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Synthesis of zwitterionic titanocene monochloride $Cp[\eta^5\text{-}C_5H_4B(C_6F_5)_3]TiCl$ containing tris(pentafluorophenyl)borane moiety in the η^5-cyclopentadienyl ring

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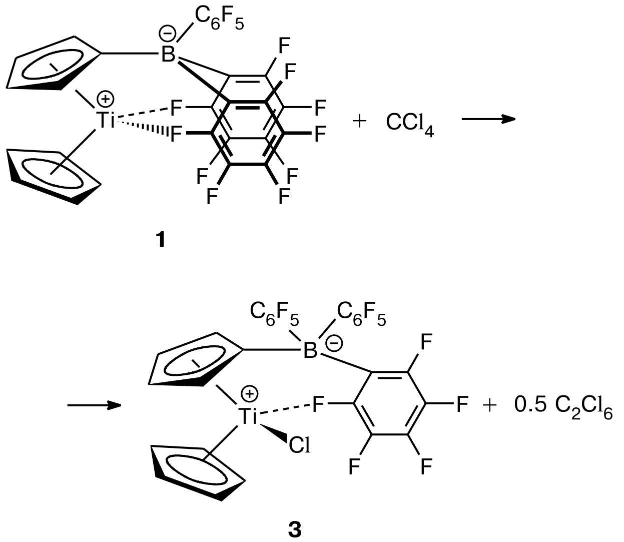
Zwitterionic Group IVB metallocenes are of considerable interest as potential catalysts for stereospecific polymerization of olefins and other reactions (see, for instance, Refs. 1—9 and references cited therein). Recently, we have reported on the first examples of the successful use of such metallocenes in catalysis of cationic ring-opening polymerization. It was found that the reaction of the zwitterionic paramagnetic trivalent titanium complex $Cp[\eta^5\text{-}C_5H_4B(C_6F_5)_3]Ti$ (**1**)[2,3] with atmospheric oxygen afforded zwitterionic titanoxane $\{Cp[\eta^5\text{-}C_5H_4B(C_6F_5)_3]Ti\}_2O$ (**2**),[8] which contains two positively charged titanium atoms per molecule and is able to catalyze polymerization of THF and ε-caprolactone.[9] This result is indicative of the high electrophilicity of the cationic centers in molecule **2**, which may be useful in performing other reactions catalyzed by the Lewis acids.

In the present paper, we report the synthesis and structure of new zwitterionic metallocene $Cp[\eta^5\text{-}C_5H_4B(C_6F_5)_3]TiCl$ (**3**), which is a chloride analog of titanoxane **2**. Complex **3** was prepared in 66% yield by the reaction of zwitterion **1** with CCl_4 at 20 °C in an Ar atmosphere (Scheme 1). Hexacloroethane was detected among organic products of the reaction. Complex **3** is dark-brown needle-like crystals (m.p. 186—187 °C (with decomp.) under Ar), which are soluble in toluene, dichlromethane, and THF and poorly soluble in CCl_4. In the solid state, complex **3** is stable under an Ar atmosphere at 20 °C, but it gradually decomposes in air. According to elemental analysis, the composition of the complex corresponds to the formula $Cp[\eta^5\text{-}C_5H_4B(C_6F_5)_3]TiCl \cdot 0.5CCl_4$.

Scheme 1



The structure of complex **3** (as the solvate with CCl_4) was established by X-ray diffraction analysis. The crystals of **3** at 110 K are monoclinic: a = 10.762(3), b = 14.617(4), c = 18.356(4) Å, β = 94.713(6)°, V = 2877.7(12) Å^3, d_{calc} = 1.850 g cm^{-3}, μ = 6.96 cm^{-1}, $P2_1/c$, Z = 4. The intensities of 18115 reflections were measured on a SMART 1000 CCD diffractometer at 110 K (Mo-Kα radiation, $2\theta_{max}$ = 58°), and 7475 observed reflections were used in subsequent calculations. The structure of **3** was solved by direct methods and refined by the full-matrix least-squares method (SHELXTL PLUS) with anisotropic and isotropic thermal parameters based on F^2 to wR_2 = 0.1034, GOOF = 1.022 for all reflections; R_1 = 0.0502 for 3784 reflections with $I > 2\sigma(I)$.

Complex **3** is a monochloro derivative of titanocene in which one of the hydrogen atoms of the η^5-Cp ring is replaced by the $B(C_6F_5)_3$ group (Fig. 1). The characteristic feature of the complex is the presence of a coordina-

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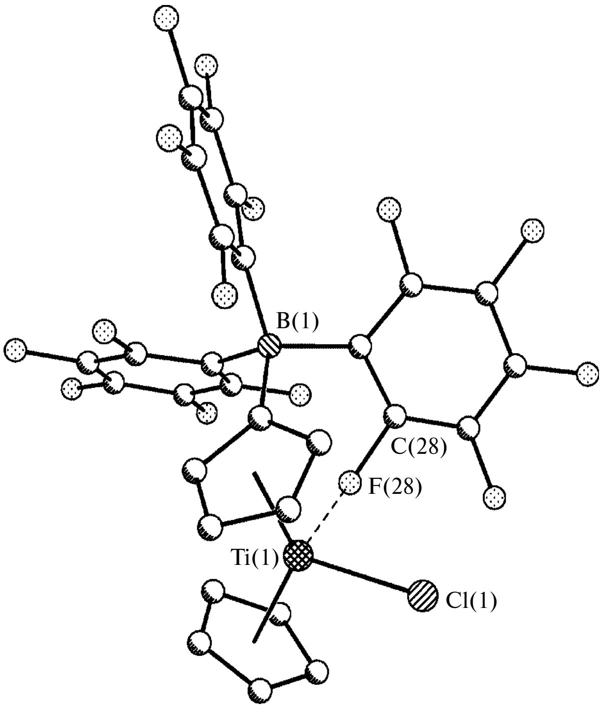

Fog. 1. Molecular structure of complex **3**.

tion bond between the *ortho*-fluorine atom (F(28)) of one of the C_6F_5 substituents and the positively charged titanium atom. The Ti(1)...F(28) distance is 2.168(2) Å, which is noticeably shorter than the analogous Ti...F distances (2.181(2)—2.252(2) Å) in other known zwitterionic titanium complexes containing the $B(C_6F_5)_3$ group in the cyclopentadienyl ligand.[2,3,8] Due to the coordination of the F(28) atom to the titanium atom, the C(28)—F(28) bond is elongated (1.406(3) Å) compared to the remaining C—F bonds in molecule **3** (1.338(3)—1.363(3) Å; aver. 1.352 Å). The coordination of the boron atom is approximately tetrahedral. The boron atom deviates from the plane of the Cp ring in the opposite direction with respect to the titanium atom by 0.08 Å.

The geometry of the bent sandwich in compound **3** is typical of Group IVB metallocenes. The dihedral angle between the planes of the substituted and unsubstituted Cp rings is 46.9°. The titanium atom and the F(28) and Cl(1) atoms bonded to Ti (F(28)—Ti(1)—Cl(1), 88.99(5)°; Ti(1)—F(28)—C(28), 127.9(1)°) lie approximately in the bisector plane of this dihedral angle. The Ti(1)—Cl(1) bond length is 2.302(1) Å, which is considerably shorter than the Ti—Cl distances (2.364(3) Å) in titanocene dichloride.[10] Apparently, this shortening is associated with an increase in the positive charge on the titanium atom on going from Cp_2TiCl_2 to complex **3**, which should lead to a more efficient donation of the lone electron pair of the chlorine atom to the unoccupied orbital of the Ti atom and, consequently, to an increase in the multiplicity of the Ti—Cl bond and its shortening.

At 20 °C, complex **3**, like zwitterionic titanoxane **2**, catalyzes cationic ring-opening polymerization of THF. The results of this investigation will be published elsewhere.

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