Letters to the Editor

Protolytic B—C_6F_5 bond cleavage in zwitterionic titanocene monochloride Cp[η^5-$C_5H_4B(C_6F_5)_3$]TiCl with water to form titanocene chloride hydroxide complex Cp[η^5-$C_5H_4B(C_6F_5)_2$]TiCl(μ-OH)

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Zwitterionic Group IVB metallocenes (see, for instance, reviews[1—4]) hold considerable promise for catalysis due to their high electrophilicity and, as a rule, sufficiently good solubility in nonpolar solvents, *viz.*, aromatic hydrocarbons. Recently,[4—6] we have described the first zwitterions of this type, which can catalyze cationic ring-opening polymerization. The reaction of the zwitterionic paramagnetic trivalent titanium complex Cp[η^5-$C_5H_4B(C_6F_5)_3$]Ti with an excess of CCl_4 at 20 °C afforded the zwitterionic compound Cp[η^5-$C_5H_4B(C_6F_5)_3$]TiCl (**1**) containing the $B(C_6F_5)_3$-substituted η^5-Cp ring and exhibiting catalytic activity in polymerization of THF and ε-caprolactone.[5,6] These data are indicative of high electrophilicity of the positively charged titanium atom in molecule **1**, which may be used for performing other reactions catalyzed or promoted by Lewis acids. In the present study, we report a new reaction of zwitterion **1**, which demonstrates its high electrophilicity.

We found that exposure of a toluene solution of compound **1** to water vapor at 20 °C under Ar leads to rapid protolytic cleavage of one B—C_6F_5 bond in the tris(pentafluorophenyl)borane group giving rise to pentafluorobenzene and the titanocene chloride hydroxide complex Cp[η^5-$C_5H_4B(C_6F_5)_2$]TiCl(μ-OH) (**2**), which was isolated from the mixture in 78% yield (Scheme 1). Compound **2** is also gradually formed during storage of solid zwitterion **1** in air. One may assume that the observed reaction proceeds through coordination of a water molecule to the positively charged titanium center in the starting zwitterion (see Scheme 1). Apparently, complexation with titanium sharply increases the acidity of water, resulting finally in protolysis of the B—C_6F_5 bond. Therefore, zwitterion **1** behaves in the reaction with water as typical strong Lewis acids, whose ability to increase the

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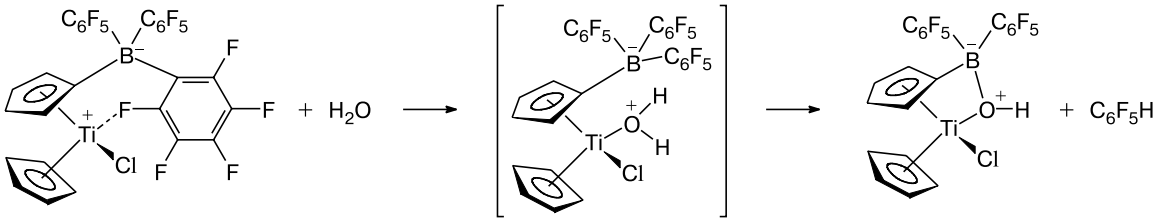
Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 1, pp. 169—171, January, 2006.
1066-5285/06/5501-0174

Scheme 1



1 **2**

acidity of water due to complexation with the latter is well known.[7] It should be noted that the B—C_6F_5 bond in tris(pentafluorophenyl)borane $B(C_6F_5)_3$ is very inert to water (after 18 days, the yield of pentafluorobenzene at 20 °C is lower than 3%).[8] In this case, the process virtually ceases at the step of formation of the corresponding complexes, *viz.*, $(C_6F_5)_3B(OH_2)$, $[(C_6F_5)_3B(OH_2)] \cdot H_2O$, and $[(C_6F_5)_3B(OH_2)] \cdot 2H_2O$.[9,10] It is known that the boron—carbon bond in tetraarylborates is also stable to water at 20 °C, whereas in polyfluorine-containing tetraarylborates ($[B(C_6F_4)_4]^-$, $\{B[3,5\text{-}(CF_3)_2C_6H_3]_4\}^-$, *etc.*), it is not cleaved under ambient conditions even with aqueous solutions of mineral acids.[11]

Complex **2** is a red-orange crystalline solid (m.p. 219 °C under Ar) stable at 20 °C under an Ar atmosphere. The structure of complex **2** (as a solvate with two toluene molecules) was established by X-ray diffraction (Fig. 1).

The crystals of **2** at 120 K are triclinic: space group $P\bar{1}$, a = 11.173(1) Å, b = 12.768(1) Å, c = 13.104(2) Å, α = 65.360(3)°, β = 73.375(3)°, γ = 77.086(3)°, V = 1616.6(3) Å^3, Z = 2 (Z' = 1), d_{calc} = 1.559 g cm^{-3}. X-ray diffraction data were collected on a Smart 1000 CCD diffractometer. The final R factors were R_1 = 0.0588 (for 3934 reflections with $I > 2\sigma(I)$), wR_2 = 0.1492, GOOF = 1.066 (for 6107 independent reflections with $\theta > 52°$).

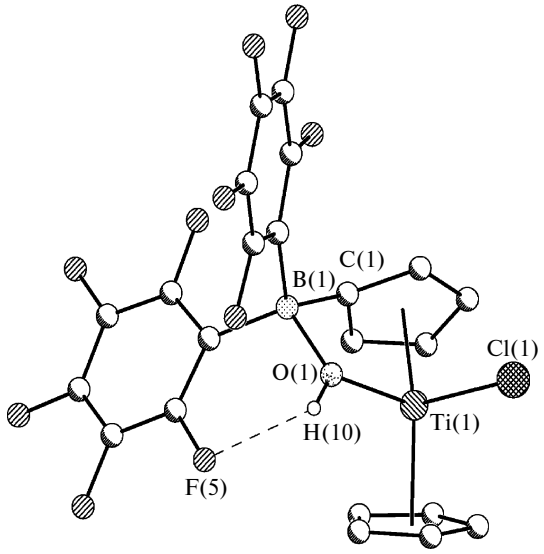


Fig. 1. Molecular structure of complex **2**.

An interesting structural feature of complex **2** is the presence of the Ti—O—B bridge (Ti(1)—O(1), 2.040(2) Å; B(1)—O(1), 1.540(4) Å) the formation of which leads to a deviation of the boron atom from the plane of the Cp ring by 0.69 Å toward the titanium atom and a decrease in the C(1)—B(1)—O(1) bond angle to 93.5(2)°. Other angles at the boron atom are close to the tetrahedral angle. The dihedral angle between the planes of the substituted and unsubstituted C_5 rings in molecule **2** is 45.9°. The titanium atom and the O(1) and Cl(1) atoms coordinated to Ti (O(1)—Ti(1)—Cl(1), 97.48(7)°; Ti(1)—O(1)—B(1), 107.6(2)°) lie approximately in the bisector plane of this dihedral angle. The Ti(1)—Cl(1) bond length in complex **2** (2.358(1) Å) is similar to the corresponding distance (2.364(3) Å) in titanocene dichloride[12] but is substantially larger than that in the starting zwitterion **1** (2.302(1) Å).[5,6] This result can be explained by a decrease in the positive charge on the titanium atom in complex **2** compared to that in zwitterion **1**, which should lead to a less efficient donation of the chlorine lone electron pair to the unoccupied orbital of titanium and, consequently, to an elongation of the Ti—Cl bond. The hydroxide hydrogen atom in compound **2** forms a shortened intramolecular contact with the F(5) atom (H(10)—F(5), 2.24 Å).

Earlier, complex **2** has been obtained[13] in a small amount on recrystallization of boryl-substituted titanocene dichloride $Cp[\eta^5\text{-}C_5H_4B(C_6F_5)_2]TiCl(\mu\text{-}Cl)$ from dichloromethane. Apparently, traces of water present in the solvent serve as a source of the hydroxide group in the reaction product.

This study was financially supported by the Russian Foundation for Basic Research (Project No. 05-03-32515).

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Received November 14, 2005