Highly fluorous zirconocene(IV) complexes and their catalytic applications in the polymerization of ethylene

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ABSTRACT

The catalytic activities of the highly fluorous systems formed by the zirconocene(IV) complexes [Zr{η^5-C$_5$H$_4$SiMe$_2$C$_2$H$_4$R$_F$}$_2$Cl$_2$] (R$_F$ = C$_6$F$_{13}$ (**4a**), C$_{10}$F$_{21}$ (**4b**)) or [Zr-{η^5-C$_5$H$_3$(SiMe$_2$C$_2$H$_4$C$_6$F$_{13}$)$_2$}$_2$Cl$_2$] (**5a**) and MMAO in toluene have been studied and compared with analogous nonfluorous systems generated from [Zr{η^5-C$_5$H$_4$SiMe$_3$}$_2$Cl$_2$] and [Zr{η^5-C$_5$H$_5$}$_2$Cl$_2$]. Although less active than the reference systems, the fluorous catalysts are stable over prolonged polymerization times, giving rise to polymers with similar molecular weights to those obtained with [Zr{η^5-C$_5$H$_4$SiMe$_3$}$_2$Cl$_2$].

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1. Introduction

Group 4 metallocenes, especially zirconocenes, constitute a fundamental contribution to the development of olefin polymerization catalysis, since their homogeneous and single-site nature render them highly active and selective for this purpose [1–6]. By tailoring of the environment of the metal center, polymer properties such as the molecular weight, molecular weight distribution, stereochemistry, comonomer incorporation and branching can be successfully controlled, giving access to a range of new polymeric materials [7–10].

Traditionally, research in this area has focused on catalyst design directed to improve catalyst performance and to gain control over the structure and properties of the resultant polymers [11–15]. In recent years, the development of novel approaches for facile catalyst recycling has become one of the most challenging goals in homogeneous transition metal catalysis [16]. In this regard, the use of fluorous biphase systems (FBS), which exploits the temperature-dependent miscibilities of organic and fluorous solvents, has emerged as one of the most promising methods for catalyst recovery that is especially suitable for water sensitive catalyst systems [17–22]. Furthermore, the concept of fluorous catalysis without fluorous solvent has also been recently introduced, which is based on the temperature-dependent solubility of solid fluorous catalyst in a nonfluorinated solvent [23,24]. Catalysts can be made fluorous phase soluble by attaching fluorocarbon moieties to ligands. The most effective fluorocarbon moieties are linear or branched perfluoroalkyl chains with high carbon number, usually called fluorous ponytails [25–28]. These ligands have been previously introduced in group 4 metallocenes. Thus, a series of zirconium(IV) complexes of the type [Zr{η^5-C$_5$H$_4$SiMe$_{3-n}$(R$_F$)$_n$}$_2$Cl$_2$] (R$_F$ = CH$_2$CH$_2$C$_6$F$_{13}$, C$_8$F$_{17}$; CH$_2$C$_6$F$_5$) were described [29–31]. These complexes possess one to three fluorous alkyl or aryl groups attached to each cyclopentadienyl ligand through a silicon atom. Mono- and bis(η^5-cyclopentadienyl)titanium(IV) complexes containing one or two (perfluorooctyl)ethyldimethylsilyl groups were reported by Čermák et al. [32,33].

In some cases, an insulating alkyl group was inserted between the Si atom and the perfluorinated chains in order to decrease the strong electron-withdrawing effects of the latter. Studies on the olefin polymerization activity of these complexes upon treatment with MAO in organic and FBS phases were carried out. A marked influence of the fluorous group and the alkyl spacer has been observed, with the catalytic activity and molecular weights of the resulting polymers decreasing when the fluorinated substituents were directly attached to silicon. Accordingly, the fluorinated

zirconocenes gave the best results in polymerization when an ethylene spacer was used [29]. Other interesting observations were the increased stability and productivity over time that characterizes the fluorous zirconocene systems. This phenomenon might be indicative of a lower degree of occlusion of the catalyst during the polymerization process, favored by phase segregation of the fluorous metallocene moiety from the growing polymer matrix.

Following this work on fluorous zirconocenes we were interested in increasing their fluorine content by preparing derivatives that bear a longer fluorous tail or more than one fluorous silyl substituent, in order to study their effects in olefin polymerization.

2. Results and discussion

### 2.1. Synthesis of the fluorinated dichlorozirconocenes 4b and 5a

The target complexes were synthesized following the methodology previously applied for the fluorous compound Zr{η^5-$C_5H_4(SiMe_2C_2H_4C_6F_{13})$}$_2Cl_2$ (4a) [29]. The latter was also prepared for comparative purposes (Scheme 1).

The required precursors, fluorous chlorosilanes 1a and 1b, were prepared by catalytic hydrosilylation of 1,1,2-trihydroperfluorooctene for 1a, and 1,1,2-trihydroperfluorododecene for 1b [34]. The fluorous monosilyl-substituted cyclopentadienes 2a and 2b were synthesized by addition of freshly prepared LiCp ($Cp = C_5H_5$) to a thf solution of the suitable chlorosilane (1a and 1b, respectively). Compound 2b was obtained in 68% yield after distillation as a light yellow oil, which consists of a mixture of 1-, 2- and 5-silyl isomers, the last being the major (70%), as deduced from the comparison of the ^1H NMR spectrum of the mixture with literature values for related compounds [35]. Thus, the ^1H NMR spectrum of 2b exhibits an intense singlet at δ 0.04 ppm and a broad resonance at δ 3.42 ppm, that can be assigned respectively to the SiMe$_2$ group and the H atom attached to the sp^3 carbon of the 5-silyl isomer. Signals of the SiMe$_2$ groups of the 1- and 2-isomers are somewhat deshielded (δ 0.22 ppm) because they are directly bound to a sp^2 carbon, whereas the corresponding CH$_2$ protons resonate at δ 3.06 ppm. Lithiation of the monosilyl-substituted cyclopentadiene 2a and subsequent reaction with 1a afforded an isomeric mixture of disilyl-substituted cyclopentadienes 3a in the

form of a light yellow oil in 76 % yield. Disubstituted cyclopentadienes like 3a can exist in seven different isomers that interconvert through proto- and metallotropic migrations (Chart 1) [32,36]. Detection of all of the individual isomers at room temperature by ^1H NMR spectroscopy was not possible due to the overlapping SiMe$_2$ signals and broadening of the resonances corresponding to the aliphatic protons of the ring. In the ^1H NMR spectrum of isomeric mixture 3a, three main sets of signals are present in an approximately 47:31:22 ratio at room temperature corresponding to the SiMe$_2$ groups (singlets) and the CH$_2$Si groups (multiplets). The set of highest intensity corresponds to the 5,5-isomer (isomer a in Chart 1), which is characterized by its SiMe$_2$ and CH$_2$Si resonances at δ 0.23 and 0.50 ppm, respectively. Comparison with the values found in the literature for related compounds [37] suggests that the second most intense set of signals could correspond to two isomers (set b, Chart 1), whereas the set of signals of lowest intensity is due to four isomers (set c, Chart 1). The most characteristic resonances of set b, those due to the protons in the 5 position, appear at δ 3.60 ppm, while the methylene protons in the same position for set c give rise to two multiplets at δ 3.09 and 3.12 ppm. Considering that the product obtained from the deprotonation and complexation of isomeric compounds 3a (complex 5a, Scheme 1) consists exclusively of the 1,3-disubstituted isomer, it seems reasonable to assume that the major component of mixture b is isomer 2,5-. For the same reason, we favor isomers 1,3- or 1,4- as the major components of mixture c, rather than 1,2- or 2,3-isomers.

The new fluorous zirconocene(IV) dichlorides 4b and 5a were prepared by lithiation of the corresponding silylcyclopentadienes 2b and 3a, followed by reaction with ZrCl$_4$ (Scheme 1). Complexes 4b and 5a were obtained as white, air-stable, crystalline solids in moderate yields (42 and 30%, respectively) after recrystallization. NMR data for 4b are unexceptional and confirm the proposed molecular structure. The NMR spectra of complex 5a displayed diastereotopic SiMe groups due to the prochirality of the 1,3-substituted Cp–Zr moiety.

Complexes 4b and 5a displayed higher solubility in hydrocarbon solvents than the previously reported perfluoroalkyl dichlorotitanocenes [32]. However, when compared with the monosilyl-substituted derivative 4a, we observed that the introduction of

a: R$_F$ = (CH$_2$)$_2$C$_6$F$_{13}$
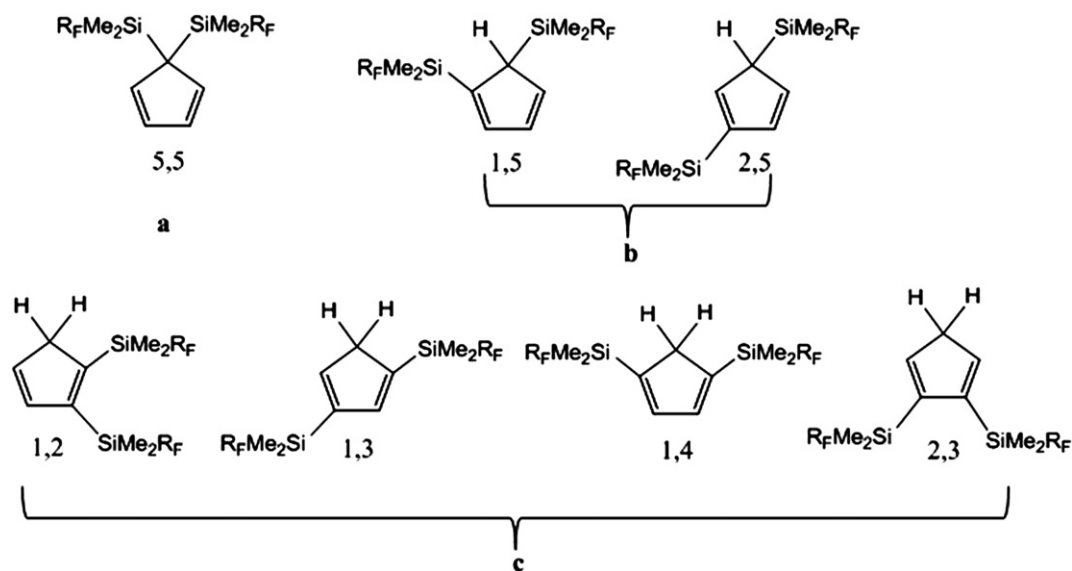b: R$_F$ = (CH$_2$)$_2$C$_{10}$F$_{21}$
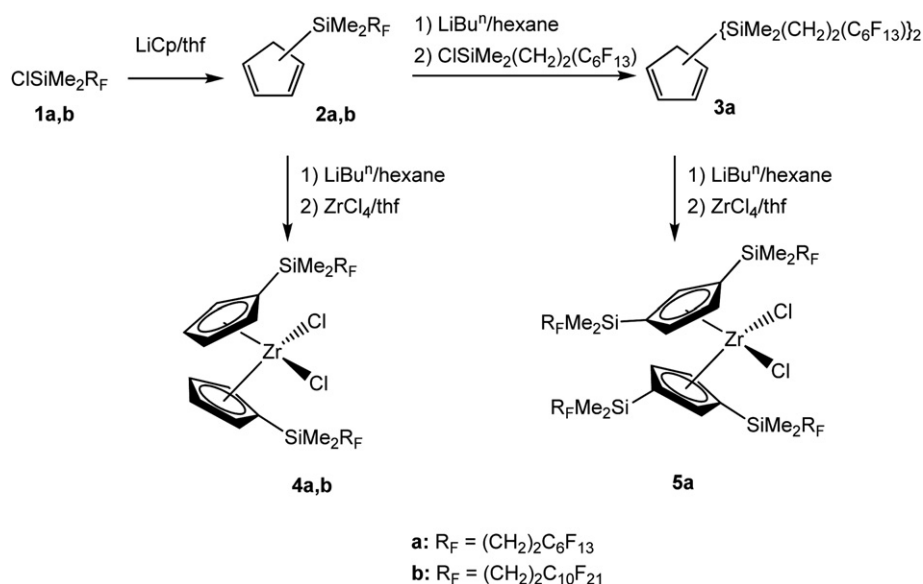
Scheme 1.

Chart 1. Possible isomers of compound **3a**.

a second ponytail per cyclopentadienyl ring in **5a** did not increase the solubility of the complex. Thus, both complexes **4a** and **5a** were slightly soluble in hexane, pentane or benzene, showed medium solubility in chloroform and dichloromethane and were soluble in thf. Complex **4b**, bearing the longest perfluoroalkyl chain, was less soluble in hydrocarbon solvents, being only slightly soluble in hexane, pentane, benzene, dichloromethane or thf and showing medium solubility in chloroform. Whereas complex **4a** displayed modest solubility in perfluorohexane (FC-72), complexes **4b** and **5a** were virtually insoluble in this solvent. However, they had moderate solubility in a mixture C_6D_6/C_6F_6 1:1, **5a** at room temperature and **4b** at 55 °C.

2.2. Crystal structure of 5a

Crystals of **5a** suitable for X-ray diffraction were obtained by recrystallization from dichloromethane. The asymmetric unit for **5a** contains half a molecule, the other half being generated by a binary crystallographic axis. Two independent molecules exhibiting no significant differences are found in the unit cell. An ORTEP representation of one of them is shown in Fig. 1. The compound exhibits a bent-metallocene structure, with a pseudo-tetrahedral ligand arrangement around the Zr atom and the Cp ligands slightly
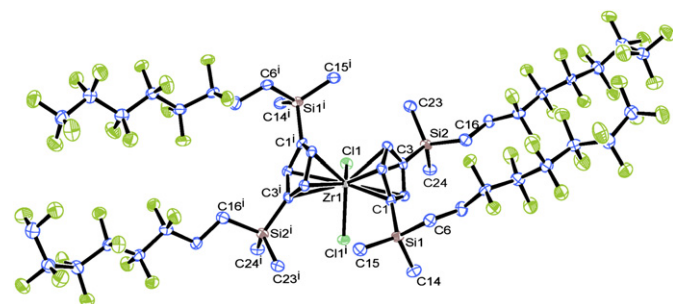
asymmetrically η^5-bonded to the latter (the Zr–C distances range from 2.490 to 2.562 Å). As found in the complexes $Zr\{\eta^5\text{-}C_5H_4(SiMe_3)_2\}_2X_2$ (X = F, Cl, Br, I) and in the parent $Zr(\eta^5\text{-}C_5H_5)_2Cl_2$ [38,39], the two Cp rings are in a staggered conformation. The Zr-centroid distance in **5a** (2.21 Å) is similar to that of the latter compounds and the monosilyl-substituted derivatives **4a** [29] and $Zr(\eta^5\text{-}C_5H_4Si-Me_3)_2Cl_2$ [38]. The fluorinated alkyl chains are radiating away from the $ZrCl_2$ part of the molecule at close to perpendicular angles (C6–Si1–C1–C2 = 101.4(3)°; C16–Si2–C3–C4 = 81.6(4)°). This disposition places both methyl groups of each $SiMe_2CH_2CH_2R_F$ group outside of the C_5 ligand plane (C14–Si1–C1–C2 = −15.9(4)°, C15–Si1–C1–C2 = −142.0(3)°, C23–Si2–C3–C4 = −34.5(4)°, C24–Si2–C3–C4 = 160.4(3)°) on the side of the Zr atom. This is in contrast to what is found for the complexes $Zr(\eta^5\text{-}C_5H_4SiMe_3)_2Cl_2$, $Zr\{\eta^5\text{-}C_5H_4(SiMe_3)_2\}_2X_2$ and **4a**, where one of the methyl groups of each $SiMe_3$ group is lying pseudo-coplanar to the ligand C_5 plane. This distribution of the methyl groups in **5a** causes the centroid–Zr–centroid angle to be the smallest (127.9°) among the former compounds (129.6° and 130.8° in **4a** and $Zr\{\eta^5\text{-}C_5H_4(Si-Me_3)_2\}_2Cl_2$, respectively), in order to minimize steric repulsion between the methyl and the chloride ligands. The Cl–Zr–Cl′ angle of 97.35(5)° is similar to that of the catalytically active $Zr(\eta^5\text{-}C_5H_5)_2Cl_2$ (97°) and complex **4a** (96.50(3)°). As previously found for the related titanocene derivatives [32] and a fluorous rhodium diphosphine complex [40], the fluoroalkyl chains of neighboring molecules line up, thus creating separate domains that contain either fluoroalkyl chains or zirconocene units (Fig. 2).

2.3. Polymerization experiments

Previous studies carried out on the polymerization of zirconocene(IV) dichlorides substituted with one fluorous silyl group per cyclopentadienyl ring showed that they form active ethylene polymerization catalysts when reacted with an excess of methylaluminoxane (MAO, Al/Zr = 500) in toluene [29]. Although their activity is lower than that of the nonfluorous reference system [Zr(η^5-C_5H_4SiMe_3)_2Cl_2] under the same conditions, these fluorous zirconocene systems display increased robustness and consequently increased productivity over prolonged polymerization times. Ethylene polymerization experiments were carried out using

Fig. 1. ORTEP view of compound **5a**. Selected bond distances (Å) and angles (°): Zr(1)–Cl(1) = 2.4558(10); Zr(1)–Cg = 2.209; Cl(1)–Zr(1)–Cl(1) = 97.35(5); Cg–Zr(1)–Cg = 127.89. Si(1)–C(1), 1.881(4); Si(2)–C(3), 1.871(4); Cl(1)–Zr(1)–Cl(1) = 97.35(5); Cg–Zr(1)–Cg = 127.89; C(6)–Si(1)–C(1)–C(5), −57.0(4); C(6)–Si(1)–C(1)–C(2), 101.4(3); C(16)–Si(2)–C(3)–C(2), −75.4 (4); C(16)–Si(2)–C(3)–C(4), 81.6(4).
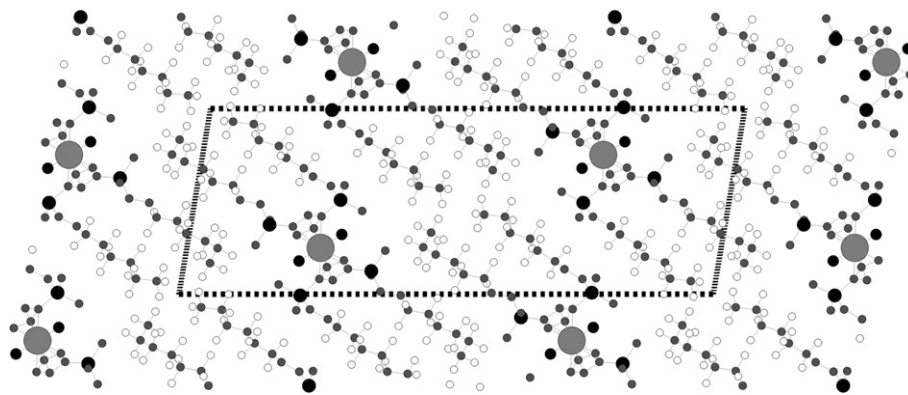
Fig. 2. View of the crystallographic packing from the *b*-axis direction.

the new compounds **4b** and **5a** as precatalysts, to study the effect of introducing higher fluorine content.

In order to tune the polymerization conditions and have reference data for known catalysts, we have studied two reference complexes, $ZrCp_2Cl_2$ and $Zr(CpSiMe_3)_2Cl_2$. Based on preliminary polymerization tests, we decided to use the following experimental conditions: toluene (150 mL), $T = 30\,°C$, 2.2 μmoles of the Zr complex, cocatalyst (MMAO): Al/Zr = 900. The reactions were performed in a glass reactor under 3 bar of ethylene. The catalyst was suspended or dissolved in the solvent, and the mixture was saturated with ethylene at the working temperature. MMAO was added with a syringe, and the ethylene consumption was continuously monitored. We found that using the silylated precatalyst $Zr(CpSiMe_3)_2Cl_2$ as a reference was difficult under these conditions due to its very high activity. After 1 min, stirring became hindered due to precipitation of the polymer. The activity measured under these conditions was ca. $15.2 \cdot 10^3$ kg of PE $mol^{-1}\,bar^{-1}\,h^{-1}$, corresponding to a yield of polyethylene of 1.67 g. The high polymerization activity and the resulting temperature variation caused the reproducibility of the experiments to be too poor to allow a comparison of the catalytic activities and the molecular weights of the polymer obtained. More accurate data were gathered in the case of the complex $ZrCp_2Cl_2$, which was an order of magnitude less active. Table 1 summarizes the results obtained from independent experiments, expressed as yield of polyethylene and total measured activity in each case. Although the fluorous catalysts showed lower activities than the nonfluorous systems, they remained active for longer periods of time, resulting in higher productivity. Thus, the amount of polyethylene obtained when using precatalysts **4a**, **4b** and **5a** is comparable to that obtained with $ZrCp_2Cl_2$ and higher than that for $Zr(CpSiMe_3)_2Cl_2$.

More accurate comparison of the activity profiles of the whole series of complexes can be made from the instantaneous catalytic activity curves, which are obtained from ethylene consumption data. Fig. 3 compares the instantaneous activity curves obtained for some

of the experiments run with $ZrCp_2Cl_2$, **4a**, **4b** and **5a**. As can be ascertained from Fig. 3, the catalyst system based on the nonfluorous complex underwent rapid activation, attaining an activity maximum after 4 min, but its activity dropped to nearly zero after ca. 30 min. On the contrary, the fluorous catalysts, although only moderately active, are very stable judged by the corresponding activity curves, which show that the activity is maintained for longer periods of time. In a separate experiment with complex **5a**, where ethylene consumption was monitored for 7 h, the activity reached a flat maximum at ca. 1.7 h, and then started to decay slowly. After 7 h, the catalyst kept ca. 60% of the activity recorded at $t = 1.7$ h.

We found some reproducibility problems that we believe are connected with the low solubility of the complexes. These problems were especially severe in the case of $Zr(\eta^5\text{-}C_5H_4SiMe_2C_2H_4C_{10}F_{21})_2Cl_2$ (**4b**), which showed a somewhat erratic behavior. Since we observed that activity of these compounds tends to increase slowly with time, it seems likely that the activation of the precatalysts with MMAO is hindered by their insolubility. In spite of this reproducibility issue, it can be concluded that the activity drops slightly when the fluorine content is increased (Table 1, entries 3 and 4 vs entry 2; Fig. 3). Additionally, the increased half-life time of complex **5a** supports our previous assumption that occlusion of the active site in the precipitated polyethylene becomes less favored for the fluorous complexes compared to nonfluorous precatalysts, at least when the polymerization is performed in nonfluorous solvents and compared to reference compound $Zr(CpSiMe_3)_2Cl_2$.

Table 1
Polymerization activities.[a]

Entry	Precatalyst	PE yield, g (activity)[b]			
		$t = 10$ min	$t = 30$ min	$t = 60$ min	$t = 420$ min
1	$ZrCp_2Cl_2$	3.20 (2907)	3.94 (1194)		
2	**4a**			4.95 (749)	
3	**4b**			3.46 (524)	
4	**5a**			2.29 (346)	4.05 (83)

[a] Polymerization conditions: toluene (150 mL), $T = 30\,°C$, ethylene pressure = 3 bar, 2.2 μmoles of the Zr complex, cocatalyst (MMAO): Al/Zr = 900.
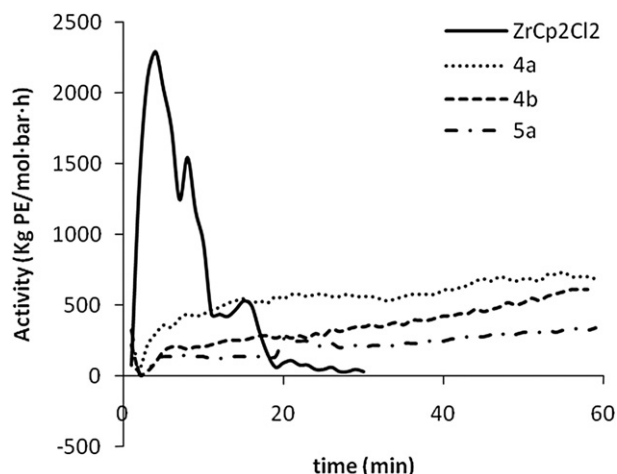[b] kg of PE/mol Zr bar h.

Fig. 3. Catalytic activity curves for complexes $ZrCp_2Cl_2$, **4a**, **4b** and **5a**.

Table 2
GPC and DSC data.

Entry	Precatalyst	Reaction time (min)	M_n (10^3 g mol^{-1})	M_w/M_n	T_{m2} (°C)[a]	ΔH_2 (J g^{-1})[b]
1	ZrCp$_2$Cl$_2$	10	133	3.3	138.1	66.7
2	ZrCp$_2$Cl$_2$	30	136	2.8	140.0	150.4
3	Zr(CpSiMe$_3$)$_2$Cl$_2$	60	261	4.8	138.6	140.4
4	**4a**	60	256	4.2	143.5	126.9
5	**4b**	60	264	4.3	139.6	133.3
6	**5a**	60	219	4.4	141.8	132.1
7	**5a**	420	222	5.1	139.3	121.0

[a] Melting temperature determined by DSC (second heating run).
[b] Enthalpy of melting determined by DSC (second heating run).

The polymers obtained with the reference precatalysts and complexes **4a**, **4b** and **5a** were subjected to GPC analyses. The number-averaged molecular weights (M_n) thus obtained were within the range reported for zirconocene precatalysts [11]. Unimodal distributions were obtained for all the samples, with high polydispersities (PDI $= M_w/M_n$), which values ranged from 2.8 to 5.1. This is not surprising considering the slow initiation and the long polymerization times used, which cause the effects of heterogenization of the reaction mixtures due to precipitation of the polymer and local temperature fluctuations to be more pronounced. This effect is clearly shown in the case of complex **5a**. In this case, PDI underwent an increase from 4.4 to 5.1 when the polymerization time was extended from 1 to 7 h.

In contrast to what was found for the pentafluorophenyl-substituted zirconocenes [41], the molecular weight of the polymers obtained with the fluorous precatalysts is not significantly affected by the use of more electron-withdrawing substituents. Indeed, complexes **4a**, **4b** and **5a** give rise to polymers with M_n that are essentially identical with that of Zr(CpSiMe$_3$)$_2$Cl$_2$ and higher than that of the parent ZrCp$_2$Cl$_2$.

DSC analyses of the polymers (Table 2) confirmed the presence of long ethylene sequences that crystallize with a behavior similar to those of HDPE samples. The associated enthalpy values are characteristic of polyethylene with about 50% of crystallinity (except for polymer in entry 1 that is lower). For two samples (entries 2 and 5) a second crystallization peak has been observed during the cooling due to a small fraction characterized by a larger number of structural defects or much lower molecular weight.

3. Conclusions

New highly fluorous zirconocene(IV) dichloride complexes have been prepared, bearing one (**4b**) or two (**5a**) fluorous silyl groups per cyclopentadienyl ring. They are only moderately soluble in hydrocarbons and even less soluble in perfluorocarbons, with the disilyl-substituted derivative being more soluble than the mono-substituted one. The fluorous complexes form active catalysts in ethylene polymerization upon reaction with methylaluminoxane (Al/Zr = 900). Although their activity is lower than that of the nonfluorous reference precatalysts Zr(η^5-C$_5$H$_4$SiMe$_3$)$_2$Cl$_2$ and ZrCp$_2$Cl$_2$, they exhibit increased robustness over the latter compounds, which supports previously reported results regarding the fluorous system **4a**, and may be indicative of phase segregation between the fluorinated catalyst system and the precipitating polymer during the polymerization process. Contrary to previous findings, the molecular weights (M_n) of the polyethylene obtained with complexes **4a**, **4b** and **5a** are similar to that obtained when using a Zr(CpSiMe$_3$)$_2$Cl$_2$, showing that the molecular weights are little affected by the introduction of the electron-withdrawing perfluoroalkyl substituents.

4. Experimental

4.1. General considerations

All experiments were carried out under dry nitrogen using standard Schlenk techniques. Solvents were dried and distilled prior to use following literature procedures. Elemental analyses were performed by Dornis und Kolbe, Mikroanalytisches Laboratorium (Mülheim, Germany). ^{1}H (300.1 MHz) and ^{13}C (75.5 MHz) NMR spectra were recorded on a Varian INOVA 300 and Bruker DRX 300 spectrometer at 25 °C, unless otherwise stated, and were referenced internally (^{1}H, ^{13}C) to residual solvent resonances. CpLi was prepared by thermal cracking of dicyclopentadiene and collection of the cyclopentadiene distillate in a solution of LiBu^n (1.6 mol L^{-1} in hexane). Chlorodimethyl(1H,1H,2H,2H-perfluorooctyl)silane (**1a**), chlorodimethyl(1H,1H,2H,2H-perfluorododecyl)silane (**1b**) [34,42] and [dimethyl(1H,1H,2H,2H-perfluoroctyl)silyl]cyclopentadiene (**2a**) [29] were prepared by reported methods. All other reagents were purchased from commercial sources and used without further purification. Polymer molecular weights were obtained by size exclusion chromatography (SEC) by using a Waters Alliance GPCV 2000 Series System apparatus equipped with three Waters Styragel HT 6E columns (MW 5000–10,000,000) and one Waters Styragel HT 3 (MW 500–30,000) column, with an average particle size of 10 mm, a differential refractive index (DRI) and a differential viscometer as detectors. Polymer solutions were prepared with amounts of 2.5–3 mg of polymer in 4 mL of 1,2,4-trichlorobenzene (TCB) containing a small amount of antioxidant (BHT) to prevent degradation and eluted at 145 °C, 1 mL/min flow rate. The calibration was made with narrow MWD polystyrene standards and calculations were carried out using the Millennium software package. Melting (T_m), crystallization (T_c) temperatures and thermal transition-associated enthalpy values of the polymer samples were determined by differential scanning calorimetry (DSC) with a Perkin–Elmer DSC-7 instrument equipped with a CCA-7 cooling device and referenced to the melting transitions of indium and n-heptane (156.1 and −90.61 °C, respectively). The polymer sample mass was 10 mg and aluminum cups were used. Any difference in thermal history of the polymer samples was eliminated by a first heating cycle of the specimen at a heating rate of 20 °C min^{-1} to 200 °C, cooling at 20 °C min^{-1} to 0 °C, and then recording the second scan from 0 °C to 200 °C.

4.2. [Dimethyl(1H,1H,2H,2H-perfluorododecyl)silyl]cyclopentadiene (2b)

Freshly distilled cyclopentadiene (0.98 mL, 12 mmol) was added to a cooled (0 °C) solution of LiBu^n (12.6 mmol) in hexane (50 mL). After 3 h of stirring, the solvent was removed in vacuo and the resulting white solid was washed with pentane. The LiCp thus obtained was dissolved in 50 mL of thf at −78 °C and added to a solution of ClSiMe$_2$C$_2$H$_4$C$_{10}$F$_{21}$ (**1b**) (7.31 g, 10.84 mmol) in thf (20 mL) at 0 °C. The reaction mixture was allowed to warm to ambient temperature and stirred overnight. Volatiles were removed under vacuum and the residue was extracted with pentane. The residue was evaporated to dryness to afford an orange oil. The product was Kugelrohr distilled (140 °C, 1.0 mbar) to give a light yellow oil (4.96 g, 68% yield). MS: m/z 670 (calcd. 670.1). Anal. Calcd. for C$_{19}$H$_{15}$F$_{21}$Si: C, 34.04; H, 2.26; F, 59.51; Si, 4.19. Found: C, 34.14; H, 2.18; F, 59.74; Si, 4.29. The ^{1}H NMR spectrum was complicated by the presence of 1- and 2-silyl isomers (minor) next to the 5-silyl isomer (major, 70%). ^{1}H NMR (CDCl$_3$) δ 0.04 (s, SiMe$_2$, 5-(R$_F$SiMe$_2$)C$_5$H$_5$ isomer), 0.22 (s, SiMe$_2$, 1- and 2-(R$_F$SiMe$_2$)C$_5$H$_5$ isomers), 0.71 (m, CH$_2$–Si, 5-(R$_F$SiMe$_2$)C$_5$H$_5$ isomer), 0.97 (m, CH$_2$Si, 1- and 2-(R$_F$SiMe$_2$)C$_5$H$_5$ isomers), 2.01 (m, CH$_2$–CF$_2$, all isomers),

3.06 (m, 5-CH$_2$ of 1- and 2-(R$_F$SiMe$_2$)C$_5$H$_5$ isomers), 3.42 (bs, CH of 5-(R$_F$SiMe$_2$)C$_5$H$_5$ isomer), 6.55, 6.65, 6.73, 6.89 (olefinic H, all isomers); ^{13}C{^{1}H} NMR (CDCl$_3$) δ −4.0, −3.5, −3.1, 4.3, 5.5 (CH$_3$, CH$_2$−Si, all isomers), 26.2 (t, $^2J_{CF}$ = 23.4 Hz, CH$_2$CF$_2$), 50.7 (bs, 5-CH of 5-(R$_F$SiMe$_2$)C$_5$H$_5$ isomer), 111.1, 119.2 (CF$_2$), 131.1, 132.8, 133.0, 138.5, 143.3 (olefinic C, all isomers).

4.3. Bis[dimethyl(1H,1H,2H,2H-perfluoroctyl)silyl]cyclopentadiene (3a)

CpSiMe$_2$C$_2$H$_4$C$_6$F$_{13}$ (2a) (1.31 g, 2.79 mmol) was added to a cooled (0 °C) solution of LiBu^n (2.93 mmol) in hexane (40 mL), with formation of a white suspension. The reaction mixture was stirred for 3 h at ambient temperature. After removal of the solvent in vacuo, the solid was washed with pentane and dried under vacuum. The Li[CpSiMe$_2$C$_2$H$_4$C$_6$F$_{13}$] was dissolved in 30 mL of pre-cooled (−78 °C) thf and the solution was added by cannula to a solution of 1a (1.16 g, 2.63 mmol) in thf (20 mL) at 0 °C. After stirring for 48 h, the solvent was removed in vacuo and the product was extracted with pentane (50 mL). The filtrate was evaporated to dryness to give an orange oil, which was Kugelrohr distilled (130 °C, 0.1 mbar) to give a light yellow oil (1.75 g, 76% yield). MS: m/z 874 (calcd. 874.1). Anal. Calcd. for C$_{25}$H$_{24}$F$_{26}$Si$_2$: C, 34.33; H, 2.77; F, 56.48; Si, 6.42. Found: C, 34.17; H, 2.84; F, 56.63; Si, 6.50. The ^{1}H- and ^{13}C-NMR spectra display signals due to isomers a (47%), b (31%) and c (22%). Assignment of the ^{1}H-NMR resonances was done by comparison with literature [34]; ^{1}H NMR (CDCl$_3$) δ 0.03 (s, SiMe$_2$, isomers c), 0.12 (s, SiMe$_2$, isomer a), 0.23 (s, SiMe$_2$, isomers b), 0.50 (m, CH$_2$−Si, isomer a), 0.68 (m, CH$_2$−Si, isomers c), 0.91 (m, CH$_2$−Si, isomers b), 1.93 (m, CH$_2$−CF$_2$, all isomers), 3.09, 3.12 (m, 5-CH$_2$ of isomers c), 3.60 (bs, 5-CH of isomers b), 6.55 (d, $^3J_{HH}$ = 4.6 Hz, α-H of isomer a), 6.73, 6.87 (bs, olefinic H of isomers b or c), 6.80 (d, $^3J_{HH}$ = 4.6 Hz, β-H of isomer a), 6.92, 6.96 (m, olefinic H of isomers b or c). ^{13}C{^{1}H} NMR (CDCl$_3$) δ −3.8, −3.2, −2.1, 4.0, 4.3, 5.4 (CH$_3$ and CH$_2$−Si of all isomers), 26.3 (m, CH$_2$−CF$_2$), 54.0 (bs, CH of isomer b), 111.2, 115.54, 118.8 (CF$_2$), 132.2, 135.1 (olefinic C of isomer a), 133.4, 143.5 (olefinic C of isomers b and c).

4.4. Bis[dimethyl(1H,1H,2H,2H-Perfluorododecyl)silyl-cyclopentadienyl]zirconium dichloride (4b)

LiBu^n (1.05 mL of a 1.6 mol L^{-1} solution in hexane, 1.68 mmol) was added to a cooled (0 °C) solution of 2b (1.07 g, 1.60 mmol) in hexane. The mixture was stirred for 3 h, solvent was removed and the product was washed with pentane and dried under vacuum. The crude Li[C$_5$H$_5$SiMe$_2$C$_2$H$_4$C$_{10}$F$_{21}$] was dissolved in pre-cooled (−78 °C) thf (100 mL) and was added dropwise over 0.5 h to a cooled (0 °C) solution of ZrCl$_4$ (0.18 g, 0.74 mmol) in thf (100 mL). After 2 days of stirring the solvent was removed in vacuo and the solid residue was extracted with pentane (75 mL). The solvent was evaporated in vacuo and the product was recrystallized from warm toluene (75 mL) to afford a white product (0.46 g, 42% yield). The compound is only slightly soluble in hexane, pentane, benzene, FC-72, dichloromethane or thf. It shows medium solubility in chloroform. Anal. Calcd. for C$_{38}$H$_{28}$Cl$_2$F$_{42}$Si$_2$Zr: C, 30.41; H, 1.88; F, 53.16; Si, 3.74. Found: C, 30.55; H, 1.73; F, 53.08; Si, 3.85. ^{1}H NMR (CDCl$_3$) δ 0.37 (s, 6H, SiMe$_2$), 0.97 (m, 2H, CH$_2$−Si), 2.02 (m, 2H, CH$_2$−CF$_2$), 6.52 (bs, 2H, α-C$_5$H$_4$), 6.65 (bs, 2H, β-C$_5$H$_4$); ^{1}H NMR (C$_6$D$_6$/C$_6$F$_6$ (1:1), 55 °C) δ 0.32 (s, 6H, SiMe$_2$), 0.97 (m, 2H, CH$_2$−Si), 2.05 (m, 2H, CH$_2$−CF$_2$), 6.10 (t, $^3J_{HH}$ = 2.5 Hz, 2H, α-C$_5$H$_4$), 6.41 (t, $^3J_{HH}$ = 2.5 Hz, 2H, β-C$_5$H$_4$); ^{13}C{^{1}H} NMR (C$_6$D$_6$/C$_6$F$_6$ (1:1), 55 °C) δ −4.0 (SiMe$_2$), 6.0 (CH$_2$−Si), 25.5 (t, $^2J_{CF}$ = 23.9 Hz, CH$_2$−CF$_2$), 114.5 (C$_5$H$_4$), 124.3 (ipso-C C$_5$H$_4$), 125.7 (C$_5$H$_4$), C$_{10}$F$_{21}$ signals not observed.

4.5. Bis[bis{dimethyl(1H,1H,2H,2H-perfluoroctyl)silyl}-cyclopentadienyl]zirconium dichloride (5a)

LiBu^n (2.03 mL of a 1.6 mol L^{-1} solution in hexane, 3.25 mmol) was added to a cooled (0 °C) solution of 3a (2.71 g, 3.10 mmol) in hexane. After 3 h of stirring the solvent was removed to give a white solid. The crude Li[C$_5$H$_4$(SiMe$_2$C$_2$H$_4$C$_6$F$_{13}$)$_2$] was dissolved in thf at −78 °C and added drop wise to a cooled (0 °C) solution of ZrCl$_4$ (0.35 g, 1.48 mmol) in thf (40 mL). After stirring for 48 h at room temperature volatiles were removed and the residue was extracted with boiling toluene. Recrystallization from CH$_2$Cl$_2$ (50 mL) gave the product as white needles (0.84 g, 30% yield). The product is only slightly soluble in hexane, pentane or benzene, shows medium solubility in chloroform and dichloromethane and is soluble in thf. Anal. Calcd. for C$_{50}$H$_{46}$Cl$_2$F$_{52}$Si$_4$Zr: C, 31.45; H, 2.43. Found: C, 31.26; H, 2.52. ^{1}H NMR (CDCl$_3$) δ 0.38, 0.41 (s, 12H, diastereotopic SiMe), 0.92 (m, 4H, CH$_2$−Si), 3.82 (m, 4H, CH$_2$−CF$_2$), 6.47 (s, 2H, CH$_{arom}$), 7.03 (s, 1H, CH$_{arom}$); ^{1}H NMR (C$_6$D$_6$/C$_6$F$_6$ 1:1, 400 MHz) δ 0.41, 0.43 (s, 12H, SiMe$_2$), 0.98 (m, 4H, CH$_2$−Si), 2.02 (m, 4H, CH$_2$−CF$_2$), 6.50 (d, 2H, 4- and 5-CH, $^4J_{HH}$ = 1.7 Hz), 7.11 (d, 1H, 2-CH, $^4J_{HH}$ = 1.7 Hz); ^{13}C{^{1}H} NMR (C$_6$D$_6$/C$_6$F$_6$ 1:1) δ −4.4, −4.2 (diastereotopic SiMe), 6.1 (CH$_2$−Si), 25.5 (t, $^2J_{CF}$ = 23.7 Hz, CH$_2$−CF$_2$), 120.1 (C$_5$H$_3$), 142.9 (C$_5$H$_3$), ipso-C's of C$_5$H$_3$ and C$_8$F$_{17}$ signals not observed.

4.6. Ethylene polymerization

In a typical polymerization experiment, a solution of the pre-catalyst (2 μmol) in 150 mL of toluene was transferred under a nitrogen atmosphere to a Fischer−Porter reactor equipped with a septum-capped port. The reactor was flushed three times with ethylene, and then allowed to equilibrate with this gas at the working conditions (3 bar, 30 °C), using a thermostated water bath. Then a solution of MMAO in toluene was added with a syringe counter pressure through a septum-capped port. Ethylene consumption was continuously monitored. At the specified reaction time, the gas inlet was closed, the reactor vented and the reaction mixture poured into ca. 500 mL of methanol acidified with HCl, in order to precipitate the polymer. The precipitate was separated by filtration and dried under vacuum until constant weight.

4.7. Crystal data for 5a

C$_{50}$H$_{46}$Cl$_2$F$_{52}$ Si$_4$ Zr, M_r = 1909.35, crystal size 0.40 × 0.06 × 0.05 mm^3, crystallized from CH$_2$Cl$_2$, monoclinic, space group P2/n, a = 13.7513(11) Å, b = 6.6494(5) Å, c = 39.165(3) Å, β = 99.718(4)°, V = 3529.8(5) Å^3, Z = 2, D_x = 1.796 mg/m^3, μ = 0.473 mm^{-1}, T = 100(2) K. X-ray diffraction data were collected on a Bruker-Nonius X8Apex-II CCD diffractometer, graphite mon-ochromated MoK$_{α1}$ radiation, λ = 0.71073 Å and a Kryoflex low-temperature device. 25552 reflections measured, 9696 unique reflections (R_{int} = 0.0972) which were used in all calculations. Data reduction up to θ = 29.50° by program SAINT. After correction for Lorentz polarisation effects and absorption by multiscan method applied by SADABS [43], the structure was solved by direct methods (SIR-2002) [44] and refined against all F^2 data by full-matrix least-squares techniques (SHELXL97) [45]. The final R1 = 0.0677 [I > 2σ (I)], wR2 = 0.1413 (all data). Good-of-fit on F^2 = 0.988, largest difference peak and hole = 0.686 and −1.082 e Å^{-3} respectively.

Acknowledgments

Appendix A. Supplementary material

CCDC 766405 contains the supplementary crystallographic data for Compound **5a**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac. uk/data_request/cif.

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