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Control of symmetry in active cationic *ansa*-zirconocene species: catalyst preparation, characterization and ethylene–norbornene copolymerization

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Abstract

New bis-hydrocarbyl complexes of methylene bridged *ansa*-metallocenes $[H_2C(C_5Me_2H_2)_2]ZrR_2$ {R = Me (**1**), CH_2Ph (**2**), CH_2SiMe_3 (**3**), Ph (**4**)} have been prepared. They form catalytically active intermediates with borane or borate depending on solvent and Zr–R group. Specifically, $[H_2C(Me_2C_5H_2)_2]Zr(CH_2Ph)_2$ (**2**) produced an ion pair upon treatment with $B(C_6F_5)_3$ whereas $[H_2C(Me_2C_5H_2)_2]Zr(CH_2SiMe_3)_2$ (**3**) produced a zwitterionic species, identified by ^1H, ^{13}C, and ^{19}F NMR spectroscopy. Copolymerization of ethylene and norbornene for the metallocene dichloride/MAO and bis-hydrocarbyl complex/borate systems was compared.

Keywords: *ansa*-Zirconocene; Bent metallocene; Borane; Borate; Copolymerization; Ethylene; Ion pair; Norbornene; Zwitterion

1. Introduction

Many different group 4 metallocene hyrodrocarbyl complexes have been previously synthesized, characterized and used industrially for α-olefin (co)polymerization in combination with borane or borate cocatalysts [1]. These catalytic precursors are attractive since they bypass the use of a large amount of methylaluminoxane (MAO), and production of polymer ash and metal content [2]. Borane and borate cocatalysts can be used in equivalent amounts, but then hydrocarbyl derivatives of the zirconocene are required [3]. In these reactions, UV–Vis light, heat and solvent sensitivity of the species create synthetic challenges. Alternative to preparing non-MAO catalytic systems for olefin polymerization is the ternary system, wherein an aluminum reagent is used to give the metallocene "alkyl complex" in situ followed by the use of a non-metallic cocatalyst such as borane or borate [4,5].

To date, many reactions of hydrocarbyl metallocene and Lewis acidic $B(C_6F_5)_3$ or other borate salt such as $[Me_2PhHN][B(C_6F_5)_4]$ and $[Ph_3C][B(C_6F_5)_4]$ have been studied to elucidate the nature of the active metallocene species [6]. Two species exist: the zwitterion and the ion pair. For the ion-pair polymerization activity is generally higher [7]. The cocatalyst may change the environmental sphere and reactivity [8]. In this paper, we describe the synthesis and characterization of bis-hydrocarbyl complexes of methylene bridged *ansa*-zirconocenes. These complexes demonstrate different reactivity towards cocatalysts; metallocene dihalide/MAO for

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norbornene and ethylene copolymerization activities have been compared.

2. Results and discussion

*2.1. Preparation and characterization of complexes **1–4***

The dichloride complex $[H_2C(C_5Me_2H_2)_2]ZrCl_2$ was used to afford hydrocarbyl complexes **1** through **4** as illustrated in Scheme 1 [9,10].

The chemical stability of each hydrocarbyl complex of potential industrial importance was investigated. Complexes **1** through **4** were stable at 80 °C for one day (toluene, benzene), whereas $[H_2C(C_5Me_2H_2)_2]ZrPh_2$ underwent reaction in toluene at 80 °C to eliminate benzene [11], but resisted decomposition in CH_2Cl_2.

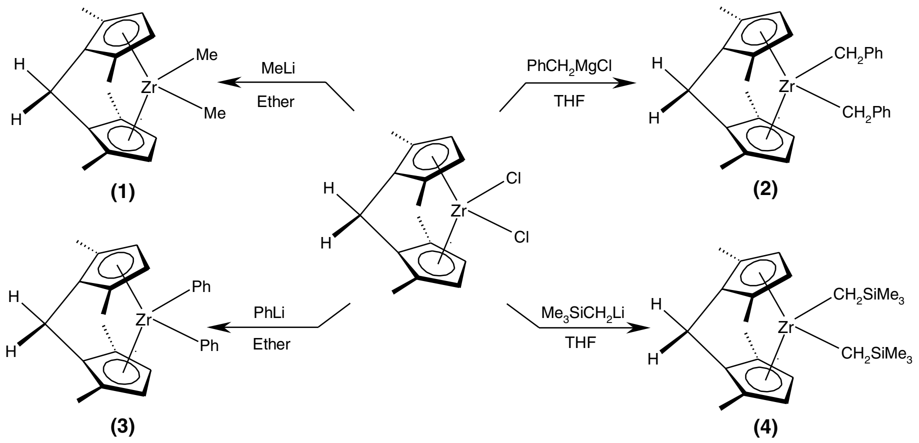
2.2. Formation and identification of the zirconocene ion pair

In general the zircononcene bis-hydrocarbyl complex undergoes reaction with a cocatalyst to form a species that exhibits some level of olefin polymerization activity [12]. Specifically, the Lewis acidic $B(C_6F_5)_3$ serves to abstract a hydrocarbyl group (R^-) to give an electron poor metal center. The ability for borane to perform alkyl-group abstraction depends on M–R bond strength and the ability for R^- to stabilize a negative charge. Depending on the extent of charge separation, there may be either a zwitterion or a complete separation into an ion pair from which changes in polymerization activity arise [13]. Unlike $B(C_6F_5)_3$, salt cocatalysts such as $[Me_2PhHN][B(C_6F_5)_4]$ and $[Ph_3C][B(C_6F_5)_4]$ attack the M–R group giving an active ionic species. Thus, reactions with borates were favored entropically over boranes as inferred from Scheme 2. So far, many reactions of hydrocarbyl metallocenes with aryl boranes or borate salt such as $[Me_2PhHN][B(C_6F_5)_4]$ and $[Ph_3C][B(C_6F_5)_4]$ both inpolar and non-polar solvents have been studied to elucidate the nature of the cationic metallocene active species [14,15].

We have investigated the reactivity of hydrocarbyl complexes with each cocatalyst in different solvent and the stability of the active species. An equimolar amount of hydrocarbyl complex and cocatalyst were combined into solution and monitored by observation of color change or oil formation and by NMR spectroscopy.

*2.2.1. The formation and characterization of an ion pair with complex $[H_2C(C_5Me_2H_2)_2]ZrMe_2$ (**1**)*

The complex $[H_2C(Me_2C_5H_2)_2]ZrMe_2$ underwent reaction with $[Me_2PhHN][B(C_6F_5)_4]$ and $[Ph_3C][B(C_6F_5)_4]$ immediately to give an oil precipitate not able to be characterized by NMR spectroscopy. Also combining $[H_2C(Me_2C_5H_2)_2]ZrMe_2$ with $[Ph_3C][B(C_6F_5)_4]$ in CH_2Cl_2 gave an immediate red color change to give



Scheme 1. New methylene bridged bis-hydrocarbyl *ansa*-zirconocene complexes **1**–**4**.

$$[H_2C(Me_2C_5H_2)_2]ZrR_2 + Me_2PhNHB(C_6F_5)_4 \longrightarrow \{H_2C(Me_2C_5H_2)_2ZrR\}^+\{RB(C_6F_5)_4\}^- + PhCH_3 + Me_2PhN$$

$$[H_2C(Me_2C_5H_2)_2]ZrR_2 + Ph_3CB(C_6F_5)_4 \longrightarrow \{H_2C(Me_2C_5H_2)_2ZrR\}^+\{RB(C_6F_5)_4\}^- + Ph_3CCH_2Ph$$

$$[H_2C(Me_2C_5H_2)_2]ZrR_2 + B(C_6F_5)_3 \longrightarrow \{H_2C(Me_2C_5H_2)_2ZrR\}^+\{RB(C_6F_5)_3\}^-$$

Scheme 2. Hydrocarbyl complexes with various cocatalysts.

^{1}H NMR spectral peaks assigned to $\{[H_2C(Me_2C_5H_2)_2]Zr(CH_3)\}^+\{B(C_6F_3)_4\}^-$ (**1a**).

2.2.2. The formation and characterization of an ion pair from complex $[H_2C(Me_2C_5H_2)_2]Zr(CH_2Ph)_2$ (2)

The complex $[H_2C(Me_2C_5H_2)_2]Zr(CH_2Ph)_2$ underwent reaction with $[Me_2PhHN][B(C_6F_5)_4]$, $[Ph_3C][B(C_6F_5)_4]$ and $B(C_6F_5)_3$ immediately in toluene to give a soluble ion pair characterized by ^{1}H NMR spectroscopy as $\{[H_2C(Me_2C_5H_2)_2]Zr(CH_2Ph)\}^+\{B(C_6F_5)_4\}^-$ (**2a**). However, the complex $[H_2C(Me_2C_5H_2)_2]$- $Zr(CH_2Ph)_2$ underwent decomposition in the presence of $[Ph_3C][B(C_6F_5)_4]$ and $B(C_6F_5)$.

2.2.3. The formation and characterization of an ion pair from complex $[H_2C(Me_2C_5H_2)_2]Zr(CH_2SiMe_3)_2$ (3)

The complex $[H_2C(Me_2C_5H_2)_2]Zr(CH_2SiMe_3)_2$ underwent reaction immediately with $[Me_2PhHN][B(C_6F_5)_4]$ in both toluene and CH_2Cl_2 to give a soluble species identified by ^{1}H NMR spectroscopy. $\{[H_2C(Me_2C_5H_2)_2]\ Zr(CH_2SiMe_3)\}^+\{B(C_6F_3)_4\}^-$ (**3a**) after treatment with $[Me_2PhHN][B(C_6F_5)_4]$ was green in CH_2Cl_2. The same species **3a** was not produced from the cocatalyst $[Ph_3C][B(C_6F_5)_4]$ either in toluene or CH_2Cl_2 even at elevated temperature, and gave a product of decomposition with $B(C_6F_5)_3$ in CH_2Cl_2.

2.2.4. The formation and characterization of an ion pair from complex $[H_2C(Me_2C_5H_2)_2]ZrPh_2$ (4)

The complex $[H_2C(Me_2C_5H_2)_2]ZrPh_2$ immediately underwent reaction with $[Me_2PhHN][B(C_6F_5)_4]$ and $[Ph_3C][B(C_6F_5)_4]$ but then quickly decomposed. However, $\{[H_2C(Me_2C_5H_2)_2]ZrPh\}^+\{B(C_6F_5)_4\}^-$ (**4a**) produced from the cocatalyst $[Ph_3C][B(C_6F_5)_4]$ in toluene was green and characterized from assignments made in the ^{1}H NMR spectrum. In contrast, the complex **4** did not react with $B(C_6F_5)_3$, even in CH_2Cl_2. ^{1}H NMR spectral signals of identified species **2a**–**4a** in each solvent are listed in Section 4.

2.2.5. Specific reactions of $[H_2C(Me_2C_5H_2)_2]Zr(CH_3)_2$ (1), $[H_2C(Me_2C_5H_2)_2]Zr(CH_2Ph)_2$ (2), and $[H_2C(Me_2C_5H_2)_2]Zr(CH_2SiMe_3)_2$ (3) with $B(C_6F_3)_3$

Complexes **1**, **2** and **3** showed distinctive reactivity with $B(C_6F_3)_3$ [16]. The ion pair $\{[H_2C(Me_2C_5H_2)_2]Zr(CH_3)\}^+\{(CH_3)B(C_6F_5)_3\}^-$ (**1b**) was obtained clearly in toluene, but became an immiscible oil in benzene. When **3** was treated with $B(C_6F_5)_3$ the species **3b** was formed; structural differences were observed by ^{1}H, ^{13}C NMR and ^{19}F NMR spectroscopy. All complexes **1**, **2** and **3** exhibited C_{2v} molecular symmetry in solution, as determined by NMR spectroscopy and were strictly speaking ion pairs in which the anion is located outside the metal coordination sphere [17] as in complexes **1**, **2** and **3**. It is proposed that the species $\{[H_2C(Me_2C_5H_2)_2]Zr(CH_2Ph)\}^+\{(CH_2Ph)B(C_6F_5)_4\}^-$ (**2b**) exists as an ion pair in toluene with one benzyl group bound to boron in the anion, assigned by ^{1}H NMR spectroscopy (Fig. 2). Thus, two hydrogens of the methylene bridge and the four Cp methyls and hydrogens were chemically shift equivalent as reflected by the ^{1}H NMR and ^{13}C NMR spectrum; these signals are consistent with the assignment

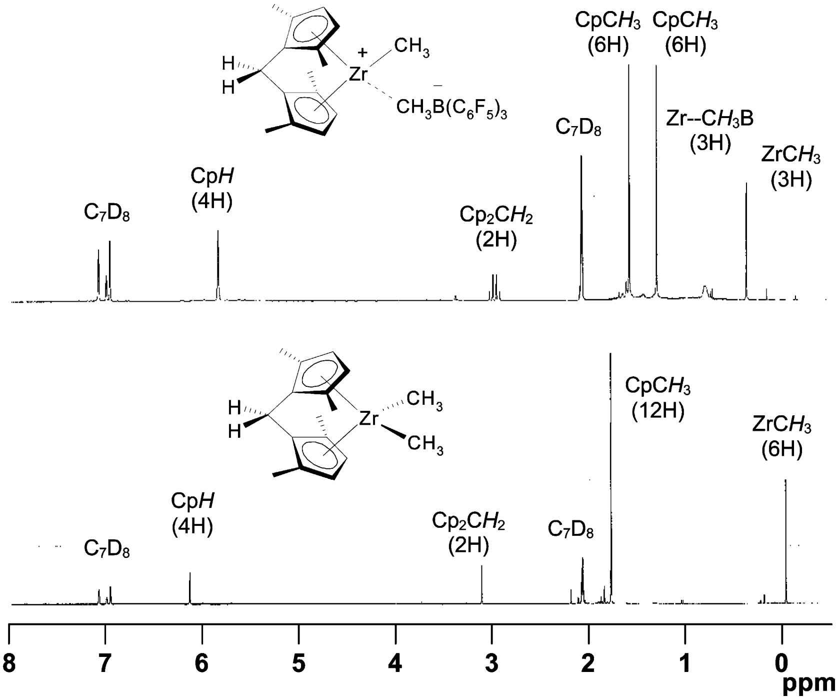


Fig. 1. ^{1}H NMR of C_{2v} symmetric complex **1** and C_s symmetric **1b**.

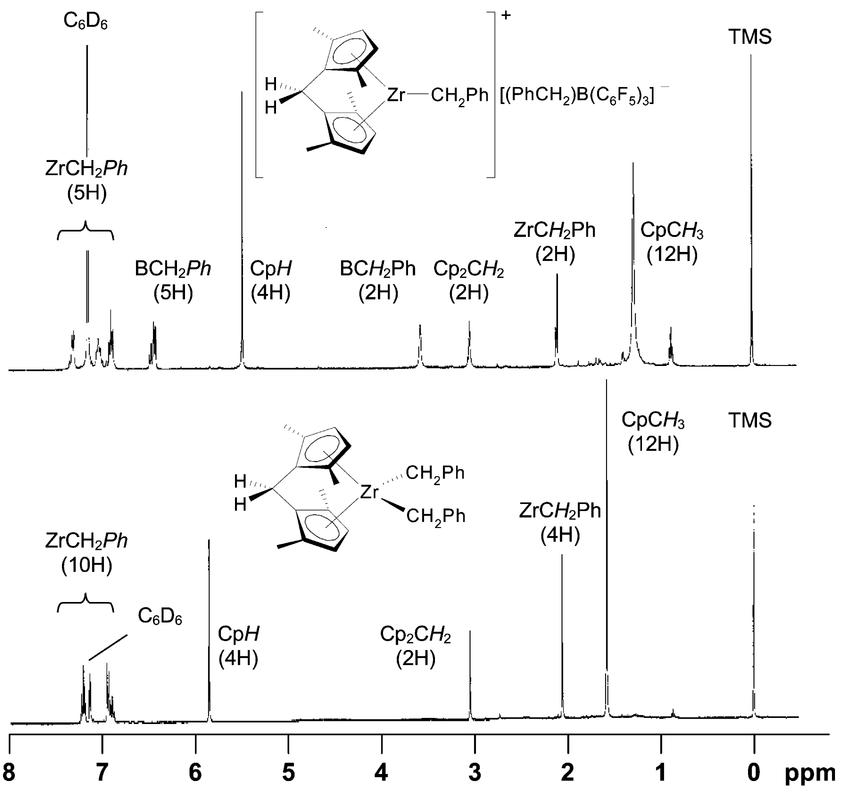


Fig. 2. ^{1}H NMR of C_{2v} symmetric complexes **2** and **2b**.

of C_{2v} symmetry [18]. Also two distinct benzyl groups are spectroscopically observed; one is present at the metal center while the other is connected to the anion.

In contrast, $\{[H_2C(Me_2C_5H_2)_2]Zr(CH_3)\}^+\{(CH_3)B(C_6F_5)_3\}^-$ (**1b**) and $\{[H_2C(Me_2C_5H_2)_2]Zr(CH_2SiMe_3)\}^+\{(Me_3SiCH_2)B(C_6F_5)_3\}^-$ (**3b**) exist as an ion pair, judging from the C_s molecular symmetric species in ^{1}H and ^{13}C NMR spectrum instead of C_{2v} symmetry (Figs. 1 and 3). This would place a weak positive and a negative charge at zirconium and boron, respectively. In this way one methyl or (trimethylsilyl)methyl group is covalently bonded to zirconium while another interacts with borane. The two Cp hydrogen and methyl groups in **1b** and **3b** were inequivalent and the methylene bridge hydrogens were diastereotopic. Additionally, there exist two doublets for the $[H_2C]$ bridge resonances in **3b**, whereas the $[H_2C]$ signal in **1b** is assignable as an AB quartet (Fig. 3). In this way, both **1b** and **3b** can be considered as a contact ion pair with C_s molecular symmetry. In addition, the spectrum of **3b** shows that the (trimethylsilyl)methyl group interacting with borane features methyl groups in two different environments in the ^{1}H NMR spectrum suggesting that one methyl group is interacting closely with borane. In **3b** there exists three separate upfield carbon NMR signals associated with $\{(Me_3SiCH_2)B(C_6F_5)_3\}^-$ below ca. 10 ppm in the ^{13}C NMR spectrum, along with distinctive Cp methyl signals, supporting C_s molecular symmetry. Thus, **3b** might be better represented as $\{[H_2C(Me_2C_5H_2)_2]Zr(CH_2SiMe_3)\}^{\delta+}\{(Me_3SiCH_2)B(C_6F_5)_3\}^{\delta-}$ with partial charges at zirconium and boron.

Only three resonances in each ^{19}F NMR spectrum were observed for **2b** and **3b**; these shifts were different from those of free $B(C_6F_5)_3$, indicating an interaction between borane and an alkyl group. As shown in Scheme 3, the ability to form metallocene ions with $B(C_6F_5)_3$ depends on the Zr–R group.

Reactions of **1**–**4** with the different cocatalysts in different solvent are summarized in Table 1.

2.3. Copolymerization of ethylene–norbornene using the ion paired metallocene species

Since methylene bridged *ansa*-zirconocenes $[H_2C(Me_2C_5H_2)_2]ZrCl_2$ (**5**) were known for high copolymerization activity with ethylene and norbornene, all species here from **5** were tested for this copolymerization activity with borane or borate. Unlike for MAO systems, use of a scavenging agent such as triisobutylaluminum (TIBA) was required here in the polymerization solution. Owing to the insolubility of $[Me_2PhHN][B(C_6F_5)_4]$ and $B(C_6F_5)_3$ in toluene at room temperature, the formation of the active species was carried out under heating at 60 °C. In contrast, cocatalyst solubility was greater in CH_2Cl_2, and thus preactivation could be carried out at room temperature. All identified ionic species (**2a**, **3a** and **2b)** exhibited copolymerization activity comparable to the **5**/MAO system; the results of

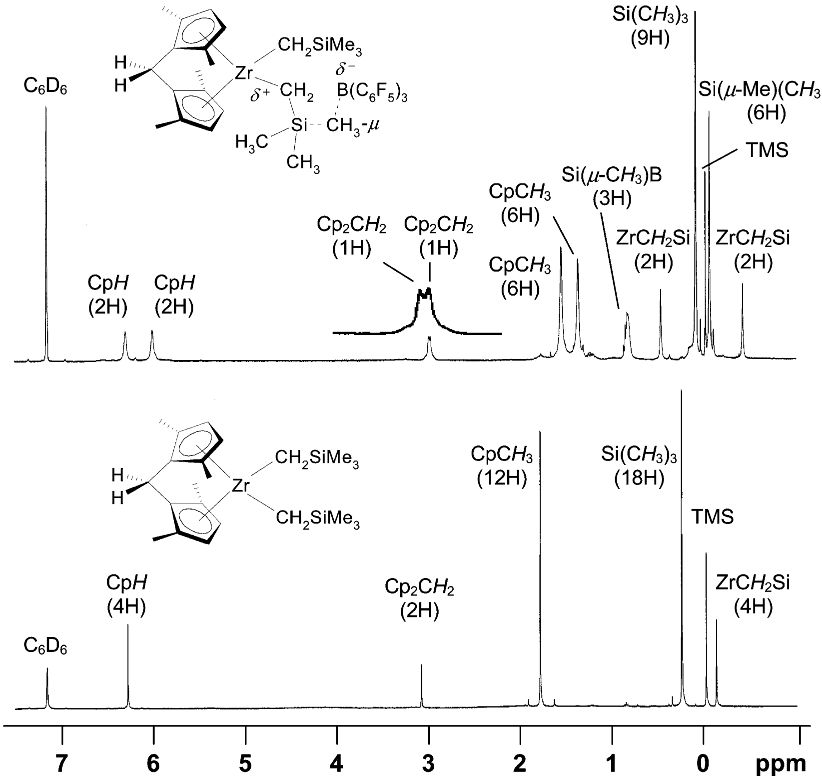
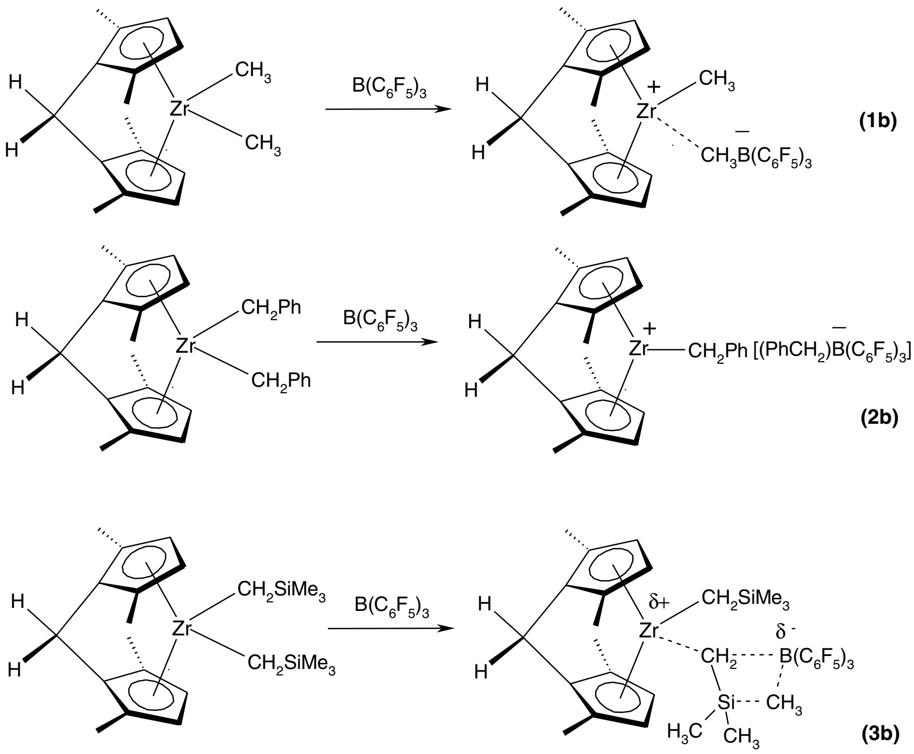


Fig. 3. ^{1}H NMR of C_{2v} symmetric complex **3** and C_s symmetric **3b**.



Scheme 3. Reactions of $\{[H_2C(Me_2\ C_5H_2)_2]ZrR_2$with $B(C_6F_5)_3\}$.

copolymerization of ethylene–norbornene are summarized in Table 2. The active species $\{[H_2C(Me_2C_5H_2)_2]ZrPh\}\{B(C_6F_5)_4\}$ (**4a**) did not produce a copolymer. Despite known catalysis for the $CpTiPh_2$/MAO system producing isotactic polypropylene and known nickel (II) catalysis, we suggest that in this system the propagation

Table 1
Reactivity of hydrocarbyl complexes and cocatalysts in solvents (25 °C)

	Cocatalyst:	$[Me_2PhHN][B(C_6F_5)_4]$		$[Ph_3C][B(C_6F_5)_4]$		$B(C_6F_5)_3$	
	Solvent:	C_7D_8	CD_2Cl_2	C_7D_8	CD_2Cl_2	C_7D_8	CD_2Cl_2
Catalyst	**1**	Oil[a]	Decomp.	Oil	**1a**	**1b**	Decomp.
	2	**2a**	**2a**	**2a**	Decomp.	**2b**	Decomp.
	3	**3a**	**3a**	N.R.[b]	N.R.	**3b**	Decomp.
	4	**4a**[c]	**4a**[c]	**4a**[c]	Decomp.	N.R	N.R.

[a] Immediate reaction giving an immiscible oil not characterized by NMR spectroscopy.

[b] No reaction at room temperature or elevated temperature.

[c] The reaction formed an oil which quickly decomposed.

Table 2
Ethylene–norbornene copolymerization results[a]

Species	Catalyst	Cocatalyst	Yield(g)[c]	Activity[d]	T_g (°C)	M_w	M_w/M_n
2a	**2**	$[Me_2PhHN][B(C_6F_5)_4]$	34.7	26.3	239	102,000	1.6
2a	**2**	$[Ph_3C][B(C_6F_5)_4]$	26.2	19.9	229	123,000	1.6
2a[b]	**2**	$[Me_2PhHN][B(C_6F_5)_4]$	26.8	16.2	233	N/A	N/A
3a	**3**	$[Me_2PhHN][B(C_6F_5)_4]$	30.4	23.1	234	127,000	1.6
3a	**3**	$[Ph_3C][B(C_6F_5)_4]$	26.4	20.0	230	117,000	1.6
3a[b]	**3**	$[Me_2PhHN][B(C_6F_5)_4]$	–[f]	–	–	–	–
4a	**4**	$[Me_2PhHN][B(C_6F_5)_4]$	–[f]	–	–	–	–
2b	**2**	$B(C_6F_5)_3$	18.1	13.7	222	139,000	1.6
3b	**3**	$B(C_6F_5)_3$	–[f]	–	–	–	–
5c[e]	**5**	MAO	55.1	41.3	228	10,800	1.6
2d[g]	**2**	MAO	50.0	33.3	–	–	–

[a] Polymerization conditions: zirconocene 4 μmol, TIBA 1 mL, toluene 150 mL (56 wt% norbornene), T_p = 70 °C, P_p = 60 psi.

[b] Preactivation of catalyst with cocatalyst in CH_2Cl_2 at room temperature for 2 min was conducted.

[c] Yield is defined as the weight of copolymer obtained.

[d] Activity in kg COC/mmol of Zr•h.

[e] Polymerization conditions: zirconocene 4 μmol, Al/Zr = 2000, toluene 150 mL (56 w% norbornene), T_p = 70°C, P_p = 60 psi, without preactivation.

[f] No polymerization occurred.

[g] Polymerization conditions: zirconocene 4.5 μmol, Al/Zr = 2000, toluene 150 mL (56 wt% norbornene), T_p = 70°C, P_p = 60 psi, without preactivation.

step fails to proceed due to the presence of a Zr–Ph group [20]. In addition, **2a** from $[Me_2PhHN][B(C_6F_5)_4]$ in CH_2Cl_2 exhibited moderate copolymerization activity, while **3a** from $[Me_2PhHN][B(C_6F_5)_4]$ in CH_2Cl_2 shows no activity for copolymerization. Interestingly $\{[H_2C(Me_2C_5H_2)_2]Zr(CH_2SiMe_3)\}^{\delta+}\{(Me_3SiH_2C)B(C_6F_5)_3\}^{\delta-}$ (**3b**) did not form polymer, suggesting that the zirconium center is too electron rich to conduct polymerization. For the active species of $[H_2C(Me_2C_5H_2)_2]ZrMe_2$ with borane or borate, less than one gram of copolymer was produced compared with the yields given in Table 2. However, this complex is used in a ternary system (**1** with triisobutylaluminum and $[Ph_3C][B(C_6F_5)_4]$), where the activity was 18 kg COC/mmol of Zr•h. In this respect, cocatalyst decreases in the order $[Me_2PhHN][B(C_6F_5)_4] > [Ph_3C][B(C_6F_5)_4] > B(C_6F_5)_3$ when considering a given hydrocarbyl. The nature of a given hydrocarbyl group does affect the stability of the ionic species and ultimately olefin polymerization activity [21]. Catalytic use of MAO in copolymerization requires a larger stochiometric amount than borate use does, but the basic properties (such as T_g, M_w and PDI values) of the resulting polymers were quite similar [19].

3. Conclusion

In summary, four bis-hydrocarbyl methylene bridged *ansa*-metallocenes were synthesized and gave stable ion pairs with cocatalysts $[Me_2PhHN][B(C_6F_5)_4]$, $[Ph_3C][B(C_6F_5)_4]$ and $B(C_6F_5)_3$. The activity of borane towards these hydrocarbyl complexes is dependent on the Zr–R group. The preactivated $[H_2C(C_5Me_2H_2)_2]Zr(CH_2Ph)_2$/$[Me_2PhHN][B(C_6F_5)_4]$ system shows the highest activity in norbornene/ethylene copolymerzation.

4. Experimental

4.1. General techniques and reagents

All manipulations were performed using a combination of glove box, high vacuum, and Schlenk techniques. Solvents were purified and degassed by standard procedures prior to use. All available reagents were purchased commercially and used as received unless otherwise noted in the experimental procedure. Elemental analyses were performed using a Perkin–Elmer 2400 CHN Elemental

Analyzer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Advance 400DRX spectrometer operating at 399.9 MHz and 100.6 MHz, respectively. ^{1}H NMR and ^{13}C NMR spectral chemical shifts are reported in ppm relative to $SiMe_4$ ($\delta = 0$) and were referenced internally, relative to the protio solvent impurity ($\delta = 7.26$ and $\delta = 77.0$ for $CDCl_3$). All coupling constants are reported in hertz. The glass transition temperature values (T_g) were measured using a TA instrument DSC2010. The sample was first heated to 300 °C, then cooled to 30 °C (20 °C/min), and then reheated to 250 or 300 °C (20 °C/min). The data reported here were taken from the second heating. The average molecular weight (M_w) and distribution (MWD) of E–N copolymers were measured by gel permeation chromatography (GPC) using a Waters Millennium instrument with three Waters chromatographic columns. Chloroform was used as a solvent with a flow rate 1 mL/min at 37 °C. The polystyrene (PS) standards, with narrow molecular weight distribution, were used for the calibration of molecular weights versus retention time of the column set.

4.2. Representative gas tight NMR tube reaction

Deuterated toluene (1.0 mL) or CH_2Cl_2 (1.0 mL) was added to the solid mixture of complex $[H_2C(Me_2C_5H_2)_2]Zr(CH_2Ph)_2$ (10 mg, 0.02 mmol) and cocatalyst $[Me_2PhHN][B(C_6F_5)_4]$ (17 mg, 0.02 mmol). The formation of yellow $\{[H_2C(Me_2C_5H_2)_2]Zr(CH_2Ph)\}^+\{B(C_6F_5)_4\}^-$ was instantaneous and quantitative as determined by ^{1}H NMR spectroscopy.

*4.3. Dimethyl {methylene-bis(2,5-dimethylcyclopentadienyl)}zirconium (**IV**), [$H_2C(Me_2C_5H_2)_2$]$ZrMe_2$ (**1**)*

MeLi (1.45 mL, 0.232 mmol, 1.6 M diethyl ether solution) was added slowly by syringe to $[H_2C(Me_2C_5H_2)_2]ZrCl_2$ (0.35 g, 0.97 mol) in diethyl ether (30 mL) (using THF did not work) at −78 °C. After stirring the yellow reaction mixture at room temperature for 10 min, the volatiles were removed in vacuo and the solid residue was extracted with pentane (150 mL). The solution was concentrated to 10 mL and cooled to −78 °C, to give crystals of $[H_2C(Me_2C_5H_2)_2]ZrMe_2$ which were not isolated. The solvent was then removed to give a yellow sticky product $[H_2C(Me_2C_5H_2)_2]ZrMe_2$ by the ^{1}H NMR spectrum (0.31 g, 66%). This material was used without further purification. ^{1}H NMR (C_6D_6, $\delta = 7.15$): 1.79 {$CH_2(\mathit{Me}_2C_5H_2)_2$, 12H, s}, 3.11 {$C\mathit{H}_2(Me_2C_5H_2)_2$, 2H, s}, 6.19 {$CH_2(Me_2C_5\mathit{H}_2)_2$, 4H, s}, 0.08 ($Zr\mathit{Me}$, 6H, s). ^{13}C NMR ($C_6D_6$, $\delta = 128.0$): 28.5 {$Zr\mathit{Me}_2$, 6C, t, $^1J_{C-H} = 115$ Hz}, 15.5 {$CH_2(\mathit{Me}_2C_5H_3)_2$, 4C, q, $^1J_{C-H} = 127$ Hz}, 20.7 {$\mathit{C}_2(Me_2C_5H_3)_2$, 1C, t, $^1J_{C-H} = 132$ Hz}, 98.1 *ipso* $CH_2(Me_2\mathit{C}_5H_3)_2$, 2C, s, 116.6 {$CH_2(Me_2\mathit{C}_5H_3)_2$, 4C, d, $^1J_{C-H} = 161$ Hz}, 119.8 {$(Me_2\mathit{C}_5H_3)_2$, 4C, s}.

*4.4. Dibenzyl {methylene-bis(2,5-dimethylcyclopentadienyl)}zirconium (**IV**), [$H_2C(C_5Me_2H_2)_2$]$Zr(CH_2Ph)_2$ (**2**)*

$PhCH_2MgCl$ (1.90 mL, 0.370 mol, 2.0 M in THF solution) was added slowly by a syringe to a solution of $[H_2C(Me_2C_5H_2)_2]ZrCl_2$ (0.58 g, 0.161 mol) in THF (50 mL) at room temperature. After stirring the yellow reaction mixture at room temperature for 12 h, the volatiles were removed in vacuo and the residue was extracted into pentane (450 mL). The solution was concentrated to 10 mL and cooled to −78 °C, giving $[H_2C(Me_2C_5H_2)_2]$ $Zr(CH_2Ph)_2$ as yellow crystals isolated by filtration (0.31 g, 66%). ^{1}H NMR (C_6D_6, $\delta = 7.15$): 1.58 {$CH_2(\mathit{Me}_2C_5H_2)_2$, 12H, s}, 3.05 {$C\mathit{H}_2(Me_2C_5H_2)_2$, 2H, s}, 2.06 {$ZrC\mathit{H}_2(C_6H_5)$, 4H, s}, 5.87 {$CH_2$ (Me_2- $C_5\mathit{H}_2)_2$, 4H, s}, 7.22 {$ZrCH_2(C_6\mathit{H}_5)$, t, 4H, $^3J_{H-H} = 8$ Hz}, 6.94 {$ZrCH_2(C_6\mathit{H}_5)$, d, 4H, $^3J_{H-H} = 8$ Hz}, 6.91 {$ZrCH_2(C_6\mathit{H}_5)$, t, 2H, $^3J_{H-H} = 8$ Hz}. ^{13}C NMR (C_6D_6, $\delta = 128.0$): 15.1 $CH_2(\mathit{Me}_2C_5H_3)_2$, 4C, q, $^1J_{C-H} = 127$ Hz, 20.7 {$Zr\mathit{C}_2(C_6H_5)$, 4C, t, $^1J_{C-H} = 136$ Hz}, 60.5 {$\mathit{C}_2(Me_2C_5H_3)_2$, 1C, t, $^1J_{C-H} = 116$ Hz}, 96.5 {*ipso* $CH_2(Me_2\mathit{C}_5H_3)_2$, 2C, s}, 117.7 {$CH_2(Me_2\mathit{C}_5H_3)_2$, 4C, d, $^1J_{C-H} = 171$ Hz}, 120.4 {$(Me_2\mathit{C}_5H_3)_2$, 4C, s}, 121.1 {$ZrCH_2(\mathit{C}_6H_5)$, 4C, d, $^1J_{C-H} = 151$ Hz}, 125.9 {$ZrCH_2(\mathit{C}_6H_5)$, 2C, d, $^1J_{C-H} = 161$ Hz}, 128.8 {$ZrCH_2$ (C_6H_5), 4C, d, $^1J_{C-H}$ = not resolved}, 152.6 {*ipso* $ZrCH_2(\mathit{C}_6H_5)$, 2C, s}. CHN analysis calculated for $C_{29}H_{32}Zr$: C, 73.83; H, 6.84. Found: C, 73.79; H, 6.94%.

*4.5. Bis(trimethylsilylmethyl) {methylene-bis(2,5-dimethylcyclopentadienyl)}zirconium (**IV**), [H_2C-($Me_2C_5H_2)_2$]$Zr(CH_2SiMe_3)_2$ (**3**)*

Me_3SiCH_2Li (1.0 M in pentane solution, 3.4 mL, 0.340 mol, 2.4 eq.) was added slowly by syringe to $[H_2C(Me_2C_5H_2)_2]ZrCl_2$ (0.50 g, 0.139 mol) dissolved in THF (50 mL) at room temperature. After stirring the yellow reaction mixture at room temperature for 12 h, the volatiles were removed in vacuo and the residue was extracted into pentane (250 mL). The solution was concentrated to 10 mL and cooled to −78 °C, giving pale yellow crystals of $[H_2C(Me_2C_5H_2)_2]$ $Zr(CH_2SiMe_3)_2$ isolated by filtration (0.16 g, 34%). ^{1}H NMR (C_6D_6, $\delta = 7.15$): 1.80 {$CH_2(\mathit{Me}_2C_5H_2)_2$, 12H, s}, 3.09 {$C\mathit{H}_2(Me_2C_5H_2)_2$, 2H, s}, 6.28 {$ZrC\mathit{H}_2(C_6$ $H_5)_2$, 4H, s}, −0.12 ($ZrC\mathit{H}_2SiMe_3$, 4H, s), 0.26 ($ZrCH_2Si\mathit{Me}_3$, 18H, s). ^{13}C NMR (C_6D_6, $\delta = 128.0$): 3.6 {$ZrCH_2Si\mathit{Me}_3$ 9C, t, $^1J_{C-H} = 118$ Hz}, 15.8 {$CH_2(\mathit{Me}_2C_5H_3)_2$, 4C, q, $^1J_{C-H} = 127$ Hz}, 20.5 {$Zr\mathit{C}_2SiMe_3$, 4C, t, $^1J_{C-H} = 132$ Hz}, 41.4 {$\mathit{C}_2(Me_2C_5H_3)_2$, 1C, t, $^1J_{C-H} = 104$ Hz}, 102.2 {*ipso* CH_2 (Me_2-$\mathit{C}_5H_3)_2$, 2C, s}, 115.4 {$CH_2(Me_2\mathit{C}_5H_3)_2$, 4C, d, $^1J_{C-H} = 171$ Hz}, 119.6 {$(Me_2\mathit{C}_5H_3)_2$, 4C, s}. CHN analysis calculated for $C_{23}H_{40}Si_2Zr$: C, 59.54; H, 8.69. Found: C, 58.73; H, 8.49%.

4.6. *Diphenyl {methylene-bis(2,5-dimethylcyclopentadienyl)}zirconium (IV),* $[H_2C(Me_2C_5H_2)_2]ZrPh_2$ *(**4**)*

PhLi (1.8 M in cyclohexane/diethyl ether, 2.0 mL, 0.361 mol, 2.6 eq.) was added slowly by a syringe to a solution of $[H_2C(Me_2C_5H_2)_2]ZrCl_2$ (0.50 g, 0.139 mol) in diethyl ether (30 mL) at room temperature. After stirring this reaction mixture (yellow) for 12 h, the volatiles were removed in vacuo and the residue was extracted into pentane (250 mL). The solution was then concentrated to 10 mL and cooled to −78 °C, giving $[H_2C(Me_2C_5H_2)_2]ZrPh_2$ as pale yellow crystals, isolated by filtration (0.09 g, 20%). ^{1}H NMR (C_6D_6, $\delta = 7.15$): 1.89 {$CH_2(\mathit{Me}_2C_5H_2)_2$, 12H, s}, 3.27 {$CH_2(\mathit{Me}_2C_5H_2)_2$, 12H, s}, 6.14 {$ZrC\mathit{H}_2(C_6H_5)_2$, 4H, s}, 7.64 {$Zr(C_6\mathit{H}_5)$, d, 4H, $^3J_{\mathrm{H–H}} = 8$ Hz}, 7.18–7.11 {$Zr(C_6\mathit{H}_5)$, m, 6H}. ^{13}C NMR (C_6D_6, $\delta = 128.0$): 15.3 {$CH_2(\mathit{Me}_2C_5H_3)_2$, 4C, q, $^1J_{\mathrm{C–H}} = 128$ Hz}, 68.3 {$\mathit{C}_2(Me_2C_5H_3)_2$, 1C, t, $^1J_{\mathrm{C–H}} = 129$ Hz}, 97.2 {*ipso* $CH_2(Me_2C_5H_3)_2$, 2C, s}, 117.9 {$CH_2(Me_2\mathit{C}_5H_3)_2$, 4C, d, $^1J_{\mathrm{C–H}} = 171$ Hz}, 121.1 {$(Me_2\mathit{C}_5H_3)_2$, 4C, s}, 126.1 {$Zr(C_6H_5)$, 4C, d, $^1J_{\mathrm{C–H}} = 161$ Hz}, 127.5 {$Zr(\mathit{C}_6H_5)$, 2C, d, $^1J_{\mathrm{C–H}} = 151$ Hz}, 136.0 {$Zr(\mathit{C}_6H_5)$, 4C, d, $^1J_{\mathrm{C–H}} = 151$}, 181.7 {*ipso* $Zr(C_6H_5)$, 2C, s}. CHN analysis calculated for $C_{29}H_{32}Zr$: C, 73.83.54; H, 6.84. Found: C, 73.79; H, 6.94%.

4.7. *The ionic pair* $\{[H_2C(Me_2C_5H_2)_2]Zr(CH_3)\}^+$-$\{B(C_6F_5)_4\}^-$ *(**1a**)*

^{1}H NMR (CD_2Cl_2, $\delta = 5.24$): 2.13 {$CH_2(\mathit{Me}_2C_5H_2)_2$, 12H, s}, 4.25 {$C\mathit{H}_2(Me_2C_5H_2)_2$, 2H, s}, 6.19 {$CH_2(Me_2C_5\mathit{H}_2)_2$, 4H, s}, −0.08 {$ZrC\mathit{H}_3$, 3H, s}.

4.8. *The ionic pair* $\{[H_2C(Me_2C_5H_2)_2]Zr(CH_2Ph)\}^+$-$\{B(C_6F_5)_4\}^-$ *(**2a**)*

^{1}H NMR (C_7D_8, $\delta = 2.09$): 1.27 {$CH_2(\mathit{Me}_2C_5H_2)_2$, 12H, s}, 3.12 {$C\mathit{H}_2(Me_2C_5H_2)_2$, 2H, s}, 2.10 {$ZrC\mathit{H}_2(C_6H_5)$, 2H, s}, 5.52 {$CH_2(Me_2C_5\mathit{H}_2)_2$, 4H, s}, 6.89 {$ZrCH_2(C_6\ \mathit{H}_5)$, t, 2H, $^3J_{\mathrm{H–H}} = 8$ Hz}.6.79 {$ZrCH_2(C_6\mathit{H}_5)$, 2H, $^3\ J_{\mathrm{H–H}} = 8$ Hz}, 6.47 {$ZrCH_2(C_6\mathit{H}_5)$, t, 2H, $^3J_{\mathrm{H–H}} = 8$ Hz}. ^{1}H NMR (CD_2Cl_2, $\delta = 5.24$): 3.29 {$CH_2(\mathit{Me}_2C_5H_2)_2$, 12H, s}, 4.08 {$C\mathit{H}_2(Me_2C_5H_2)_2$, 2H, s}, 2.26 {$ZrC\mathit{H}_2(C_6H_5)$, 2H, s}, 6.36 {$CH_2(Me_2C_5\mathit{H}_2)_2$, 4H, s}, 7.31 {$ZrCH_2(C_6\ \mathit{H}_5)$, t, 2H, $^3J_{\mathrm{H–H}} = 8$ Hz}, 7.14 {$ZrCH_2(C_6\mathit{H}_5)$, d, 2H, $^3\ J_{\mathrm{H–H}} = 8$ Hz}, 7.10 {$ZrCH_2(C_6\mathit{H}_5)$, t, 2H, $^3J_{\mathrm{H–H}} = 8$ Hz}.

4.9. *The ionic pair* $\{[H_2C(Me_2C_5H_2)_2]Zr(CH_2SiMe_3)\}^+$ $\{B(C_6F_5)_4\}^-$ *(**3a**)*

^{1}H NMR (C_7D_8, $\delta = 2.09$): 1.31 {$CH_2(\mathit{Me}_2C_5H_2)_2$, 12H, s}, 3.10 {$\mathit{H}_2C(Me_2C_5H_2)_2$, 2H, s}, 5.50 {$H_2C(Me_2C_5\mathit{H}\ _2)_2$, 4H, s}, −0.02 ($ZrCH_2Si\mathit{Me}_3$ 9H, s), 0.04 ($ZrC\mathit{H}_2SiMe_3$, 2H, s). ^{1}H NMR (CD_2Cl_2, $\delta = 5.24$): 2.12 {$H_2C(\mathit{Me}_2\ C_5H_2)_2$, 12H, s}, 4.05 {$\mathit{H}_2C(Me_2C_5H_2)\ _2$, 2H, s}, 6.35 {$H_2C(Me_2C_5\mathit{H}_2)_2$, 4H, s}, −0.08 ($ZrCH_2Si\mathit{Me}_3$ 9H, s), 3.23 ($ZrC\mathit{H}_2SiMe_3$, 2H, s) or −0.08 ($ZrC\mathit{H}_2SiMe_3$, 2H, s).

4.10. *The ionic pair* $\{[H_2C(Me_2C_5H_2)_2]ZrPh)\}^+$-$\{B(C_6F_5)_4\}^-$ *(**4a**)*

^{1}H NMR (C_7D_8, $\delta = 2.09$): 1.91 {$CH_2(\mathit{Me}_2C_5H_2)_2$, 12H, s}, 3.32 {$\mathit{H}_2C(Me_2C_5H_2)_2$, 2H, s}, 6.11 {$H_2C(Me_2C_5\mathit{H}_2)\ _2$, 4H, s}, 7.59 {$Zr(C_6\mathit{H}_5)$, 2H, d}, {$Zr(C_6\mathit{H}_5)$, 1H, d}, 7.18 {$Zr(C_6\mathit{H}_5)$, 2H, t}.

4.11. *The ionic pair* $\{[H_2C(Me_2C_5H_2)_2]Zr(CH_3)\}^+$-$\{(CH_3)B(C_6F_5)_3\}^-$ *(**1b**)*

^{1}H NMR (C_7D_8, $\delta = 2.09$): 1.60 {$H_2C(\mathit{Me}_2C_5H_2)_2$, 6H, s}, 1.32 {$H_2C(\mathit{Me}_2C_5H_2)_2$, 6H, s}, 3.03 {$\mathit{H}_2C(Me_2C_5H_2)_2$, 1H, s}, 2.95 {$\mathit{H}_2C(Me_2C_5H_2)_2$, 1H, s}, 5.86 {$H_2C(Me_2C_5\mathit{H}_2)_2$, 4H, s}, 0.82 {$(C\mathit{H}_3)B(C_6F_5)_3$, 3H, s}, 0.38 ($ZrC\mathit{H}_3$, 3H, s).

4.12. *The ionic pair* $\{[H_2C(Me_2C_5H_2)_2]Zr(CH_2Ph)\}^+$-$\{(PhCH_2)B(C_6F_5)_3\}^-$ *(**2b**)*

^{1}H NMR (C_6D_6, $\delta = 7.15$): 1.27 {$H_2C(\mathit{Me}_2C_5H_2)_2$, 12H, s}, 3.04 {$\mathit{H}_2C(Me_2C_5H_2)_2$, 2H, s}, 2.10 {$ZrC\mathit{H}_2(C_6H_5)$, 2H, *ABq*}, 5.49 {$H_2C(Me_2C_5\mathit{H}_2)_2$, 4H, *ABq*}, 3.57 {$(C_6H_5C\mathit{H}_2)B(C_6F_5)_3$, 2H, s}, 7.30 {$ZrCH_2$ $(C_6\mathit{H}_5)$ or $(C_6\ \mathit{H}_5CH_2)B(C_6F_5)_3$, 2H, m}, 7.04 {$ZrCH_2$ $(C_6\mathit{H}_5)$ or $(C_6\ \mathit{H}_5CH_2)B(C_6F_5)_3$, 2H, m}, 6.88 {$ZrCH_2(C_6\mathit{H}_5)$ or $(C_6\ \mathit{H}_5CH_2)B(C_6F_5)_3$, 3H, m}, 6.44 {$ZrCH_2(C_6\mathit{H}_5)$ or $(C_6\ \mathit{H}_5CH_2)B(C_6F_5)_3$, 3H, m}. ^{13}C NMR ($C_6D_6$, $\delta = 128.0$): 14.2 {$H_2C(\mathit{Me}_2C_5H_3)_2$, 4C}, 22.7 {$Zr\mathit{C}_2(C_6H_5)$, 2C}, 20.5 {$B\mathit{C}_2(C_6H_5)\}(C_6F_5)$, 2C}, 53.6 {$H_2\mathit{C}(Me_2C_5H_3)_2$, 1C,}, 98.3 {*ipso* CH_2 $(Me_2\mathit{C}_5H_3)_2$, 2C}, 117.7, 129.3, 129.6, 103.4, 130.9, 131.8, 136.5, 137.0, 138.0, 138.9, 147.0, 147.5, 149.6, 150.1 {$(Me_2\mathit{C}_5H_3)_2$, 4C,4C; $ZrCH_2(\mathit{C}_6H_5)$, 2C, 2C, 1C, 1C; $BCH_2(\mathit{C}_6H_5)(C_6F_5)$, 2C, 2C, 1C, 1C; BCH_2 $(C_6H_5)(\mathit{C}_6H_5)$, 2C, 2C, 1C, 1C}. ^{19}F NMR (C_6D_6, external standard C_6F_6, $\delta = -163$): −129 {Me_3SiCH_2B $(C_6\mathit{F}_5)$, *ortho*, 6C}, −163 {$Me_3SiCH_2B(C_6\mathit{F}_5)$, *para*, 3C}, −173 {$Me_3SiCH_2B(C_6\mathit{F}_5)$, *meta*, 6C, br}.

4.13. *The ion pair* $\{[H_2C(Me_2C_5H_2)_2]Zr(CH_2SiMe_3)\}^{\delta+}\{(Me_3SiCH_2)B(C_6F_5)_4\}^{\delta-}$ *(**3b**)*

^{1}H NMR (C_6D_6, $\delta = 7.15$): 1.55 {$H_2C(\mathit{Me}_2C_5H_2)_2$, 6H, s}, 1.36 {$H_2C(\mathit{Me}_2C_5H_2)_2$, 6H, s}, 2.98 {$\mathit{H}_2C(Me_2C_5H_2)_2$, 1H, brs}, 2.96 {$\mathit{H}_2C(Me_2C_5H_2)_2$, 1H, brs}, 6.29 {$H_2C(Me_2C_5\mathit{H}_2)_2$, 2H, s}, 6.01 {$H_2C(Me_2C_5\mathit{H}_2)_2$, 2H, s}, −0.42 ($ZrC\mathit{H}_2SiMe_3$, 2H, s), 0.47 {$(Me_3SiC\mathit{H}_2)B(C_6F_5)_4$, 2H, brs}, 0.10 ($ZrCH_2Si\mathit{Me}_3$ 9H, s), −0.08 {$(\mathit{Me}_2MeSiCH_2)B(C_6F_5)_4$, 6H, s}, 0.83 {$(Me_2\mathit{Me}SiCH_2)B(C_6F_5)_4$, 3H, s}. ^{13}C NMR ($C_6D_6$, $\delta = 128$): −0.1 {$BCH_2SiMe\mathit{Me}_2 2C$}, 1.5

$\{\mathrm{ZrCH_2Si}\mathit{Me}_3\mathrm{3C}\}$, 3.0 $\{\mathrm{BCH_2Si}\mathit{Me}\mathrm{Me_2}, \mathrm{1C}\}$, 7.2 $\{\mathrm{B}\mathit{C}_2\mathrm{SiMeMe_2}, \mathrm{1C}\}$, 15.2 $\{\mathrm{H_2C}(\mathit{Me}_2\mathrm{C_5H_3})_2, \mathrm{2C}\}$, 16.0 $\{\mathrm{H_2C}(\mathit{Me}_2\mathrm{C_5H_3})_2, \mathrm{2C}\}$, 20.9 $\{\mathrm{Zr}\mathit{C}_2\mathrm{SiMe_3}, \mathrm{1C}\}$, 58.3 $\{\mathrm{H_2}\mathit{C}(\mathrm{Me_2C_5H_3})_2, \mathrm{1C}\}$, 103.4 $\{\mathit{ipso}\ \mathrm{H_2C(Me_2}\mathit{C}_5\mathrm{H_3)_2}, \mathrm{2C}\}$, 117.4, 122.4, 123.8, 124.6 $\{\mathrm{CH_2(Me_2}\mathit{C}_5\mathrm{H_3)_2}, \mathrm{2C}\}$, 136.3, 138.8, 141.0, 147.0, 147.5, 149.8 $\{\mathrm{Me_3SiCH_2B}(\mathit{C}_6\mathrm{H_5}), \mathrm{1C}\}$. ^{19}F NMR ($C_6D_6$, external standard C_6F_6, $\delta = -163$): −133 $\{\mathrm{Me_3SiCH_2B(C_6}\mathit{F}_5), \mathit{ortho}, \mathrm{6C}\}$, −159 $\{\mathrm{Me_3SiCH_2\ B(C_6}\mathit{F}_5), \mathit{para}, \mathrm{3C, br}\}$, −164 $\{\mathrm{Me_3SiCH_2B(C_6}\mathit{F}_5), \mathit{meta}, \mathrm{6C, br}\}$.

4.14. General procedure for ethylene–norbornene copolymerization

Ethylene-norbornene copolymerization was carried out using a 500 mL jacketed stainless steel reactor, equipped with a mechanical stirrer. All manipulations were carried out in an inert atmosphere using a standard Schlenk technique or a VAC dry-box. The norbornene was dissolved in toluene to obtain 150 mL of a 56% (by weight) solution. The solution was passed through the purification column and injected into the reactor. After the reactor temperature was stabilized, the TIBA–toluene solution (1 mmol, triisobutylaluminum 1.0 M in toluene) 1 mL was injected into the reactor and the reaction mixture was stirred for 15 min. The TIBA–toluene solution used as a scavenger in the polymerization reactor. For catalyst preactivation, the catalyst (4×10^{-6} mol/L) and same amount of cocatalyst (4×10^{-6} mol/L) in 2 mL toluene or CH_2Cl_2 solution was stirred for 15 min at 60 °C. After the addition of preactivated catalyst (4×10^{-6} mol/L), polymerization began as a constant ethylene pressure 60 psi to the reactor. The polymerization time was measured from the start of reaction mixture stirring. After polymerization occurred, the reactor was vented and the reaction mixture was poured into acetone (2 L). The precipitated white polymer was filtered, washed with acetone and dried in a vacuum oven at 80 °C.

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References

[1] (a) R.F. Jordan, R.F. Lapointe, P.K. Bradley, N. Baenziger, Organometallics 8 (1989) 2892;
(b) T.J. Marks, Acc. Chem. Res. 25 (1992) 57;
(c) X. Yang, C.L. Stern, T.J. Marks, Organometallics 10 (1991) 840;
(d) R.F. Jordan, Adv. Organomet. Chem. 32 (1991) 325.

[2] M. Yamaura et al., WO Pat. Appl. 20662, 1999.

[3] (a) For other hydrocarbyl group IV complexes see: V. Varga, J. Hiller, R. Gyepes, M. Polek, P. Sedmera, U. Thewalt, K. Mach, J. Organomet. Chem. 538 (1997) 63;
(b) A. Cano, T. Cuenca, P. Gómez-Sal, B. Royo, P. Royo, Organometallics 13 (1994) 1688;
(c) R. Gómez, T. Cuenca, P. Royo, Organometallics 10 (1991) 1505;
(d) S.J. Lancaster, O.B. Robinson, M. Bochmann, Organometallics 14 (1995) 2456;
(e) J.J. Eisch, K.R. Caldwell, S. Werner, G.-X.C. Krüger, Organometallics 10 (1991) 3417.

[4] (a) J.J. Eisch, A.M. Piotrowski, S.K. Brownstein, E.J. Gabe, F.L. Lee, J. Am. Chem. Soc. 107 (1985) 7219;
(b) T. Shiomura, T. Asanuma, T. Sunaga, Macromol. Rapid Commun. 18 (1997) 169;
(c) C. Götz, A. Rau, G. Luft, Macromol. Symp. 178 (2002) 93.

[5] J.J. Eisch, S.I. Pombrik, G.-X. Zheng, Organometallics 12 (1993) 3856.

[6] (a) M. Bochmann, J. Chem. Soc., Dalton Trans. (1996) 255;
(b) R.F. Jordan, C.S. Bajgur, R. Willett, B. Scott, J. Am. Chem. Soc. 108 (1986) 7410;
(c) G.G. Hlatky, H.W. Turner, R.R. Eckman, J. Am. Chem. Soc. 111 (1989) 2728;
(d) K.P. Bryliakov, E.P. Talsi, M. Bochmann, Organometallics 23 (2004) 149;
(e) M. Bochmann, S.J. Lancaster, M.B. Hursthouse, K.M.A. Malik, Organometallics 13 (1994) 2235;
(f) L.H. Doerrer, M.L.H. Green, D. Häußinger, J. Saßmannshausen, J. Chem. Soc., Dalton Trans. (1999) 2111C;
(g) D.J. Gillis, M.-J. Tudoret, M.C. Baird, J. Am. Chem. Soc. 120 (1993) 2543.

[7] (a) M.C. Sacchi, F. Forlini, S. Losio, I. Tritto, P. Locatelli, Macromol. Symp. 193 (2003) 45;
(b) D. Coevoet, H. Cramail, A. Deffieux, Macromol. Chem. Phys. 200 (1999) 1208;
(c) J.J. Eisch, S.I. Pombrik, G.-X. Zheng, Makromol. Chem. Macromol. Symp. 66 (1993) 109.

[8] (a) Y.-X. Chen, M.V. Metz, L. Li, C.L. Stern, T.J. Marks, J. Am. Chem. Soc. 120 (1998) 6287;
(b) M.-C. Chen, J.A.S. Roberts, T.J. Marks, Organometallics 23 (2004) 932;
(c) T. Shiomura, T. Asanuma, N. Inoue, Macromol. Chem. Rapid Commun. 18 (1997) 169;
(d) J.C.W. Chien, W. Song, M.D. Rausch, Macromolecules 26 (1993) 3239;
(e) J. Zhou, S.J. Lancaster, D.A. Walker, S. Beck, M. Thornton, M. Bochmann, J. Am. Chem. Soc. 123 (2001) 223;
(f) J.W. Strauch, J.-L. Fauré, S. Bredeau, C. Wang, G. Kehr, R. Fröhlich, H. Luftmann, G. Erker, J. Am. Chem. Soc. 126 (2004) 2089.

[9] B.Y. Lee, Y.H. Kim, Y.C. Won, J.W. Han, I.S. Lee, W.H. Suh, Y.K. Chung, K.H. Song, Organometallics 21 (2002) 1500.

[10] D. Balboni, I. Camurati, G. Prini, L. Resconi, S. Galli, P. Mercandelli, A. Sironi, Inorg. Chem. 40 (2001) 6588.

[11] (a) H. Lee, P.J. Desrosiers, I. Guzei, A.L. Rheingold, G. Parkin, J. Am. Chem. Soc. 120 (1998) 3255;
(b) L.E. Schock, R.D. Sanner, J. Am. Chem. Soc. 110 (1988) 7701.

[12] (a) E.Y.-X. Chen, T.J. Marks, Chem. Rev. 100 (2000) 1391;
(b) R. Choukroun, F. Wolff, C. Lorber, B. Donnadieu, Organometallics 22 (2003) 2245.

[13] G. Lanza, I.L. Fragala, T.J. Marks, Organometallics 21 (2002) 5594.

[14] A.D. Horton, A.G. Orpen, Organometallics 10 (1991) 3910.

[15] (a) A. Cano, T. Cuenca, P. Gómez-Sal, B. Royo, P. Royo, J. Organomet. Chem. 526 (1996) 227;

(b) A. Razavi, U. Thewalt, J. Organomet. Chem. 445 (1993) 111;
(c) E.P. Talsi, J.L. Eilertsen, M. Ystenes, E. Rytter, J. Organomet. Chem. 677 (2003) 10;
(d) M. Bochmann, S.J. Lancaster, Angew. Chem., Int. Ed. Engl. 33 (1994) 1634.

[16] (a) For the reaction of $B(C_6F_5)_3$ with other metallocene complexes, see: R. Choukroun, C. Lorber, C. lepetit, B. Donnadieu, Organometallics 22 (2003) 1995;
(b) A.D. Horton, J.D. With, A.J. Van der Linden, H. Van de Weg, Organometallics 15 (1996) 2672;
(c) J. Cano, P. Gómez-Sal, G. Heinz, G. Martínez, R. Royo, Inorg. Chim. Acta 345 (2003) 15;
(d) R. Choukroun, C. Lorber, B. Donnadieu, Organometallics 23 (2004) 1434.

[17] M. Bochmann, A.J. Jaggar, J.C. Nicholls, Angew. Chem., Int. Ed. Engl. 29 (1990) 780.

[18] C. Pellecchia, A. Immirzi, D. Pappalardo, A. Peluso, Organometallics 13 (1994) 3773.

[19] (a) See Ref. [10];
(b) B.Y. Lee, Y.H. Kim, Y.C. Won, C.B. Shim, D.M. Shin, Y.K. Chung, J. Organomet. Chem. 660 (2002) 161;
(c) H. Lasarov, K. Mönkkönen, T.T. Pakkanen, Macromol. Chem. Phys. 199 (1998) 1939.

[20] (a) J.A. Ewen, J. Am. Chem. Soc. 106 (1984) 6355;
(b) , Additional references hereinS. Mecking, Angew. Chem., Int. Ed. Engl. 40 (2001) 534.

[21] M. Bochmann, S.J. Lancaster, Organometallics 12 (1993) 633.