

Priority communication

Preparation of  $(Cp^*)\{C_5Me_4CH_2B(C_6F_5)_3\}ZrPh$ , a novel zwitterionic single-component alkene polymerisation catalyst

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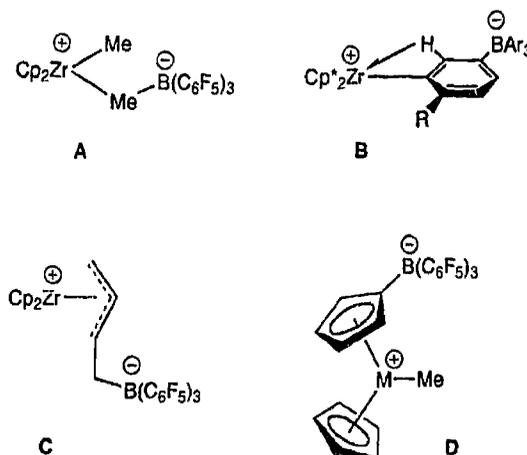
Received 5 June 1997

Abstract

$B(C_6F_5)_3$  reacts with the fulvene complex (pentamethylcyclopentadienyl)( $\pi$ - $\eta^5$ : $\sigma$ - $\eta^1$ -tetramethylfulvene)phenylzirconium ( $Cp^*FvZrPh$ ) (I) selectively under attack at the fulvene- $CH_2$  group to form the highly sensitive zwitterionic complex  $(Cp^*)\{C_5Me_4CH_2B(C_6F_5)_3\}ZrPh$  (II). Mixtures of I with either  $B(C_6F_5)_3$  or  $[CPh_3][B(C_6F_5)_4]$  are highly active for the polymerisation of ethene over a wide range of temperatures. © 1997 Elsevier Science S.A.

1. Introduction

It is now well recognised that cationic metal alkyl species  $[Cp_2MR]^+$  are the catalytically active species in metallocene-based olefin polymerisation catalysts [1–3]. Zwitterionic complexes are also known to give highly active catalysts. Two types may be distinguished: those that through dissociation or other processes are converted into cationic complexes  $[Cp_2MR]^+$  (e.g., A, B and C) [4–10],<sup>1</sup> and those which retain their zwitterionic character throughout the chain growth process, such as the borato-Cp compounds of type D [15]. We are interested in compounds of the second type in order to control anion influence and solubility without impairing the Lewis acid character of the metal centre judged necessary for efficient catalysis.



We have recently prepared complexes of type D in which a cyclopentadienyl ligand carries an anionic tris(pentafluorophenyl)borato substituent by reaction of the  $[C_5H_4B(C_6F_5)_3]^{2-}$  dianion with zirconium and hafnium halides [15]. Here, we report a different approach to generate single-component metal-borate betaine systems, by attack of  $B(C_6F_5)_3$  on a coordinated fulvene ligand, generating complexes of the related

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<sup>1</sup> For further examples of fluoroarylborate coordination, see Refs. [11–14].

$[\text{C}_5\text{Me}_4\text{CH}_2\text{B}(\text{C}_6\text{F}_5)_3]^{2-}$  dianion which contains a  $\text{CH}_2$  spacer between the borato substituent and the Cp ring.

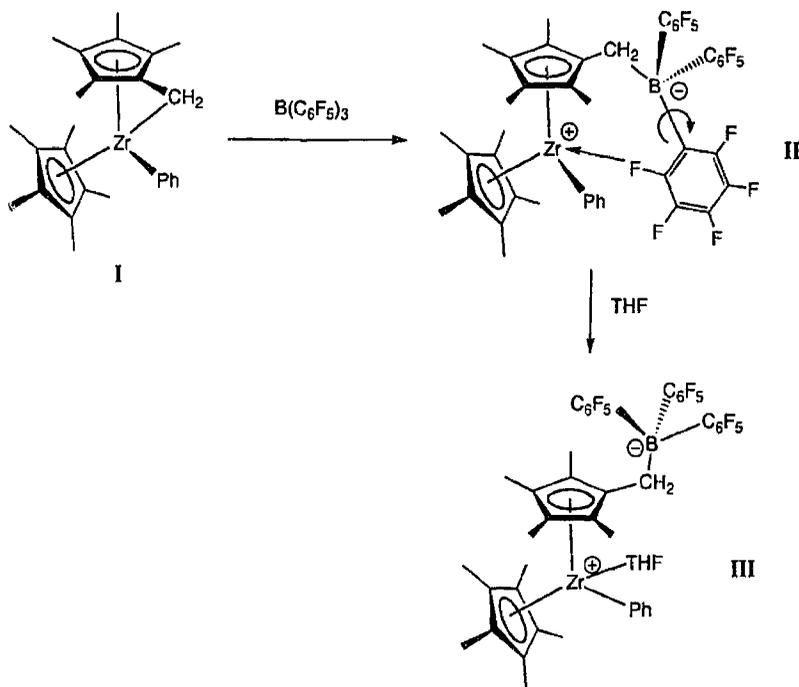
The reaction between  $\text{Cp}^*(\text{Fulv})\text{ZrPh}$  (**I**) ( $\text{Fulv} = \text{C}_5\text{Me}_4\text{CH}_2$ ) [16] with  $\text{B}(\text{C}_6\text{F}_5)_3$  in toluene at room temperature proceeds selectively with attack on the fulvene- $\text{CH}_2$  group to give a new zwitterionic zirconocene complex (**II**) (Scheme 1).

Complex (**II**) is obtained in essentially quantitative yield according to NMR data and is isolated as a very air-sensitive microcrystalline yellow solid which dissolves readily in toluene. The  $^{19}\text{F}$  NMR spectrum of **II** in  $\text{CD}_2\text{Cl}_2$  at  $-70^\circ\text{C}$  shows two *para*-fluorine [ $\delta -161.1$  (2 F) and  $-162.1$  (1 F)], three *meta*-fluorine ( $\delta -164.1$ ,  $-164.6$ ,  $-166.7$ ) and three clearly separated *ortho*-fluorine signals. Two of the three *o*-F signals appear in the usual range ( $\delta -130.4$ ,  $-132.5$ ), whereas a third, rather broad signal, integrating for 2 F atoms, is found shifted to higher field, at  $\delta -143.4$ . This chemical shift is less than values previously observed for *ortho*-fluorine atoms coordinated to metal centres, which are usually found at ca.  $\delta -170$  to  $-220$  ppm [8–14,17,18], and represents the average for a coordinated and an uncoordinated *o*-F of one of the  $\text{C}_6\text{F}_5$  substituents. Cooling to  $-90^\circ\text{C}$  led to some broadening of this signal, though further resolution could not be achieved. On adding THF to these solutions the signal at  $\delta -143.4$  disappears, while resonances for six fluorines appear in the typical *o*-F region (cf. **III**). Evidently the weak metal-fluorine interaction in **II** allows rapid interchange between the two *ortho* posi-

tions of one  $\text{C}_6\text{F}_5$  rings even at very low temperatures, and is considerably weaker than in previously reported complexes containing coordinated *ortho*-fluorines [8–14,17,18].

On addition of some THF to toluene solutions of **II**, the THF adduct **III** is formed which on cooling to  $-16^\circ\text{C}$  is isolated as yellow crystals. The complex is fluxional and shows rapid exchange with free THF above  $-30^\circ\text{C}$ . The  $^{19}\text{F}$  NMR of **III** in  $\text{CD}_2\text{Cl}_2$  at  $-70^\circ\text{C}$  is resolved into one *para*-fluorine, two *meta*-fluorine, and four *ortho*-fluorine signals. In this case, the latter are found within the usual *o*-F range, as expected, and integrate for six non-equivalent F-atoms, indicative of severely hindered  $\text{C}_6\text{F}_5$  rotation in this sterically congested complex. Unfortunately, all attempts to grow X-ray quality crystals of **II** and **III** were unsuccessful.

The reaction of complex **I** with  $\text{CPh}_3\text{B}(\text{C}_6\text{F}_5)_4$  proceeds less cleanly than in the case of  $\text{B}(\text{C}_6\text{F}_5)_3$  although the attack of  $\text{CPh}_3^+$  on the fulvene- $\text{CH}_2$  group is expected. Unfortunately, there is no clearly assignable species in the NMR. Mixtures of **I** with one equivalent of either  $\text{B}(\text{C}_6\text{F}_5)_3$  or  $[\text{CPh}_3][\text{B}(\text{C}_6\text{F}_5)_4]$  are highly active catalysts for the polymerisation of ethylene in toluene from  $80^\circ\text{C}$  to  $-78^\circ\text{C}$ , in the presence and absence of  $\text{AlMe}_3$  as a scavenger. Some of the polyethylene samples contained high molecular weight components that proved too insoluble for GPC analysis in 1,2-dichlorobenzene at  $140^\circ\text{C}$ . The apparent decrease of catalyst productivity with increasing temperature is



Scheme 1.

Table 1  
Ethene polymerisations with I/[CPh<sub>3</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] in toluene<sup>a</sup>

Temperature [°C]	Time [min]	AlMe <sub>3</sub> [μmol]	Polymer yield [g]	Productivity <sup>b</sup>	M <sub>w</sub>	M <sub>w</sub> /M <sub>n</sub>
-78	1.0	—	0.462	2772	640,000	4.3
-50	3.0	—	0.233	466	316,000	3.0
-30	2.0	—	0.120	360	168,000	3.5
-10	2.0	—	0.093	279	181,000	3.4
20	1.5	—	0.145	580	110,000	4.2
20	1.5	55	0.106	424	51,000	4.1
50	2.0	—	0.119	357	57,400	3.0
60	6.0	—	0.259	259	107,500	5.2
60	6.0	55	0.313	313	14,300	5.0
60	6.0	110	0.312	312	11,100	4.8

<sup>a</sup>Conditions: 10 μmol of I, 10 μmol of [CPh<sub>3</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>], 20 cm<sup>3</sup> of toluene, ethene 1 bar.

<sup>b</sup>In 10<sup>3</sup> g PE (mol Zr)<sup>-1</sup> h<sup>-1</sup>.

due to diffusion limitation at the low ethene pressure employed (1 bar). Some polymerisation results are listed in Tables 1 and 2.

## 2. Experimental

All reactions were carried out under strictly anaerobic conditions following procedures detailed elsewhere [19].

### 2.1. Preparation of (Cp<sup>\*</sup>)(C<sub>5</sub>Me<sub>4</sub>CH<sub>2</sub>B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>)ZrPh (III)

Complex II was prepared by addition of 20 ml of toluene to a mixture of 0.65 g (1.49 mmol) of Cp<sup>\*</sup>FlvZrPh (I) and 0.76 g (1.49 mmol) of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> at room temperature. The clear orange solution formed was stirred for 1 h and cooled to -78°C to give a yellow precipitate which was filtered off and dried under vacuum to give II (1.1 g, 1.2 mmol, 80%). The compound is very air-sensitive and readily soluble in toluene. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, -70°C, 300 MHz): δ 1.48 (s, 12H, C<sub>5</sub>Me<sub>4</sub>), 1.74 (s, 15H, C<sub>5</sub>Me<sub>5</sub>), 2.37 (br, 2H, CH<sub>2</sub>-B), 6.53 (d, *J* = 7.3 Hz, 2H, *o*-CH of Ph), 7.05 (t, *J* = 7.3 Hz, 1H, *p*-CH of Ph), 7.18 (m, *J* = 7.3 Hz, 2H,

*m*-CH of Ph). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, -70°C): δ 11.0 (s, C<sub>5</sub>Me<sub>5</sub>), 11.5 (s, 2C, C<sub>5</sub>Me<sub>4</sub>), 12.0 (s, 2C, C<sub>5</sub>Me<sub>4</sub>), 22.7 (br, 1C, CH<sub>2</sub>-B), 123.5 (s, 2C, C<sub>5</sub>Me<sub>4</sub>); 123.7 (s, 2C, *o*-CH of Ph); 124.0 (s, C<sub>5</sub>Me<sub>5</sub>), 124.2 (s, 2C, C<sub>5</sub>Me<sub>4</sub>), 126.1 (s, 1C, *p*-CH of Ph); 127.8 (s, 2C, *m*-CH of Ph), 132.7 (s, 1C, *ipso*-C of C<sub>5</sub>Me<sub>4</sub>), 199.4 (s, 1C, *ipso*-C of Ph). <sup>19</sup>F NMR (CD<sub>2</sub>Cl<sub>2</sub>, -70°C): δ -130.4 (d, br, 2F, *o*-F), -132.5 (d, *J* = 21 Hz, 2F, *o*-F), -143.4 (br, 2F, *o*-F), -161.1 (t, *J* = 21 Hz, 2F, *p*-F), -162.1 (t, *J* = 21 Hz, 1F, *p*-F), -164.1 (t, br, 2F, *m*-F), -164.6 (t, br, 2F, *m*-F), -166.7 (t, br, 2F, *m*-F). <sup>11</sup>B NMR (CD<sub>2</sub>Cl<sub>2</sub>, -70°C): δ -13.2.

The THF adduct (Cp<sup>\*</sup>)(C<sub>5</sub>Me<sub>4</sub>CH<sub>2</sub>B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>)ZrPh(THF) (III) is prepared similarly except that a couple drops of THF were added to the above reaction mixture. Cooling to -16°C gives a yellow crystalline solid (70%). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 25°C, 300 MHz): δ 1.19 (s, 6H, CH<sub>3</sub> of C<sub>5</sub>Me<sub>4</sub>), 1.33 (s, 15H, Cp<sup>\*</sup>); 1.48 (s, 6H, CH<sub>3</sub> of C<sub>5</sub>Me<sub>4</sub>), 1.54 (br, 4H, THF), 2.79 (br, 2H, CH-B), 3.53 (m, 4H, THF), 6.55 (d, *J* = 7.0 Hz, 2H, *o*-CH of Ph), 7.07 (t, *J* = 7.0 Hz, 1H, *p*-CH of Ph), 7.16 (t, *J* = 7.0 Hz, 2H, *m*-CH of Ph). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, -50°C): δ 10.5 (1C, C<sub>5</sub>Me<sub>4</sub>), 11.4 (1C, C<sub>5</sub>Me<sub>4</sub>), 11.5 (1C, C<sub>5</sub>Me<sub>4</sub>), 11.7 (C<sub>5</sub>Me<sub>5</sub>), 12.9 (1C, C<sub>5</sub>Me<sub>4</sub>), 21.5 (br, 1C, CH<sub>2</sub>-B), 26.0 (2C, THF), 68.3 (2C, THF), 122.1 (1C, *o*-CH of Ph), 123.9

Table 2  
Ethene polymerisations with I/B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> in toluene<sup>a</sup>

Temperature [°C]	Time [min]	Polymer yield [g]	Productivity <sup>b</sup>	M <sub>w</sub>	M <sub>w</sub> /M <sub>n</sub>
-70	4.0	0.485	970	861,000	3.0
-50	3.0	0.392	784	482,500	3.8
-20	3.0	0.200	400	234,500	2.5
20	3.0	0.185	370	128,000	3.0
20 <sup>c</sup>	2.0	0.101	342	167,000	2.4

<sup>a</sup>Conditions: 10 μmol of I, 10 μmol of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>, 20 cm<sup>3</sup> of toluene, ethene 1 bar.

<sup>b</sup>In 10<sup>3</sup> g PE (mol Zr)<sup>-1</sup> h<sup>-1</sup>.

<sup>c</sup>5 μmol I, 5 μmol B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>.

( $C_5Me_5$ ), 125.0 (1C, *p*-CH of Ph), 135.6 (1C, *o*-CH of Ph), 127.0 (1C, *m*-CH of Ph), 127.3 (1C, *m*-CH of Ph), 143.6 (1C,  $C_5Me_4$ ), 126.8 (1C,  $C_5Me_4$ ), 125.3 (1C,  $C_5Me_4$ ), 123.0 (1C,  $C_5Me_4$ ), 121.4 (1C,  $C_5Me_4$ ), 194.7 (1C, *ipso*-C of Ph).  $^{19}F$  NMR ( $CD_2Cl_2$ ,  $-90^\circ C$ ): *o*-F:  $\delta$  -130.1 (br, 1F), -131.2 (br, 3F), -134.3 (br, 1F), -134.6 (br, 1F); *p*-F:  $\delta$  -163.1 (br, 3F); *m*-F:  $\delta$  -166.5 (br, 4F), -167.7 (br, 2F).  $^{11}B$  NMR ( $C_6D_6$ ,  $25^\circ C$ ):  $\delta$  -12.0. Anal. Calc. for  $C_{48}H_{42}BF_{15}OZr$ : C, 56.4; H, 4.1. Found C, 56.4; H, 4.0.

## 2.2. Ethene polymerisations

Toluene was saturated at the stated temperature with ethylene under 1 bar pressure. The appropriate amount of a standard solution of the complex (**I**) (and of  $AlMe_3$  where applicable) was injected, followed by a solution of  $B(C_6F_5)_3$  or  $[CPh_3][B(C_6F_5)_4]$  in toluene. Immediate rapid polymerisation was observed. The polymerisations were terminated by the injection of methanol and the polymers were precipitated with methanol/HCl, washed with methanol and dried to a constant weight. Molecular weights and polydispersities were determined by gel permeation chromatography.

## Acknowledgements

This work was supported by the Engineering and Physical Sciences Research Council. We thank RAPRA Technology, Shawbury, for GPC measurements.

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