

$\text{Cp}_2^* \text{Zr}(\mu\text{-C}_4\text{H}_6)\text{B}(\text{C}_6\text{F}_5)_3$, a first example of a stable unbridged homogeneous metallocene–betaine Ziegler catalyst system

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Abstract

Addition of the strong organometallic Lewis acid $\text{B}(\text{C}_6\text{F}_5)_3$ to $(\eta^4\text{-butadiene})\text{ZrCp}_2^*$ ($\text{Cp}^* = \eta^5\text{-pentamethylcyclopentadienyl}$) yields the open-chain metallocene–hydrocarbylborate–betaine complex **2**. The novel betaine complex **2** is an active homogeneous single component metallocene Ziegler catalyst for α -olefin polymerization. © 1997 Elsevier Science S.A.

Keywords: Homogeneous catalysis; Metallocenes; Ziegler catalysts; Betaine; Polymerization

1. Introduction

The use of homogeneous Ziegler catalysts based on the Group 4 metallocenes has initiated an important new development in α -olefin polymerization [1]. It is widely agreed that Cp_2ZrR^+ cations (or their respective *ansa*-metallocene analogues containing specifically designed substituent patterns) are to be regarded as the active species of these extremely active and often highly stereoselective new catalyst systems [2,3]. Commonly the generation of the active catalyst system is carried out by reacting the respective metallocene dihalide precursor (e.g. the parent compound Cp_2ZrCl_2 in the most simple case) with a large excess of methylalumoxane $[-(\text{CH}_3\text{AlO})_n-]$ in e.g. toluene. Since a large excess of the methylalumoxane activator has usually to be employed (Al:Zr ratios of $> 10^3$ are not uncommon) the search for alternative methods of activation has recently been pursued intensively. Catalytically active alkylmetallocene cations have thus been obtained by treatment of the dialkylmetallocenes with trityl- or trialkylammonium ions (both employed with an inert anion such as BPh_4^-) [4]. Also the strong Lewis acid tris(pentafluorophenyl)borane has been employed for generating active homogeneous metallocene Ziegler catalysts [5].

2. Results and discussion

It might be advantageous to try to avoid the in situ generation of the active catalyst species altogether by developing stable, isolable organometallic complexes that become active upon addition of the α -olefin monomer to then immediately initiate the actual polymerization process. Such complexes require a structural composition where the active metallocene cation and the accompanying non-nucleophilic anion are present in the same molecule and are connected by means of a hydrocarbyl chain. Ideal catalysts of this type would be the neutral metallocene–betaine systems **B**. Such compounds would upon contact with e.g. ethene instantaneously react with insertion of the olefin into the reactive Zr–C bond and thus initiate the polymerization process. Betaines **B** would probably constitute ideal single component catalyst systems. However, the cyclic betaine isomers **A** should probably be more stable and easier to synthesize. In these compounds the electron-deficit of the metallocene cation is diminished by internal coordination of a suitable component of the anionic part X of the molecule. The position of the $\text{A} \rightleftharpoons \text{B}$ equilibrium and the rate of equilibration will then determine the quality of the overall catalyst system.



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We have recently found a first example of a single component metallocene Ziegler catalyst system of the type A, namely the 1:1 addition product **1** of $B(C_6F_5)_3$ to (butadiene)zirconocene [6,7]. Complex **1** is a very active α -olefin polymerization catalyst. Reversible cleavage of the stabilizing C–F coordination to the zirconium center has been observed to occur prior to the insertion process. In addition the primary ethene and propene insertion products respectively have been observed by NMR spectroscopy at low temperature with this system [8].

We have now, to our knowledge for the first time, prepared a non-cyclic, open metallocene–hydrocarbyl–betaine of the general type **B** and characterized it with regard to its most important structural and chemical properties. The synthesis was carried out by reacting (η^4 -butadiene)bis(pentamethylcyclopentadienyl)zirconium with tris(pentafluorophenyl)borane in a 1:1 molar ratio at room temperature in toluene. After three days a black precipitate of the product **2** (containing one equivalent of toluene in the solid state) was formed. The stable compound **2** was isolated in close to 90% yield [m.p. 105°C, DSC, decomp.; UV (toluene, $c = 8.4 \times 10^{-4} \text{ mol l}^{-1}$): $\lambda_{\text{max}} = 462 \text{ nm}$ (ϵ 950), 568 nm (ϵ 740)]. Single crystals for the X-ray structure analysis were obtained from toluene.

In the crystal two η^5 -pentamethylcyclopentadienyl ligands are coordinated to the zirconium center of **2** (D1–Zr–D2 137.8°, where D1 and D2 denote the centroids of the Cp* ligands) in addition to a $\text{CH}_2\text{CHCH}-\text{CH}_2\text{B}(\text{C}_6\text{F}_5)_3$ moiety. The latter is linked to zirconium only through the carbon atoms C1 to C3 in a distorted η^3 -allyl bonding situation. The Zr–C1 bond is short (2.337(4) Å). The Zr–C2 distance is markedly longer at 2.488(4) Å and the Zr–C3 separation (2.722(4) Å) is found to be close to the limit of the zirconium to carbon bonding range. Consequently the C2–C3 bond (1.362(6) Å) is much shorter than the C1–C2 linkage (1.426(6) Å). The Zr–(C1–C3) unit in **2** can thus be described as a markedly distorted (π -allyl)zirconium unit [9]. Alternatively, the specific bonding situation encountered in **2** may be regarded as another example of a ‘ π -agostic’ metal complex situation, similar to what was previously observed in a few cases of remotely related cyclic heterobimetallic allylmetallocene systems [10].

The most remarkable structural feature of the betaine complex **2** is that the formally cationic metallocene center does not attain coordinative saturation by intramolecular C–F fluoride coordination from the $B(\text{C}_6\text{F}_5)_3$ unit. On the contrary, in **2** the $B(\text{C}_6\text{F}_5)_3$ end of the metallocene–alkyl–tris(aryl)borate dipole is clearly oriented away from the bent metallocene unit. In the crystal a molecular arrangement is found that takes care of a maximal spatial separation between boron and zirconium (dihedral angles Zr–C1–C2–C3 –64.2(3)°,

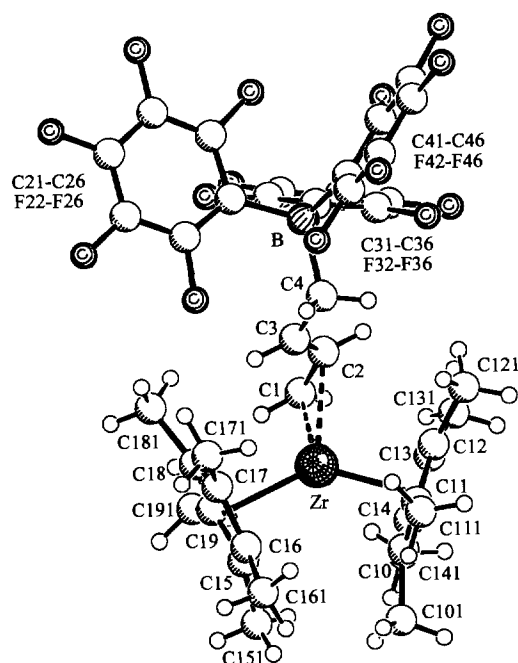
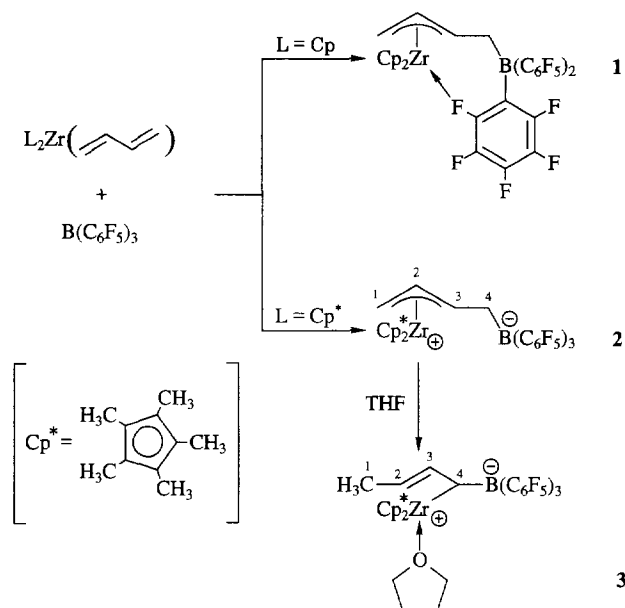


Fig. 1. A view of the molecular geometry of the zirconocene–borate–betaine complex **2** in the crystal. Selected bond lengths (Å) and angles (deg): Zr–C1 2.337(4), Zr–C2 2.488(4), Zr–C3 2.722(4), Zr–C4 3.856(4), C1–C2 1.426(6), C2–C3 1.362(6), C3–C4 1.500(6), C4–B 1.670(6), B–C21 1.654(6), B–C31 1.643(6), B–C41 1.667(6); C1–Zr–C2 34.2(2), Zr–C1–C2 78.7(2), C1–C2–C3 126.3(4), C2–C3–C4 124.3(4), C3–C4–B 113.9(3), C4–B–C21 116.4(4), C4–B–C31 104.8(3), C4–B–C41 109.0(3).

C2–C3–C4–B 87.7(5)°). Complex **2** comes very close to the ideal situation of a non-bridged open metallocene– μ -hydrocarbyl–borate betaine **B** (Fig. 1, see above).

The spectroscopic data support an analogous structure of **2** in toluene- d_8 solution. The complex is chiral ($^1\text{H}/^{13}\text{C}$ NMR resonances of the diastereotopic Cp* ligands at δ 1.36, 1.34/123.6, 122.8, 10.9, 10.8). The π -allyl unit exhibits ^1H NMR signals at δ 0.80, 2.99 (1-H, H'), 6.36 and 5.68 (2-H, 3-H; ^{13}C NMR signals at 75.4, 144.5 and 125.0). The hydrogen atoms of the CH_2 group adjacent to boron are diastereotopic (δ 1.68, 2.28; C-4: δ 30.4). In contrast to the behavior of the cyclic metallocene betaine complex **1**, which shows 15 different ^{19}F NMR resonances at low temperature with one clearly separated signal of the single divalent o -F- C_6F_4 atom, and exhibits dynamic NMR behavior at elevated temperature, complex **2** is not dynamic in toluene- d_8 . Down to the lowest monitoring temperature (193 K) the ^{19}F NMR spectrum of **2** (at 564 MHz) shows three sharp signals (o -, m -, p - C_6F_5) of the $\text{RB}(\text{C}_6\text{F}_5)_3$ moiety. In the coordinating solvent THF- d_8 a simplified spectrum of **2** is monitored, in which the diastereotopies that were observed in toluene- d_8 are lost. In THF complex **2** is not stable for prolonged periods of time. During ca. 10 h in THF- d_8 **2** is rearranged to an isomeric THF- d_8 stabilized σ -allyl metal-

locene betaine complex **3** with formal 1,4-hydrogen migration [11].



Complex **2** catalyzes the polymerization of ethene (in toluene solution at room temperature, 1 bar, reaction time 5 min, activity $a = 50$ g of polyethylene/mmol Zr h; m.p. 121 °C) as well as propene (catalyst formed in situ from 35 mg (0.084 mmol) of $\text{Cp}_2^*\text{Zr}(\text{butadiene})$ and 100 mg (0.195 mmol) of $\text{B}(\text{C}_6\text{F}_5)_3$ in 200 ml of toluene; polymerization in the presence of 2 ml of triisobutylaluminum as internal drying agent (2 bar propene pressure, 2 h reaction time), three temperatures: -20°C , $a = 18$ g polypropylene/mmol Zr h bar, $M_w \approx 3000$; 0°C , $a = 60$, $M_w \approx 1000$; $+20^\circ\text{C}$, $a = 50$, $M_w \approx 650$). The molecular weight determination of the polypropylene formed was carried out by ^1H NMR spectroscopy; the end group analysis also indicated that chain transfer had occurred predominantly by a β -methyl elimination pathway (signals of the $-\text{CH}=\text{CH}_2$ polymer end groups at δ 4.98, 5.02 (2H) and 5.75 (1H)). In addition a ca. 2% chain transfer having taken place by means of β -H elimination was found (^1H NMR signals of the $-\text{C}(\text{CH}_3)=\text{CH}_2$ end group at δ 4.74 and 4.80 in toluene- d_8). The overall mode of chain transfer mechanism and the resulting molecular weights are as typically found for polypropylene formation at a homogeneous bis(pentamethylcyclopentadienyl)zirconium derived Ziegler catalyst system [12].

The polypropylene formed at the catalyst **2** is atactic as expected (determined by ^{13}C NMR methyl pentade analysis [13]). The α -olefin polymerization reactions with the catalyst system **2** were also carried out in toluene- d_8 solution at low temperature under direct ^1H NMR observation. Unlike the reactions with the cyclic fluoride-bridged system **1** [8], we were not able to

observe any kinetically stabilized intermediates in the initiation phase of the α -olefin polymerization process when starting from **2**. Apparently, at the single component Ziegler catalyst system **2** the rapid formation of the polymer chain takes place immediately upon exposure to the α -olefin above the critical initiation temperature.

The (butadiene)metallocene/ $\text{B}(\text{C}_6\text{F}_5)_3$ method has been applied successfully to generate very active homogeneous Ziegler catalyst systems derived from the typical highly substituted *ansa*-metallocene complexes developed for practical industrial applications [1,3]. We are currently investigating which of these sterically congested systems prefer open-chain metallocene betaine structures (analogous to **2**) and in which cases fluorine-bridged metallacycles (analogous to **1**) are involved.

3. Experimental details

3.1. Synthesis of **2**

The reaction of 80 mg (0.19 mmol) of (butadiene) ZrCp_2^* [14] with 110 mg (0.22 mmol) of $\text{B}(\text{C}_6\text{F}_5)_3$ [15] in 50 ml of toluene (3 days, ambient temperature) yielded 172 mg of **2** (88%), a black colored solid (contains 1 molar equiv. of toluene), m.p. 105 °C (DSC, decomp.). Anal. Found: C, 56.51; H, 4.47. $\text{C}_{42}\text{H}_{36}\text{BF}_{15}\text{Zr} \cdot \text{C}_7\text{H}_8$ (1019.9) Calc.: C, 57.71; H, 4.35%. ^1H NMR (600 MHz, 303 K, toluene- d_8): δ 6.36 (m, 1H, 2-H), 5.68 (m, 1H, 3-H), 2.99 (br d, $^3J(\text{H,H}) = 11.7$ Hz, 1H, 1-H), 2.28 (br, 1H, 4-H), 1.68 (br, 1H, 4-H'), 1.36, 1.34 (each s, each 15H, CH_3 of Cp^*), 0.80 (m, 1H, 1-H') ppm. ^{13}C NMR (150.8 MHz, 303 K, toluene- d_8): δ 149.0 ($^1J(\text{C,F}) = 244$ Hz, *o*- $\text{B}(\text{C}_6\text{F}_5)_3$), 144.5 (C-2), 139.1 ($^1J(\text{C,F}) = 244$ Hz, *p*- $\text{B}(\text{C}_6\text{F}_5)_3$), 137.6 ($^1J(\text{C,F}) = 250$ Hz, *m*- $\text{B}(\text{C}_6\text{F}_5)_3$), 125.0 (C-3), 123.6, 122.8 (each quart. C of Cp^*), 75.4 (C-1), 30.4 (C-4), 10.9, 10.8 (each CH_3 of Cp^*) ppm. ^{19}F NMR (564.3 MHz, 303 K, toluene- d_8): δ -166.8 ($^3J(\text{F,F}) = 21$ Hz, 6F, *m*-F), -163.2 ($^3J(\text{F,F}) = 21$ Hz, 3F, *p*-F), -132.8 ($^3J(\text{F,F}) = 21$ Hz, 6F, *o*-F) ppm. ^1H NMR (600 MHz, 303 K, THF- d_8): δ 5.87 (m, 1H, 2-H), 5.73 (m, 1H, 3-H), 2.20 (d, $^3J(\text{H,H}) = 10.3$ Hz, 2H, 1-H), 1.96 (s, 30H, CH_3 of Cp^*), 1.85 (br, 2H, 4-H) ppm. ^{13}C NMR (150.8 MHz, 303 K, THF- d_8): δ 149.0 ($^1J(\text{C,F}) = 244$ Hz, *o*- $\text{B}(\text{C}_6\text{F}_5)_3$), 138.0 ($^1J(\text{C,F}) = 250$ Hz, *p*- $\text{B}(\text{C}_6\text{F}_5)_3$), 138.6 (C-2), 137.3 ($^1J(\text{C,F}) = 250$ Hz, *m*- $\text{B}(\text{C}_6\text{F}_5)_3$), 131.3 (C-3), 124.2 (quart. C of Cp^*), 74.0 ($^1J(\text{C,H}) = 140$ Hz, C-1), 31.0 (C-4), 11.6 (CH_3 of Cp^*) ppm. ^{19}F NMR (564.3 MHz, 303 K, THF- d_8): δ -168.3 ($^3J(\text{F,F}) = 20$ Hz, 6F, *m*-F), -165.5 ($^3J(\text{F,F}) = 20$ Hz, 3F, *p*-F), -132.0 ($^3J(\text{F,F}) = 22$ Hz, 6F, *o*-F) ppm. IR; $\tilde{\nu} = 3672, 3606, 3537, 2964, 2920, 2866, 1641, 1608, 1512, 1458, 1385, 1267, 1082, 961, 804, 773, 675$ cm^{-1} .

3.2. X-ray crystal structure analysis of 2

$C_{49}H_{44}BF_{15}Zr$, $M_r = 1019.87$, crystal size $0.5 \times 0.4 \times 0.1$ mm, $a = 17.083(1)$, $b = 16.012(1)$, $c = 18.370(1)$ Å, $\beta = 116.49^\circ$, $V = 4497.3(5)$ Å³, $\rho_{\text{calc}} = 1.506$ g cm⁻³, $\mu = 3.42$ cm⁻¹, empirical absorption correction, $Z = 4$, monoclinic, space group $P2_1/c$ (No. 14), Enraf–Nonius MACH-3 diffractometer, $\lambda = 0.71073$ Å, $T = 223$ K, 7851 measured reflections ($\pm h, +k, -l$), $[(\sin \theta)/\lambda]_{\text{max}} = 0.59$ Å⁻¹, 7587 independent and 4986 observed reflections [$I \geq 2\sigma(I)$], 593 refined parameters, $R = 0.044$, $wR^2 = 0.112$. Programs used: SHELXS-86, SHELXL-93, SCHAKAL-92. Further details of the X-ray crystal structure analysis of **2** can be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, under the reference number CSD-405296.

3.3. Rearrangement to give 3

After 10 h in THF- d_8 only the NMR signals of the rearrangement product **3** were observed. ¹H NMR (600 MHz, 299 K, THF- d_8): δ 5.45 (m, 1H, 3-H), 4.60 (m, 1H, 2-H), 2.07 (s, 30H, CH₃ of Cp*), 2.00 (m, 1H, 4-H), 1.31 (d, ³J(H,H) = 6.2 Hz, 3H, 1-H) ppm. ¹³C NMR (150.8 MHz, 299 K, THF- d_8): δ 149.1 (¹J(C,F) = 246 Hz, *o*-B(C₆F₅)₃), 138.4 (¹J(C,F) = 245 Hz, *p*-B(C₆F₅)₃), 137.6 (C-3), 137.1 (¹J(C,F) = 246 Hz, *m*-B(C₆F₅)₃), 124.2 (quart. C of Cp*), 119.0 (¹J(C,H) = 148 Hz, C-2), 29.4 (C-4), 18.4 (¹J(C,H) = 125 Hz, C-1), 11.4 (¹J(C,H) = 127 Hz, CH₃ of Cp*) ppm. ¹⁹F NMR (564.3 MHz, 299 K, THF- d_8): δ -169.5 (³J(F,F) = 20 Hz, 6F, *m*-F), -167.2 (³J(F,F) = 20 Hz, 3F, *p*-F), -132.4 (³J(F,F) = 21 Hz, *o*-F) ppm.

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