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Synthesis and X-ray Crystal Structure Determination of New Zwitterionic Complexes of Titanocene

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The reaction of $(\eta^5\text{-}^iPrC_5H_4)_2Ti(Me_3SiC_2SiMe_3)$ (**2**) with $B(C_6F_5)_3$ in toluene at room temperature produces the zwitterionic titanium(III) complex $(\eta^5\text{-}^iPrC_5H_4)[\eta^5\text{-}\{1,3\text{-}^iPrC_5H_3B(C_6F_5)_3\}]Ti$ (**3**) in which the 3-hydrogen atom of one of the C_5 rings is substituted by a $B(C_6F_5)_3$ group. The complex is analogous in its structure to the previously described titanium(III) zwitterion $Cp[\eta^5\text{-}C_5H_4B(C_6F_5)_3]Ti$ (**1**) formed in the interaction of $B(C_6F_5)_3$ with $Cp_2Ti(Me_3SiC_2SiMe_3)$. A characteristic feature of both zwitterionic complexes is the presence of coordinative bonds between the *ortho*-fluorine atoms of two C_6F_5 substituents and the positively charged titanium center. Complex **1** is also obtained by the reaction of $B(C_6F_5)_3$ with $Cp_2Ti(PhC_2SiMe_3)$. The oxidation of **1** and **3** by air oxygen affords the zwitterionic titanoxanes $\{Cp[\eta^5\text{-}C_5H_4B(C_6F_5)_3]Ti\}_2O$ (**4**) and $\{(\eta^5\text{-}^iPrC_5H_4)[(\eta^5\text{-}\{1,3\text{-}^iPrC_5H_3B(C_6F_5)_3\}]Ti\}_2O$ (**5**), respectively, which contain two zwitterionic units in the molecule. In each of these units, only one *ortho*-fluorine atom of a $B(C_6F_5)_3$ group is involved in the coordination to the titanium atom. Complex **1** readily reacts also with acetone to give the zwitterionic adduct $Cp[\eta^5\text{-}C_5H_4B(C_6F_5)_3]Ti(Me_2CO)$ (**6**)**,** wherein the molecule of acetone is bonded to the Ti(III) center through the oxygen atom. In this adduct too, only one *ortho*-fluorine atom of a $B(C_6F_5)_3$ group is coordinated to the metal.

Introduction

Zwitterionic metallocenes of the group IVB metals are a very promising class of compounds owing to their ability to catalyze the olefin polymerization in the absence of Lewis-acidic cocatalysts. The first syntheses of such metallocenes have been described in 1989 by Hlatky et al.[1] Subsequently, a large number of similar betaine complexes has been prepared and structurally characterized (see e.g. ref 2 and refs 3−6). In the majority of presently known zwitterionic titanocene, zirconocene, and hafnocene derivatives, a metal atom is in the +4 oxidation state and contains at least one σ-bonded organic group.

Recently, we have reported[7] on the synthesis and structure of a novel type of zwitterionic metallocene which was isolated from the interaction of the bis(trimethylsilyl)acetylene complex of titanocene $Cp_2Ti(Me_3SiC_2SiMe_3)$[8] with $B(C_6F_5)_3$ in toluene at room temperature. It turned out that in the course of this reaction electrophilic substitution of a hydrogen atom in one of the $\eta^5\text{-}C_5H_5$ rings by a $B(C_6F_5)_3$ group takes place and a zwitterionic complex of trivalent titanium, $Cp[\eta^5\text{-}C_5H_4B(C_6F_5)_3]Ti$ (**1**), containing no σ-bonded organic radicals at the metal atom is produced. Later, in studying the interaction of $B(C_6F_5)_3$ with the phenyl(trimethylsilyl)acetylene complex of permethyltitanocene $Cp^*_2Ti(PhC_2SiMe_3)$[8b,9] at 20 °C, we observed[10] electrophilic substitution of a hydrogen atom in one of the methyl groups of the Cp* ring by a $B(C_6F_5)_3$ moiety. As a result of this reaction, the zwitterionic Ti(III) complex $Cp^*[\eta^5\text{-}C_5Me_4CH_2B(C_6F_5)_3]Ti$ was formed. Under similar conditions, the reaction of $Cp^*_2Zr(PhC_2SiMe_3)$[11] with $B(C_6F_5)_3$ afforded a zwitterionic Zr(IV) derivative, $Cp^*[\eta^5\text{-}C_5Me_4CH_2B(C_6F_5)_3]ZrC(Ph){=}CH(SiMe_3)$, containing a σ-alkenyl group at the zirconium center.[10]

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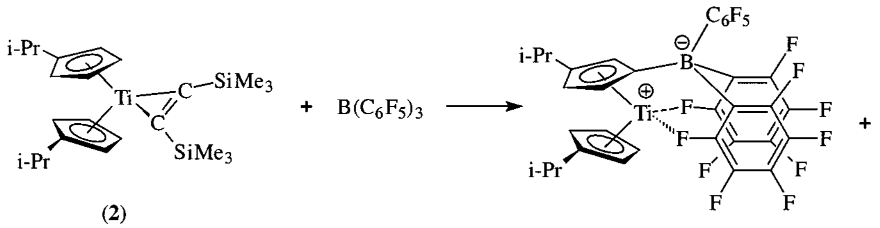
Scheme 1



(2)

(3)

+ $Me_3SiC{\equiv}CSiMe_3$ + $Me_3SiCH_2CH_2SiMe_3$ + cis/trans-$Me_3SiCH{=}CHSiMe_3$

In the present paper, data on the reactivity of the acetylene complexes $Cp_2Ti(PhC_2Ph)$,[12] $Cp_2Ti(PhC_2SiMe_3)$,[8b,13] and $(\eta^5\text{-}^iPrC_5H_4)_2Ti(Me_3SiC_2SiMe_3)$ (**2**) toward $B(C_6F_5)_3$ are reported. Also, selected reactions of the obtained Ti(III) zwitterions with oxygen and acetone are described. These studies have led to the synthesis of a series of new zwitterionic complexes of titanocene, including those containing two zwitterionic units in the molecule.

Results and Discussion

Reactions of Acetylene Complexes $Cp_2Ti(PhC_2SiMe_3)$, $Cp_2Ti(PhC_2Ph)$, and $(\eta^5\text{-}^iPrC_5H_4)_2Ti(Me_3SiC_2SiMe_3)$ (2) with $B(C_6F_5)_3$. The reactions were carried out in toluene solution at room temperature and equimolar ratio of the reagents. Under these conditions, the interaction of $Cp_2Ti(PhC_2SiMe_3)$ with $B(C_6F_5)_3$ gave the same zwitterionic titanium(III) complex **1**, which was isolated by us[7] from the reaction of $B(C_6F_5)_3$ with $Cp_2Ti(Me_3SiC_2SiMe_3)$ (see above). However, the use of $Cp_2Ti(PhC_2SiMe_3)$ instead of $Cp_2Ti(Me_3SiC_2SiMe_3)$ strongly diminished the rate of the process. The tolane complex of titanocene $Cp_2Ti(PhC_2Ph)$ did not react with $B(C_6F_5)_3$ at all under the same conditions, not even over a period of a month. Thus, the replacement of Me_3Si groups in the acetylene ligand by Ph substituents decreases sharply the reactivity of the corresponding acetylene complex $Cp_2Ti(R^1C_2R^2)$ toward $B(C_6F_5)_3$.

The reaction of $B(C_6F_5)_3$ with acetylene complex **2**, which was prepared by the interaction of $(\eta^5\text{-}^iPrC_5H_4)_2TiCl_2$ with Mg in the presence of $Me_3SiC{\equiv}CSiMe_3$ in THF (see "Experimental Procedure"), proceeds in the same way as in the case of $Cp_2Ti(Me_3SiC_2SiMe_3)$ and $Cp_2Ti(PhC_2SiMe_3)$. As a result of the reaction, the zwitterionic Ti(III) complex $(\eta^5\text{-}^iPrC_5H_4)[\eta^5\text{-}\{1,3\text{-}^iPrC_5H_3B(C_6F_5)_3\}]Ti$ (**3**), containing a $B(C_6F_5)_3$ group in 3-position of the Cp ring relative to the ^{i}Pr substituent, is produced (see Scheme 1).

The isolated complex is a dark blue paramagnetic crystalline solid, which rapidly decomposed on contact with oxygen. The structure of **3** has been determined by an X-ray diffraction study (see Figure 1 and Table 1), which revealed the presence of coordinative bonds between the *ortho*-fluorine atoms (F(22) and F(34)) of two C_6F_5 rings and the positively charged titanium center (the Ti(1)···F(22) and Ti(1)···F(34) distances are 2.264(2) and 2.256(2) Å, respectively). As a result of the coordination of the F(22) and F(34) atoms to titanium, the C(22)−F(22) and C(34)−F(34) bonds become longer (1.401(3) and 1.394(3) Å, respectively) as compared with other C−F bonds in the molecule of **3** (1.341−1.360 Å,

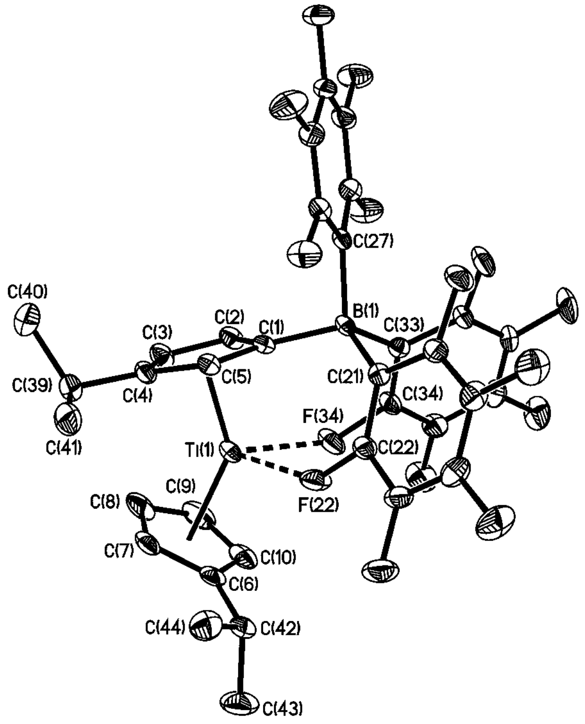


Figure 1. Molecular structure of complex **3** in the crystal at the 30% probability level for thermal ellipsoids.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 3

Bond Lengths			
Ti(1)−C(1)	2.255(3)	Ti(1)−C(8)	2.325(3)
Ti(1)−C(2)	2.308(3)	Ti(1)−C(9)	2.304(3)
Ti(1)−C(3)	2.360(3)	Ti(1)−C(10)	2.333(3)
Ti(1)−C(4)	2.369(3)	Ti(1)−Cp(2)	2.021(3)
Ti(1)−C(5)	2.302(3)	Ti(1)−F(22)	2.264(2)
Ti(1)−Cp(1)	1.980(3)	Ti(1)−F(34)	2.256(2)
Ti(1)−C(6)	2.418(3)	C(22)−F(22)	1.401(3)
Ti(1)−C(7)	2.373(3)	C(34)−F(34)	1.394(3)

Bond Angles			
Cp(1)−Ti(1)−Cp(2)	139.3(3)	Cp(2)−Ti(1)−F(34)	106.1(2)
Cp(1)−Ti(1)−F(22)	108.5(4)	F(22)−Ti(1)−F(34)	72.27(8)
Cp(1)−Ti(1)−F(34)	105.7(3)	Ti(1)−F(22)−C(22)	141.0(2)
Cp(2)−Ti(1)−F(22)	108.5(3)	Ti(1)−F(34)−C(34)	140.8(2)

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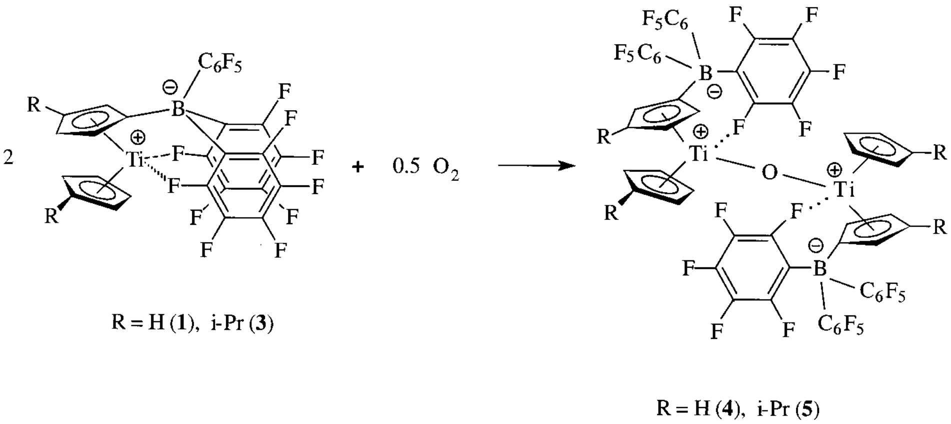
Scheme 2



av 1.354 Å). A similar structure has been established for the above-mentioned zwitterionic complex **1**; however in this complex the Ti···F distances (2.248(2) and 2.223(3) Å) are somewhat shorter than those in **3**. This fact can be explained by a decrease in a partial positive charge on the titanium atom in **3** due to the electron-donating effect of the ^{i}Pr groups.

The ESR spectrum of **3** in toluene at 300−350 K shows a doublet signal (9 G) with $g = 1.966$ and $a(F) = 8.3$ G, thus indicating the retention of only one Ti···F coordinative bond in the complex under such conditions. On cooling the solution to 230 K, the spectrum becomes more complicated: it can be tentatively treated now as superposition of the above-mentioned doublet and a triplet (∼5 G) with $g = 1.978$ and $a(2F) = 7.5$ G. The latter suggests that at 230 K a considerable part of complex **3** retains both coordinative Ti···F bonds in toluene solution.

The geometry of the bent sandwich in **3** is not exceptional. The planes of the C_5 rings form a dihedral angle of 38.4°. The titanium atom and the coordinated F(22) and F(34) atoms are located approximately in the bisector plane of this angle. The coordination environment at titanium can be described as pseudotetrahedral, with the large Cp(1)−Ti(1)−Cp(2) angle (139.3(3)°) and small F(22)−Ti(1)−F(34) angle (72.27(8)°) due to the size difference between the Cp ligand and fluorine atom (Cp(1) and Cp(2) are the centroids of Cp rings C(1)−C(5) and C(6)−C(10), respectively). The Ti(1)−Cp(1) distance (1.980(3) Å) is somewhat shorter than Ti(1)−Cp(2) (2.021(3) Å), which can be due to the bonding of the Cp ring C(1)−C(5) to titanium via the C−B−C−C−F bridges. The Ti(1)−F(34)−C(34) and Ti(1)−F(22)−C(22) angles are virtually the same (140.8(2) and 141.0(2) Å). The mutual orientation of the Cp ligands in **3** is close to staggered conformation. In complex **1**, the Cp ligands are in eclipsed conformation. The pseudotorsion C(4)−Cp(1)−Cp(2)−C(6) angle in **3** characterizing the relative orientation of the ^{i}Pr groups is 88°. The Ti−C distances are in the range 2.30−2.42 Å. The boron atom is located nearly exactly in the plane of the C_5 ring: its displacement from this plane (in the direction away from the Ti atom) is only 0.06 Å. The C(39) and C(42) atoms of the ^{i}Pr groups are displaced from the plane of the corresponding C_5 ring in the same direction by 0.12 and 0.09 Å, respectively. Coordination at the boron is essentially tetrahedral.

Oxidation of Complexes 1 and 3 by Oxygen. For the transformation of the above-mentioned Ti(III) zwitterionic complexes into the corresponding Ti(IV) derivatives, the oxidation of **1** and **3** by oxygen was carried out in toluene at room temperature. During the course of the reactions, a change in color of the reaction solutions from initial dark blue to brownish-red was observed, and new complexes $\{Cp[\eta^5\text{-}C_5H_4B(C_6F_5)_3]Ti\}_2O$ (**4**) and $\{(\eta^5\text{-}^{i}PrC_5H_4)[(\eta^5\text{-}\{1,3\text{-}^{i}PrC_5H_3B(C_6F_5)_3\}]Ti\}_2O$ (**5**), respectively, were produced. A study of these complexes by analytical and spectral means as well as by an X-ray analysis has shown that they have unusual structures of zwitterionic titanoxanes (see Scheme 2).

Complex **4** is a red crystalline substance practically insoluble in aromatic and aliphatic hydrocarbons. The complex is moderately stable in air: its melting point does not change after keeping **4** in air for 1 h. However, if the time of the contact of **4** with air is increased to 3 h, its melting point is somewhat decreased. The IR spectrum of **4** (Nujol mull) contains, in addition to the bands of $\eta^5\text{-}C_5H_5$, $\eta^5\text{-}C_5H_4$, and $B(C_6F_5)_3$ moieties, a broad intense absorption band at 731 cm^{-1} belonging to vibrations of the Ti−O−Ti group. According to elemental analysis, the complex contains (after drying for 5−10 min at 20 °C in a vacuum) half a mole of toluene per mole of **4**. For carrying out the X-ray diffraction study of **4**, the crystals of the complex were not dried in a vacuum. Under such conditions, the content of toluene in **4** increased to two moles.

Complex **5** is also a red crystalline solid practically insoluble in aromatic and aliphatic hydrocarbons. Its IR spectrum is characterized by a broad intense absorption band of the Ti−O−Ti group at 730 cm^{-1}. The crystals of the complex contain one mole of toluene per mole of **5**.

The structures of **4** and **5** are shown in Figures 2 and 3, respectively. The selected bond distances and angles for **4** and **5** are listed in Tables 2 and 3. The unit cell of **4** contains two crystallographically independent molecules (**4A** and **4B**) differing from each other only by the mutual orientation of the noncoordinated C_6F_5 rings.

A remarkable feature of complexes **4** and **5** is the presence of two zwitterionic units in their molecules. In each of these units, only one *ortho*-fluorine atom of a $B(C_6F_5)_3$ group is coordinated to the metal. The Ti(1)···F(22) and Ti(2)···F(40) distances in **4** and **5** (see Tables 2 and 3) are notably shorter than the analogous

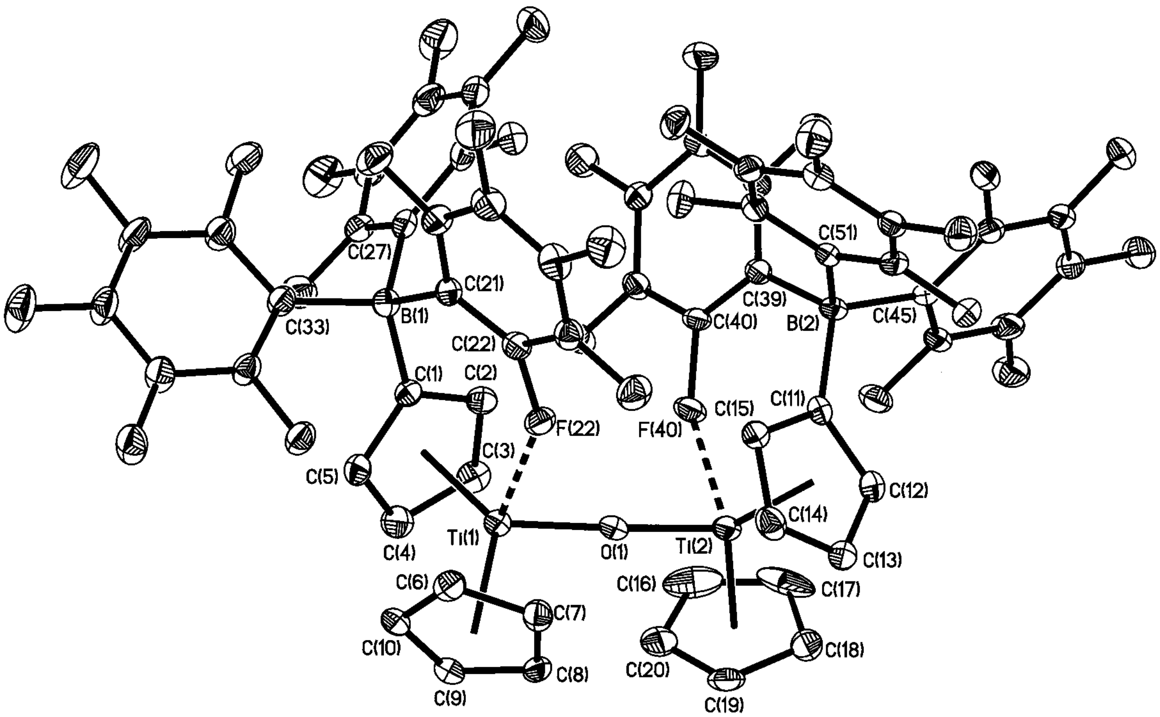


Figure 2. Molecular structure of complex **4** in the crystal at the 30% probability level for thermal ellipsoids.

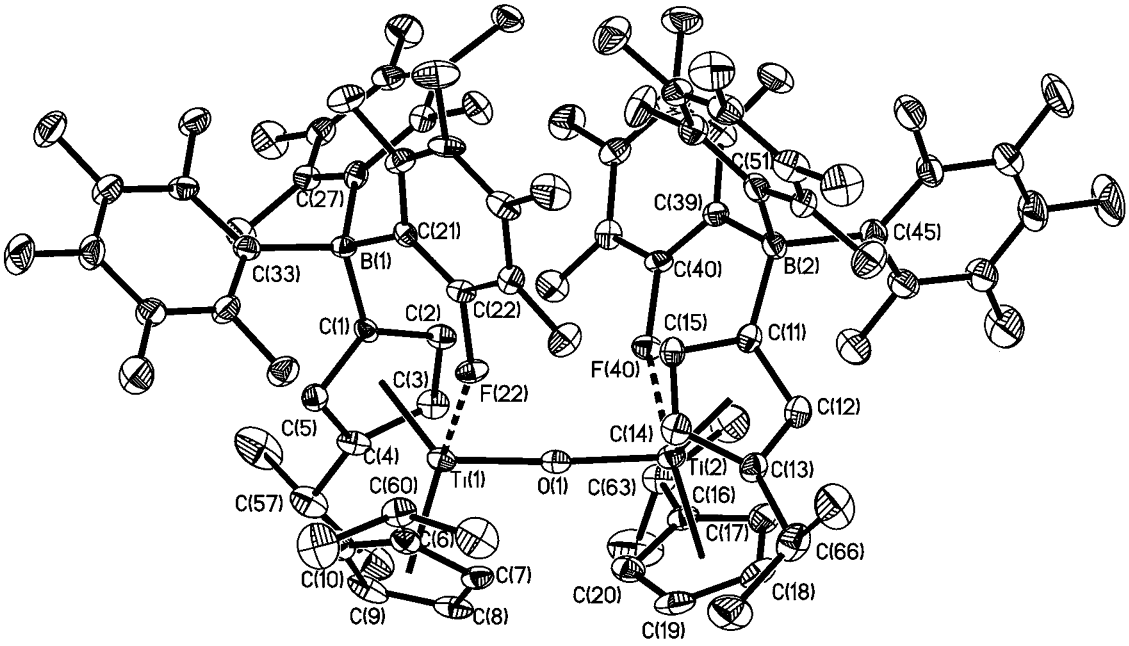


Figure 3. Molecular structure of complex **5** in the crystal at the 30% probability level for thermal ellipsoids.

distances in **1** and **3**, which can be explained by the higher oxidation state of titanium in **4** and **5** as compared to that in **1** and **3**. The coordinated C−F bonds in **4** and **5** are again noticeably longer than other C−F bonds in these molecules (av 1.351 and 1.351 Å in **4A** and **4B**, respectively; 1.350 Å in **5**). The Ti(1)−O(1)−Ti(2) bond angle in both complexes is close to 180°. The Ti−O bond lengths range from 1.83 to 1.85 Å. The Ti(1)−F(22)−C(22) and Ti(2)−F(40)−C(40) angles are 147.1(2)° and 147.9(1)° for **4A**, 145.8(2)° and 148.5(2)° for **4B**, and 148.8(2)° and 149.1(2)° for **5**.

The bis(cyclopentadienyl)titanium fragments in **4** and **5** have a typically bent sandwich geometry. The dihedral angles between the planes of the C_5 rings in sandwich moieties are 45−46°. The titanium atom as well as the oxygen and coordinated fluorine atoms in each of the zwitterionic units of **4** and **5** are disposed practically in the bisector plane of the corresponding dihedral angle formed by the pair of C_5 rings. The dihedral angle between these bisector planes in **4A**, **4B**, and **5** is 81.7°, 79.9°, and 88.9°, respectively; that is, the sandwich fragments in both complexes are turned almost by 90° relative to each other.

The titanium atoms in **4** and **5** again have a pseudotetrahedral coordination environment. In each of the zwitterionic units of **4** and **5**, as in **1** and **3**, the distance between the Ti atom and the centroid of the C_5 ring containing a $B(C_6F_5)_3$ group is somewhat shorter than

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 4A/4B

	Bond Lengths		
Ti(1)−C(1)	2.434(3)/2.419(3)	Ti(2)−C(12)	2.376(3)/2.383(4)
Ti(1)−C(2)	2.332(3)/2.334(3)	Ti(2)−C(13)	2.333(4)/2.332(4)
Ti(1)−C(3)	2.330(4)/2.336(4)	Ti(2)−C(14)	2.330(4)/2.335(4)
Ti(1)−C(4)	2.315(4)/2.314(4)	Ti(2)−C(15)	2.338(3)/2.356(4)
Ti(1)−C(5)	2.369(3)/2.354(3)	Ti(2)−C(16)	2.382(4)/2.394(4)
Ti(1)−C(6)	2.372(3)/2.372(4)	Ti(2)−C(17)	2.352(4)/2.372(4)
Ti(1)−C(7)	2.368(3)/2.382(4)	Ti(2)−C(18)	2.362(4)/2.372(4)
Ti(1)−C(8)	2.383(3)/2.352(4)	Ti(2)−C(19)	2.338(4)/2.336(4)
Ti(1)−C(9)	2.346(3)/2.374(4)	Ti(2)−C(20)	2.391(4)/2.392(4)
Ti(1)−C(10)	2.381(3)/2.380(4)	Ti(2)−O(1)	1.831(2)/1.833(2)
Ti(1)−O(1)	1.846(2)/1.851(2)	Ti(2)−F(40)	2.241(2)/2.185(2)
Ti(1)−F(22)	2.184(2)/2.181(2)	Ti(2)−Cp(3)	2.031(3)/2.041(3)
Ti(1)−Cp(1)	2.044(3)/2.025(3)	Ti(2)−Cp(4)	2.055(3)/2.056(3)
Ti(1)−Cp(2)	2.070(3)/2.053(3)	C(22)−F(22)	1.398(4)/1.394(4)
Ti(2)−C(11)	2.414(3)/2.423(4)	C(40)−F(40)	1.386(3)/1.395(4)
	Bond Angles		
Cp(1)−Ti(1)−Cp(2)	134.4(1)/133.4(1)	Cp(3)−Ti(2)−F(40)	104.9(1)/104.6(1)
Cp(1)−Ti(1)−F(22)	102.0(1)/102.1(1)	Cp(4)−Ti(2)−F(40)	101.8(1)/101.1(1)
Cp(2)−Ti(1)−F(22)	104.5(1)/105.7(1)	Cp(3)−Ti(2)−O(1)	109.3(1)/108.9(1)
Cp(1)−Ti(1)−O(1)	108.6(1)/108.9(1)	Cp(4)−Ti(2)−O(1)	108.4(1)/108.7(1)
Cp(2)−Ti(1)−O(1)	108.7(1)/101.4(1)	O(1)−Ti(2)−F(40)	88.66(8)/91.39(9)
O(1)−Ti(1)−F(22)	88.05(8)/86.55(9)	Ti(2)−F(40)−C(40)	147.9(1)/148.5(2)
Ti(1)−F(22)−C(22)	147.1(2)/145.8(2)	Ti(1)−O(1)−Ti(2)	176.6(1)/178.5(1)
Cp(3)−Ti(2)−Cp(4)	133.8(1)/133.9(1)		

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 5

	Bond Lengths		
Ti(1)−C(1)	2.416(5)	Ti(2)−C(12)	2.395(5)
Ti(1)−C(2)	2.325(4)	Ti(2)−C(13)	2.375(5)
Ti(1)−C(3)	2.348(4)	Ti(2)−C(14)	2.330(4)
Ti(1)−C(4)	2.386(5)	Ti(2)−C(15)	2.329(5)
Ti(1)−C(5)	2.383(5)	Ti(2)−C(16)	2.428(5)
Ti(1)−C(6)	2.478(4)	Ti(2)−C(17)	2.385(5)
Ti(1)−C(7)	2.399(5)	Ti(2)−C(18)	2.341(5)
Ti(1)−C(8)	2.341(5)	Ti(2)−C(19)	2.354(5)
Ti(1)−C(9)	2.341(5)	Ti(2)−C(20)	2.428(5)
Ti(1)−C(10)	2.387(5)	Ti(2)−O(1)	1.848(3)
Ti(1)−O(1)	1.847(3)	Ti(2)−F(40)	2.226(3)
Ti(1)−F(22)	2.219(3)	Ti(2)−Cp(3)	2.044(5)
Ti(1)−Cp(1)	2.044(5)	Ti(2)−Cp(4)	2.077(5)
Ti(1)−Cp(2)	2.070(5)	C(22)−F(22)	1.404(5)
Ti(2)−C(11)	2.428(5)	C(40)−F(40)	1.409(5)
	Bond Angles		
Cp(1)−Ti(1)−Cp(2)	134.3(2)	Ti(1)−O(1)−Ti(2)	176.3(2)
Cp(1)−Ti(1)−F(22)	101.7(2)	Cp(3)−Ti(2)−F(40)	101.3(2)
Cp(2)−Ti(1)−F(22)	105.3(2)	Cp(4)−Ti(2)−F(40)	105.0(2)
Cp(1)−Ti(1)−O(1)	108.4(2)	Cp(3)−Ti(2)−O(1)	108.5(2)
Cp(2)−Ti(1)−O(1)	108.9(2)	Cp(4)−Ti(2)−O(1)	107.8 (2)
O(1)−Ti(1)−F(22)	87.3(1)	O(1)−Ti(2)−F(40)	89.0(1)
Ti(1)−F(22)−C(22)	148.8(2)	Ti(2)−F(40)−C(40)	149.1(2)
Cp(3)−Ti(2)−Cp(4)	135.1(2)		

the corresponding distance from the centroid of the other C_5 ring which does not contain a $B(C_6F_5)_3$ moiety (see Tables 2 and 3, where Cp(1), Cp(2), Cp(3), and Cp(4) are the centroids of the C_5 rings C(1)−C(5), C(6)−C(10), C(11)−C(15), and C(16)−C(20), respectively). The C_5 rings in the Ti(1) sandwich of both titanoxanes are in eclipsed conformation, while the C_5 rings in the Ti(2) sandwich are in staggered conformation. The pseudotorsion angles C(4)−Cp(1)−Cp(2)−C(6) and C(13)−Cp(3)−Cp(4)−C(16) in **5** are 151.5° and 171°, respectively.

An interesting structural peculiarity of complexes **4** and **5** is the considerably stronger deviation of the boron atoms from the plane of the corresponding C_5 ring (in the direction away from the Ti atom) than those in **1** and **3**, which is a consequence of the steric overcrowding of the molecules of **4** and **5**. In the case of **4**, these deviations are 0.27−0.28 Å, and even larger deviations of the boron atoms (0.40 Å for B(1) and 0.38 Å for B(2)) were found in the structure of **5**. The secondary carbon atoms of the ^{i}Pr groups in **5** also deviate considerably stronger (by 0.37 Å for C(57), 0.21 Å for C(60), 0.33 Å for C(66), 0.19 Å for C(63)) than in **3** from the corresponding C_5 ring plane, the strongest deviations being observed for the ^{i}Pr groups in the boron-containing rings. The Ti−C distances range from 2.32 to 2.44 Å in **4A**, from 2.31 to 2.42 Å in **4B**, and from 2.33 to 2.48 Å in **5**.

Reaction of Complex 1 with Acetone. When the toluene solution of **1** is treated by an equimolar amount of dry acetone at room temperature, the color of the reaction mixture gradually turns from dark blue to green, and within 48 h green air-sensitive paramagnetic crystals of the acetone complex $Cp[\eta^5\text{-}C_5H_4B(C_6F_5)_3]Ti(Me_2CO)$ (**6**) are precipitated (see Scheme 3). The ESR spectrum of **6** in toluene solution at 300 K exhibits an intense broadened (9 G) singlet signal with $g = 1.970$. Cooling of the solution of **6** to 210 K leads to further broadening of the signal (18 G).

An X-ray diffraction study of the toluene solvate of the complex, $\mathbf{6}\cdot 0.5PhCH_3$, has shown that in **6** as in **4** and **5** only one *ortho*-fluorine atom (F(22); see Figure 4) of a $B(C_6F_5)_3$ group is involved in the bonding to the positively charged titanium center. The Ti(1)···F(22) distance in **6** is 2.252(2) Å (Table 4), which is noticeably longer than the similar Ti···F distances in **1**, **4**, and **5**. Correspondingly, the coordinated C(22)−F(22) bond in **6** (1.364(3) Å) is elongated to a considerably lesser extent than those in **1**, **4**, and **5** (the average value of the length of the noncoordinated C−F bonds in **6** is equal to 1.349 Å).

The acetone ligand in the molecule of **6** is bonded to titanium through the oxygen atom. The Ti(1)−O(1) distance in **6** is 2.146(2) Å, while the C(39)−O(1) bond length is 1.226(3) Å, which is somewhat longer than that in free aliphatic ketones (av 1.21 Å[14]). The C(40)−C(39)−O(1), C(41)−C(39)−O(1), and C(40)−C(39)−C(41) bond angles are close to 120°.

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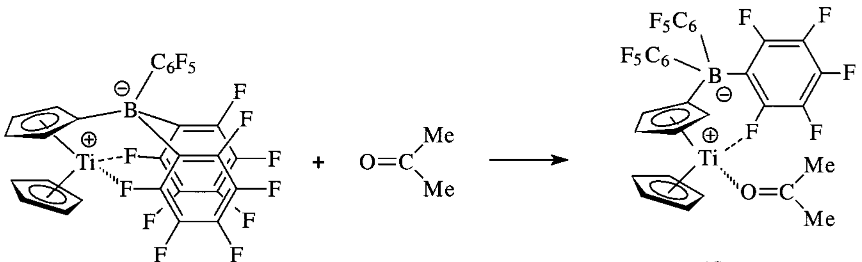
[14] Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O., Watson, D. G.; Taylor, R. In *Structure Correlation*; Bürgi, H.-B., Dunitz, J. D., Eds.; Weinheim-New York, 1994; Vol. 2, p 751.

Scheme 3



(6)

(1)

The ν_{CO} band (1681 cm^{-1}) in the IR spectrum of **6** is shifted by 38 cm^{-1} in the low-frequency region relative to the corresponding ν_{CO} band of free acetone. This indicates the considerable weakening of the C=O bond of the acetone molecule as a result of its coordination with the positively charged titanium center of **1**.

The titanium atom and the O(1) and F(22) atoms in complex **6** form a plane which bisects the dihedral angle (42.1°) between the planes of the C_5 rings. Besides the oxygen atom, all other non-hydrogen atoms of the acetone ligand are located in this bisector plane as well. The Ti(1)–O(1)–C(39) and Ti(1)–F(22)–C(22) angles in **6** are 143.2(2)° and 147.3(2)°, respectively.

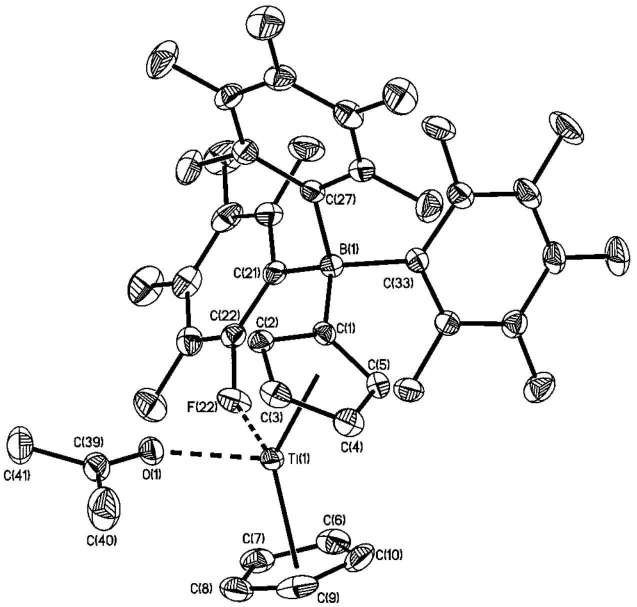


Figure 4. Molecular structure of complex **6** in the crystal at the 30% probability level for thermal ellipsoids.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for 6

Bond Lengths			
Ti(1)–C(1)	2.409(3)	Ti(1)–C(9)	2.368(3)
Ti(1)–C(2)	2.323(3)	Ti(1)–C(10)	2.341(3)
Ti(1)–C(3)	2.322(3)	Ti(1)–Cp(2)	2.050(3)
Ti(1)–C(4)	2.326(3)	Ti(1)–O(1)	2.146(2)
Ti(1)–C(5)	2.372(3)	Ti(1)–F(22)	2.252(2)
Ti(1)–Cp(1)	2.022(3)	C(22)–F(22)	1.364(3)
Ti(1)–C(6)	2.342(3)	C(39)–O(1)	1.226(3)
Ti(1)–C(7)	2.359(3)	C(39)–C(40)	1.472(5)
Ti(1)–C(8)	2.404(3)	C(39)–C(41)	1.476(5)
Bond Angles			
Cp(1)–Ti(1)–Cp(2)	139.0(2)	Ti(1)–F(22)–C(22)	147.3(2)
Cp(1)–Ti(1)–F(22)	104.4(8)	Ti(1)–O(1)–C(39)	143.2(2)
Cp(1)–Ti(1)–O(1)	108.7(3)	O(1)–C(39)–C(40)	122.1(3)
Cp(2)–Ti(1)–F(22)	104.6(4)	O(1)–C(39)–C(41)	120.3(3)
Cp(2)–Ti(1)–O(1)	106.9(5)	C(40)–C(39)–C(41)	117.6(3)
F(22)–Ti(1)–O(1)	73.48(8)		

Coordination at titanium in **6** as in **1** and **3**–**5** is pseudotetrahedral with a Cp(1)–Ti(1)–Cp(2) angle of 139.0(2)° and a F(22)–Ti(1)–O(1) angle of 73.48(8)° (Cp(1) and Cp(2) are the centroids of the substituted and unsubstituted C_5 rings, respectively). The Ti(1)–Cp(1) distance (2.022(3) Å) is again somewhat shorter than Ti(1)–Cp(2) (2.050(3) Å). The Cp ligands are in staggered conformation. The Ti–C distances span the range 2.32–2.41 Å. The displacement of the boron atom from the plane of the corresponding C_5 ring (in the direction opposite to the Ti atom) is approximately the same (0.26 Å) as in **4** but considerably smaller than in **5**.

Conclusion

In the course of our study, a series of new zwitterionic complexes of titanocene (**3**–**6**) have been prepared and structurally characterized. Complexes **3** and **6** are the Ti(III) derivatives, while the Ti atoms in **4** and **5** are in the +4 oxidation state. In compound **3**, two *ortho*-fluorine atoms of a $B(C_6F_5)_3$ unit are coordinated to the metal, and in such a way the titanium atom in **3** acquires a pseudotetrahedral coordination environment. In compounds **4**–**6**, one of the coordination sites at titanium is occupied by oxygen, and as a consequence, only one *ortho*-fluorine atom of the $B(C_6F_5)_3$ moiety is bonded here to the metal.

Complex **3** is analogous in its structure to the previously described Ti(III) zwitterion **1**.[7] However, a study of **3** by the ESR method allowed us to demonstrate for the first time that the coordinative bonds between fluorine atoms of a $B(C_6F_5)_3$ group and the positively charged titanium center in Ti(III) zwitterionic metallocenes can exist not only in the crystal but also in solutions. The ESR spectra of **3** also evidence a sufficiently high strength of these coordinative Ti···F bonds: one of them is retained in toluene solution even at 77 °C, while at −43 °C a considerable part of **3** retains both Ti···F bonds in the solution. In the case of **1** and **6**, the ESR spectra do not provide any information on the state of these compounds in toluene medium.

Complexes **4** and **5** have unusual structures of zwitterionic titanoxanes and are the first examples of metallocenes that contain two zwitterionic units in the molecule. The complexes are sterically overcrowded. The presence of two positively charged titanium(IV) centers in **4** and **5** makes these complexes very promising for catalysis.

Table 5. Crystal Data, Data Collection, and Structure Refinement Parameters for 3−6

	3	**4**	**5**	**6**
formula	$C_{34}H_{21}BF_{15}Ti$	$C_{56}H_{18}B_2F_{30}OTi_2$ $2C_7H_8$	$C_{68}H_{42}B_2F_{30}OTi_2$ C_7H_8	$C_{31}H_{15}BF_{15}OTi$ $^1/_2C_7H_8$
molecular wt	773.22	1578.39	1654.57	793.21
cryst syst	monoclinic	monoclinic	monoclinic	triclinic
space group, *Z*	$P2_1/c$, 4	$P2_1/c$, 8	$P2_1/n$, 4	$P\bar{1}$, 2
a, Å	14.007(3)	11.198(3)	15.585(3)	9.096(2)
b, Å	11.252(2)	45.383(13)	22.012(4)	13.153(3)
c, Å	20.389(2)	24.336(7)	20.934(4)	15.561(3)
α, deg				67.83(3)
β, deg	100.52(3)	91.40(3)	105.59(3)	77.16(3)
γ, deg				71.89(3)
V, $Å^3$	3159(1)	12364(6)	6917(2)	1627.0(6)
D(calc), g cm^{-3}	1.626	1.696	1.589	1.619
temperature, K	200(2)	110(2)	200(2)	200(2)
diffractometer	STOE-IPDS	SMART 1000 CCD	STOE-IPDS	STOE-IPDS
θ range (deg)	1.81−22.51	2.18−27.56	1.64−24.31	1.84−24.19
μ(Mo Kα, $\lambda = 0.71073$ Å), cm^{-1}	3.85	3.97	3.59	3.85
no. of collected reflns	7424	12 1271	20 200	4858
no. of ind reflns	3913	28 451	10 921	4858
no. of obsd reflns ($I > 2\sigma(I)$)	2931	10 509	4751	3612
no. of params	464	2008	969	472
R_1 (on *F* for obsd reflns)	0.037	0.053	0.052	0.042
wR_2 (on F^2 for all reflns)	0.087	0.095	0.107	0.112
ρ_{max}/ρ_{min}, e $Å^{-3}$	0.278/−0.280	0.615/ −0.638	0.678/−0.354	0.353/−0.275

Finally, acetone adduct **6** is the first example of a complex of a zwitterionic metallocene with a carbonyl compound. The acetone ligand in this complex is coordinated to titanium via the oxygen atom, and the C═O bond in acetone is considerably weakened as a result of the complexation. The latter suggests that zwitterionic metallocenes of such a type could be used as catalysts for reactions of nucleophilic addition to the carbonyl group of aldehydes and ketones.

Experimental Section

Unless mentioned otherwise, all operations were performed in an Ar atmosphere with careful exclusion of air and moisture using standard Schlenk techniques. Solvents were purified in the usual manner and freshly distilled prior to use over sodium (toluene, *n*-hexane) or from sodium/benzophenone (THF) under Ar. The starting $Cp_2Ti(PhC_2Ph)$, $Cp_2Ti(PhC_2SiMe_3)$, and **1** were prepared according to published procedures.[7b,8b,12] The compounds $(\eta^5\text{-}^iPrC_5H_4)_2TiCl_2$ and $B(C_6F_5)_3$ were purchased from Strem and used without further purification. The NMR spectra were recorded on a Bruker ARX 400 spectrometer. The ESR spectra were registrated on a Varian E12A spectrometer. The IR spectra were taken on a JFS-25 Bruker instrument.

Synthesis of $Cp[\eta^5\text{-}C_5H_4B(C_6F_5)_3]Ti$ (1) by the Reaction of $Cp_2Ti(PhC_2SiMe_3)$ with $B(C_6F_5)_3$. An amount of 0.76 g (1.5 mmol) of $B(C_6F_5)_3$ was dissolved in 20 mL of toluene under Ar, and the obtained solution was added to 0.42 g (1.19 mmol) of solid $Cp_2Ti(PhC_2SiMe_3)$. The resulting red-brown mixture was then filtered and allowed to stand in an Ar atmosphere at room temperature. During the course of the reaction, the solution gradually turned dark blue, and within a month dark blue crystals of zwitterionic complex **1** were precipitated. The crystals were separated from the mother liquor by decanting, washed with a small amount of toluene, and dried at 20 °C in a vacuum. Yield of **1** is 0.30 g (70%), mp 163−164 °C (dec) under Ar; lit. mp 161−163 °C (dec) under Ar.[7] The decanted solution was then analyzed by the GLC-MS method, which revealed the presence of free phenyl(trimethylsilyl)acetylene in the mixture.

Synthesis of $(\eta^5\text{-}^iPrC_5H_4)_2Ti(Me_3SiC_2SiMe_3)$ (2). $(\eta^5\text{-}^iPrC_5H_4)_2TiCl_2$ (0.943 g, 2.83 mmol), 0.069 g (2.84 mmol) of finely shaved magnesium, and 0.65 mL (2.89 mmol) of bis(trimethylsilyl)acetylene in 15 mL of THF were stirred at room temperature under Ar for 2.5 h, after which the resulting dark solution was filtered and evaporated in a vacuum to dryness at 20 °C. The residue was dissolved in 15 mL of *n*-hexane, and the *n*-hexane solution, after filtration, was evaporated at room temperature in a vacuum to give a dark yellow oily liquid representing complex **2**.

The yield of **2** is 1.088 g (89%). Anal. Calcd for $C_{24}H_{40}TiSi_2$: C, 66.63; H, 9.32. Found: C, 67.22; H, 9.67. ^1H NMR (C_6D_6, δ): −0.21 (s, 18H, $SiMe_3$); 1.05 (d, 12H, Me); 2.21 (sept, 2H, C*H*Me_2); 5.82 (m, 4H, Cp); 6.53 (m, 4H, Cp). $^{13}C\{^1H\}$ NMR (C_6D_6, δ): 1.3 ($SiMe_3$); 23.3 (CH*Me*$_2$); 29.2 (C*H*Me_2); 113.7 (Cp); 114.8 (Cp); 141.4 (Cp); 245.1 (s, C≡C). IR (Nujol mull, cm^{-1}): 1636 and 1674 (C≡C). MS (70 eV, *m*/*z*): 432 $([M])^+$, 1%), 262 $([(^iPrC_5H_4)_2Ti]^+$, 73%), 170 $([Me_3SiC_2SiMe_3]^+$, 12%), 155 $([Me_3SiC_2SiMe_3-Me]^+$, 100%).

Synthesis of $(\eta^5\text{-}^iPrC_5H_4)[(\eta^5\text{-}\{1,3\text{-}^iPrC_5H_3B(C_6F_5)_3\}]Ti$ (3). A solution of $B(C_6F_5)_3$ (1.257 g, 2.46 mmol) in 20 mL of toluene was added to a solution of **2** (1.064 g, 2.46 mmol) in 3 mL of toluene. After 24 h, the dark blue reaction mixture was evaporated to dryness in a vacuum, the residue was dissolved in 20 mL of *n*-hexane, and the resulting solution was kept after filtration overnight at room temperature in an Ar atmosphere. After 1 day, dark blue crystals of zwitterionic complex **3** were precipitated, which were separated from the mother liquor by decanting, washed with a small amount of *n*-hexane, and dried at 20 °C in a vacuum to give 1.402 g (74.1%) of **3**, mp 163−165 °C (dec) under Ar. Anal. Calcd for $C_{34}H_{21}TiBF_{15}$: C, 52.81; H, 2.74. Found: C, 52.22; H, 3.11. MS (70 eV, *m*/*z*): 512 $[B(C_6F_5)_3]^+$. The decanted solution was then analyzed by the GLC-MS method, which revealed the presence of free bis(trimethylsilyl)acetylene (96.4%), 1,2-bis(trimethylsilyl)ethane (2.6%), and *cis*/*trans*-1,2-bis(trimethylsilyl)ethylene (1%) in the mixture.

Synthesis of $\{Cp[\eta^5\text{-}C_5H_4B(C_6F_5)_3]Ti\}_2O$ (4). Complex **1** (0.595 g, 0.76 mmol) was dissolved in 25−30 mL of toluene at 60 °C under Ar in a Schlenk tube, and the resulting dark blue solution was exposed to dry air for 10−15 min after cooling to room temperature. Then the Schlenk tube was disconnected from air, and the reaction mixture was kept at 20 °C overnight. Within 24 h, fine red crystalline aggregates of complex **4** were formed on the bottom and the walls of the vessel. The crystals were separated by decanting, carefully washed with toluene, and dried for 5−10 min at 20 °C in a vacuum. The yield of **4** is 0.283 g (53%), mp 244−246 °C (dec) under Ar. Anal. Calcd for $C_{56}H_{18}Ti_2B_2OF_{30}\cdot 1/2C_6H_5CH_3$ (%): C, 49.62; H, 1.54. Found: C, 50.05; H, 1.36. IR (Nujol mull, cm^{-1}): 3136(w), 3122(w), 1644(m), 1515(vs), 1378(m), 1278(m), 1106(sh), 1092(s, br), 973(s, br), 952(m), 852(s), 731(s, br), 695(m). MS (250

°C, 70 eV, *m*/*z*): 686 ($\{(C_5H_5)[C_5H_4B(C_6F_5)_3]TiO{-}F\}^+$, 2%), 512 ($[B(C_6F_5)_3]^+$, 3%), 474 ($[B(C_6F_5)_3{-}2F]^+$, 2%), 410 ($[C_5H_5B(C_6F_5)_2]^+$, 2%), 344 ($[C_5H_5TiC_5H_4(C_6F_5)]^+$, 5%), 324 ($\{[C_5H_5TiC_5H_4(C_6F_5)]{-}HF\}^+$, 9%), 277 ($\{[C_5H_5TiC_5H_4(C_6F_5)]{-}TiF\}^+$, 10%), 193 ($[(C_5H_5)(C_5H_4)TiO]^+$, 10%), 175 ($\{[(C_5H_5)(C_5H_4)TiO]\text{-}H_2O\}^+$, 13%), 168 ($[C_6F_5H]^+$, 100%), 151 ($[C_5H_5TiF_2]^+$, 17%), 148 ($[C_6F_4]^+$, 11%), 132 ($[C_5H_5TiF]^+$, 26%), 131 ($[C_5H_5TiF_2{-}HF]^+$, 5%), and 65 ($[C_5H_5]^+$, 38%).

Synthesis of $\{(\eta^5\text{-}^iPrC_5H_4)[(\eta^5\text{-}\{1,3\text{-}^iPrC_5H_3B(C_6F_5)_3\}]Ti\}_2O$ (5). Complex **3** (0.454 g, 0.589 mmol) was dissolved in 15 mL of toluene at 60 °C under Ar in a Schlenk tube, and the resulting dark blue solution was exposed to dry air after cooling to room temperature and filtration. Within 24 h, dark red crystalline aggregates of complex **5** were formed on the bottom and the walls of the vessel. The crystals were separated by decanting, washed with toluene, and dried at 20 °C in a vacuum to give 0.130 g (26.8%) of **5**, mp 241−242 °C (dec) under Ar. Anal. Calcd for $C_{68}H_{38}Ti_2B_2OF_{30}\cdot C_6H_5CH_3$: C, 54.58; H, 2.81. Found: C, 54.21; H, 2.62. IR (Nujol mull, cm^{-1}): 730 (Ti−O−Ti).

Synthesis of $Cp[\eta^5\text{-}C_5H_4B(C_6F_5)_3]Ti(Me_2CO)$ (6). Complex $\mathbf{1}\cdot C_6H_5CH_3$ (0.286 g, 0.366 mmol) was dissolved in 10−12 mL of toluene at 60 °C under Ar in a Schlenk tube, and the resulting dark blue solution was treated after filtration with 0.03 mL (0.41 mmol) of dry acetone. The color of the mixture rapidly turned from blue to greenish, and within 48 h green crystals of **6** were formed on the bottom and the walls of the vessel. The crystals were separated by decanting, carefully washed with toluene, and dried for 1−2 min at 20 °C in a vacuum to give 0.157 g (51%) of complex **6**, mp 192−193 °C (dec) under Ar. Anal. Calcd for $C_{31}H_{15}TiOBF_{15}$: C, 49.84; H, 2.02. Found: C, 50.11; H, 2.27. IR (Nujol mull, cm^{-1}): 1681 (C═O). MS (250 °C, 70 eV, *m*/*z*): 689 [M − acetone]$^+$. The crystals of **6** for the X-ray diffraction study were not dried in a vacuum. Under such conditions, they contained half a mole of toluene per mole of **6**.

X-ray Crystallographic Study. Data for **3**, **5**, and **6** were collected with a STOE-IPDS diffractometer (Rostock) and for **4** with SMART 1000 CCD (Moscow) using graphite-monochromated Mo Kα radiation. The structures were solved by direct methods (SHELXS-86)[15] and refined by full-matrix least-squares against F^2 (SHELXL-93).[16] The hydrogen atoms were included at calculated positions. All other non-hydrogen atoms except the atoms of the disordered solvate molecules were refined anisotropically. Cell constants and other experimental details are listed in Table 5. XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations.

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Supporting Information Available: Tables of crystal data and structure refinement, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates for **3**, **4**, **5**, and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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