

# Perfluorofluorenyl anions and their use as co-catalysts in the zirconocene-promoted polymerization of olefins

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## Abstract

Fluorofluorenes [1,2,3,4,5,6,7,8-octafluoro-9-(pentafluorophenyl)-9H-fluorene (**OFPF**), 1,2,3,4,5,6,7,8-octafluoro-9-(2,4-trifluoromethylphenyl)-9H-fluorene (**OTTF**), and 1,2,3,4,5,6,7,8-octafluorofluorene (**OFF**)] react with sodium hydride or with lithium alkyls to give fluorofluorenyl anions which have been characterized in solution by <sup>19</sup>F NMR spectroscopy. **OFPF** is deprotonated by ethylenediamine, by HMPT and by 1,7-diazo-bicyclo(5,4)-undec-7-ene (**DBU**), as shown by <sup>1</sup>H and <sup>19</sup>F NMR spectrometry. The new compound [*rac*-ethylene-bis(η<sup>5</sup>-4,5,6,7-tetrahydroindenyl)]diallylzirconium(IV) (**ZRAL**), as prepared from [*rac*-ethylene-bis(η<sup>5</sup>-4,5,6,7-tetrahydroindenyl)]dichloridezirconium(IV) and allylmagnesium chloride, undergoes allyl abstraction with **OFPF**, CPh<sub>3</sub>[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>], and B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> forming zirconium-containing cations, as established by <sup>1</sup>H and <sup>19</sup>F NMR spectrometry. Toluene/pentafluoroanisole solutions of the fluorinated anions, in combination with **ZRAL**, catalyze the polymerization of ethylene, with an activity comparable to that of MAO or CPh<sub>3</sub>[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>], a remarkable increase of activity being observed with the **ZRAL/OFPF** system.

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## 1. Introduction

Significant stabilization of carbanions is known to be induced by fluoro- or perfluoroaryl substituents [1,2]. Of special relevance to this paper is the observation that fluoro-substituted species such as B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> [3], rather than the parent non-fluorinated derivative B(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>, are useful co-catalysts for the polymerization of olefins [4]. Moreover, patents have recently appeared on the use

of boron-free species such as 1,2,3,4,5,6,7,8-octafluoro-9-(pentafluorophenyl)-9H-fluorene as activators of Group 4 metallocenes in the α-olefin polymerization process [5].

In the framework of our studies on cyclopentadienyl derivatives of early transition elements, we became interested in fluorosubstituted fluorenyl metal derivatives and this paper reports the formation of fluorenyl anions by reaction of **OFPF**, **OTTF**, and **OFF**, see Chart 1, with sodium hydride or lithium alkyls and with Lewis bases such as bidentate amines, HMPT and **DBU**. Moreover, it will be shown that the new *ansa*-metallocene zirconium(IV) diallyl derivative **ZRAL** undergoes allyl transfer by reaction with **OFPF**, CPh<sub>3</sub>[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] and B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> affording active species for the ethylene

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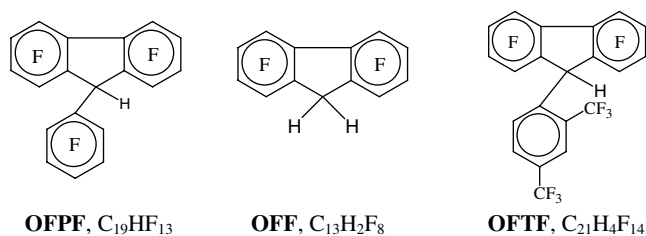


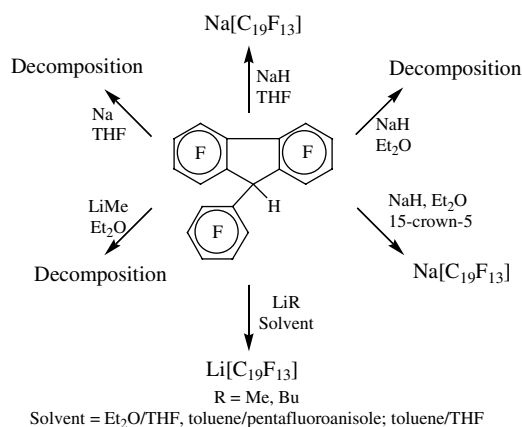
Chart 1.

polymerization and the ethylene/propylene copolymerization reactions.

## 2. Results and discussion

### 2.1. Synthesis and spectroscopic properties of the perfluorofluorenyl anions

Deprotonation of **OPPF**, C<sub>19</sub>H<sub>13</sub>F<sub>13</sub>, by NaH or LiH in DME was reported by Vlasov et al. [6] who described the formation of the [C<sub>19</sub>F<sub>13</sub>]<sup>−</sup> anion, stated to be “the first example of a perfluorinated benzocyclopentadienyl anion”. We treated **OPPF** with finely divided sodium in THF, Scheme 1, and noted di-hydrogen evolution accompanied by the formation of a colourless solid. The <sup>19</sup>F NMR spectrum of the solution showed that consistent amounts of the starting material were still present. A gasvolumetric control of the reaction showed di-hydrogen evolution up to a H<sub>2</sub>/**OPPF** molar ratio of 0.18, thus suggesting that a parasitic reaction had occurred. On the other hand, **OPPF** and NaH interact smoothly in THF at room temperature with evolution of one mol of H<sub>2</sub> per mol of C<sub>19</sub>H<sub>13</sub>F<sub>13</sub>. The <sup>19</sup>F NMR spectrum (vide infra) of the resulting yellow solution shows the presence of the [C<sub>19</sub>F<sub>13</sub>]<sup>−</sup> anion as the unique product. However, all attempts to isolate the sodium compound failed due to decomposition on solvent evaporation.



Scheme 1.

Treatment of **OPPF** with NaH in Et<sub>2</sub>O affords solutions of the [C<sub>19</sub>F<sub>13</sub>]<sup>−</sup> anion (<sup>19</sup>F NMR) which decomposes to give insoluble, unidentified materials. On the other hand, when this reaction is performed in the presence of 1,4,7,10-pentaoxacyclopentadecane (15-crown-5), quantitative dihydrogen evolution (gas-volumetric measurement) and formation of [C<sub>19</sub>F<sub>13</sub>]<sup>−</sup> (<sup>19</sup>F NMR), stable in solution for at least 15 h, is observed, see Scheme 1.

Quantitative formation of Li[C<sub>19</sub>F<sub>13</sub>] was observed by treating **OPPF** with LiMe in Et<sub>2</sub>O/THF or with LiBu in toluene/THF mixtures, see Scheme 1. The polarity of the solvent may be changed by using pentafluoroanisole instead of THF, with similar results. On the other hand, when Et<sub>2</sub>O alone was used as medium, separation of a colourless solid was observed and a <sup>19</sup>F NMR spectrum of the solution showed only the signals of the starting **OPPF**.

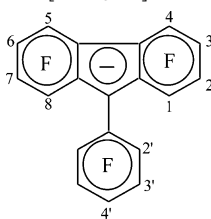
**OTTF** [5,7] reacts with LiBu in toluene/pentafluoroanisole (PFA), vide infra, affording the [C<sub>21</sub>H<sub>3</sub>F<sub>14</sub>]<sup>−</sup> anion, as evidenced by <sup>19</sup>F NMR spectrometry. However, the lithium derivative is rather unstable and decomposes during spectrum acquisition. We have also observed that the lithium derivative is stabilized by a donor solvent such as THF, a stable solution being obtained in a C<sub>6</sub>D<sub>5</sub>CD<sub>3</sub>/d<sub>8</sub>-THF 9/1 mixture. Spectral data are reported in Table 1 together with those of the other fluorinated anions.

The spectral data by Vlasov et al. [6] on both the [C<sub>9</sub>F<sub>13</sub>]<sup>−</sup> anion and the precursor **OPPF** [7] have been confirmed, thus verifying that the <sup>19</sup>F NMR resonances of the anion are shifted to high fields with respect to the corresponding neutral compound **OPPF** (the fluorine nuclei in positions 3' experience the largest shift). The nature of both the medium and the cation (lithium, sodium, sodium/crown ether) has a relatively small effect on the chemical shifts, see Table 1.

The experimental observations reported above suggest that the [C<sub>19</sub>F<sub>13</sub>]<sup>−</sup> and the [C<sub>21</sub>H<sub>3</sub>F<sub>14</sub>]<sup>−</sup> anions are stable in media characterized by relatively high dielectric constants such as THF or in the presence of complexing agents for the cation. In solvents of lower polarity or in the solid state, interactions between the cation and the anion are strong enough to promote decomposition, with probable formation, inter alia, of sodium fluoride. Such instability in the presence of strong interactions between fluorinated hydrocarbons and alkali metal cations has also been reported by Seppelt and co-workers [8] for the [C<sub>6</sub>F<sub>5</sub>]<sup>−</sup> anion, its stability depending on the nature of the cation and increasing in the order Li<sup>+</sup> < Na<sup>+</sup> < K<sup>+</sup> < Cs<sup>+</sup> < TI<sup>+</sup> < [Na(18-crown-6)]<sup>+</sup>.

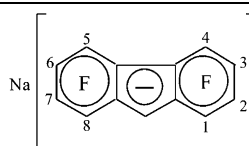
It is interesting to note that 1,2,3,4,5,6,7,8-octafluorofluorene (**OFF**), is reduced either by sodium or by NaH in THF with quantitative formation of the [C<sub>13</sub>H<sub>2</sub>F<sub>8</sub>]<sup>−</sup> anion identified by <sup>19</sup>F NMR spectrometry. This suggests that the decomposition of [C<sub>19</sub>F<sub>13</sub>]<sup>−</sup> or

Table 1

 $^{19}\text{F}$  NMR spectra of **OFTF** and of the  $[\text{C}_{19}\text{F}_{13}]^-$ ,  $[\text{C}_{13}\text{HF}_8]^-$ , and  $[\text{C}_{21}\text{H}_3\text{F}_{14}]^-$  anions

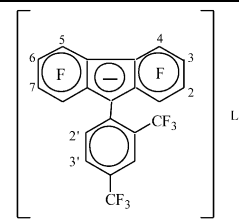
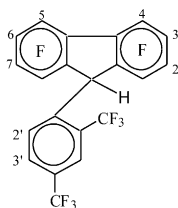
Nucleus	Na $[\text{C}_{19}\text{F}_{13}]/\text{THF}$	Li $[\text{C}_{19}\text{F}_{13}]/\text{THF}$	Na(15-crown-5) $[\text{C}_{19}\text{F}_{13}]/\text{Et}_2\text{O}$	Li $[\text{C}_{19}\text{F}_{13}]$ toluene/THF	Li $[\text{C}_{19}\text{F}_{13}]$ toluene/PFA <sup>a</sup>
1,8	-141.0 (2 F, m)	-141.3 (2 F, m)	-139.2 (2 F, m)	-142.5 (2 F, m)	-140.4 (2 F,m)
2'	-144.8 (2 F,s)	-145.0 (2 F, m)	-142.6 (2 F, m)	-144.9 (2 F, m)	-143.6 (2 F,m)
4,5	-161.4 (2 F, m)	-161.7 (2 F, m)	-159.2 (2 F, m)	-150.1 (2 F, m)	-159.9 (2 F,m)
4'	-164.4 (1 F, m)	-165.0 (1 F, m)	-161.9 (1 F, t)	-160.5 (1 F, m)	-162.7 (1 F,t)
3,6	-168.2 (2 F,t)	-168.6 (2 F, t)	-165.9 (2 F, m)	-170.3 (2 F,t)	-166.8 (2 F,m)
2,7	-170.8 (2 F, m)	-171.2 (2 F, m)	-168.5 (2 F, t)	-170.8 (2 F,t)	-169.3 (2 F,t)
3'	-181.7 (2 F, m)	-182.1 (2 F, m)	-179.4 (2 F, m)	-181.8 (2 F,m)	-180.3 (2 F,m)

Nucleus



	THF	DME	Et <sub>2</sub> O <sup>b</sup>
1,8	-146.4 (2 F,s)	-145.8 (2 F,s)	-143.2 (2 F,s)
2,7	-159.9 (2 F,s)	-159.1 (2 F,s)	-157.8 (2 F,s)
4,5	-161.4 (2 F,m)	-161.7 (2 F,s)	-159.2 (2 F,m)
4,5	-185.7 (2 F,s)	-184.8 (2 F,s)	-180.1 (2 F,s)

Nucleus



	Toluene/THF	Toluene/THF
CF <sub>3</sub> (1)	-58.6	-59.6
CF <sub>3</sub> (2)	-63.4	-62.4
1,8	-134.9	-133.4
4,5	-142.3	-149.1
3,6	-153.6	-167.8
2,7	-153.6	-171.7

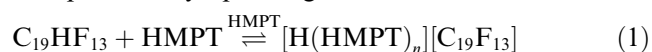
<sup>a</sup> PFA, pentafluoroanisole.<sup>b</sup> Spectrum recorded 10 min after the preparation of the solution.

$[\text{C}_{21}\text{H}_3\text{F}_{14}]^-$  anions may be due to cleavage of the C–C bond between the perfluorinated fluorenyl moiety and the aryl substituent in position 9.

## 2.2. Reaction of **OPPF** with **HMPT** or nitrogen bases

The  $^{19}\text{F}$  NMR spectrum of **OPPF** in HMPT was reported [6] to exhibit the resonances of the anion as well as those of the corresponding protonated species; ca. 30% conversion of the starting material into the corresponding anion in this medium was suggested. We have confirmed that a solution of **OPPF** in HMPT con-

tains the  $[\text{C}_{19}\text{F}_{13}]^-$  anion, equilibrium (1) being therefore presumably operating.



In order to support this hypothesis,  $^{19}\text{F}$  NMR spectra of **OPPF** in HMPT have been recorded at different temperatures and the equilibrium constants have been calculated from the intensity ratio of the -135 ppm resonance due to the fluorine atom 2' of **OPPF** [7] to that at -180 ppm assigned to the fluorine nuclei 3' of the  $[\text{C}_{19}\text{F}_{13}]^-$  anion. A van't Hoff plot gave the thermodynamic parameters of Eq. (1) which

amount to  $\Delta H = -2.6 \text{ kcal mol}^{-1}$  and  $\Delta S = -11.5 \text{ cal mol}^{-1} \text{ K}^{-1}$ , the negative entropy change being in agreement with the loss of degrees of freedom on proton solvation by HMPT. The preferred protonation site of HMPT in the gas phase is the oxygen atom due to the well-established [9] higher basicity of oxygen with respect to nitrogen in this molecule. Solvation by HMPT of the resulting cation easily explains the result.

We have further investigated the behaviour of  $\text{C}_{19}\text{HF}_{13}$  in different nitrogen-containing media. No reaction takes place with py,  $\text{NHET}_2$ ,  $\text{NH}^i\text{Pr}_2$ , and  $\text{N}^n\text{Bu}_3$ . On the other hand, complete deprotonation was observed in neat ethylenediamine or  $N,N'$ -dimethylethylenediamine, probably due to the higher stabilization of the  $[\text{HL}]^+$  system by the chelate effect typical of bidentate amines [10].

As a further test of the protonation activity, we studied the reaction of **OFPF** with **DBU**. The  $^{19}\text{F}$  NMR spectrum in  $\text{C}_6\text{D}_5\text{CD}_3/\text{C}_6\text{D}_5\text{Cl}$  9/1 of an equimolar solution of **OFPF** and **DBU** shows, see Fig. 1A, a broad spectrum probably consisting of the overlapping of the spectra of **OFPF** and of the  $[\text{C}_{19}\text{F}_{13}]^-$  anion, thus suggesting that an equilibrium situation is attained. Addition of excess **DBU** (**DBU/OFPF** molar ratio = 2–5) causes a shift of the equilibrium to the right and the resulting spectrum shows the resonances of  $[\text{C}_{19}\text{F}_{13}]^-$  only, see Fig. 1C.

Additional information on the reaction between **DBU** and **OFPF** has been obtained by examining the  $^1\text{H}$  NMR spectrum, see Fig. SM-A. On addition of one equivalent of **OFPF** to a solution of **DBU** in  $\text{C}_6\text{D}_5\text{CD}_3/\text{C}_6\text{D}_5\text{Cl}$  9/1, a high-field shift of the resonances of the amine [11] was observed attributed to the formation of the  $[\text{DBUH}]^+$  cation. Subsequent increasing of the **DBU/OFPF** molar ratio causes a downfield shift of the **DBU** resonances, probably due to the formation of hydrogen bonding within the cation, see Scheme 2.

### 2.3. $^1\text{H}$ NMR study of the interaction between **ZRAL** and **OFPF**

**ZRAL** [5b] was prepared by reacting [*rac*-ethylenebis( $\eta^5$ -4,5,6,7-tetrahydroindenyl)] dichloridezirconium-(IV) [12] with allylmagnesium chloride, Eq. (2).

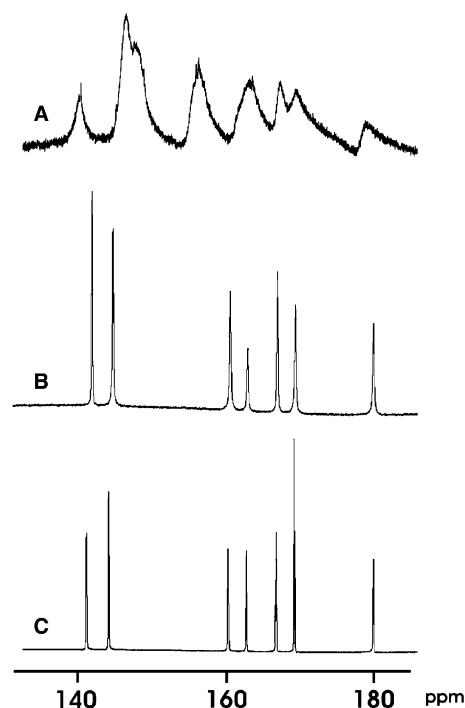
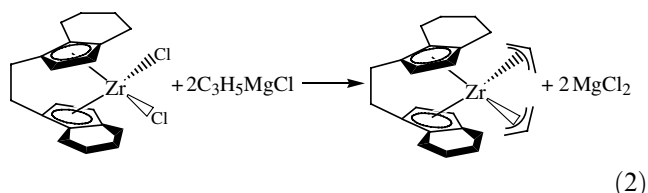
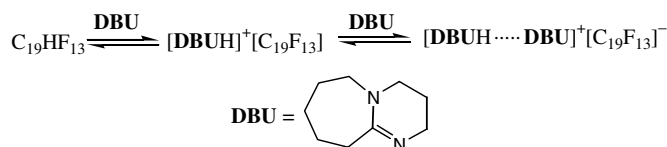


Fig. 1.  $^{19}\text{F}$  NMR spectrum of a solution ( $\text{C}_6\text{D}_5\text{CD}_3/\text{C}_6\text{D}_5\text{Cl}$  9/1) of **DBU** and **OFPF** at different molar ratios of the reagents. (A) **DBU/OFPF** = 1, (B) **DBU/OFPF** = 2, and (C) **DBU/OFPF** = 5.



The  $^1\text{H}$  NMR spectrum of **ZRAL** in  $\text{C}_6\text{D}_6$  at room temperature, see Fig. 2A, shows two narrow doublets at 5.15 ( $\text{C}^5_1$ ) and 4.62 ( $\text{C}^5_2$ ) ppm both with a coupling constant of 2.8 Hz, assigned to the two couples of protons of the five-membered rings. The two CH– and the four  $\text{CH}_2$  groups of the two allyl systems are observed at 5.54 and 2.98 ppm. In view of the highly symmetrical  $\text{AX}_4$  pattern, we assume that at least one of the two allyl- or one  $\text{C}^5$  ring of the tetrahydroindenyl ligands is  $\eta^3$ -coordinated although they may rapidly equilibrate on the NMR timescale, as generally observed for this class of compounds [13]. The four protons of the  $-\text{CH}_2-\text{CH}_2-$  bridge resonate at 2.56 ppm and appear as a strongly coupled spin system. The other signals, at 2.31 (4H), 2.11 (2H) and 1.85 (2H), 1.60 (4H) and



Scheme 2.

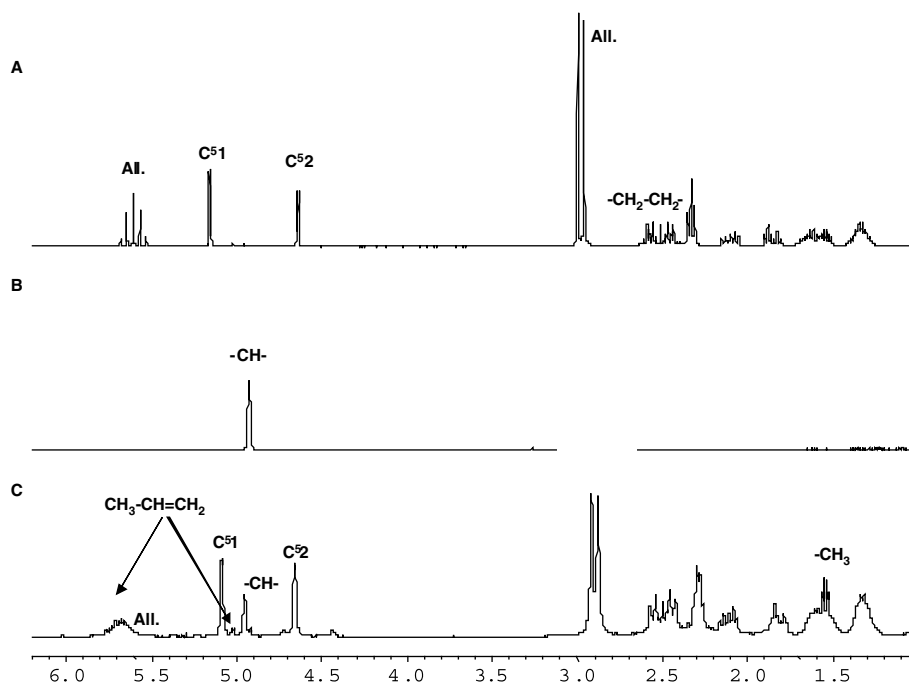


Fig. 2.  $^1\text{H}$  NMR spectrum at 294 K of: (A) **ZRAL** in  $\text{C}_6\text{D}_6$ ; (B) **OPPF** in  $\text{C}_6\text{D}_6$ ; (C) solution resulting from the reaction of **OPPF** with **ZRAL** (molar ratio = 1) in  $\text{C}_6\text{D}_6/\text{C}_6\text{D}_5\text{Cl}$  9/1.  $\text{C}^{\text{S}1}$  and  $\text{C}^{\text{S}2}$  denote the two couples of protons on the five-membered ring of the tetrahydroindenyl ligand.

1.32 (4H) ppm are assigned to the protons in positions 4, 5, 6, and 7, respectively, of the aliphatic cycle. These assignments have been confirmed on the basis of the  $^1\text{H}$ – $^1\text{H}$  COSY spectrum.

The  $^1\text{H}$  NMR spectrum of **OPPF**, see Fig. 2B, shows one proton signal at 4.92 ppm only. The  $^{19}\text{F}$  NMR signals of **OPPF** agree with those in  $\text{C}_6\text{D}_6$  [7], as follows (refer to Table 1 for atom labelling):  $-134.4$ , F(4,5);  $-142.6$ , F(2');  $-143.6$ , F(2'');  $-144.3$ , F(1,8);  $-152.0$ , F(4');  $-152.6$ , F(2,7);  $-153.7$ , F(3,3);  $-160.9$ , F(3',3'').

When **OPPF** was added to a solution of **ZRAL** (**OPPF** to **ZRAL** molar ratio = 1) in  $\text{C}_6\text{D}_6$ , an immediate reaction was observed and a solid separated out with time (2–3 h). In the  $^1\text{H}$  NMR spectrum, see Fig. 2C, the intensity of the signal at 4.92 ppm, assigned to **OPPF**, has reduced its intensity, while the two signals of the five-membered rings shift from 5.15 to 5.08 ppm (and from 4.64 to 4.67 ppm), accompanied by a general broadening of the signals of **ZRAL**. Resonances due to propylene are observed.

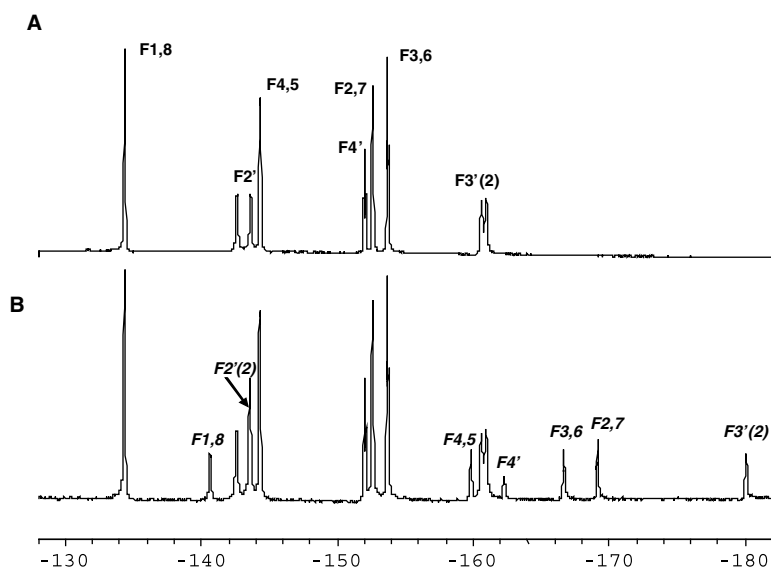


Fig. 3.  $^{19}\text{F}$  NMR spectrum at 294 K of: (A) **OPPF** in  $\text{C}_6\text{D}_6$ ; (B) solution resulting from the reaction of **OPPF** with **ZRAL** (molar ratio = 1) in  $\text{C}_6\text{D}_6/\text{C}_6\text{D}_5\text{Cl}$  9/1.

Table 2

Relative amounts of uncharged and anionic species in the reaction of **ZRAL** with **OFPF** in different media at 294 K

Run	Medium	Neutral species (%)	Anionic species (%)
1	C <sub>6</sub> D <sub>6</sub>	74	26
2 <sup>a</sup>	C <sub>6</sub> D <sub>6</sub> /THF	58	41
3	C <sub>6</sub> D <sub>6</sub> /C <sub>6</sub> D <sub>5</sub> Cl 9/1	52	46
4 <sup>b</sup>	C <sub>6</sub> D <sub>6</sub> /C <sub>6</sub> D <sub>5</sub> Cl 9/1	46	54

<sup>a</sup> THF/Zr molar ratio = 1.

<sup>b</sup> Equimolar amounts of **OFPF** and **ZRAL** were reacted in pentane, the solid was isolated and dissolved in a 9/1 C<sub>6</sub>D<sub>6</sub>/C<sub>6</sub>D<sub>5</sub>Cl mixture.

Fig. 3A shows the <sup>19</sup>F NMR spectrum of **OFPF**. A new series of resonances of the deprotonated species, see Fig. 3B, can be compared with those obtained on the product of the reaction between **OFPF** and LiH or NaH, Table 1.

As the solution contains both the neutral and the anionic forms, the molar percentage of the anionic form derived from **OFPF** can be estimated from the intensities of the <sup>19</sup>F-signals as  $100 \times \text{Int}_{\text{an}}/\text{Int}_{\text{tot}}$ , where  $\text{Int}_{\text{an}}$  is the average integral of the resonances assigned to the anionic form and  $\text{Int}_{\text{tot}}$  is the sum of the average integrals of both the uncharged and the anionic form. In C<sub>6</sub>D<sub>6</sub>, the molar percentages of the uncharged and the anionic species are 74% and 26%, respectively, see Table 2.

On the basis of similar reaction schemes reported in the literature concerning the reactivity of metallocene alkyls of Group 4 with protonated species such as alkylammonium salts [14], we suggest that the reaction reported in Scheme 3 is operative in our system, involving the protonolysis of the metal-allyl bond to give {[*rac*-ethylene-bis(η<sup>5</sup>-4,5,6,7-tetrahydroindenyl)]allylzirconium(IV)}{C<sub>19</sub>F<sub>13</sub>} and propylene, both the uncharged and the anionic fluorinated species being present in solution.

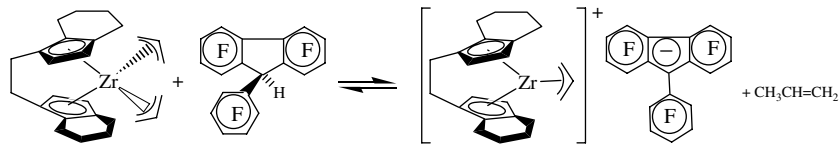
Our data are also in agreement with the formation of a cationic bimetallic species, as shown in Scheme 4. This

would be consistent with the tendency of allylic ligands to form bimetallic complexes such as Zr<sub>2</sub>Cp<sub>4</sub>Cl(C<sub>3</sub>H<sub>5</sub>)<sub>3</sub> [13a]. Also, dinuclear compounds are formed when zirconocene alkyls are reacted with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> [15] or CPh<sub>3</sub>[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] [16], or when TiCp\*Me<sub>2</sub>E (E = Me, C<sub>6</sub>F<sub>5</sub>, OC<sub>6</sub>F<sub>5</sub>, Cl) or TiCp\*Me<sub>3</sub> react with CPh<sub>3</sub>[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] [17] or B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> [18].

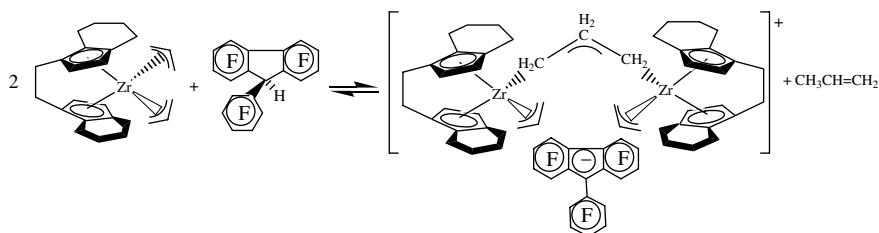
Attempts have been made to shift the reaction completely to the right, and the results are reported in Table 2. We observe that addition of *d*<sub>8</sub>-THF (molar ratio **ZRAL**/**OFPF**/*d*<sub>8</sub>-THF = 1/1/1) (Table 2, run 2) leads to an increase of the anionic form (41%); no separation of solid was observed, similar to what occurs for the lithium or sodium salts. Due to the generally recognized poisoning effect of Lewis bases on the catalytic activity [19], chlorobenzene-*d*<sub>5</sub> was used instead of THF to increase the polarity of the medium, but no precipitation of solid was observed (C<sub>6</sub>D<sub>6</sub>/C<sub>6</sub>D<sub>5</sub>Cl = 9/1 v/v), and the amount of anionic species only slightly increased (Table 2, run 3). Besides, when the yellow solid, which was separated out by mixing equimolar amounts of **ZRAL** and **OFPF** in pentane (see Section 4), was dissolved in a 9/1 (by volume) mixture of C<sub>6</sub>D<sub>6</sub> and C<sub>6</sub>D<sub>5</sub>Cl, the higher conversion (54%, see Table 2, run 4) to the anionic species was achieved. All attempts to obtain higher conversions by operating with equimolar amounts of the reagents were unsuccessful.

We believe that our <sup>1</sup>H NMR spectrum is the result of equilibria being rapid on the NMR timescale such as those reported in Schemes 3 and 4, the position of the resonances pertaining to the five-membered rings depending on the molar ratio of the contributing forms. Unfortunately, at -40 °C, the lowest temperature attainable with the C<sub>6</sub>D<sub>6</sub>/C<sub>6</sub>D<sub>5</sub>Cl mixture, we still observed a broad <sup>1</sup>H NMR spectrum which does not allow the individual species to be distinguished.

The reaction between **ZRAL** and **OFPF** was examined also in a sapphire high-pressure NMR tube



Scheme 3.



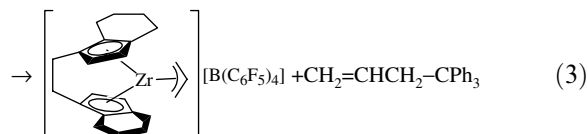
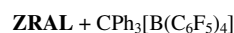
Scheme 4.

(10 mm) under an ethylene pressure of 5 bar, see Fig. 4. In Fig. 4A, the resonances of ZRAL and ethylene are observed. After addition of OFPF, the spectral features typical of ZRAL gradually change with the CH<sub>2</sub> signal of the allylic fragment turning to a triplet, thus suggesting the formation of the Zr–CH<sub>2</sub>–CH<sub>2</sub>– sequence, the resonance of polyethylene at 1.5 ppm becoming evident, see Fig. 4B. After 15 min, Fig. 4C, and especially after heating at 50 °C, Fig. 4D, the polyethylene resonance becomes one of the most intense bands in the whole spectrum.

In order to study in more detail the reaction between the fluorene corresponding to OFPF and the allylic complex ZRAL, two well-known polymerization co-catalysts, CPh<sub>3</sub>[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] and B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> [4], were also examined as potential allyl-abstracting agents. The <sup>1</sup>H NMR spectrum of the solution obtained for the 1:1 reaction of ZRAL with CPh<sub>3</sub>[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>], see Fig. 5, shows a shift of the protons of the five-membered rings from 5.15 to 6.30 ppm (C<sup>5</sup>1) and from 4.64 to 4.60 ppm (C<sup>5</sup>2). The latter signal is also broader than that of the starting compound and only two signals due to the five-membered rings are present. The appearance of a

new spin system can be observed, corresponding to CH<sub>2</sub>=CH–CH<sub>2</sub>–CPh<sub>3</sub> [20], as also confirmed by the <sup>1</sup>H–<sup>1</sup>H COSY spectrum, the distinctive chemical shifts of this species being located at 4.85 (CH<sub>2</sub>=), 5.63 (=CH–), 3.28 (CH<sub>2</sub>), 6.95–7.20 (C<sub>6</sub>H<sub>5</sub>) ppm.

By taking into consideration that the <sup>19</sup>F NMR spectrum of the [B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>–</sup> anion does not substantially change after treatment with ZRAL (Table 3), the overall reaction can be described in the following reaction:



In this case the reaction goes to completion as evidenced by the 1:1 molar ratio between the intensity of the resonances of the allyl group in CH<sub>2</sub>=CH–CH<sub>2</sub>–CPh<sub>3</sub> and those in the zirconium complex and by the absence of resonances of the starting zirconium allyl derivative ZRAL.

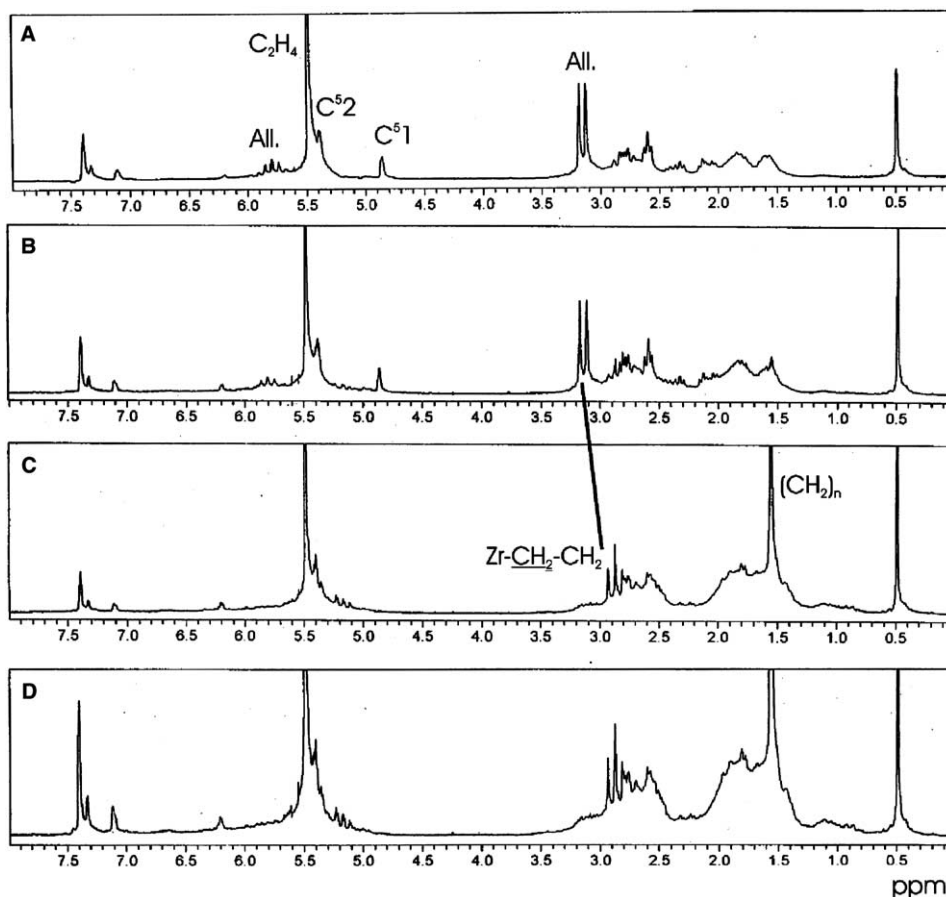


Fig. 4. <sup>1</sup>H NMR spectrum of the solution from the reaction of OFPF and ZRAL under ethylene pressure (5 bar): (A) ZRAL + C<sub>2</sub>H<sub>4</sub> at 294 K; (B) the same as (A) + OFPF; (C) the same as (B) after 15 min; (D) the same as (C) after heating at 323 K. C<sup>5</sup>1 and C<sup>5</sup>2 denote the two couples of protons on the five-membered ring of the tetrahydroindenyl ligand.

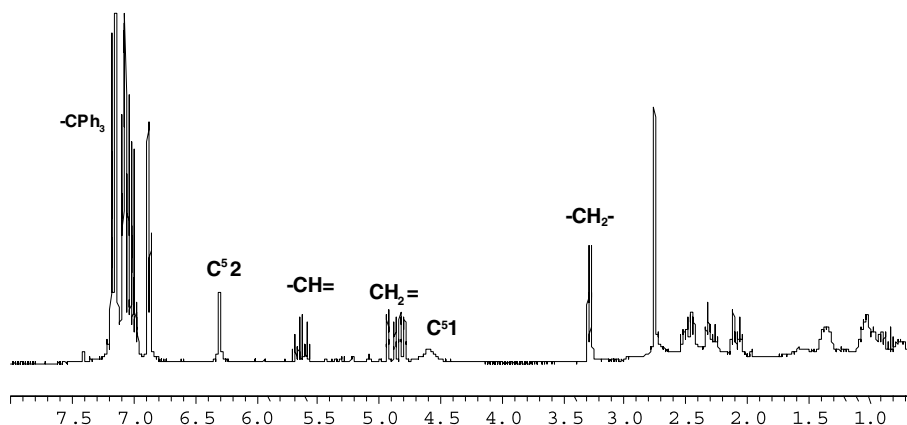


Fig. 5.  $^1\text{H}$  NMR spectrum of the solution from the reaction of **ZRAL** with  $\text{CPh}_3[\text{B}(\text{C}_6\text{F}_5)_4]$  (molar ratio = 1) in  $\text{C}_6\text{D}_6/\text{C}_6\text{D}_5\text{Cl}$  9/1 at 294 K.  $\text{C}^51$  and  $\text{C}^52$  denote the two couples of protons on the five-membered ring of the tetrahydroindenyl ligand.

Table 3

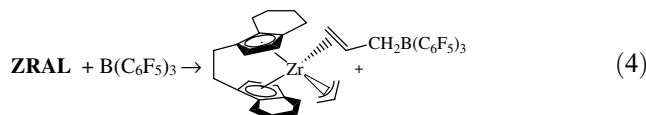
$^{19}\text{F}$  NMR spectrum of the solution ( $\text{C}_6\text{D}_6/\text{C}_6\text{D}_5\text{Cl}$  9/1, 294 K) after the reaction between **ZRAL** and  $\text{CPh}_3[\text{B}(\text{C}_6\text{F}_5)_4]$

Nucleus	$\text{CPh}_3[\text{B}(\text{C}_6\text{F}_5)_4]$	$[\text{Zr}][\text{B}(\text{C}_6\text{F}_5)_4]$
F( <i>ortho</i> )	−131.9	−132.1
F( <i>para</i> )	−162.7	−162.7
F( <i>meta</i> )	−166.6	−166.6

$[\text{Zr}] = [\text{rac-ethylene-bis}(\eta^5\text{-4,5,6,7-tetrahydroindenyl})\text{allylzirconium(IV)}]$  cation.

The reaction between **ZRAL** and  $\text{B}(\text{C}_6\text{F}_5)_3$  is more complex. The  $^1\text{H}$  NMR spectrum of the solution shows four resonances of equal intensity at 7.52, 5.89, 5.26 and 3.84 ppm attributed to the protons of the five-membered ring (see Fig. SM-B) suggesting that the bis-tetrahydroindenyl fragment has lost its symmetry. A sharp triplet at  $-0.19$  ppm, which correlates (by  $^1\text{H}-^1\text{H}$  COSY) to the resonances at 1.40 and 4.80 ppm, has been assigned to an allyl group linking zirconium and boron. The sharpness of the  $-0.19$  ppm triplet suggests coordination to zirconium; on the other hand, the broad triplet at 4.80 ppm probably indicates boron coordination, broadening being originated by the quadrupolar effect of the boron atom [15,21].

In this connection it is important to observe that when unsaturated R groups are present as ligands of the metallocene compound, formation of zwitterionic species may be observed, as in the case of the reactions of  $\text{Zr}(\text{CH}_2\text{Ph})_4$  or  $\text{ZrCp}(\text{CH}_2\text{Ph})_3$  with  $\text{B}(\text{C}_6\text{F}_5)_3$ . These reactions afford  $\text{ZrL}(\text{CH}_2\text{Ph})_2(\eta^6\text{-C}_6\text{H}_5\text{CH}_2)\text{B}(\text{C}_6\text{F}_5)_3$ ,  $\text{L} = \text{Cp}$  [22],  $\text{L} = \text{CH}_2\text{Ph}$  [23], the zirconium centre being stabilised by  $\eta^6$ -interactions with a boron-bonded benzyl group. Probably a zwitterionic species is formed in the reaction between **ZRAL** and  $\text{B}(\text{C}_6\text{F}_5)_3$ , see Eq. (4), lowering the symmetry of the bis-tetrahydroindenyl structure and thus justifying the observed increase of the  $^1\text{H}$  NMR signals in the region typical of the five-membered ring.



It is noteworthy that the  $^{19}\text{F}$ -spectrum of the solution obtained from the reaction of **ZRAL** with  $\text{B}(\text{C}_6\text{F}_5)_3$  (see Fig. SM-C) shows the resonances of the pentafluorophenyl group linked to the quaternary boron atom slightly shifted [ $-129.9$  (*o*-F),  $-162.2$  (*p*-F) and  $-165.8$  (*m*-F)] with respect to those of the  $[\text{B}(\text{C}_6\text{F}_5)_4]^-$  anion, see Table 3. The substantial absence of resonances due to the starting  $\text{B}(\text{C}_6\text{F}_5)_3$ , whose  $^{19}\text{F}$  NMR spectrum under comparable conditions shows resonances at  $-129.0$  (*o*-F),  $-141.0$  (*p*-F) and  $-160.2$  (*m*-F), suggests that, as in the case of  $\text{CPh}_3[\text{B}(\text{C}_6\text{F}_5)_4]$ , the reaction of **ZRAL** with  $\text{B}(\text{C}_6\text{F}_5)_3$  goes substantially to completion.

The reaction of **ZRAL** with the **DBU/OFPF** system was also studied. The  $^{19}\text{F}$  NMR spectrum of the solution obtained from the addition of one equivalent of **ZRAL** to  $[\text{BDUH}]^+[\text{C}_{19}\text{F}_{13}]^-$  (obtained from the reaction of **DBU** and **OFPF** in the molar ratio of 2) is substantially unchanged with respect to that of  $[\text{BDUH}]^+[\text{C}_{19}\text{F}_{13}]^-$ . On the other hand, the  $^1\text{H}$  NMR spectrum, see Fig. SM-D, undergoes radical changes, which can be summarized as follows: (a) the resonances of  $[\text{BDUH}]^+$  shift to lower fields, i.e., to the region typical of the unprotonated base; (b) the resonance attributed to the proton on nitrogen disappears; (c) resonances due to propylene are observed; (d) four resonances attributed to the protons on the five-membered rings are present instead of the two typical of the starting zirconium compound **ZRAL** (Fig. SM-E).

These experimental data suggest that incomplete protonation of an allyl ligand has occurred. Moreover, coordination of **DBU**, as formed after protonation of the allyl group to the zirconium centre probably takes place, which reduces the axial symmetry of **ZRAL**, thus inducing the protons on the five membered ring to be



Table 4  
Ethylene polymerization and ethylene-propylene co-polymerization reactions

Run	Co-catalyst	Al <sub>i</sub> /Zr	T (°C)	Time (h)	Yield (kg <sub>PE</sub> g <sub>Zr</sub> <sup>-1</sup> h <sup>-1</sup> )	Activity (mol%)	C <sub>3</sub> (×10 <sup>-3</sup> )	M <sub>n</sub> (×10 <sup>-3</sup> )	M <sub>w</sub>	MWD
1 <sup>a,b</sup>	c	300	25	1	3.4	25	–	–	–	–
2 <sup>a,b</sup>	d	300	25	1	3.5	25	–	–	–	–
3 <sup>a,b</sup>	e	300	25	1	–	–	–	–	–	–
4 <sup>a</sup>	CPh <sub>3</sub> [B(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub> ]	300	50	0.5	1.9	28	–	–	–	–
5 <sup>a</sup>	MAO	500	50	0.5	2.1	30	–	–	–	–
6 <sup>f</sup>	<b>OFPF</b>	300	50	0.5	50	440	–	95	200	2.1
7 <sup>g</sup>	<b>OFPF</b>	300	50	1	16	70	46	39.5	75	1.9
8 <sup>g</sup>	CPh <sub>3</sub> [B(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub> ]	300	50	1	31	135	45	32	70	2.2
9 <sup>g</sup>	B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub>	300	50	1	13	57	43	32.5	65	2.0
10 <sup>g</sup>	MAO	500	80	0.8	66	349	40	25	48	1.9

<sup>a</sup> [*rac*-ethylene-bis(η<sup>5</sup>-4,5,6,7-tetrahydroindenyl)]dichloridezirconium(IV) as catalytic precursor.

<sup>b</sup> Toluene (150 mL) and pentafluoroanisole (1 mL). P<sub>ethylene</sub> = 0.5 atm. TIBA has been used in runs 1–4.

<sup>c</sup> Toluene/PFA solution of Li[C<sub>19</sub>F<sub>13</sub>].

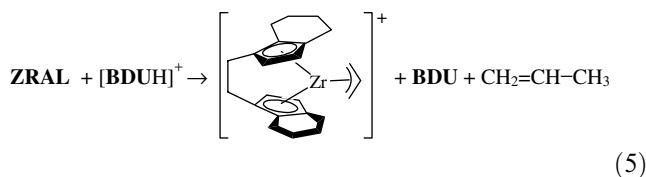
<sup>d</sup> Toluene/PFA solution of Li[C<sub>21</sub>H<sub>3</sub>F<sub>14</sub>].

<sup>e</sup> THF or Et<sub>2</sub>O solutions of M[C<sub>19</sub>F<sub>13</sub>], M = Li, Na.

<sup>f</sup> TIBA has been used as an impurity scavenger. P<sub>ethylene</sub> = 8 atm. **ZRAL** as catalytic precursor.

<sup>g</sup> TIBA has been used as an impurity scavenger. P<sub>ethylene</sub> + P<sub>propylene</sub> = 8 atm. **ZRAL** as catalytic precursor.

non-equivalent, see Eq. (5). This is in agreement with the observation that the protonation of metallocene precursors produces coordinatively unsaturated, catalytically active, cations only when ammonium salts bearing large alkyl groups are used [19].



#### 2.4. Polymerization experiments

Solutions of the lithium derivatives Li[C<sub>19</sub>F<sub>13</sub>] or Li[C<sub>21</sub>H<sub>3</sub>F<sub>14</sub>], see Table 4, prepared in toluene/PFA or in ethers, in combination with [*rac*-ethylene-bis(η<sup>5</sup>-4,5,6,7-tetrahydroindenyl)] dichloridezirconium(IV), have been evaluated as co-catalysts for the polymerisation of ethylene. Solutions of perfluorinated anions in THF or Et<sub>2</sub>O are inactive ethylene polymerization catalysts (Table 4, run 3), as these polar media coordinate to the zirconocene cation, generally accepted to be the active species [19]. On the other hand, with toluene/pentafluoroanisole solutions of the anions, polyethylene was produced, with an activity (25 kg<sub>PE</sub> g<sub>Zr</sub><sup>-1</sup> h<sup>-1</sup>, Table 4, runs 1-2) comparable to that obtained with the MAO- or the CPh<sub>3</sub>[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]/[*rac*-ethylene-bis(η<sup>5</sup>-4,5,6,7-tetrahydroindenyl)]dichloridezirconium(IV) system, Table 4, runs 4 and 5.

On the other hand, the combination **OFPF/ZRAL** in toluene, Table 4, run 6, is much more active than the previous ones, activities as high as 440 kg<sub>PE</sub> g<sub>Zr</sub><sup>-1</sup> h<sup>-1</sup> being obtained. Accordingly, the **OFPF/ZRAL** combination was used for ethylene/propylene co-polymerization, the data being reported in Table 4, run 7.

Comparison with classical catalytic compositions (zirconium compounds and boron derivatives or MAO, runs 8–10) shows that the **OFPF/ZRAL** catalytic system has comparable activities although MAO still gives the best results.

### 3. Conclusions

In this paper, the reactivity of **OFPF**, **OFTF**, and **OFF** has been studied, with special attention for **OFPF**. The <sup>19</sup>F NMR spectra of the three anions have been assigned. The sodium and lithium derivatives are stable only in solvents of high dielectric constants such as THF, HMPA, decomposition being observed in media such as toluene or diethyl ether or during attempts to isolate solid materials. This is probably due to formation of alkali fluorides.

Treatment of **OFPF** with Lewis bases such as amines, HMPT or **DBU** has shown that nitrogen bases such as pyridine or aliphatic amines do not react with **OFPF**, formation of the anion being quantitative with bidentate amines (ethylenediamine, *N,N'*-dimethylethylenediamine) due to stabilization by chelate effect. With a large excess of HMPT, the deprotonation equilibrium constant  $K = \frac{[\text{H}(\text{HMPT})_n][\text{C}_{19}\text{F}_{13}]}{[\text{C}_{19}\text{HF}_{13}]}$  is 0.007 at 298 K. A **DBU/OFPF** molar ratio of 5 is sufficient to totally convert **OFPF** into the anion.

The reactivity of **OFPF** with (1,2-ethylene-bis(η<sup>5</sup>-4,5,6,7-tetrahydroindenyl)) diallylzirconium(IV), **ZRAL**, has been also examined by <sup>1</sup>H and <sup>19</sup>F NMR techniques and compared with that of classical Ziegler–Natta co-catalyst such as B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> and CPh<sub>3</sub>[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]. The compounds [*rac*-ethylene-bis(η<sup>5</sup>-4,5,6,7-tetrahydroindenyl)]allylzirconium(IV)[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] and CPh<sub>3</sub>CH<sub>2</sub>CH=CH<sub>2</sub> are obtained from **ZRAL** and CPh<sub>3</sub>B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>. According to <sup>1</sup>H and <sup>19</sup>F NMR spectra, a zwitterionic

compound is obtained in the reaction of **ZRAL** with  $B(C_6F_5)_3$ .

In the presence of excess TIBAL, the known [*rac*-ethylene-bis( $\eta^5$ -4,5,6,7-tetrahydroindenyl)]dichloridezirconium(IV), in combination with fluorenyl anions shows a low activity in ethylene polymerization. However, the new zirconium derivative [*rac*-ethylene-bis( $\eta^5$ -4,5,6,7-tetrahydroindenyl)]diallylzirconium(IV) in combination with **OFPF** co-polymerizes ethylene and propylene with activities similar to the catalytic systems involving boron derivatives.

## 4. Experimental

### 4.1. General

Unless otherwise stated, all of the operations were carried out under an atmosphere of prepurified argon. Solvents were dried by conventional methods prior to use.

NMR spectra were measured at 25 °C on a Varian Gemini 200BB instrument operating at 200 MHz for  $^1H$  (TMS as reference), at 50.3 MHz for  $^{13}C$  (TMS as reference) and at 188 MHz for  $^{19}F$  NMR ( $CFCl_3$  as reference) or on a Varian VXR 300 spectrometer at 300 and 282 MHz for  $^1H$  and  $^{19}F$  NMR, respectively. The NMR sapphire tubes with a diameter of 10 mm, used for the high-pressure experiments, were equipped with a titanium high-pressure head, provided by ISSECC-CNR (Firenze, Italy).

The MW of the polymers were measured by using a Waters Associates 150 C High Temperature gel permeation chromatography (GPC) instrument equipped with four Waters Styragel columns: HT3, HT4, HT5, HT6 with pore dimensions of  $10^3$ ,  $10^4$ ,  $10^5$  and  $10^6$  Å, respectively, and a refractive index detector. All samples were run in 1,2,4-trichlorobenzene at 135 °C with a flow rate of 1 mL  $min^{-1}$ . The data obtained were processed with a Maxima 820 software version 3.30 (Millipore); for the calculation of the average molecular weights  $M_n$  and  $M_w$ , the universal calibration principles were applied, by selecting polystyrene standards for the calibration with MW in the 650000–2000 range.

The following compounds were commercial products, used as received: [*rac*-ethylene-bis( $\eta^5$ -4,5,6,7-tetrahydroindenyl)]dichloridezirconium(IV) (Crompton), pentafluoroanisole, PFA (Aldrich), tri-isobutylaluminum, TIBA (Crompton), methylalumoxane, MAO (Crompton). The following compounds were prepared according to literature procedures: 1,2,3,4,5,6,7,8-octa-fluoro-9-(pentafluorophenyl)-9H-fluorene (**OFPF**) [6], 1,2,3,4,5,6,7,8-octafluoro-9-(2,4-trifluoromethylphenyl)-9H-fluorene (**OFPF**) [5a], and 1,2,3,4,5,6,7,8-octafluorofluorene (**OFF**) [24].

### 4.2. Reaction of **OFPF** with NaH in THF. Preparation of THF solutions of $Na[C_{19}F_{13}]$

A solution of **OFPF** (0.096 g, 0.2 mmol) in THF (10 mL) was treated at room temperature with NaH (0.006 g, 0.25 mmol). Evolution of gas and formation of a yellow solution were observed. The solution showed the  $^{19}F$  NMR spectrum reported in Table 1. A gasvolumetric control showed that 0.67 mmol of **OFPF** in THF react at 300 K with the stoichiometric amount of NaH, 0.67 mmol of  $H_2$ , corresponding to a  $H_2/C_{19}HF_{13}$  molar ratio of 1.0, being evolved in ca. 20 min [25]. In one attempt to isolate a solid product, the solvent was partially removed in vacuo from the yellow solution and heptane was added: the solid which was recovered by filtration was almost insoluble in THF and its  $^{19}F$  NMR spectrum showed only broad resonances which did not correspond to those of either  $Na[C_{19}F_{13}]$  or **OFPF**.

### 4.3. Reactions of **OFPF**

#### 4.3.1. With NaH in $Et_2O$

A solution of **OFPF** (0.102 g, 0.21 mmol) in  $Et_2O$  (10 mL) was treated at room temperature with an equimolar amount of NaH, which caused gas evolution. After 1 h stirring, the  $^{19}F$  NMR spectrum showed no resonances attributable either to the starting material or to the anion.

#### 4.3.2. With NaH in $Et_2O$ in the presence of 1,4,7,10,13-pentaoxacyclopentadecane (15-crown-5)

A solution of **OFPF** (0.106 g, 0.22 mmol) and 15-crown-5 (0.056 g, 0.25 mmol) in  $Et_2O$  (10 mL) was treated at room temperature with NaH (0.007 g, 0.29 mmol). Evolution of gas and formation of a yellow solution were observed. The solution showed the  $^{19}F$  NMR spectrum reported in Table 1.

A gasvolumetric control of the reaction showed that 0.54 mmol of **OFPF** in  $Et_2O$  react at 298 K with the stoichiometric amount of NaH in the presence of 15-crown-5 (0.55 mmol) with evolution of 0.52 mmol of  $H_2$  ( $H_2/C_{19}HF_{13}$  molar ratio of 0.96) in ca. 15 min.

### 4.4. Preparation of solutions of $Li[C_{19}F_{13}]$ from **OFPF**

#### 4.4.1. With LiMe in THF

A solution of **OFPF** (0.102 g, 0.2 mmol) in THF (10 mL) was reacted at room temperature with a 1.6 M  $Et_2O$  solution of LiMe (0.2 mL, 0.32 mmol of LiMe). After 30 min stirring at room temperature, the yellow solution showed the  $^{19}F$  NMR spectrum reported in Table 1.

#### 4.4.2. With LiBu in toluene/pentafluoroanisole (PFA)

A solution of **OFPF** (0.5 mmol) in toluene (25 mL) and pentafluoroanisole (1 mL) cooled at  $-10$  °C was treated with 0.64 mmol of LiBu (1.6 M solution in

hexane). The solution showed the  $^{19}\text{F}$  NMR spectrum reported in Table 1. Gas evolution and formation of a yellow solution (stable at least for 48 h when stored at ca. 0 °C) were observed. Formation of  $\text{Li}[\text{C}_{19}\text{F}_{13}]$  was proved by the treatment of the yellow solution with  $\text{D}_2\text{O}$ ,  $\text{C}_{19}\text{F}_{13}\text{D}$  being identified by mass spectrometry. All attempts to isolate the lithium derivative at room temperature failed due to decomposition of the anion upon addition of low-polarity solvents.

#### 4.4.3. With LiBu in toluene/THF

A solution of **OFPF** (0.5 mmol) in toluene (27 mL) and THF (3 mL) cooled at  $-10$  °C was treated with 0.64 mmol of LiBu (1.6 M solution in hexane). The solution showed the  $^{19}\text{F}$  NMR spectrum reported in Table 1. Evolution of gas and formation of a yellow solution (stable at least for 48 h at 0 °C) were observed. All attempts to obtain the solid product failed due to decomposition.

#### 4.5. Reaction of **OFTF** with LiBu in toluene/THF. Preparation of $\text{Li}[\text{C}_{21}\text{H}_3\text{F}_{14}]$ solutions

A solution of **OFTF** (0.5 mmol) in toluene (25 mL) and THF (3 mL) cooled at  $-10$  °C was treated with 0.64 mmol of LiBu (1.6 M solution in hexane). The solution showed the  $^{19}\text{F}$  NMR spectrum reported in Table 1.

#### 4.6. Preparation of THF solutions of $\text{Na}[\text{C}_{13}\text{HF}_8]$ from **OFF**

##### 4.6.1. With NaH in THF

A suspension of NaH (8.4 mg, 0.032 mmol) in THF 1.2 mL was treated at room temperature with a solution of **OFF** (0.011 g, 0.035 mmol) in THF (2 mL). Evolution of di-hydrogen was observed, while the yellow solution showed the  $^{19}\text{F}$  NMR spectrum reported in Table 1.

##### 4.6.2. With Na in THF

A solution of **OFF** (0.020 g, 0.064 mmol) in THF (3 mL) was treated at room temperature with 0.065 mmol of Na suspended in 1.5 mL of THF. Evolution of di-hydrogen was observed, while the yellow solution showed a  $^{19}\text{F}$  NMR spectrum superimposable to that obtained in Section 4.6.1. Similar results were obtained in  $\text{Et}_2\text{O}$ , but the solutions were stable for limited periods of time.

#### 4.7. Reactivity of **OFPF** with HMPT

A NMR tube was charged with **OFPF** (0.01 g, 0.021 mmol) and HMPT (0.5 mL). After the tube was sealed, the yellow solution was examined by  $^{19}\text{F}$  NMR spectrometry. The intensities of the resonances at  $-135$  ppm [ $I_b$ , due to the F2' atom of **OFPF**] and at  $-180$  ppm [ $I_a$ , due to the two F3' atoms of the corresponding anion] were used to establish the molar ratio of the components. The data collected at different temperatures and referred

to  $I_a = 1$  were the following ( $T, I_b$ ): 295 K, 0.070; 308 K, 0.080; 323 K, 0.097; 338 K, 0.112; 353 K, 0.131; 363 K, 0.141. The equilibrium constants (temperature in parenthesis) were: 0.264 (295 K); 0.227 (308 K); 0.182 (323 K); 0.153 (338 K); 0.126 (353 K); 0.116 (363 K).

#### 4.8. Reactivity of **OFPF** with nitrogen bases

By operating under the experimental conditions described in Section 4.7, quantitative formation of the  $[\text{C}_{19}\text{F}_{13}]^-$  anion was observed by recording  $^{19}\text{F}$  NMR spectra of **OFPF** in *N,N'*-dimethylethylenediamine, or ethylenediamine. No formation of the  $[\text{C}_{19}\text{F}_{13}]^-$  anion was observed in pyridine,  $\text{NH}^i\text{Pr}_2$  or  $\text{N}^n\text{Bu}_3$  solutions of similar concentrations.

#### 4.9. Preparation of **ZRAL**

A 2 M solution of allylmagnesium chloride (7 mL, 14 mmol) in THF maintained at ca.  $-70$  °C was added to a solution of [rac-ethylene-bis(4,5,6,7-tetrahydroindenyl)]dichloridezirconium(IV) (2 g, 5.0 mmol) in THF (100 mL). The mixture was left to spontaneously warm up to room temperature and the solvent was then removed in vacuo. Toluene (100 mL) was added and the resulting mixture was subjected to evaporation in vacuo. The residue was treated with pentane (200 mL). After filtration, the solution was concentrated in vacuo at room temperature to ca. 25 mL and cooled down to ca.  $-70$  °C. The yellow microcrystalline product was recovered by filtration and dried in vacuo at room temperature (2.1 g, 98% yield) as a solid. Anal. Calc. for  $\text{C}_{26}\text{H}_{34}\text{Zr}$ : C, 71.3; H, 7.8. Found: C, 71.2; H, 7.9%.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  5.54 (quintet, 2H), 5.15 (d, 2H), 4.62 (d, 2H), 2.98 (d, 8H), 2.56 (m, 4H), 2.31 (m, 4H), 2.11 (m, 2H), 1.85 (m, 2H), 1.60 (m, 4H) 1.32 (m, 4H) ppm.

#### 4.10. Reaction of **OFPF** with [rac-ethylene-bis( $\eta^5$ -4,5,6,7-tetrahydroindenyl)]diallyl zirconium(IV) (**ZRAL**)

**OFPF** (0.39 g, 0.68 mmol) was added to a solution of **ZRAL** (0.3 g, 0.68 mmol) in pentane (15 mL). The resulting yellow precipitate was collected by filtration, washed with pentane, dried in vacuo and used for the  $^1\text{H}$  and  $^{19}\text{F}$  NMR experiments.

#### 4.11. Reaction of **OFPF** with DBU

Only the reaction of **OFPF** with **DBU** in the 1:1 molar ratio is described in detail, the reactions at different ratios (**DBU/OFPF** molar ratios 1/2 and 1/5) being performed in a similar way. A solution of **OFPF** (23.8 mg, 0.05 mmol) in 2 mL of  $\text{C}_6\text{H}_5\text{CD}_3/\text{C}_6\text{H}_5\text{Cl}$  9/1 was treated with 7.6 mg (0.05 mmol) of **DBU**. A yellow solution

of  $[\text{DBUH}]^+[\text{C}_{19}\text{F}_{13}]^-$  was obtained, which was examined by  $^1\text{H}$  and  $^{19}\text{F}$  NMR spectra.

#### 4.12. Reaction of ZRAL with $[\text{DBUH}]^+[\text{C}_{19}\text{F}_{13}]^-$

ZRAL (22 mg, 0.05 mmol) in  $\text{C}_6\text{H}_5\text{CD}_3/\text{C}_6\text{H}_5\text{Cl}$  (9:1) was treated with a solution of  $[\text{DBUH}]^+[\text{C}_{19}\text{F}_{13}]^-$ s obtained from the reaction of DBU (0.1 mmol) with OFPF (0.05 mmol). The resulting yellow solution was examined by  $^1\text{H}$  and  $^{19}\text{F}$  NMR spectra.

#### 4.13. Ethylene polymerization reactions (Table 4, runs 1–5)

##### 4.13.1. Preparation of the catalytic precursor

The zirconium derivative [*rac*-ethylene-bis( $\eta^5$ -4,5,6,7-tetrahydroindenyl)]dichloridezirconium(IV) (0.063 g, 0.15 mmol) was dissolved in dry toluene (140 mL) and stirred for 30 min at room temperature until a yellow solution was obtained. By operating at ca.  $-10^\circ\text{C}$ , an equimolar solution of the perfluorofluorenyl anion was added and the resulting solution was used for the ethylene polymerization experiments. Only traces of polyethylenewere obtained in the absence of co-catalyst.

##### 4.13.2. Polymerization experiments

A 250 mL glass reactor was charged with dry toluene (ca. 150 mL), TIBA (0.45 mmol) and 1.5 mL of the solution obtained as described above ( $\text{Zr} = 0.0015$  mmol), pressurized with 0.5 atm of ethylene. After 60 min stirring at  $25^\circ\text{C}$  with ethylene being fed in order to maintain a constant pressure, gases were vented and methanol containing a small amount of aqueous HCl was added to quench the polymerization. The polymer was filtered, washed with methanol and then dried in vacuo at ca.  $40^\circ\text{C}$  for about 8 h. Details of the polymerization runs are reported in Table 4.

#### 4.14. Polymerization experiments with ZRAL, Table 4, runs 6–10

Toluene (500 mL) containing 0.75 mmol of tri-isobutylaluminum (TIBAL) were charged into a 1 L stainless-steel autoclave. After thermostating at  $50^\circ\text{C}$ , a toluene solution (10 mL) containing ZRAL (0.0025 mmol) and OFPF (0.0025 mmol) was introduced. The reactor was pressurized (8 atm) with ethylene and the mixture stirred for 30 min, ethylene being in order to keep a constant pressure in the reactor. The reactor was then depressurized and 5 mL of methanol were introduced. The polymer was recovered by addition of methanol (1 L, acidified with hydrochloric acid), filtration and drying in vacuo at  $40^\circ\text{C}$  for 8 h. Polyethylene (50 g) was obtained [ $M_n = 95000$ ;  $MW = 200000$ ;  $MWD = 2.1$ ].

Ethylene/propylene co-polymerizations (runs 7–10) were performed similarly by pressurizing the reactor with an equimolar mixture of ethylene and propylene.

The NMR experiment under 5 atm of ethylene pressure was performed by recording spectra at fixed times of a  $\text{C}_6\text{D}_6$  solution of OFPF and ZRAL introduced into a sapphire tube.

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#### Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2005.07.105.

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