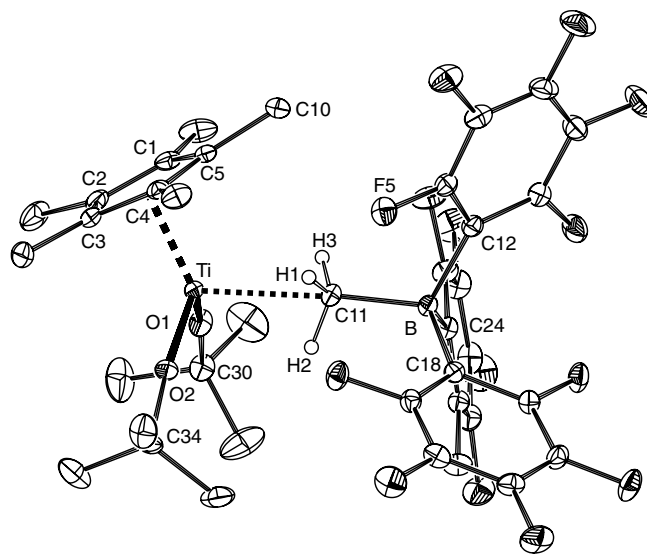


Fig. 1. The PLATON drawing of **5** (30% probability ellipsoids) with atom labeling scheme. Hydrogen atoms except those residing on the bridging C(11) atom are omitted for clarity.

ligand, two *tert*-butoxy groups and by  $\mu$ -Me group binding together the anionic  $[MeB(C_6F_5)_3]^{0-}$  and the  $[(\eta^5-C_5Me_5)Ti(Ot-Bu)_2]^{0+}$  moieties. There is no apparent steric crowding imposed by the ligands. The distance of the least-squares plane of the cyclopentadienyl ring to the titanium atom (2.0445(7) Å) is within two esd's equal to the Ti–Cg (Cg is the centroid of the cyclopentadienyl ring) distance, and the maximum deviation of 0.160(3) Å for the methyl carbon atom C(10) from the above plane opposite to titanium falls into the values found in not crowded half-sandwich  $[(\eta^5-C_5Me_4t-Bu)TiCl_3]$  or  $\{[(\eta^5-C_5Me_4t-Bu)TiCl_2]_2O\}$  complexes [12]. Likewise, the C–C bonds in *tert*-butoxy groups as well as the C–F bonds in the  $C_6F_5$

Table 1  
Selected bond lengths (Å) and bond angles (°) for compound **5**

Ti–Cg <sup>a</sup>	2.0464(7)	Ti–C(1)	2.387(1)
Ti–C(2)	2.332(1)	Ti–C(3)	2.350(1)
Ti–C(4)	2.390(1)	Ti–C(5)	2.421(1)
Ti–O(1)	1.766(1)	Ti–O(2)	1.756(1)
Ti–C(11)	2.436(1)	B–C(11)	1.679(2)
C <sub>ring</sub> –C <sub>ring</sub> (Cp)	1.412–1.427(2)	C <sub>ring</sub> –C <sub>Me</sub>	1.497–1.504(2)
B–C(12)	1.655(2)	B–C(18)	1.649(2)
B–C(24)	1.655(2)	O(1)–C(30)	1.438(1)
O(2)–C(34)	1.441(1)	C–F(range) <sup>b</sup>	1.339–1.358(2)
C–C <sub>Me</sub> (Ot-Bu)	1.503–1.523(3)	C–C(Ph) <sup>b</sup>	1.368–1.393(3)
Cg–Ti–O(1)	118.26(4)	Cg–Ti–O(2)	119.61(4)
Cg–Ti–C(11)	113.98(4)	O(1)–Ti–O(2)	106.80(6)
O(1)–Ti–C(11)	97.64(5)	O(2)–Ti–C(11)	96.35(5)
Ti–O(1)–C(30)	166.1(1)	Ti–O(2)–C(34)	169.9(1)
Ti–C(11)–B	169.0(1)	C(11)–B–C(12)	112.9(1)
C(11)–B–C(18)	112.3(1)	C(11)–B–C(24)	100.9(1)
C(12)–B–C(24)	113.2(1)	C(12)–B–C(18)	104.3(1)
C(18)–B–C(24)	113.6(1)	B–C(11)–H(1)	113(1)
B–C(11)–H(2)	105(1)	B–C(11)–H(3)	105(1)

<sup>a</sup> Cg denotes the centroid of C(1–5) cyclopentadienyl ring.

<sup>b</sup> Range of values for all the three  $C_6F_5$  groups.

groups fall into narrow distance ranges (Table 1), not indicating a steric crowding. The *tert*-butoxytitanium moieties are bent at the oxygen atom comparably to  $[(\eta^5\text{-C}_5\text{HMe}_4)_2\text{-Ti}(\text{O}t\text{-Bu})]$  [13] or  $[\{\text{Ti}(\text{O}t\text{-Bu})_3\}\{\text{Co}(\text{CO})_3\}]$  [14], and the Ti–O bond lengths (Table 1) are shorter with respect to that in the former (1.8425(14) Å) and longer with respect to those in the latter compound (1.738(9)–1.743(5) Å). The tetrahedral coordination about the boron atom is also distorted showing the angles C(11)–B–C(24) and C(12)–B–C(18) smaller than the other boron-centered angles (Table 1). The B–C(11) bond length is only slightly longer than the B–C<sub>ipso</sub> bond lengths, and B–C(11)–H angles clearly indicate that the methyl group is regularly  $\sigma$ -bonded to the boron atom. A larger value of the B–C(11)–H(1) angle (113(1)°) against the other two hydrogen-containing angles of 105(1)° and 105(1)° is connected with the bent bridging links (Ti–C(11)–B 169.0(1)°). Accordingly, the Ti–H(1) distance of 2.42(2) Å is longer than the Ti–H(2) and Ti–H(3) distances of 2.28(2) Å and 2.29(2) Å, respectively. The Ti–C(11) distance of 2.436(1) Å is longer than  $\sigma$ -Ti–C bonds in  $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{TiCH}_2\text{CMe}_3]$  (2.231(5) Å) [15] and a number of titanocene cyclopentadienyl ring-tethered titanacyclopentanes (2.208(2)–2.270(5) Å) [16], however, it approaches the length of Ti–C(sp<sup>2</sup>) bonds to the  $\eta^5\text{-C}_5\text{Me}_5$  ring in **5** (Table 1) and generally in all titanocene compounds. Since the methyl C(11) atom has an sp<sup>3</sup> hybridization its bonding to titanium has to be accomplished via agostic bonding of its C–H bonds. All conditions for its occurrence are fulfilled: the d<sup>0</sup> titanium atom has empty orbitals to interact with the  $\sigma$ -C–H bonding orbital, the Ti–C and Ti–H distances are comparable, and angles Ti–C–H are smaller than 100° [17]. The agostic interaction with one C–H bond on each of two vicinal methyl groups of the decamethyltitanocene cation resulted in attraction of both the methyl groups toward titanium so that the agostic Ti–H/Ti–C distances were 2.16(3) Å/2.685(5) Å and 2.20(3) Å/2.652(4) Å [18]. Compared to the parameters for **5**, the Ti–H distances are only slightly shorter with respect to Ti–H(2) and Ti–H(3), and the Ti–C distances considerably longer than Ti–C(11). A very similar orientation of the bridging methyl group in zirconocene contact ion pairs  $[\text{Me}_4\text{C}_2(\eta^5\text{-C}_5\text{H}_4)_2\text{ZrMe}]^+[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$  [19a], *rac*- $[\text{Me}_2\text{Si}\{\eta^5\text{-C}_5\text{H}_2(2\text{-Me-4-}t\text{-Bu})\}_2\text{ZrMe}]^+[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$  [19], and  $[\{\eta^5\text{-C}_5\text{H}_3(1,2\text{-Me}_2)\}_2\text{ZrMe}]^+[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$  [19b] was 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.

## 2.2. Conclusions

High thermal stability of **5** probably results from a lower Lewis acidity of the titanium atom induced by *tert*-butoxy ligands capable of back-donation of electron density. Apparently for the same reasons compound **5** is catalytically inactive for polymerization of ethene. The <sup>1</sup>H, <sup>19</sup>F and 1D NOESY NMR spectra proved the ISIP structure in C<sub>6</sub>D<sub>6</sub> solution, however, a broad signal for the borate

methyl group does not allow us to determine the <sup>1</sup>J<sub>CH</sub> coupling constants whose reduced value would be indicative for the presence of agostic interaction [17a,20]. The crystal structure determination of **5** confirmed the Ti···Me–B bridging moiety, which is analogous to that found in zirconocene cationic complexes [9,19]. The position of bridging methyl group with respect to the titanium atom allows us to consider a remarkable agostic bonding contribution to a generally accepted electrostatic bonding attraction. The cationic moiety is apparently unstable in solvent-separated ion pair as observed for **5** in polar CD<sub>2</sub>Cl<sub>2</sub> solvent or for **6** containing the  $[\text{B}(\text{C}_6\text{F}_5)_4]^-$  anion.

## 3. Experimental

### 3.1. Chemicals and methods

All reactions with moisture and air-sensitive compounds were carried out under argon or on a high-vacuum line using all-sealed glass devices equipped with breakable seals. Li(*Ot*-Bu) (1.0 M solution in hexane), LiMe (1.6 M solution in diethylether) and LiAlH<sub>4</sub> were obtained from Aldrich and used as received.  $[\text{B}(\text{C}_6\text{F}_5)_3]$ ,  $[(\eta^5\text{-C}_5\text{Me}_5)\text{TiCl}_3]$  and  $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$  were purchased from Strem, and the former two purified by crystallization from hexane. Solvents tetrahydrofuran (THF), hexane, and toluene were dried by refluxing over LiAlH<sub>4</sub> and stored as solutions of dimeric titanocene  $[(\mu\text{-}\eta^5\text{-}\eta^5\text{-C}_{10}\text{H}_8)(\mu\text{-H})_2\{\text{Ti}(\eta^5\text{-C}_5\text{H}_5)\}_2]$  [21]. <sup>1</sup>H (299.98 MHz), <sup>13</sup>C (75.44 MHz) and <sup>19</sup>F (282.22 MHz) NMR spectra were recorded on a Varian Mercury 300 spectrometer at 298 K if not noticed otherwise. Chemical shifts ( $\delta$ /ppm) are given relative to the solvent signal (C<sub>6</sub>D<sub>6</sub>:  $\delta_{\text{H}}$  7.15,  $\delta_{\text{C}}$  128.00; CD<sub>2</sub>Cl<sub>2</sub>:  $\delta_{\text{H}}$  5.32,  $\delta_{\text{C}}$  54.00). EI-MS spectra of **5** were measured on a VG-7070E mass spectrometer at 70 eV. Crystalline 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. Infrared spectra of hexane solutions of **1–4** under argon in KBr cuvettes were measured on a Magna 550 Nicolet spectrometer in the range 400–4000 cm<sup>-1</sup>. KBr pellets of **5** were prepared in a glovebox Labmaster 130 (mBraun) and then measured in an air-protecting cuvette on a Nicolet Avatar FT IR spectrometer in the range 400–4000 cm<sup>-1</sup>.

### 3.2. Synthesis of permethylcyclopentadienyl(chloro)titanium *tert*-butanolates

Pentamethylcyclopentadienyl(chloro)titanium *tert*-butanolates were prepared by reacting  $[(\eta^5\text{-C}_5\text{Me}_5)\text{TiCl}_3]$  with one or two equivalents of Li(*Ot*-Bu) [22].

#### 3.2.1. $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ti}(\text{O}t\text{-Bu})_2\text{Cl}]$ (**1**)

Hexane solution of Li(*Ot*-Bu) (1.0 M, 17.4 ml, 17.4 mmol) was added dropwise within 2.5 h to a precooled solution of  $[(\eta^5\text{-C}_5\text{Me}_5)\text{TiCl}_3]$  (2.51 g, 8.7 mmol) in 50 ml of THF at –15 °C. The reaction mixture was heated to

room temperature, stirred for additional 3 h and then all volatiles were evaporated in vacuum. A crude product was extracted into hexane. Distillation of crude product at 90 °C/0.1 mm Hg gave compound **1** as a yellow oily liquid. Yield 2.84 g (88%).

<sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): 1.31 (s, 18H, OMe<sub>3</sub>); 2.03 (s, 15H, C<sub>5</sub>Me<sub>5</sub>). <sup>13</sup>C {<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>): 12.83 (C<sub>5</sub>Me<sub>5</sub>); 32.51 (OMe<sub>3</sub>); 84.64 (OMe<sub>3</sub>); 125.45 (C<sub>5</sub>Me<sub>5</sub>). IR (hexane solution, cm<sup>-1</sup>): 1358 (s), 1230 (m), 1188 (s), 1174 (s, sh), 1016 (vs), 993 (vs), 792 (m), 575 (m), 567 (m, sh), 567 (m, sh), 482 (w), 472 (w), 429 (m), 403 (m).

### 3.2.2. [(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)Ti(Ot-Bu)Cl<sub>2</sub>] (**2**)

The above described procedure was used starting from Li(Ot-Bu) solution (1.0 M, 8.4 ml, 8.4 mmol) and [(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)TiCl<sub>3</sub>] (2.43 g, 8.3 mmol). After workup, a crude product was recrystallized from hexane to give analytically pure **2** as orange crystals. Yield 2.21 g (82%).

<sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): 1.30 (s, 9H, OMe<sub>3</sub>); 1.98 (s, 15H, C<sub>5</sub>Me<sub>5</sub>). <sup>13</sup>C {<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>): 13.34 (C<sub>5</sub>Me<sub>5</sub>); 31.68 (OMe<sub>3</sub>); 90.50 (OMe<sub>3</sub>); 131.05 (C<sub>5</sub>Me<sub>5</sub>). EI-MS (50 °C): *m/z* (relative abundance, %) 326 (*M*<sup>+</sup>; 7), 311 ([*M*-Me]<sup>+</sup>; 9), 291 ([*M*-Cl]<sup>+</sup>; 2), 272 (12), 270 ([*M*-C<sub>4</sub>H<sub>8</sub>]<sup>+</sup>; 18), 256 (14), 255 (23), 254 (55), 253 (36), 252 ([*M*-*t*-BuOH]<sup>+</sup>; 78), 251 (9), 250 (8), 236 (12), 235 (12), 234 (27), 218 (9), 217 (16), 216 (11), 215 (9), 213 (14), 176 (8), 140 (9), 136 (11), 135 ([C<sub>5</sub>Me<sub>5</sub>]<sup>+</sup>; 100), 119 (46), 105 (38), 91 (29). IR (hexane solution, cm<sup>-1</sup>): 1363 (s), 1233 (m), 1172 (s), 1065 (w), 1005 (vs), 796 (m), 758 (m), 580 (m), 479 (w), 450 (s), 406 (s).

### 3.3. Synthesis of permethylcyclopentadienyl(methyl)titanium *tert*-butanolates

#### 3.3.1. [(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)Ti(Ot-Bu)<sub>2</sub>Me] (**3**)

Cold diethylether solution of LiMe (1.6 M, 4.5 ml, 7.2 mmol) was dropwise added to a stirred solution of **1** (2.64 g, 7.2 mmol) in 25 ml of toluene precooled to -60 °C. The reaction mixture was allowed warming to -40 °C, stirred for 1 h at this temperature, and degassed in vacuum. After warming to ambient temperature the mixture was left standing for 5 h in dark. Volatiles were evaporated in vacuum, and an oily residue was extracted in hexane. Pure **3** was obtained after distillation at 75 °C/0.1 mm Hg as a yellowish oily liquid of **3**. Yield 2.34 g (94%).

<sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): 0.50 (s, 3H, TiMe); 1.30 (s, 18H, OMe<sub>3</sub>); 1.94 (s, 15H, C<sub>5</sub>Me<sub>5</sub>). <sup>13</sup>C {<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>): 11.79 (C<sub>5</sub>Me<sub>5</sub>); 32.68 (OMe<sub>3</sub>); 37.64 (TiMe); 80.47 (OMe<sub>3</sub>); 119.62 (C<sub>5</sub>Me<sub>5</sub>). IR (hexane solution, cm<sup>-1</sup>): 1357 (s), 1228 (m), 1197 (vs), 1180 (s), 1137 (w), 1106 (w), 1065 (w), 1033 (vs), 1012 (vs), 903 (w), 790 (m), 758 (w), 694 (w), 635 (w), 604 (m), 553 (m), 502 (m), 463 (w), 415 (m).

#### 3.3.2. [(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)Ti(Ot-Bu)Me<sub>2</sub>] (**4**)

The above described protocol for **3** was used starting from LiMe solution (1.6 M, 9.8 ml, 15.6 mmol) and **2** (2.55 g, 7.8 mmol). Crude product was extracted in hexane

and purified by distillation at 70 °C/0.1 mm Hg to give a yellowish oily liquid of **4**. Yield 1.79 g (84%).

<sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): 0.40 (s, 6H, TiMe); 1.44 (s, 9H, OMe<sub>3</sub>); 1.83 (s, 15H, C<sub>5</sub>Me<sub>5</sub>). <sup>13</sup>C {<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>): 11.72 (C<sub>5</sub>Me<sub>5</sub>); 32.37 (OMe<sub>3</sub>); 47.81 (TiMe); 82.32 (OMe<sub>3</sub>); 120.94 (C<sub>5</sub>Me<sub>5</sub>). IR (hexane solution, cm<sup>-1</sup>): 1360 (s), 1232 (m), 1190 (vs), 1135 (w), 1111 (w), 1065 (w, sh), 1037 (vs), 904 (w), 883 (w), 795 (m), 758 (w), 694 (w), 625 (w, br), 550 (m), 520 (s), 462 (w), 414 (w).

### 3.4. Synthesis of [(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)Ti(Ot-Bu)<sub>2</sub>][MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>] (**5**)

A solution of **3** (0.40 g, 1.17 mmol) in 15 ml of toluene was added to a solution of [B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>] (0.60 g, 1.17 mmol) in 20 ml of toluene. The reaction mixture was stirred for 2 h and then concentrated to cca. 20 ml. Heating of the mixture to 60 °C followed by slow cooling to room temperature gave yellow-orange crystals of **5**. Yield 0.81 g (81%).

<sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): 0.45 (br s, 3H, MeB); 1.01 (s, 18H, OMe<sub>3</sub>); 1.63 (s, 15H, C<sub>5</sub>Me<sub>5</sub>). <sup>13</sup>C {<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>): 12.17 (C<sub>5</sub>Me<sub>5</sub>); 31.59 (OMe<sub>3</sub>); 90.18 (OMe<sub>3</sub>); 130.71 (C<sub>5</sub>Me<sub>5</sub>); 137.44 (d of multiplets, <sup>1</sup>J<sub>CF</sub> = 246 Hz, *m*-CF); 139.79 (d of multiplets, <sup>1</sup>J<sub>CF</sub> = 242 Hz, *p*-CF); 148.87 (d of multiplets, <sup>1</sup>J<sub>CF</sub> = 235 Hz, *o*-CF); BMe and BC<sub>*ipso*</sub> were not observed. <sup>19</sup>F (C<sub>6</sub>D<sub>6</sub>): -132.85 (m, 6F, *o*-F); -160.45 (m, 3F, *p*-F); -165.45 (br s, 2F, *m*-F). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): 0.39 (br s, 3H, MeB); 1.35 (s, 18H, OMe<sub>3</sub>); 2.13 (s, 15H, C<sub>5</sub>Me<sub>5</sub>). selected <sup>13</sup>C {<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>): 13.09 (C<sub>5</sub>Me<sub>5</sub>); 32.34 (OMe<sub>3</sub>); 129.54 (C<sub>5</sub>Me<sub>5</sub>)<sup>19</sup>F (CD<sub>2</sub>Cl<sub>2</sub>): -133.50 (m, 6F, *o*-F); -161.34 (m, 3F, *p*-F); -167.47 (br s, 6F, *m*-F). EI-MS (300 °C): *m/z* (relative abundance, %) 856 (*M*<sup>+</sup>; not observed), 512 ([B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>]<sup>+</sup>; 14), 364 ([BF(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>]<sup>+</sup>; 16), 258 (7), 227 (10), 216 ([BF<sub>2</sub>(C<sub>6</sub>F<sub>5</sub>)]<sup>+</sup>; 17), 197 (11), 136 (32), 135 ([C<sub>5</sub>Me<sub>5</sub>]<sup>+</sup>; 100), 134 (29), 133 (20), 121 (29), 119 (56). IR (KBr, cm<sup>-1</sup>): 2982 (w), 2938 (vw), 2870 (vw), 1642 (w), 1514 (s), 1460 (vs), 1381 (w), 1365 (w), 1280 (w), 1269 (w), 1174 (m), 1160 (m), 1099 (s), 1090 (s), 1006 (s), 974 (vs), 912 (vw), 895 (w), 876 (vw), 798 (m), 770 (vw), 758 (w), 747 (vw), 730 (w), 668 (vw), 654 (vw), 627 (vw), 570 (vw), 492 (vw), 433 (vw).

### 3.5. NMR scale synthesis of [(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)Ti(Ot-Bu)<sub>2</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (**6**)

A NMR tube was charged with [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (0.0424 g, 0.046 mmol) and shortly cooled in liquid nitrogen. A cold solution (-78 °C) of **3** (0.0160 g, 0.046 mmol) in 1.0 ml of CD<sub>2</sub>Cl<sub>2</sub> was slowly dropped to the precooled solid borate. The tube was immediately cooled by liquid nitrogen, degassed in vacuum, sealed and stored in liquid nitrogen, then placed in the NMR probe at 223 K where it was examined for <sup>1</sup>H, <sup>13</sup>C, and <sup>19</sup>F nuclei.

<sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 223 K): 1.40 (s, 18H, OMe<sub>3</sub>); 2.18 (s, 15H, C<sub>5</sub>Me<sub>5</sub>). Selected <sup>13</sup>C {<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 223 K): 13.09 (C<sub>5</sub>Me<sub>5</sub>); 32.06 (OMe<sub>3</sub>); 88.98 (OMe<sub>3</sub>);

129.52 ( $C_5Me_5$ ).  $^{19}F$  ( $CD_2Cl_2$ , 223 K):  $-133.8$  (m, 6F, *o-F*);  $-163.4$  (m, 3F, *p-F*);  $-167.3$  (m, 6F, *m-F*).

*Note.* The stoichiometric amount of the formed  $MeCPh_3$  was also observed ( $^1H$  NMR ( $CD_2Cl_2$ , 223 K): 2.14 (s, 3H, *MeC*); 7.01–7.08 (m, 6H,  $CH_{ortho}$ , *Ph*); 7.15–7.28 (m, 9H,  $CH_{meta}$  and  $CH_{para}$ , *Ph*).

### 3.6. Attempted ethene polymerization with **5**

In a high vacuum system a magnetically stirred saturated solution of **5** in toluene (10.0 ml) was exposed to gaseous ethene at the pressure of 730 Torr. After the solution was saturated with ethene, no further consumption of ethene was observed. The yellow color of the solution did not change during admission of ethene and for the next one hour. After addition of 20 ml of methanol no polymer precipitated.

### 3.7. X-ray crystallography

Red plates of **5** were inserted into Lindemann glass capillaries in a glovebox and sealed by a wax. Diffraction data were collected on a Nonius KappaCCD diffractometer and analyzed by the HKL program package [23]. The structure was solved by direct methods (SIR-92, [24]) and refined by full-matrix least-squares on  $F^2$  (SHELXL-97 [25]). Relevant crystallographic data are given in Table 2. 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(11) atom. These were identified on difference electron density maps and refined with isotropic thermal motion parameters.

Table 2

Crystallographic data, data collection and structure refinement data for compound **5**

Chemical formula	$C_{37}H_{36}BF_{15}O_2Ti$
Molecular weight	856.37
Crystal system	Monoclinic
Space group	$P2_1/c$ (No.14)
<i>a</i> (Å)	10.0010(1)
<i>b</i> (Å)	17.2540(2)
<i>c</i> (Å)	22.2030(3)
$\beta$ (°)	101.3370(7)
<i>V</i> (Å <sup>3</sup> ), <i>Z</i>	3756.53(8), 4
$d_{calc}$ (g cm <sup>-3</sup> )	1.514
$\mu$ (Mo K $\alpha$ ) (mm <sup>-1</sup> )	0.336
<i>F</i> (000)	1744
Crystal size (mm <sup>3</sup> )	0.5 × 0.5 × 0.25
<i>T</i> (K)	150(2)
$\theta$ range (°)	3.05–27.49
<i>hkl</i> range	–12/12; –22/22; –28/28
Diffractions collected	8593
Unique diffractions	7435
Parameters	528
<i>R</i> , <i>wR</i> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.0361, 0.0915
<i>R</i> , <i>wR</i> (all data)	0.0440, 0.0966
<i>S</i>	1.027
$\Delta\rho_{max,min}$ (e/Å <sup>3</sup> )	0.320, –0.408

## 4. Supplementary material

CCDC 624680 contain the supplementary crystallographic data for **5**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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## References

- [1] (a) K. Yokota, T. Inoue, S. Naganuma, H. Shozaki, N. Tomotsu, M. Kuramoto, N. Ishihara, in: W. Kaminski (Ed.), *Metalloorganic Catalysts for Synthesis and Polymerization*, Springer, Berlin, 1999, p. 435; (b) J. Schellenberg, N. Tomotsu, *Prog. Polym. Sci.* 27 (2002) 1925; (c) J. Pinkas, A. Lyčka, P. Šindelář, R. Gyepes, V. Varga, J. Kubišta, M. Horáček, K. Mach, *J. Mol. Catal. A* 257 (2006) 14–25.
- [2] (a) H.-H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger, R.M. Waymouth, *Angew. Chem., Int. Ed. Engl.* 34 (1995) 1143; (b) W. Kaminski, M. Arndt, *Adv. Polym. Sci.* 127 (1997) 144; (c) M. Bochmann, *J. Chem. Soc., Dalton Trans.* (1996) 255; (d) E.Y.-X. Chen, T.J. Marks, *Chem. Rev.* 100 (2000) 1391; (e) G.W. Coates, *J. Chem. Soc., Dalton Trans.* (2002) 467.
- [3] (a) D.J. Gillis, M.-J. Tudoret, M.C. Baird, *J. Am. Chem. Soc.* 115 (1993) 2543; (b) R. Quyoum, Q. Wang, M.-J. Tudoret, M.C. Baird, *J. Am. Chem. Soc.* 116 (1994) 6435; (c) Q. Wang, M.C. Baird, *Macromolecules* 28 (1995) 8021; (d) F. Barsan, M.C. Baird, *J. Chem. Soc., Chem. Commun.* (1995) 1065; (e) M.C. Baird, *Chem. Rev.* 100 (2000) 1471.
- [4] Q. Wang, D.J. Gillis, R. Quyoum, D. Jeremic, M.-J. Tudoret, M.C. Baird, *J. Organomet. Chem.* 527 (1997) 7.
- [5] (a) Q. Wang, R. Quyoum, D.J. Gillis, M.-J. Tudoret, D. Jeremic, B.K. Hunter, M.C. Baird, *Organometallics* 15 (1996) 693; (b) M.J. Sarsfield, S.W. Ewart, T.L. Tremblay, A.W. Roszak, M.C. Baird, *J. Chem. Soc., Dalton Trans.* (1997) 3097.
- [6] (a) A.E. Fenwick, K. Phomphrai, M.G. Thorn, J.S. Vilaro, C.A. Trefun, B. Hanna, P.E. Fanwick, I.P. Rothwell, *Organometallics* 23 (2004) 2146; (b) K. Phomphrai, A.E. Fenwick, S. Sharma, P.E. Fanwick, J.M. Caruthers, W.N. Delgass, M.M. Abu-Omar, I.P. Rothwell, *Organometallics* 25 (2006) 214.
- [7] V. Amo, R. Andres, E. de Jesus, F.J. de la Mata, J.C. Flores, R. Gomez, M.P. Gomez-Sal, J.F.C. Turner, *Organometallics* 24 (2005) 2331.
- [8] (a) A.D. Horton, *Organometallics* 15 (1996) 2675; (b) C.L. Beswick, T.J. Marks, *Organometallics* 18 (1999) 2410; (c) S. Zhang, W.E. Piers, X.L. Gao, M. Parvez, *J. Am. Chem. Soc.* 122 (2000) 5499; (d) C. Zuccaccia, N.G. Stahl, A. Macchioni, M.C. Chen, J.A. Roberts, T.J. Marks, *J. Am. Chem. Soc.* 126 (2004) 1448; (e) S. Beck, M.H. Prosenc, H.H. Brintzinger, *J. Mol. Catal. A-Chem.* 128 (1998) 41.
- [9] S. Beck, S. Lieber, F. Schaper, A. Geyer, H.H. Brintzinger, *J. Am. Chem. Soc.* 123 (2001) 1483.

- [10] C.L. Beswick, T.J. Marks, *J. Am. Chem. Soc.* 122 (2000) 10358.
- [11] E.J. Stoebenau, R.F. Jordan, *J. Am. Chem. Soc.* 128 (2006) 8162.
- [12] L. Lukešová, R. Gyepes, J. Pinkas, M. Horáček, J. Kubišta, J. Čejka, K. Mach, *Collect. Czech. Chem. Commun.* 70 (2005) 1589.
- [13] M. Horáček, I. Císařová, J. Čejka, J. Karban, L. Petrusová, K. Mach, *J. Organomet. Chem.* 577 (1999) 103.
- [14] D. Selent, R. Beckhaus, J. Pickhardt, *Organometallics* 12 (1993) 2857.
- [15] G.A. Luinstra, L.C. ten Kate, H.J. Heeres, J.W. Pattiasina, A. Meetsma, J.H. Teuben, *Organometallics* 10 (1991) 3227.
- [16] (a) M. Horáček, P. Štěpnička, R. Gyepes, I. Císařová, I. Tišlerová, J. Zemánek, J. Kubišta, K. Mach, *Chem. Eur. J.* 6 (2000) 2397;  
(b) L. Lukešová, P. Štěpnička, K. Fejfarová, R. Gyepes, I. Císařová, M. Horáček, J. Kubišta, K. Mach, *Organometallics* 21 (2002) 2639.
- [17] (a) M. Brookhart, M.L.H. Green, *J. Organomet. Chem.* 250 (1983) 395;  
(b) D. Braga, F. Grepioni, E. Tedesco, K. Biradha, G.R. Desiraju, *Organometallics* 16 (1997) 1846;  
(c) T.S. Thakur, G.R. Desiraju, *Chem. Commun.* (2006) 552.
- [18] M.W. Bouwkamp, J. de Wolf, I. del Hierro Morales, J. Gercama, A. Meetsma, S.I. Troyanov, B. Hessen, J.H. Teuben, *J. Am. Chem. Soc.* 124 (2002) 12956.
- [19] (a) S. Beck, M.H. Prosenc, H.-H. Brintzinger, R. Goretzki, N. Herfert, G. Fink, *J. Mol. Catal. A-Chem.* 111 (1996) 67;  
(b) X. Yang, C.L. Stern, T.J. Marks, *J. Am. Chem. Soc.* 116 (1994) 10015.
- [20] (a) G. Erker, W. Frömberg, K. Angermund, R. Schlund, C. Krüger, *J. Chem. Soc., Chem. Commun.* (1986) 372;  
(b) M. Brookhart, M.L.H. Green, L.-L. Wong, *Prog. Inorg. Chem.* 36 (1988) 1;  
(c) I. Hyla-Kryspin, R. Gleiter, C. Krüger, R. Zwieter, G. Erker, *Organometallics* 9 (1990) 517;  
(d) M.L.H. Green, A.K. Hughes, N.A. Popham, A.H.H. Stephens, L.-L. Wong, *J. Chem. Soc., Dalton Trans.* (1992) 3077.
- [21] H. Antropiusová, A. Dosedlová, V. Hanuš, K. Mach, *Trans. Met. Chem. (London)* 6 (1981) 90.
- [22] I.M.M. Fussig, D. Fletcher, R.J. Whitby, *J. Organomet. Chem.* 470 (1994) 109.
- [23] Z. Otwinowski, W. Minor, HKL DENZO and SCALEPACK program package by Nonius. For a reference see Z. Otwinowski, W. Minor, *Methods Enzymol.* 276 (1997) 307.
- [24] A. Altomare, M.C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, G. Polidori, *J. Appl. Cryst.* 27 (1994) 435.
- [25] G.M. Sheldrick, SHELXL97. Program for Crystal Structure Refinement from Diffraction Data, University of Göttingen, Göttingen, 1997.