

# Electrophilic reactivity of the zwitterionic titanocene monohalides $\text{Cp}[\eta^5\text{-C}_5\text{H}_4\text{B}(\text{C}_6\text{F}_5)_3]\text{TiX}$ ( $\text{X} = \text{Cl}, \text{Br}$ ): Reactions with water and methanol

L.I. Strunkina<sup>a</sup>, M.Kh. Minacheva<sup>a</sup>, K.A. Lyssenko<sup>a</sup>, P.V. Petrovskii<sup>a</sup>, N.E. Mysova<sup>a</sup>,  
B.N. Strunin<sup>a</sup>, V.V. Burlakov<sup>a</sup>, U. Rosenthal<sup>b</sup>, V.B. Shur<sup>a,\*</sup>

<sup>a</sup> *A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Vavilov Street 28, 119991 Moscow, Russia*

<sup>b</sup> *Leibniz-Institut für Katalyse e.V. an der Universität Rostock, Albert-Einstein-Strasse 29a, D-19059 Rostock, Germany*

Received 28 May 2007; received in revised form 25 June 2007; accepted 28 June 2007

Available online 4 July 2007

## Abstract

The paper reports new data evidencing for a high electrophilicity of the positively charged titanium atom in the previously described zwitterionic titanocene monochloride  $\text{Cp}[\eta^5\text{-C}_5\text{H}_4\text{B}(\text{C}_6\text{F}_5)_3]\text{TiCl}$  (**1**) and titanocene monobromide  $\text{Cp}[\eta^5\text{-C}_5\text{H}_4\text{B}(\text{C}_6\text{F}_5)_3]\text{TiBr}$  (**2**), containing a  $\text{B}(\text{C}_6\text{F}_5)_3$  group in one of the  $\text{C}_5$  rings. It has been established that on a contact of a toluene solution of these zwitterions with water vapour at 20 °C under Ar, a rapid protolytic cleavage of the otherwise inert  $\text{B-C}_6\text{F}_5$  bond in the tris(pentafluorophenyl)borane moiety occurs to afford pentafluorobenzene and the corresponding halogenide hydroxide complex of titanocene  $\text{Cp}[\eta^5\text{-C}_5\text{H}_4\text{B}(\text{C}_6\text{F}_5)_2]\text{TiX}(\mu\text{-OH})$ , where  $\text{X} = \text{Cl}$  (**3**),  $\text{Br}$  (**4**). An X-ray diffraction study of the complexes has shown that the hydroxide group in **3** and **4** is bonded via the oxygen atom both to the titanium and boron atoms. Under similar conditions, the interaction of zwitterion **1** with methanol gives rise to pentafluorobenzene and the chloride methoxide complex of titanocene  $\text{Cp}[\eta^5\text{-C}_5\text{H}_4\text{B}(\text{C}_6\text{F}_5)_2]\text{TiCl}(\mu\text{-OCH}_3)$ . It has been suggested that the driving force of the protolysis of the  $\text{B-C}_6\text{F}_5$  bond in **1** and **2** is a sharp increase in the acidity of water or methanol molecule as a result of their complexation with the positively charged titanium centre in the starting zwitterion.

© 2007 Elsevier B.V. All rights reserved.

**Keywords:** Boron; Lewis acids; Titanium; Zwitterionic metallocenes; X-ray structures

## 1. Introduction

Over the last two decades, there has been considerable progress in coordination and catalytic chemistry of zwitterionic metallocenes of the Group IVB metals (see, e.g., reviews [1–4] and papers [5–16]), representing uncharged analogues of the well-known cationic Group IVB metallocenes, whose discovery more than 20 years ago had a profound influence on the development of studies into catalytic Ziegler-type olefin polymerization (for reviews, see e.g. [17–20]). A great interest in zwitterionic Group

IVB metallocenes is due to their high electrophilicity and, as a rule, sufficiently good solubility in nonpolar solvents such as aromatic hydrocarbons, which makes these remarkable betaine species very promising for catalysis of polymerization and other processes. Recently, we have described the first zwitterions of such a type, which are able to catalyze cationic ring-opening polymerization [4,16,21]. It has been shown, in particular, that the interaction of the zwitterionic paramagnetic titanium(III) complex  $\text{Cp}[\eta^5\text{-C}_5\text{H}_4\text{B}(\text{C}_6\text{F}_5)_3]\text{Ti}$  [22] with an excess of  $\text{CCl}_4$  affords the zwitterionic titanocene monochloride  $\text{Cp}[\eta^5\text{-C}_5\text{H}_4\text{B}(\text{C}_6\text{F}_5)_3]\text{TiCl}$  (**1**) containing a  $\text{B}(\text{C}_6\text{F}_5)_3$  substituent in one of the  $\text{C}_5$  rings and exhibiting catalytic activity in the polymerization of  $\epsilon$ -caprolactone [16]. Similarly, the

\* Corresponding author.

E-mail address: [vbshur@ineos.ac.ru](mailto:vbshur@ineos.ac.ru) (V.B. Shur).

reaction of  $\text{Cp}[\eta^5\text{-C}_5\text{H}_4\text{B}(\text{C}_6\text{F}_5)_3]\text{Ti}$  with an excess of 1,2-dibromoethane resulted in the formation of the corresponding monobromide zwitterionic complex  $\text{Cp}[\eta^5\text{-C}_5\text{H}_4\text{B}(\text{C}_6\text{F}_5)_3]\text{TiBr}$  (**2**) which proved to be also active in the cationic ring-opening polymerization [16]. These data are indicative of a high electrophilicity of the positively charged titanium atom in **1** and **2** which can be used for the accomplishment of other processes catalyzed or promoted by Lewis acids. In the present article, the reactions of **1** and **2** with water and methanol are reported. These new reactions of zwitterionic complexes **1** and **2** impressively illustrate their high electrophilicity.

For a short preliminary account of a small part of this study, see [23].

## 2. Results and discussion

As is known, the  $\text{B-C}_6\text{F}_5$  bond is very inert towards water at room temperature. Thus, the yield of pentafluorobenzene in the interaction of water with  $\text{B}(\text{C}_6\text{F}_5)_3$  does not exceed 3% even after 18 days at 20 °C [24]. Here, the process virtually stops at the stage of formation of the corresponding aqua complexes, viz.,  $(\text{C}_6\text{F}_5)_3\text{B}(\text{OH}_2)$ ,  $[(\text{C}_6\text{F}_5)_3\text{B}(\text{OH}_2)] \cdot \text{H}_2\text{O}$  and  $[(\text{C}_6\text{F}_5)_3\text{B}(\text{OH}_2)] \cdot 2\text{H}_2\text{O}$  [25]. The boron-carbon bond in tetraarylborates is also stable to water at room temperature, whereas in polyfluorine-containing tetraarylborates ( $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ ,  $\{\text{B}[3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3]_4\}^-$ , etc.), it is not cleaved under ambient conditions even with aqueous solutions of mineral acids [26,27].

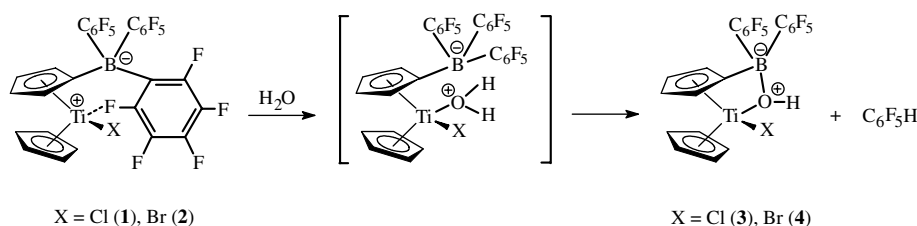
A quite different behavior in the reaction with water is demonstrated by zwitterionic complex **1**. It turned out that in this case an exposure of a toluene solution of **1** to water vapour at 20 °C under Ar leads to a rapid protolytic cleavage of one of the  $\text{B-C}_6\text{F}_5$  bonds in the tris(pentafluorophenyl)borane moiety to afford pentafluorobenzene and the chloride hydroxide complex of titanocene  $\text{Cp}[\eta^5\text{-C}_5\text{H}_4\text{B}(\text{C}_6\text{F}_5)_2]\text{TiCl}(\mu\text{-OH})$  (**3**) which was isolated from the reaction mixture in an analytically pure state in a 87% yield. The same compound **3** is gradually formed on keeping of solid **1** in air. The reaction of zwitterion **2** with water at room temperature occurs in a similar fashion, giving rise to pentafluorobenzene and the corresponding bromide hydroxide complex of titanocene  $\text{Cp}[\eta^5\text{-C}_5\text{H}_4\text{B}(\text{C}_6\text{F}_5)_2]\text{TiBr}(\mu\text{-OH})$  (**4**) in 90% isolated yield.

One may assume that the reactions found proceed through coordination of a water molecule to the positively charged titanium centre in the starting zwitterion (Scheme 1). Apparently, the complexation with titanium sharply increases the acidity of water, resulting finally in the protolysis of the  $\text{B-C}_6\text{F}_5$  bond. Thus, zwitterions **1** and **2** behave in the reaction with water as typical strong Lewis acids whose ability to increase the acidity of water due to its complexation is well known [28]. According to [25b,29], the above-mentioned complexation of water with  $\text{B}(\text{C}_6\text{F}_5)_3$  [25] leads also to an enhancement in its acidity but presumably this effect is here insufficiently strong for the efficient protolysis of the  $\text{B-C}_6\text{F}_5$  bond to occur at room temperature.

Complexes **3** and **4** are orange-red crystalline solids stable at 20 °C in an Ar atmosphere. The room-temperature  $^1\text{H}$  NMR spectra of **3** and **4** in  $\text{CDCl}_3$  exhibit a singlet for the unsubstituted  $\eta^5\text{-C}_5\text{H}_5$  ring and four distinct multiplets for the boryl-substituted Cp ligand, thus indicating nonfluxional structures of the complexes. Correspondingly, the room-temperature  $^{19}\text{F}$  NMR spectra of **3** and **4** in  $\text{CDCl}_3$  indicate the presence of two inequivalent  $\text{C}_6\text{F}_5$  groups in the  $\text{B}(\text{C}_6\text{F}_5)_2$  unit. Finally, the  $^{11}\text{B}$  NMR spectra of **3** and **4** show  $^{11}\text{B}$  resonances at  $\delta -1.13$  and  $-1.36$  ppm, respectively, which are indicative of the four-coordinate character of the boron atoms in both complexes. Complex **3** has earlier been obtained by Bochmann and co-workers [8] on recrystallization of boryl-substituted titanocene dichloride  $\text{Cp}[\eta^5\text{-C}_5\text{H}_4\text{B}(\text{C}_6\text{F}_5)_2]\text{TiCl}(\mu\text{-Cl})$  from dichloromethane. Apparently, traces of water present in the solvent are a source of the hydroxide group in the resulting product. The NMR data for **3** reported in this work are in a good accord with those of our study.

The structures of complex **3** (as a toluene solvate  $\mathbf{3} \cdot 2\text{C}_6\text{H}_5\text{CH}_3$ ) and complex **4** (as a benzene solvate  $\mathbf{4} \cdot 1.5\text{C}_6\text{H}_6$ ) have been confirmed by X-ray diffraction studies. The unit cell of **4** contains two crystallographically independent molecules (**4A** and **4B**) slightly differing from each other in the mutual orientation of the  $\text{C}_5$  rings. The molecular structure of one of these independent molecules (**4A**) is shown in Fig. 1. Complex **3** has a similar structure. The selected bond distances and angles for **3**, **4A** and **4B** are given in Table 1. The numbering of atoms for **3** is the same as for **4**.

A characteristic feature of complexes **3** and **4** is the presence in their molecules of the  $\text{Ti-O-B}$  bridge, the formation



Scheme 1.

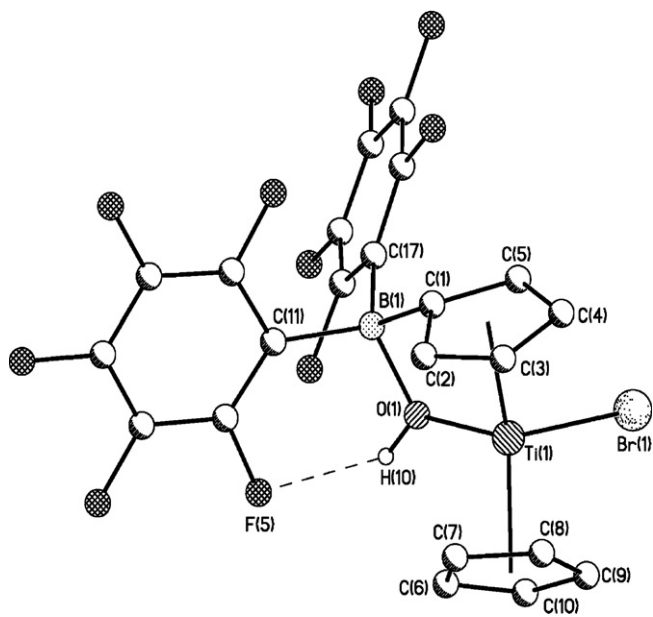
Fig. 1. Molecular structure of complex **4A** in the crystal.

Table 1  
Selected bond lengths (Å) and angles (°) in complex **3** · 2C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub> and in two independent molecules (**A** and **B**) of complex **4** · 1.5C<sub>6</sub>H<sub>6</sub>

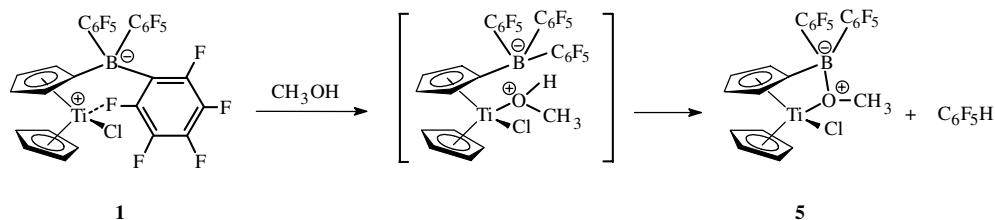
	<b>3</b>	<b>4A</b>	<b>4B</b>
Ti(1)–O(1)	2.040(2)	2.039(3)	2.017(4)
Ti(1)–Cl(1)	2.3581(11)	–	–
Ti(1)–Br(1)	–	2.5026(11)	2.5453(11)
Ti(1)–C(1)	2.301(3)	2.300(5)	2.281(5)
Ti(1)–C(2)	2.321(4)	2.287(5)	2.281(5)
Ti(1)–C(3)	2.383(4)	2.377(5)	2.375(5)
Ti(1)–C(4)	2.382(3)	2.372(5)	2.376(5)
Ti(1)–C(5)	2.325(4)	2.329(5)	2.313(5)
Ti(1)–C(6)	2.381(3)	2.349(5)	2.375(5)
Ti(1)–C(7)	2.331(4)	2.331(5)	2.336(5)
Ti(1)–C(8)	2.355(4)	2.345(5)	2.354(5)
Ti(1)–C(9)	2.361(4)	2.384(5)	2.350(5)
Ti(1)–C(10)	2.364(4)	2.353(5)	2.349(5)
B(1)–O(1)	1.540(4)	1.532(6)	1.541(6)
B(1)–C(1)	1.622(5)	1.599(8)	1.603(8)
B(1)–C(11)	1.623(5)	1.638(8)	1.615(7)
B(1)–C(17)	1.624(5)	1.623(8)	1.615(8)
Ti(1)–Cp(1)	2.016(3)	2.003(5)	1.994(5)
Ti(1)–Cp(2)	2.038(3)	2.031(5)	2.028(5)
O(1)–Ti(1)–Cl(1)	97.48(7)	–	–
O(1)–Ti(1)–Br(1)	–	96.83(9)	95.35(9)
Cp(1)–Ti(1)–Cp(2)	134.1(1)	133.7(2)	134.1(2)
B(1)–O(1)–Ti(1)	107.55(18)	107.7(3)	108.3(3)
O(1)–B(1)–C(1)	93.5(2)	94.3(4)	92.8(4)
O(1)–B(1)–C(11)	112.1(3)	112.8(4)	112.2(4)
O(1)–B(1)–C(17)	110.7(3)	110.1(4)	109.9(4)
C(1)–B(1)–C(11)	111.8(3)	112.2(4)	112.9(4)
C(1)–B(1)–C(17)	114.7(3)	118.2(4)	115.2(4)
C(11)–B(1)–C(17)	112.7(3)	108.7(4)	112.4(4)

of which leads to a deviation of the boron atom from the Cp ring plane towards the titanium atom (by 0.66 Å) and to a decrease in the O(1)–B(1)–C(1) bond angle (to 93.5(2)° in **3**, to 94.3(4)° in **4A** and to 92.8(4)° in **4B**). Other

angles at the boron atom are close to a normal tetrahedral value. In the starting zwitterions **1** and **2**, the boron atom deviates from the corresponding C<sub>5</sub> ring plane in the direction away from the titanium atom (by 0.077(5) Å in **1** and by 0.081(7) Å in **2**) [16]. The Ti(1)–O(1) and B(1)–O(1) distances in **3** (2.040(2) and 1.540(4) Å) are comparable with those in **4** (2.039(3) and 1.532(6) Å in **4A**, 2.017(4) and 1.541(6) Å in **4B**). The Ti(1)–Cl(1) bond length in **3** (2.3581(11) Å) and the Ti(1)–Br(1) bond lengths in **4A** (2.5026(11) Å) and **4B** (2.5453(11) Å) are close to the corresponding Ti–Hal distances in Cp<sub>2</sub>TiCl<sub>2</sub> (Ti–Cl 2.364(3) Å [30]) and Cp<sub>2</sub>TiBr<sub>2</sub> (Ti–Br 2.534(2) Å [31]) but are substantially larger than the Ti–Hal bond length in the starting zwitterions **1** (Ti–Cl 2.302(1) Å) and **2** (Ti–Br 2.460(1) Å) [16], respectively. This result can be explained by a decrease in the positive charge on the titanium atom on going from **1** to **3** and from **2** to **4**, which should lead to a less efficient donation of the halogen lone electron pair to the unoccupied orbital of the titanium and, as a consequence, to an elongation of the Ti–Hal bond.

The geometry of the bent sandwich in **3** and **4** is not exceptional. The planes of the C<sub>5</sub> rings form a dihedral angle of 45.9° in **3**, 46.4° in **4A**, 45.4° in **4B**. The titanium atom as well as the halogen and oxygen atoms are disposed practically in the bisector plane of this dihedral angle. The dihedral angle between the C<sub>5</sub> ring planes in the starting zwitterions **1** and **2** is considerably greater (67.2°) [16] than in **3** and **4**. The coordination environment at titanium in **3** and **4** can be described as pseudotetrahedral, with the large Cp(1)–Ti(1)–Cp(2) bond angle (134.1(1)° in **3**, 133.7(2)° in **4A**, 134.1(2)° in **4B**) and small O(1)–Ti(1)–Hal(1) angle (97.48(7)° for Hal = Cl in **3**, 96.83(9)° for Hal = Br in **4A** and 95.35(9)° for Hal = Br in **4B**) due to the size difference between the Cp ligand and halogen and oxygen atoms (Cp(1) and Cp(2) are the centroids of the Cp rings C(1)–C(5) and C(6)–C(10), respectively). The B(1)–O(1)–Ti(1) angles are 107.55(18)°, 107.7(3)° and 108.3(3)° for **3**, **4A** and **4B**, respectively. The mutual orientation on the Cp ligands in both complexes is close to an eclipsed conformation. The Ti–C distances span the range 2.301(3)–2.383(4) Å in **3**, 2.287–2.384(5) Å in **4A** and 2.281(5)–2.376(5) Å in **4B**. The hydroxide hydrogen atom in **3** and **4** forms a shortened intramolecular contact with the F(5) atom (the H(10)···F(5) distance is 2.24 Å in **3**, 2.49 Å in **4A** and 2.32 Å in **4B**). The values of the X-ray structural parameters obtained for **3** · 2C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub> in our study are close to those for **3** reported in [8]. For other complexes containing C<sub>5</sub>H<sub>4</sub>BX<sub>2</sub> and C<sub>5</sub>H<sub>4</sub>B(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> ligands, see, e.g., [32–35].

Although methanol is a still weaker Brønsted acid than water, it is also able to cleave one of the B–C<sub>6</sub>F<sub>5</sub> bonds in **1** at 20 °C. As a result of the reaction, pentafluorobenzene and the corresponding chloride methoxide complex of titanocene Cp[η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>B(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>]TiCl(μ-OCH<sub>3</sub>) (**5**) contaminated with a small amount of **3** are produced (Scheme 2). Unfortunately, our attempts to purify complex **5** and to grow its crystals suitable for an X-ray diffraction study failed. Nevertheless, the structure of this complex was



Scheme 2.

reliably proved by NMR spectroscopy. Thus, the  $^1\text{H}$  NMR spectrum of **5** shows, in addition to singlets for the  $\eta^5\text{-C}_5\text{H}_5$  and  $\text{CH}_3\text{O}$  groups, four distinct multiplets for the boryl-substituted  $\text{Cp}$  ring, which is in accord with the presence of the  $\text{Ti-O-B}$  bridge in the molecule of **5**. Correspondingly, the  $^{11}\text{B}$  NMR spectrum of **5** in  $\text{CDCl}_3$  is observed at  $\delta -0.27$  ppm, thus indicating on the presence of four-coordinate boron atom in the complex. So close similarity of the NMR spectra of **5** to those of **3** and **4** (see above) evidences for the structural resemblance of these compounds. The formation of small quantity of **3** in the interaction of **1** with methanol is due apparently to traces of moisture in the reaction system.

### 3. Conclusion

The results of our study revealed the remarkable property of zwitterionic complex **1** to increase sharply the Brønsted acidity of water and methanol. As a consequence, both these very weak Brønsted acids acquire the ability to cleave efficiently one of the otherwise inert  $\text{B-C}_6\text{F}_5$  bonds in **1** at room temperature with the formation of pentafluorobenzene and complexes **3** and **5**, respectively, containing the  $\text{Ti-O-B}$  bridge. Under similar conditions, the interaction of zwitterion **2** with water affords pentafluorobenzene and complex **4**, analogous in its structure to **3** and **5**. The key step of these reactions is, apparently, the coordination of a water or methanol molecule to the positively charged titanium(IV) centre of the starting zwitterion. The subsequent intramolecular proton transfer from the coordinated water or methanol species to the  $\text{B-C}_6\text{F}_5$  bond leads to the final products of the reaction. The results obtained in the present study together with the previously reported data on the catalytic activity of complexes **1** and **2** in the cationic ring-opening polymerization of  $\epsilon$ -caprolactone [16] evidence for a high electrophilicity of these zwitterionic metal-locenes, which is of interest for organic synthesis and catalysis.

### 4. Experimental

Experiments were carried out under Ar using standard Schlenk techniques. Starting **1** and **2** were prepared by the methods described in [16]. Toluene and benzene were purified in the usual manner and freshly distilled before use over sodium under Ar. The  $^1\text{H}$  and  $^{11}\text{B}$  NMR spectra were recorded on a Bruker AV-400 spectrometer, the  $^{19}\text{F}$

NMR spectra were registered on a Bruker AV-300 spectrometer. The  $^1\text{H}$  chemical shifts are given relative to TMS, the  $^{11}\text{B}$  chemical shifts are given relative to external  $\text{BF}_3 \cdot \text{OEt}_2$ , the  $^{19}\text{F}$  chemical shifts are given relative to external  $\text{CFCl}_3$ . GLC-MS analyses were performed on a VG 7070E instrument (ionization energy 70 eV, temperature of ion source 150 °C) using the capillary SE-54 column (30 °C).

#### 4.1. Reaction of complex 1 with water

An amount of 0.09 g (0.112 mmol) of  $\mathbf{1} \cdot 0.5\text{CCl}_4$  was dissolved under Ar in 5.5 ml of dry toluene in one Schlenk tube, and 0.5 ml of deaerated water was placed under Ar in the other Schlenk tube. Then, the both Schlenk tubes were connected with one another and the toluene solution of **1** was stirred in water vapour under Ar at 20 °C. In the course of stirring, dark reddish-brown colour of the starting reaction mixture rapidly disappeared and after 10 min an orange-red solution was formed. After 45 min of stirring, the resulting solution was concentrated to ca. 1.2–1.5 ml and kept overnight. In the next day, the precipitated orange-red crystals of complex **3** were separated from the mother liquor by decanting and dried at 20 °C for 3 h in vacuum. The yield of **3** is 0.056 g (87%). Anal. Calc. for  $\text{C}_{22}\text{H}_{10}\text{TiBClF}_{10}\text{O}$ : C, 46.00; H, 1.75. Found: C, 45.84; H, 1.65%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 20 °C, 400.13 MHz,  $\delta$ , ppm): 7.23 (br, 1H, OH), 6.94 (m, 1H,  $\text{C}_5\text{H}_4\text{B}$ ), 6.53 (m, 1H,  $\text{C}_5\text{H}_4\text{B}$ ), 6.51 (s, 5H,  $\text{C}_5\text{H}_5$ ), 6.26 (m, 1H,  $\text{C}_5\text{H}_4\text{B}$ ), 4.78 (m, 1H,  $\text{C}_5\text{H}_4\text{B}$ ).  $^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 20 °C, 128.38 MHz,  $\delta$ , ppm):  $-1.13$ .  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 20 °C, 282.40 MHz,  $\delta$ , ppm):  $-134.80$  (m, 2F, *o*- $\text{C}_6\text{F}_5$ ),  $-135.52$  (m, 2F, *o*- $\text{C}_6\text{F}_5$ ),  $-156.87$  (t, 1F,  $J_{\text{F-F}} = 20.6$  Hz, *p*- $\text{C}_6\text{F}_5$ ),  $-157.11$  (t, 1F,  $J_{\text{F-F}} = 20.4$  Hz, *p*- $\text{C}_6\text{F}_5$ ),  $-162.25$  (m, 2F, *m*- $\text{C}_6\text{F}_5$ ),  $-162.89$  (m, 2F, *m*- $\text{C}_6\text{F}_5$ ). For carrying out the X-ray diffraction study, the crystals of **3** were dried in vacuum at 20 °C for 2 min. Under such conditions, the crystals of the complex contained two moles of toluene per mole of **3**. The analysis of organic products of the reaction by the GLC-MS method revealed the presence of pentafluorobenzene in the reaction solution.

#### 4.2. Reaction of complex 2 with water

An amount of 0.08 g (0.093 mmol) of  $\mathbf{2} \cdot 0.5 \text{C}_2\text{H}_4\text{Br}_2$  was dissolved under Ar in 4 ml of dry toluene in one Schlenk tube, and 0.4 ml of deaerated water was charged

under Ar in the other Schlenk tube. Then, the both Schlenk tubes were connected with each other and the toluene solution of **2** was stirred at 20 °C in water vapour under an Ar atmosphere. During the course of stirring, dark brown colour of starting **2** gradually disappeared and after 15 min a red-orange solution was produced. After 1 h, the resulting mixture was concentrated to ca. 1.2–1.5 ml and allowed to stand at 20 °C overnight. In the next day, the precipitated orange-red crystals of complex **4** were separated by decanting and dried at 20 °C in vacuum for 3 h. Despite drying, the obtained complex contained one mole of toluene per mole of **4**. The yield of **4** · PhCH<sub>3</sub> is 0.06 g (90%). Anal. Calc. for C<sub>22</sub>H<sub>10</sub>TiBBrF<sub>10</sub>O · C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>: C, 48.98; H, 2.55. Found: C, 48.52; H, 2.55%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 20 °C, 400.13 MHz, δ, ppm): 7.55 (br, 1H, OH), 6.81 (m, 1H, C<sub>5</sub>H<sub>4</sub>B), 6.62 (m, 1H, C<sub>5</sub>H<sub>4</sub>B), 6.56 (s, 5H, C<sub>5</sub>H<sub>5</sub>), 6.30 (m, 1H, C<sub>5</sub>H<sub>4</sub>B), 4.80 (m, 1H, C<sub>5</sub>H<sub>4</sub>B). <sup>11</sup>B NMR (CDCl<sub>3</sub>, 20 °C, 128.38 MHz, δ, ppm): -1.36. <sup>19</sup>F NMR (CDCl<sub>3</sub>, 20 °C, 282.40 MHz, δ, ppm): -134.81 (m, 2F, *o*-C<sub>6</sub>F<sub>5</sub>), -135.42 (m, 2F, *o*-C<sub>6</sub>F<sub>5</sub>), -156.86 (t, 1F, *J*<sub>F-F</sub> = 20.2 Hz, *p*-C<sub>6</sub>F<sub>5</sub>), -157.07 (t, 1F, *J*<sub>F-F</sub> = 20.2 Hz, *p*-C<sub>6</sub>F<sub>5</sub>), -162.28 (m, 2F, *m*-C<sub>6</sub>F<sub>5</sub>), -162.85 (m, 2F *m*-C<sub>6</sub>F<sub>5</sub>). Crystals of **4** suitable for a structure determination were grown from dry benzene and contained 1.5 mol of C<sub>6</sub>H<sub>6</sub> per mole of **4**. In organic products of the reaction, pentafluorobenzene was found by the GLC-MS method.

#### 4.3. Reaction of complex with methanol

An amount of 0.2 g (0.25 mmol) of **1** · 0.5CCl<sub>4</sub> was dissolved under Ar in 10 ml of dry toluene in one Schlenk tube, and in the other Schlenk tube a solution of sodium methoxide in methanol was prepared from 0.12 g (5.22 mmol) of metallic sodium and 1 ml of dry CH<sub>3</sub>OH. Then, the both Schlenk tubes were connected with one another and the toluene solution of **1** was stirred in methanol vapour at 22 °C under Ar. After 1.5 h of stirring, there was a colour change of the reaction mixture from reddish-brown to wine-red, and after 6–7 h a rose-red solution was formed. The subsequent removal of the solvent and drying in vacuum at 20 °C for 2 h gave a red solid (0.17 g) containing a mixture (83 : 17) of complexes **5** and **3** according to the <sup>1</sup>H, and <sup>11</sup>B NMR spectra. <sup>1</sup>H NMR of **5** (CDCl<sub>3</sub>, 20 °C, 400.13 MHz, δ, ppm): 7.51 (m, 1H, C<sub>5</sub>H<sub>4</sub>B), 6.86 (m, 1H, C<sub>5</sub>H<sub>4</sub>B), 6.53 (s, 5H, C<sub>5</sub>H<sub>5</sub>), 6.36 (m, 1H, C<sub>5</sub>H<sub>4</sub>B), 6.25 (m, 1H, C<sub>5</sub>H<sub>4</sub>B), 3.64 (s, 3H, OCH<sub>3</sub>). <sup>11</sup>B NMR of **5** (CDCl<sub>3</sub>, 20 °C, 128.38 MHz, δ, ppm): -0.27. In organic products of the reaction, pentafluorobenzene was found by GLC-MS.

#### 4.4. X-ray crystallographic study

X-ray diffraction experiments were carried out with a Bruker SMART 1000 CCD diffractometer (complex **3**)

Table 2  
Crystal data and structure refinement parameters for **3** and **4**

	<b>3</b>	<b>4</b>
Empirical formula	C <sub>22</sub> H <sub>10</sub> BClF <sub>10</sub> OTi · 2C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	C <sub>22</sub> H <sub>10</sub> BBBrF <sub>10</sub> OTi · 1.5C <sub>6</sub> H <sub>6</sub>
Molecular weight	758.73	736.08
Dimension (mm <sup>3</sup> )	0.40 × 0.20 × 0.16	0.42 × 0.02 × 0.02
<i>T</i> (K)	100	100
Crystal system	Triclinic	Orthorhombic
Space group	<i>P</i> $\bar{1}$	<i>Pca</i> 2 <sub>1</sub>
<i>a</i> (Å)	11.1735(13)	12.400(3)
<i>b</i> (Å)	12.7684(15)	17.430(4)
<i>c</i> (Å)	13.1044(15)	26.060(5)
$\alpha$ (°)	65.360(3)	90.00
$\beta$ (°)	73.375(3)	90.00
$\gamma$ (°)	77.086(3)	90.00
<i>V</i> (Å <sup>3</sup> )	1616.6(3)	5632(2)
<i>Z</i> ( <i>Z'</i> )	2(1)	8(2)
$\rho_{\text{calc}}$ (g cm <sup>-3</sup> )	1.559	1.736
Linear absorption, $\mu$ (cm <sup>-1</sup> )	4.36	18.16
Diffractometer	SMART CCD	APEX II CCD
Scan type	$\omega$	$\omega$
<i>F</i> (000)	768	2920
2 $\theta_{\text{max}}$ (°)	52	54
Reflections measured	7740	56948
Independent reflections	6107	12540
Observed reflections [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	3934	8536
Number of parameters	552	814
<i>R</i> <sub>1</sub>	0.0588	0.0454
<i>wR</i> <sub>2</sub>	0.1492	0.0832
GOF	1.066	0.954
$\Delta\rho_{\text{max}}/\Delta\rho_{\text{min}}$ (e Å <sup>-3</sup> )	0.788/-0.354	0.502/-0.635

and a Bruker APEX II CCD diffractometer (complex **4**) at 100 K, using graphite monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71072$  Å,  $\omega$  scans). Reflection intensities were integrated using SAINT software [36] and absorption correction was performed semi-empirically using SADABS program [37]. The structures were solved by direct method and refined by the full-matrix least-squares against  $F^2$  in anisotropic approximation for non-hydrogen atoms. The positions of hydrogen atoms were calculated geometrically. Crystal data and structure refinement parameters for **3** and **4** are given in Table 2. All calculations were performed using the SHELXTL software [38].

### Acknowledgement

The work was supported by the Russian Foundation for Basic Research (Project Code 05-03-32515).

### Appendix A. Supplementary material

CCDC 616777 and 633103 contain the supplementary crystallographic data for **3** and **4**. 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. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.06.062.

### References

- [1] W.E. Piers, Chem. Eur. J. 4 (1998) 13.
- [2] G. Erker, Acc. Chem. Res. 34 (2001) 309.
- [3] G. Erker, Chem. Commun. (2003) 1469.
- [4] U. Rosenthal, V.V. Burlakov, P. Arndt, W. Baumann, A. Spannenberg, V.B. Shur, Eur. J. Inorg. Chem. (2004) 4739.
- [5] H. van der Heijden, B. Hessen, A.G. Orpen, J. Am. Chem. Soc. 120 (1998) 1112.
- [6] L.W.M. Lee, W.E. Piers, M. Parvez, S.J. Rettig, V.G. Young, Organometallics 18 (1999) 3904.
- [7] A.H. Cowley, G.S. Hair, B.G. McBarnett, R.A. Jones, Chem. Commun. (1999) 437.
- [8] S.J. Lancaster, S. Al-Benna, M. Thornton-Pett, M. Bochmann, Organometallics 19 (2000) 1599.
- [9] G.S. Hair, R.A. Jones, A.H. Cowley, V. Lynch, Organometallics 20 (2001) 177.
- [10] G.S. Hair, R.A. Jones, A.H. Cowley, V. Lynch, Inorg. Chem. 40 (2001) 1014.
- [11] M. Hill, G. Kehr, G. Erker, O. Kataeva, R. Fröhlich, Chem. Commun. (2004) 1020.
- [12] M. Hill, G. Erker, G. Kehr, R. Fröhlich, O. Kataeva, J. Am. Chem. Soc. 126 (2004) 11046.
- [13] V.V. Burlakov, P. Arndt, W. Baumann, A. Spannenberg, U. Rosenthal, Organometallics 23 (2004) 4160.
- [14] V.V. Burlakov, P. Arndt, W. Baumann, A. Spannenberg, U. Rosenthal, Organometallics 23 (2004) 5188.
- [15] V. Varga, P. Šindelář, I. Čišarová, M. Horáček, J. Kubišta, K. Mach, Inorg. Chem. Commun. 8 (2005) 222.
- [16] L.I. Strunkina, M.Kh. Minacheva, K.A. Lyssenko, V.V. Burlakov, W. Baumann, P. Arndt, B.N. Strunin, V.B. Shur, J. Organomet. Chem. 691 (2006) 557.
- [17] M. Bochmann, J. Chem. Soc., Dalton Trans. (1996) 255.
- [18] R.F. Jordan, Adv. Organomet. Chem. 32 (1991) 325.
- [19] E.Y.-X. Chen, T.J. Marks, Chem. Rev. 100 (2000) 1391.
- [20] M. Bochmann, J. Organomet. Chem. 689 (2004) 3982.
- [21] V.V. Burlakov, A.V. Letov, P. Arndt, W. Baumann, A. Spannenberg, Ch. Fisher, L.I. Strunkina, M.Kh. Minacheva, Ya.S. Vygodskii, U. Rosenthal, V.B. Shur, J. Mol. Catal. A 200 (2003) 63.
- [22] V.V. Burlakov, S.I. Troyanov, A.V. Letov, L.I. Strunkina, M.Kh. Minacheva, G.G. Furin, U. Rosenthal, V.B. Shur, J. Organomet. Chem. 598 (2000) 243.
- [23] L.I. Strunkina, M.Kh. Minacheva, K.A. Lyssenko, P.V. Petrovskii, V.V. Burlakov, U. Rosenthal, V.B. Shur, Izv. Akad. Nauk, Ser. Khim. (2006) 169 [Russ. Chem. Bull., Int. Ed. Engl. 55 (2006) 174].
- [24] A.G. Massey, A.J. Park, J. Organomet. Chem. 5 (1966) 218.
- [25] (a) A.A. Danopoulos, J.R. Galsworthy, M.L.H. Green, S. Cafferkey, L.H. Doerrer, M.B. Hursthouse, Chem. Commun. (1998) 2529; (b) L.H. Doerrer, M.L.H. Green, J. Chem. Soc., Dalton Trans. (1999) 4325; (c) T. Beringhelli, D. Maggioni, G. D'Alfonso, Organometallics 20 (2001) 4927.
- [26] H. Nishida, N. Takada, M. Yoshimura, T. Sonoda, H. Kobayashi, Bull. Chem. Soc. Jpn. 57 (1984) 2600.
- [27] O.I. Kachurin, A.P. Zarskii, L.I. Velichko, N.A. Zaraiskaya, N.M. Matvienko, Z.A. Okhrimenko, Izv. Akad. Nauk, Ser. Khim. (1995) 1895 [Russ. Chem. Bull. 44 (1995) 1815 (Engl. Transl.)].
- [28] G.A. Olah (Ed.), Friedel-Crafts and Related Reactions, Interscience/Wiley, New York/London, 1963.
- [29] (a) C. Bergquist, B.M. Bridgewater, C.J. Harlan, J.R. Norton, R.A. Friesner, G. Parkin, J. Am. Chem. Soc. 122 (2000) 10581; (b) G.S. Hill, L. Manojlovic-Muir, K.W. Muir, R.J. Puddephatt, Organometallics 16 (1997) 525.
- [30] A. Clearfield, D.K. Warner, C.H. Saldarriaga-Molina, R. Ropal, Can. J. Chem. 53 (1975) 1622.
- [31] P.G. Jones, C. Kienitz, C. Thone, Z. Kristallogr. 26 (1994) 85.
- [32] M.T. Reetz, H. Brümmer, M. Kessler, J. Kuhnigk, Chimia 49 (1995) 501.
- [33] R. Duchateau, S.J. Lancaster, M. Thornton-Pett, M. Bochmann, Organometallics 16 (1997) 4995.
- [34] L.H. Doerrer, A.J. Graham, D. Haussinger, M.L.H. Green, J. Chem. Soc., Dalton Trans. (2000) 813.
- [35] S.J. Lancaster, A.J. Mountford, D.L. Hughes, M. Schormann, M. Bochmann, J. Organomet. Chem. 680 (2003) 193.
- [36] SMART V5.051 and SAINT V5.00, Area Detector Control and Integration Software, Bruker AXS Inc., Madison, WI-53719, USA, 1998.
- [37] G.M. Sheldrick, SADABS, Bruker AXS Inc., Madison, WI-53719, USA, 1997.
- [38] G.M. Sheldrick, SHELXTL-97, Version 5.10, Bruker AXS Inc., Madison, WI-53719, USA, 1997.