Letters to the Editor

Synthesis of a zwitterionic metallocene of a new type by the reaction of the bis(trimethylsilyl)acetylene complex of titanocene with tris(pentafluorophenyl)borane

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In recent years, ever increasing interest has been shown in the synthesis of zwitterionic cyclopentadienyl complexes of group IVB metals (see the review[1]); this is due to the fact that such bipolar complexes are promising single-component catalysts for stereospecific polymerization of olefins. Syntheses of zwitterionic zirconocene derivatives were the most successful along this line. For titanium and hafnium, only a few examples of zwitterionic metallocenes of this type have been reported. In all the zwitterions synthesized, the metal atom occurs in the +4 oxidation state and has at least one σ-bonded organic group.

In the present communication, we report on the synthesis and structure of a zwitterionic metallocene of a new type, which is formed in the reaction of the bis(trimethylsilyl)acetylene complex of titanocene $(\eta^5\text{-}C_5H_5)_2Ti(Me_3SiC_2SiMe_3)$[2,3] with an equimolar amount of $B(C_6F_5)_3$ in toluene at 20 °C in an Ar atmosphere. This reaction, accompanied by the displacement of the acetylene ligand, involves electrophilic substitution of a hydrogen atom in one Cp ring by a $B(C_6F_5)_3$ group (Scheme 1) and gives a zwitterionic complex of trivalent titanium, $(\eta^5\text{-}C_5H_5)\{\eta^5\text{-}[C_5H_4B(C_6F_5)_3]\}Ti$ (**1**), which contains no organic radicals σ-bonded to the metal.

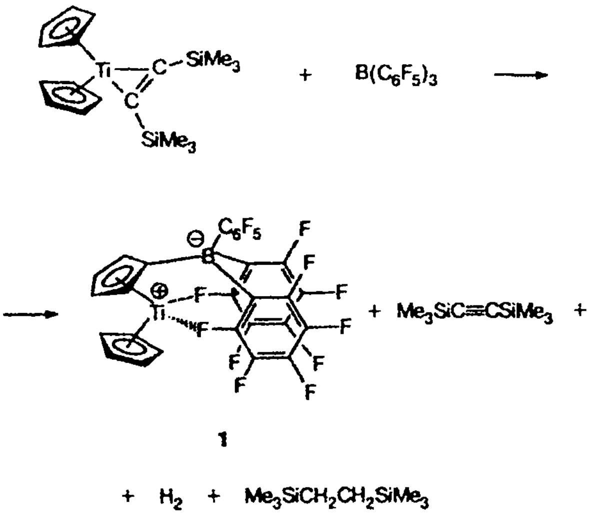
Complex **1** was obtained as dark blue paramagnetic crystals (m.p. 161—163 °C (decomp.) in an Ar atmosphere) readily soluble in THF and less soluble in toluene. The solid complex is stable under Ar at 20 °C but rapidly decomposes in the presence of atmospheric oxygen and moisture. The formation of compound **1** is accompanied by evolution of dihydrogen (0.11 moles per mole of the initial acetylene complex). The organic reaction products were found to contain bis(trimethylsilyl)acetylene and 1,2-bis(trimethylsilyl)ethane in 4 : 1 ratio.

The structure of complex **1** (which crystallizes as a solvate with a toluene molecule) was established by X-ray diffraction analysis. The crystals of **1** are monoclinic, space group $P2_1/n$, $a = 10.216(3)$ Å, $b = 14.813(6)$ Å, $c = 19.924(7)$ Å, $\beta = 91.40(5)°$, $V = 3014(2)$ Å^3, $Z = 4$, $d_{calc} = 1.721$ g cm^{-3}. The structure

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 5, pp. 1022—1024, May, 1999.

1066-5285/99/4805-1012 $22.00

Scheme 1



was solved by the direct methods and refined in the anisotropic approximation to R = 0.0484 (4090 reflections and 469 parameters).

It can be seen from Fig. 1 that complex **1** is a bis(cyclopentadienyl) derivative of Ti^{III} in which one hydrogen atom of the η^5-C_5H_5 ring is replaced by a $B(C_6F_5)_3$ group. An interesting feature of the structure of **1** is the presence of coordination bonds between the *ortho*-fluorine atoms (F(1) and F(6)) of two C_6F_5 substituents and the positively charged titanium atom (Ti···F(1), 2.248(2) Å; Ti···F(6), 2.223(3) Å). The coordination of the F(1) and F(6) atoms with titanium results in the C(12)—F(1) and C(18)—F(6) bonds being longer (1.401(4) and 1.382(5) Å) than other C—F bonds in molecule **1** (1.330—1.364 Å, aver. 1.348 Å). The geometry of the wedge-shaped sandwich in molecule **1** is not exceptional. The planes of the substituted and unsubstituted C_5 rings form a dihedral angle of 36.2°. The titanium atom and the C(12)—F(1) and C(18)—F(6) bonds coordinated to it (bond angles F(1)—Ti—F(6), 74.0(1)°; Ti—F(1)—C(12), 139.7(2)°; and Ti—F(6)—C(18), 139.9(2)°) are arranged approximately in the bisecting plane of this dihedral angle. Despite the fact that two C_6F_5 groups are bound to titanium, the boron atom virtually does not deviate from the plane of the C_5 ring. The coordination at the boron atom is nearly tetrahedral.

Electrophilic substitution of a hydrogen atom in the η^5-C_5H_5 ring by a $B(C_6F_5)_3$ group has been observed previously[4] in a study of the reaction of $B(C_6F_5)_3$ with zirconacyclopentadiene metallacycle $(\eta^5\text{-}C_5H_5)_2\overline{Zr\text{—}C(Me)\text{=}C(Me)C(Me)\text{=}C}(Me)$. However, unlike complex **1**, the zwitterionic metallocene $(\eta^5\text{-}C_5H_5)\{\eta^5\text{-}[C_5H_4B(C_6F_5)_3]\}Zr\text{—}C(Me)\text{=}C(Me)\text{—}C(Me)\text{=}CHMe$ formed in this case is a derivative of Zr^{IV} and contains a σ-bonded trimethylpentadienyl group.

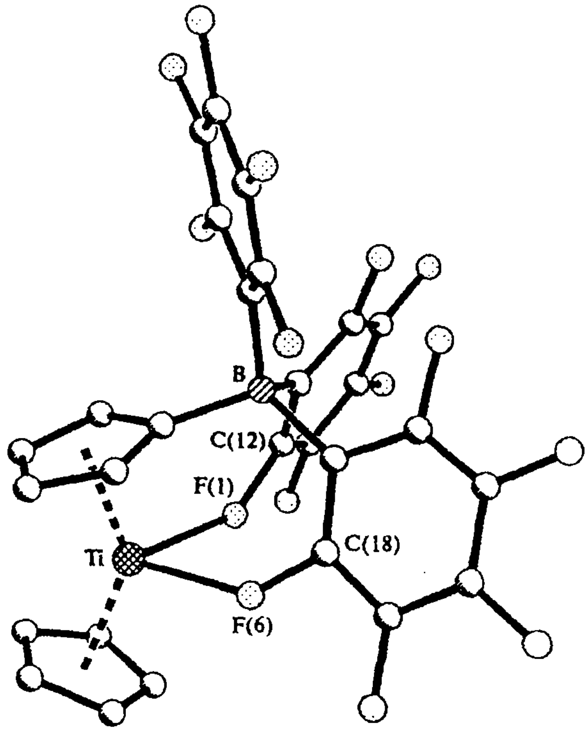


Fig. 1. Molecular structure of complex **1**.

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Received November 23, 1998;
in revised form February 15, 1999