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Zwitterionic complexes arising from the reaction of tucked-in titanocenes with tris(pentafluorophenyl)borane

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Abstract

Single tucked-in titanocene [Ti(η^5 -C₅Me₅)(η^5 : η^1 -C₅Me₄CH₂)] adds to B(C₆F₅)₃ to give the paramagnetic cationic complex [Ti(η^5 -C₅Me₅){ η^5 -C₅Me₄CH₂B(C₆F₅)₃]] (1). Doubly tucked-in titanocene [Ti(η^5 -C₅Me₅){ η^3 : η^4 -C₅Me₃(CH₂)₂] reacts with B(C₆F₅)₃ by one methylene group to give [Ti(η^5 -C₅Me₅){ η^5 : η^1 -C₅Me₃(CH₂)CH₂B(C₆F₅)₃]] (6). The crystal structure of 6 revealed that one hydrogen of the methylene group attached to boron agostically interacts with Ti(IV). © 2004 Elsevier B.V. All rights reserved.

Keywords: Titanium; Tucked-in titanocene; Borate ligand; Zwitterions; Cationic complexes; X-ray crystallography

Cationic complexes of Group IV transition metals form one of the most frequently addressed classes of organometallic compounds in the last decade. Enormous wave of interest arose with the discovery of synthetic routes to well defined titanocene and zirconocene cationic complexes containing $[BMe(C_6F_5)_3]^-$ [1] or $[B(C_6F_5)_4]^-$ [2] species as counteranions. Using these complexes, the mechanism of polymerizations on single site metallocene catalysts is now well established and the results seem to be applicable to single site catalysts generated by methylalumoxane (MAO), the systems which are difficult to investigate owing to a large molar excess of MAO which is necessary to obtain highly ac-

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tive catalysts. The field of cationic catalysts for polymerization of olefins has been the subject of a large number of review articles in recent years [3].

Alkene moieties were used for the formation of catalytic ion pairs in various ways. Erker and co-workers [4] used zirconocene (Zr(II))–butadiene complex and [B(C₆F₅)₃] to form a "girdle" zwitterion. Analogously, [BH(C₆F₅)₂] [5] adds across Zr–C bond of a zirconocene–alkene complex [Zr(PMePh₂)(η^2 -RCH = CH₂)Cp₂] (R = H, Et, C₆H₅) to give a similar "girdle" complex with an agostic Zr–H–B bond [6]. A girdle type ion pair complex was also obtained by addition of [B(C₆F₅)₃] to a zirconocene diacetylide complex [7]. Moreover, [B(C₆F₅)₃] attacks the cyclopentadienyl ligand in zirconocene complexes with disubstituted alkynes to form an alkenylzirconocene ion pair with the borane directly attached to the Cp ring [8]. In this respect, the titanocene

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and zirconocene-alkyne complexes react in various ways depending on the nature of the ancillary ligands. [Ti(η^2 -Me₃SiC=CSiMe₃)(η^5 -C₅H₅)₂] reacts with [B(C₆F₅)₃] under partial evolution of hydrogen and partial hydrogenation of the liberated alkyne, whereas one of the ring carbon atoms of one Cp ligand bears the $[B(C_6F_5)_3]^-$ anion with *ortho*-fluorine atoms of its two C_6F_5 groups coordinated to the titanium atom. The valency of Ti(II) is increased to Ti(III) [9]. The analogous permethylated titanocene complex $[Ti(\eta^2-Me_3SiC \equiv CPh)(\eta^5-C_5Me_5)_2]$ liberated hydrogen and the alkyne to give $[Ti(\eta^5 C_5Me_5$ { η^5 - $C_5Me_4CH_2B(C_6F_5)_3$ } (1), whereas the analogous permethylated zirconocene complex transfers one hydrogen atom from one cyclopentadienyl methyl group to the alkyne to give alkenyl compound 2 with an agostic Zr-H bond and zwitterionic structure [10a]. Complex rac-[Ti(η^2 -Me₃SiC=CSiMe₃)(ebthi)] (ebthi = 1,2-ethylene-1,1'-bis(η^5 -tetrahydroindenyl)) reacts with $[B(C_6F_5)_3]$ to give zwitterionic Ti(III) η^2 -(trimethylsilyl)ethynylboranate complex 3. The redox reaction of Ti(II) to Ti(III) is accompanied by elimination of the trimethylsilyl group [10b] (see Chart 1). The pendant double bonds attached to cyclopentadienyl rings were so far explored only sparingly: the allyl group at a cyclopentadienylamidozirconium complex was hydroborated by $[BH(C_6F_5)_2]$ [11], the allyldimethylsilyl group in dibenzylzirconocene was π -coordinated to a benzylzirconocene cation [12], ω -alkenylpermethylzirconocene [13], and ω -alkenyloxyzirconocene cations contained the π coordinated double bond to the Zr cation [14].

Here, we report the formation of zwitterionic complexes from the most simple "olefinic" precursors, tucked-in titanocenes $[Ti(\eta^5-C_5Me_5)(\eta^5:\eta^1-C_5Me_4CH_2)]$ (4) [15] or $[Ti(\eta^5-C_5Me_5)\{\eta^3:\eta^4-C_5Me_3(CH_2)_2\}]$ (5) [15c,16], and $[B(C_6F_5)_3]$. Compound 4 reacted with $[B(C_6F_5)_3]$ in the most simple way: by transmetallation of the methylene group by the Lewis acid boron atom (Eq. (1)). Both valence electrons from previous σ -Ti-CH₂ bond were used in the new covalent B-CH₂ bond giving rise to a zwitterionic structure 1 (Eq. (1)). The structure of the product was determined by X-ray diffraction analysis of single crystals to be identical with that reported by Rosenthal and co-workers [10a]. The compound was further characterized by IR, EI-MS and EPR spectra.¹

$$\begin{array}{c} & & \\$$

In contrast to synthesis of **1** from the Ti(II) alkyne complex where elimination of hydrogen was compatible with a redox mechanism [10], in the present case the methylene group underwent a clean transmetallation without changing the Ti valency. The presence of d¹ electron in the initial tucked-in titanocene was proved by photoelectron spectra showing vertical ionization energy of this electron to be 5.54 eV and by strongly anisotropic ESR spectra at $g_{av} = 1.953$, which both are attributable to a typical alkyltitanocene species with a σ -Ti-C bond [15c]. The non-volatility of compound **1** precluded the measurement of the photoelectron spectra, however, the d¹ state of the metal was demonstrated by ESR spectrum in toluene solution with g = 1.976, $a_{Ti} = 11.2$ G, and a = 2.2 G (triplet, $\approx 1:2:1$). The small

¹ Compound 4 [Ti(III){ $\eta^1:\eta^5-C_5Me_4(CH_2)$ }($\eta^5-C_5Me_5$)] was obtained by thermolysis of [Ti(III)Me(η⁵-C₅Me₅)₂] [15b,c], purified by sublimation and finally by crystallization from hexane. The solution of 4 in toluene (0.317 g in 10 ml, 1.0 mmol) was mixed with a solution of [B(C₆F₅)₃] (Strem, recrystallized from toluene) (0.1 M, 10 ml), and after stirring at ambient temperature a brown reaction solution was concentrated and cooled to -5 °C overnight. A crop of brown crystals of 5 was separated and dried in vacuo. Yield 0.60 g (72%). EI-MS (direct inlet, 70 eV, 200 °C): m/z (relative abundance, %) 829 (M⁺; not observed), 513 (20), 512 ([B(C₆F₅)₃]⁺; 100), 511 (24), 444 (13), 413 (6), 364 (5), 318 (8), 317 (22), 316 ($[(C_5Me_5)_2Ti-2H]^+$; 77), 315 (13), 299 (7), 296 (9), 295 (6), 277 (18), 258 (7), 227 (12), 176 (6), 148 (7), 129 (10). IR (KBr, cm⁻¹): 2950 (m,sh), 2917 (s), 2867 (m), 1643 (s), 1603 (m), 1514 (vs), 1456 (vs,b), 1384 (m), 1274 (m), 1083 (s), 1024 (w), 977 (s), 801 (vw), 787 (w), 769 (w), 750 (vw), 698 (vw), 572 (vw). EPR (toluene, 22 °C): g = 1.976, $a_{Ti} = 11.2$ G, triplet 1:2:1 a = 2.2 G; (toluene, -140 °C): $g_1 = 2.001$, $g_2 = 1.986$, $g_3 = 1.944$, $g_{av} = 1.977$.

coupling constant probably arises from interaction of the unpaired electron with 2 equivalent *ortho*-fluorine nuclei. Such an interaction has been observed in the solid [Ti(η^5 -C₅H₅)(η^5 -C₅H₄B(C₆F₅)₃] [9] and can be anticipated in the solution of **1**. In toluene glass, the spectrum of a rhombic symmetry is much less anisotropic than in its tucked-in precursor because of a change from trigonal to pseudotetrahedral coordination of the titanium atom. The solution ESR parameters for **1** (g = 1.980, $a_{Ti} = 11.0$ G) are comparable with those of **3** which showed, however, much broader signals ($\Delta H = 6.7$ G) [10b].

The doubly tucked-in compound $[Ti(\eta^5-C_5Me_5)$ $\{\eta^3:\eta^4-C_5Me_3(CH_2)_2\}]$ (5) reacted cleanly with one equivalent of $[B(C_6F_5)_3]$ to afford yellow diamagnetic $[Ti(\eta^5-C_5Me_5)\{\eta^5:\eta^1-C_5Me_3(CH_2)CH_2B(C_6F_5)_3\}]$ (6) (Eq. (2)). ² Its structure was established by X-ray diffraction analysis of single crystals. ³ Compound 6 was further characterized by elemental analysis, IR spectra (KBr pellet) and EI-MS spectra, the latter showing the molecular and fragment ions of the tucked-in titanocene and $[B(C_6F_5)_3]$ and no molecular ion of 6, however. The

² A solution of $[B(C_6F_5)_3]$ (0.1 M, 10 ml) was mixed with a toluene solution (10 ml) made from crystalline 5 [16b] (0.316 g, 1.0 mmol) under vigorous stirring at room temperature. The reaction solution was turning through green-brown to yellow-brown. After stirring for 2 h, the solution was concentrated to ca. 5 ml and cooled to -5 °C. The first crop of yellow plate crystals of 6 was separated, dried in vacuo, and used for characterization. Yield of 0.48 g (58%). EI-MS (direct inlet, 70 eV, 200 °C): m/z (relative abundance, %) 828 (M+-; not observed), 513 (20), 512 ([B(C₆F₅)₃]⁺; 100), 511 (24), 444 (13), 413 (6), 364 (5), 318 (8), 317 (22), 316 ([(C₅Me₅)₂Ti-2H]⁺; 77), 315 (13), 299 (7), 296 (9), 295 (6), 277 (18), 258 (7), 227 (12), 176 (6), 148 (7), 129 (10). IR (KBr, cm⁻¹): 2958 (m), 2918 (s), 2862 (m), 1642 (m), 1604 (vw), 1515 (s), 1457 (vs,b), 1384 (m), 1276 (m), 1084 (s), 1021 (w), 978 (s), 890 (vw), 819 (vw), 797 (w), 770 (w), 751 (w), 731 (w), 706 (vw), 696 (vw), 673 (w), 616 (vw), 574 (vw), 466 (w). Calcd. for C₄₅H₃₆BF₁₅Ti: C, 58.72; H, 3.94. Found: C, 58.65; H, 3.89.

³ Structure determination for **6**: $C_{38}H_{28}BF_{15}Ti \cdot C_7H_8$ (*M* = 920.45); triclinic, space group $P\bar{1}$ (No. 2); T = 150(2) K, a = 10.9240(2) Å, b = 17.9780(3) Å, c = 22.8620(4) Å, $\alpha = 106.1240(9)^{\circ}, \ \beta = 99.9290(9)^{\circ}, \ \gamma = 107.5030(10)^{\circ}; \ V = 3949.80(12)$ \check{A}^3 , Z = 4, $D_c = 1.548 \text{ Mg/m}^3$, $\mu(Mo \text{ K}\alpha) = 0.322 \text{ mm}^{-1}$, yellow plate from toluene, $0.50 \times 0.25 \times 0.17 \text{ mm}^3$, θ range for data collection 1.0– 27.5°, F(000) = 1872; 70 917 collected, 17 977 unique and 12 016 observed ($I > 2\sigma(I)$ diffractions, 1053 parameters, final R = 6.11%, wR = 15.81% for observed diffractions, R = 9.44% for all data, GOF = 1.026, residual electron density +1.078, -0.656 e Å⁻³. The racemic crystal contains two independent molecules of 6 and the molar equivalent of toluene of crystallization. Diffraction data were collected on a Nonius KappaCCD diffractometer and analyzed by the HKL program package [21]. The structures were solved by direct methods (SIR-92, [22]) and refined by full-matrix least-squares on F^2 (SHELXL-97 [23]). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were fixed and refined in their theoretical positions except those residing at carbon atoms C107/C207 and C106/ C206. These were identified on difference electron density maps and refined with isotropic thermal motion parameters. The racemic crystal contains one molecule of toluene of crystallization per one molecule of 1. CCDC Reference No. 256174.

¹H and ¹³C NMR spectra could not be measured (in C_6D_6) because of low solubility of **6**.



The molecular structure of one of the two independent molecules of 6 (molecule 1) is shown in Fig. 1 and important molecular parameters for this molecule are listed in Table 1. The geometric parameters for molecule 2 differ less than 3-fold esd's. The molecule consists of a tucked-in titanocene and borate species linked via one methylene group and these two species do not exert any contact interaction. The single tucked-in titanocene moiety possesses a moderately bent structure with the angle subtended by the two least-squares cyclopentadienyl planes $\varphi = 17.2(1)^{\circ}$. This angle is larger than angles φ observed in doubly tucked-in complexes (8.3–12.4°) [17] and in single tucked-in complex $[Ti{\eta^5-C_5Me_4(Si Me_2CH_2CH_2CF_3$ $\eta^5: \eta^1-C_5Me_3(CH_2)(SiMe_2CH_2CH_2)$ CF_3] (7) ($\varphi = 13.5(1)^{\circ}$) [18]. The value of the angle at the bridging carbon Ti1-C107-C102 64.8(1)° falls between the values found in 4 [15a] and 7 $(67.4(3)^\circ)$ [18]. Similarly to 4 and 5, the Ti1–Cg1 distance is shorter by ca. 0.05 Å than that of the unperturbed cyclopentadienyl ring (see Table 1). It is of interest that the



Fig. 1. The PLATON drawing of 6 (30% probability ellipsoids) with atom labeling scheme. Labels of C(123) and C(132) and hydrogen atoms except the methylene ones are omitted for clarity.

Table 1 Selected bond lengths (\AA) and bond angles (°) for molecule 1 of **6**

$Ti(2)-Cg(2)^{a}$ Ti(1)-C(102) Ti(1)-C(104)	1.997(3) 2.101(3)
Ti(1)-C(102) Ti(1)-C(104)	2 101(3)
Ti(1) - C(104)	_ (<i>b</i>)
	2.516(3)
Ti(1)–C(107)	2.267(3)
$Ti(1)-C_{ring}Cp(2)$	2.303-2.365(3)
C(102)–C(103)	1.451(4)
C(104)–C(105)	1.409(4)
C(102)–C(107)	1.421(4)
$C_{ring}-C_{ring}Cp(2)$	1.417-1.430(4)
B(1)–C(106)	1.695(4)
C–F(range)	1.339-1.360(4)
Ti(1)-C(107)-C(102)	64.8(1)
C(106)-B(1)-C(121)	110.2(2)
C(106)-B(1)-C(133)	101.4(2)
C(121)-B(1)-C(133)	113.1(2)
φ^{c}	17.2(1)
	$\begin{array}{l} \text{Ti}(1)-\text{C}(104)\\ \text{Ti}(1)-\text{C}(107)\\ \text{Ti}(1)-\text{C}(107)\\ \text{Ti}(1)-\text{C}_{ring}\text{Cp}(2)\\ \text{C}(102)-\text{C}(103)\\ \text{C}(104)-\text{C}(105)\\ \text{C}(102)-\text{C}(107)\\ \text{C}_{ring}-\text{C}_{ring}\text{Cp}(2)\\ \text{B}(1)-\text{C}(106)\\ \text{C}-\text{F}(range)\\ \text{Ti}(1)-\text{C}(107)-\text{C}(102)\\ \text{C}(106)-\text{B}(1)-\text{C}(121)\\ \text{C}(106)-\text{B}(1)-\text{C}(123)\\ \text{C}(121)-\text{B}(1)-\text{C}(133)\\ \varphi^{c} \end{array}$

^a Cg(1) and Cg(2) denote the centroids of C(101-105) and C(111-115) cyclopentadienyl rings, respectively.

^b Nonbonding distance.

^c The dihedral angle subtended by the least-squares planes of cyclopentadienyl rings.

C-C bond lengths opposite to the two carbons bearing the methylene groups are the shortest (1.409(4)) and 1.415(4) Å) and the Ti1-C104 bond the longest 2.516(3) Å as it is common in doubly tucked-in titanocenes [17].⁴ It shows that the effect of the bridging-to-boron methylene group is similar to the effect of the tucked-in methylene. Indeed, the C106 carbon atom is declined from the least-squares plane of the cyclopentadienyl ligand toward titanium by 0.627(4) Å similar to C107 (0.862(4) Å), whereas the methyl carbon atoms are declined farther away from titanium by about 0.1 Å. However, the C101–C106 bond length of 1.497(4) Å is within the error of measurement identical with the C-C bonds between methyl and ring carbon atoms (1.500-1.508(4) Å). Compared with the structure of 1, this bond is shorter than the bond in 1 (1.514(5) Å and correspondingly, the B1–C106 bond of 1.695(4) Å is longer with respect to the analogous bond in 1 (1.649(6) Å) [10a]. The hydrogen atoms of both methylene groups (C106, C107) were found and isotropically refined to give C-H bond lengths in the range 0.97(3)-1.02(3) Å. The shortest distance between the titanium atom and hydrogen attached to C106 (H(162)) was 2.21(3) Å, which is the distance found in decamethyltitanocene cation for agostic hydrogens of two vicinal methyl groups to titanium [19]. Hence, the bonding interaction of this agostic hydrogen to titanium induces the large bending of C106 toward titanium and coordinatively and electronically saturates the Ti(IV) ion so that the Ti–F interaction known for complex **1** is absent. A more electropositive zirconium, however, showed agostic interactions with both the *ortho*-proton of the phenyl group and proton(s) of the methylene group in the thermodynamically stable [ZrPh(C₅Me₅){C₅Me₄CH₂B (C₆F₅)₃)}] complex arising from the reaction of the phenylzirconocene tucked-in complex [ZrPh(C₅Me₅)-{C₅Me₄(CH₂)}] with [B(C₆F₅)₃] [20].

The pentafluorophenyl groups in 6 are inequivalent with respect to the methylene group as follows from different valence angles at the boron atom (see Table 1). This can be caused by various intra- and inter-molecular interactions in the solid state.

Neither the Ti(III) compound 1 nor the Ti(IV) compound 6 showed polymerization activity toward ethene in toluene at 1 bar pressure and 20 °C.

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⁴ The doubly tucked-in ligand is also called "allyldiene" $η^3$: $η^{4-}$ assigning the presence of trimethylallyl group in the ring and two double bonds between methylenes and ring carbon atoms [16a]. Indeed, methylene-to-ring bonds are shorter than the bond linking the corresponding ring carbon atoms [17], and the absence of d electrons proved by photoelectron spectroscopy shows on a backbonding interaction of Ti(II) with these double bonds [15c].

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