

Fluorous Zirconocene(IV) Complexes and Their Olefin Polymerization Activity in Toluene and Fluorous Biphasic Solvent Systems[†]

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The synthesis (**4a–d**) and structure (**4a,c**) of the four crystalline, water-stable, hydrocarbon- and perfluorocarbon (PFC)-soluble fluorine zirconocene(IV) dichloride precatalysts $[\text{Zr}\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_{3-n}(\text{R}_F)_n\}_2\text{Cl}_2]$ ($n = 1$, $\text{R}_F = \text{CH}_2\text{CH}_2\text{C}_6\text{F}_{13}$ (**4a**), C_8F_{17} (**4b**), $\text{CH}_2\text{C}_6\text{F}_5$ (**4c**); $n = 3$, $\text{R}_F = \text{CH}_2\text{C}_6\text{F}_5$ (**4d**)), possessing one to three fluorine alkyl or aryl groups attached to the cyclopentadienyl ligand through a silicon atom and an additional methylene (**4c,d**) or ethylene (**4a**) spacer or no spacer at all (**4b**), are reported. A nonfluorine analogue of **4a**, $[\text{Zr}\{\eta^5\text{-C}_5\text{H}_4\text{-SiMe}_2\text{C}_8\text{H}_{17}\}_2\text{Cl}_2]$ (**4e**), was prepared for comparison, and **4a** was easily converted to its dimethyl derivative $[\text{Zr}\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{CH}_2\text{CH}_2\text{C}_6\text{F}_{13}\}_2\text{Me}_2]$ (**5a**). The ethylene polymerization activities of the zirconocene dichlorides were compared to those of the known bis-(trimethylsilyl)cyclopentadienyl zirconium dichloride $[\text{Zr}\{\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3\}_2\text{Cl}_2]$ (**4f**), in both toluene and fluorine biphasic solvent (FBS) systems. In the case of **4b** a PE with a bimodal molecular weight distribution and a significantly lower molecular weight was obtained. Polymerization data and polymer properties for **4a–d**, compared to data for **4f**, show a marked influence of the fluorine groups and the alkyl spacer (e.g. methylene in **4c** or ethylene in **4a**). FBS conditions result in PE with a higher average molecular weight. Evidence on the nature of the active species formed when these precatalysts were treated with an excess of methylaluminoxane (MAO) is presented.

Introduction

Fluorine phase catalysis using fluorinated catalysts in a fluorine biphasic solvent system (FBS; i.e., a mixture of hydrocarbon and perfluorocarbon—PFC—solvents) is of considerable interest, mainly in relation to catalyst recycling.¹ In addition, PFCs have also received attention because of their unique solvent properties (low polarity, inertness, low dielectric constant, high solubility of gases, low heats of evaporation). They offer advantages in terms of environmental considerations (nontoxic) and, in the case of polymerization reactions, improved properties of the polymers.²

We are here interested in fluorine metallocene based olefin polymerization precatalysts. Olefin polymerization catalysts consisting of group 4 metallocene dichloride precatalysts and methylaluminoxane (MAO) have received significant industrial interest.³ They belong to the most highly active and selective classes of catalysts for α -olefin polymerization, and they offer unique possibilities for controlling polymer structure and properties.⁴ While catalyst recovery is not a major issue in coordination polymerization (low catalyst loading), we reasoned that the fluorine character of the catalyst, optionally supplemented by a fluorine reaction medium (pure PFC solvent or FBS conditions), would affect the polymerization mechanism and could possibly lead to improved physical properties of the polymers produced. Examples of coordination polymerization in PFC solvents are extremely rare,⁵ despite their interesting solvent properties that are related to those of super-

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[†] Dedicated to Professor Jan H. Teuben at the occasion of his retirement and in recognition of his important contributions to the field of early-transition-metal chemistry and α -olefin polymerization catalysis.

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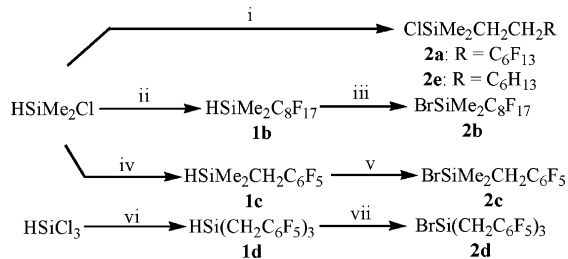
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Scheme 1



Reagents and conditions: i, $\text{RCH}=\text{CH}_2$, $\text{RhCl}(\text{PPh}_3)_3$ (5%), toluene, reflux; ii, $\text{C}_8\text{F}_{17}\text{I}$, LiBu^n , Et_2O ; $-78\text{ }^\circ\text{C}$; iii, Br_2 , CCl_4 , $60\text{ }^\circ\text{C}$; iv, $\text{C}_6\text{F}_5\text{CH}_2\text{Br}$, Mg , Et_2O , $25\text{ }^\circ\text{C}$; v, Br_2 , pentane, $25\text{ }^\circ\text{C}$; vi, $\text{C}_6\text{F}_5\text{CH}_2\text{Br}$, Mg , Et_2O , $25\text{ }^\circ\text{C}$; vii, Br_2 , hexane, $25\text{ }^\circ\text{C}$.

critical CO_2 but available at atmospheric pressure (in contrast to *sc*- CO_2).^{1c,2,6}

Finally, it should be noted that although the cyclopentadienyl group is one of the most ubiquitous ligands in organometallic chemistry, only a few such ligands bearing fluorine or short fluoroalkyl substituents have been reported.⁷ Notably in these complexes, the electronic effect of the fluorous group on the metal center is significant, as it is directly bound to a metal-coordinated carbon atom. We here report on the synthesis (4a–d) and structure (4a,c) of the four crystalline, hydrocarbon- and PFC-soluble fluorous zirconocene(IV) dichlorides $[\text{Zr}\{\eta^5\text{-C}_5\text{H}_4(\text{SiMe}_{3-n}(\text{R}_F)_n)\}_2\text{Cl}_2]$ ($n = 1$, $\text{R}_F = \text{CH}_2\text{CH}_2\text{C}_6\text{F}_{13}$ (4a), C_8F_{17} (4b), $\text{CH}_2\text{C}_6\text{F}_5$ (4c); $n = 3$, $\text{R}_F = \text{CH}_2\text{C}_6\text{F}_5$ (4d)) and some first investigations into their olefin polymerization activity in both conventional and fluorous biphasic systems (FBS) upon treatment with MAO as cocatalyst. Part of this work was previously communicated.⁸ More recently, the synthesis of related titanium compounds was reported⁹ and there has been work by the Gladysz group on (2-(perfluoroalkyl)ethyl)cyclopentadienyl complexes.¹⁰

Results and Discussion

Synthesis of the Fluorous Zirconocene Dichlorides 4a–d and Non-Fluorous 4e. The chosen precursors for the zirconocene dichlorides 4a–e, the fluorous halosilanes 2a–d and nonfluorous 2e, were synthesized in good to quantitative yield (Scheme 1).

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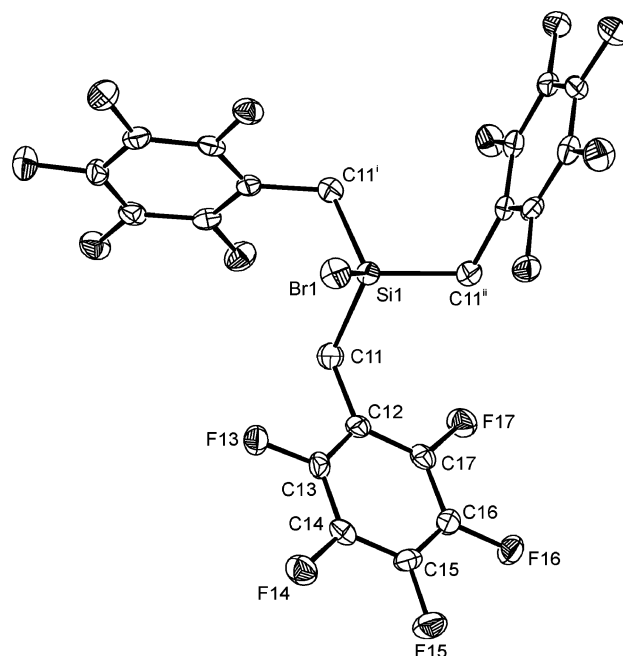
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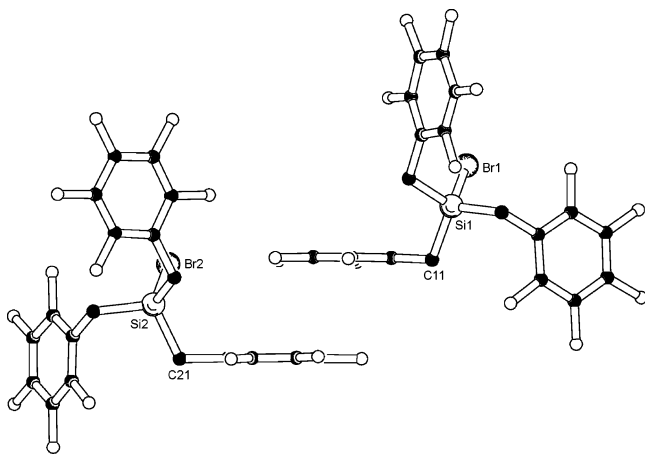
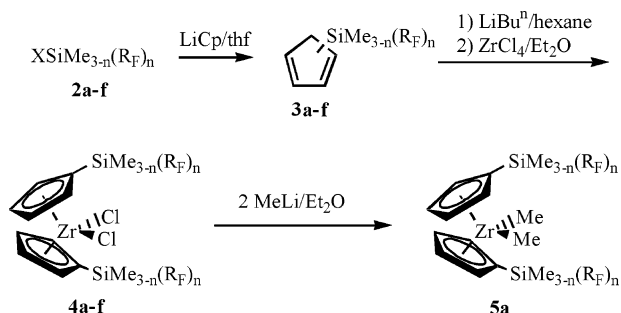


Figure 2. Stacking between the pentafluorophenyl rings of the two independent molecules of **2d**. The rings are nearly parallel with a dihedral angle of 0.02° . The interplanar distance is approximately 3.14 \AA . Because the rings are shifted with respect to each other, the distance between the ring centers is significantly longer ($4.2098(17) \text{ \AA}$). Due to this shift, atom F16 of ring 1 is above the center of ring 2 (distance $\text{F16-Cg02} = 3.121(2) \text{ \AA}$). Atoms F25 and F26 of ring 2 are directly above carbon atoms C17 and C15 of ring 1 ($\text{F25-C17} = 3.158(4) \text{ \AA}$; $\text{F26-C15} = 3.176(4) \text{ \AA}$).

Scheme 2



- a: X = Cl, n = 1, $\text{R}_F = (\text{CH}_2)_2\text{C}_6\text{F}_{13}$
 b: X = Br, n = 1, $\text{R}_F = \text{C}_8\text{F}_{17}$
 c: X = Br, n = 1, $\text{R}_F = \text{CH}_2\text{C}_6\text{F}_5$
 d: X = Br, n = 3, $\text{R}_F = \text{CH}_2\text{C}_6\text{F}_5$
 e: X = Cl, n = 1, $\text{R}_F = \text{C}_8\text{H}_{17}$
 f: X = Cl, n = 0

\AA).¹⁵ Also, the tetrahedral hybridization of the Si atoms with angles of $108.37(10)$ – $110.55(9)^\circ$ is comparable to that in other bromotrialkylsilanes and compounds **4a,c** (vide infra). Interestingly, the pentafluorophenyl rings of the two independent molecules of **2d** are π -stacked but with significant ring slippage (Figure 2).

The target compounds **4a–e** were prepared (Scheme 2) by slight modification of a reported procedure for $[\text{Zr}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Cl}_2]$ (**4f**).¹⁶ Addition of LiCp (Cp = C_5H_5) in THF to **2a–e** gave in good yield the fluorinated silyl-substituted cyclopentadienes **3a–e** as a mixture of the 1-, 2- and 5-silyl isomers (the last being the major species by ca. 80%).¹⁷ Lithiation and reaction with solid ZrCl_4 produced the new fluorinated zirconocene(IV) dichlorides **4a–e** in moderate to good yields as colorless (**4a**), off-white (**4c,d**), or pale yellow (**4b**) air-stable, highly

hydrocarbon-soluble, crystalline solids or as a brown oil (**4e**) with satisfactory analyses and multinuclear ambient-temperature NMR spectra. Complex **4a** was easily converted to its dimethyl derivative $[(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{CH}_2\text{CH}_2\text{C}_6\text{F}_{13})_2\text{ZrMe}_2]$ (**5a**).

Low-temperature NMR spectra (300 MHz) of toluene- d_8 solutions of **4a,c** were recorded from 25 to -80°C (for assignments, see the Experimental Section) and revealed that even at low temperature (-80°C) the fluxional M–Cp rotational processes are still operative and fast on the NMR time scale.¹⁸ The spectra recorded under the same conditions for the precatalyst **4b** (i.e. with the C_8F_{17} tail; see the Experimental Section for assignments) merit more explanations: the α - and β -proton signals, of the monosubstituted-cyclopentadienyl ligand (δ 6.30 and 5.70 at ambient temperature), gradually disappear to the profit of four equal-intensity signals (δ 6.34, 6.15, 5.64, and 5.46 at -80°C); in the meantime, the singlet observed for the SiMe_2 protons (δ 0.61 at ambient temperature) splits into two new signals at δ 0.75 and 0.67 at -80°C , the fluxional M–Cp rotational process becoming slower than the NMR time scale, indicative of either a C_2 - or C_v -symmetric isomer (*rac* or *meso* forms).

Complexes **4a–d** have a much higher hydrocarbon solubility than the previously reported group 4 fluorinated metallocenes $[\text{M}\{\eta^5\text{-C}_5\text{H}_4(\text{C}_6\text{F}_5)_2\text{Cl}_2\}]$ (M = Ti,^{7b} Zr^{7c}). Moreover, in contrast to **4f**, they clearly display, albeit modest, solubility in PFC solvents: e.g., FC-72 (ca. 1 g/L). The partition coefficient P ($P = C_{\text{fluorous phase}}/C_{\text{organic phase}}$, where C is the concentration of the complex in the solvent, i.e. *c*- $\text{C}_6\text{F}_{11}\text{CF}_3$ and toluene, respectively) for complexes **4a–c** reflected a trend similar to that observed in the case of fluorinated phosphines,¹⁹ i.e., a steady increase with the F weight percentage of the molecule (cf. $P_{4c} = 0.09$, wt % F 24.7; $P_{4a} = 0.23$, wt % F 44.9; $P_{4b} = 0.78$, wt % F 51.9); these values indicate a relatively small affinity of the molecules for the fluorinated phase but possibly enough to induce surface activity.²⁰

Crystal Structures of 4a–c. Compounds **4a,c** were successfully subjected to structural characterization by single-crystal X-ray crystallography. The single crystals of **4a,c** contained discrete $[\text{Zr}\{\eta^5\text{-C}_5\text{H}_4(\text{SiMe}_2\text{R}_F)_2\text{Cl}_2\}]$ molecules ($\text{R}_F = \text{CH}_2\text{CH}_2\text{C}_6\text{F}_{13}$ (**4a**) $\text{CH}_2\text{C}_6\text{F}_5$ (**4c**)) (Figures 3 and 4, respectively). Compound **4b** could not be refined satisfactorily, due to significant disorder in the perfluorooctyl groups ($R = 22\%$); hence, the crystallographic data are not reported here. However, we can conclude from this analysis that **4b** also has a regular bent-metallocene structure, similar to that of **4a**. The asymmetric unit for **4c** contained a single molecule, whereas it contained half a molecule in **4a**, the other half being generated by a 2-fold rotation. The stereochemistry around the Zr atom was invariably that found in previously studied bent-sandwich complexes of the type $[\text{ML}_2\text{X}_2]$ (M = Zr, Hf; L = η^5 -cyclopentadienyl or

(18) DSC analysis of crystalline **4a,c** in the solid state, from ambient temperature to the melting point, shows no evidence of polymorphism as one could have expected with such fluxional groups (e.g. $\text{CH}_2\text{C}_6\text{F}_{13}$ as in **4a**).

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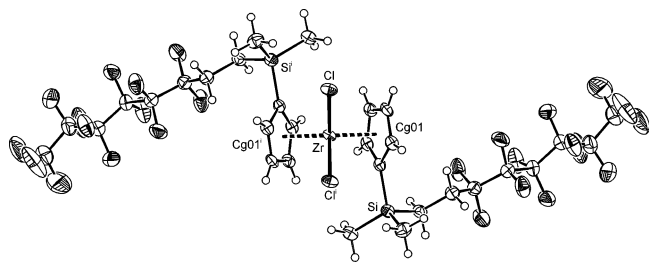


Figure 3. Molecular structure of compound **4a**. Displacement ellipsoids are drawn at the 50% probability level, and H atoms are omitted for clarity. Symmetry operation: (i) $-x, y, 0.5 - z$. Selected bond lengths (Å) and angles (deg): Zr–Cl = 2.4524(7), Zr–Cg01 = 2.1987(12); Cl–Zr–Cl' = 96.50(3), Cg01–Zr–Cg01' = 129.61(5).

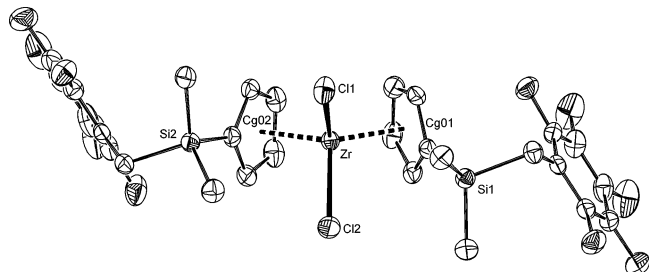


Figure 4. Molecular structure of compound **4c**. Displacement ellipsoids are drawn at the 50% probability level, and H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Zr–Cl1 = 2.4571(6), Zr–Cl2 = 2.4379(6), Zr–Cg01 = 2.2091(11), Zr–Cg02 = 2.2157(11); Cl1–Zr–Cl2 = 99.48(2), Cg01–Zr–Cg02 = 127.94(4).

an analogue)²¹ and can be conveniently described as a distorted tetrahedron by considering the ligand L^- as a sterically demanding unidentate moiety. The cyclopentadienyl ring is slightly asymmetrically η^5 -bonded to the Zr atom (with Zr–C distances ranging from 2.480(3) to 2.530(3) Å in **4a** and from 2.489(2) to 2.545(2) Å in **4c**, the shift resulting from the steric hindrance of the bulky $\text{SiMe}_2\text{CH}_2\text{CH}_2\text{C}_6\text{F}_{13}$ group) with similar Zr–centroid distances (Zr–Cg = 2.1987(12) Å in **4a** and 2.2091(11) and 2.2157(11) Å in **4c**).

Compound **4a** possess 2-fold symmetry in the solid state (Figure 3) with the Si atoms pointing in opposite directions, as observed for the related complex **4f** with a smaller SiMe_3 substituent.²² The fluorine tails lie on one side of the molecule, the two chlorine atoms occupying the other one. The Si atoms are pushed above the cyclopentadienyl plane by 0.335(1) Å, resulting in a Cg01–Zr–Cg01' angle of 129.61(5)° (cf. 129.1° for **4f**).²² The Cl–Zr–Cl' angle of 96.50(3)° is wider than in **4f** (93.7°) but close to the 97° measured for the catalytically highly active zirconocene dichloride complex $[\text{Zr}\{\eta^5\text{-C}_5\text{H}_5\}_2\text{Cl}_2]$.

Triclinic **4c** crystallized as the *rac* conformer with C_1 symmetry (Figure 4). In contrast to **4a**, the Si atoms on the Cp rings in **4c** are eclipsed with a stridre Cl atoms, as observed for $[\text{Zr}\{\eta^5\text{-C}_5\text{H}_4\text{CH}_2\text{Ph}\}_2\text{Cl}_2]$ ²³ or the geo-

Table 1. Polymerization Activities for **4a–d,f** in Toluene^a

entry	precatalyst	activity (kg of PE ((mol of Zr) h) ⁻¹)	
		$t = 5$ min	$t = 30$ min
1	4a		443
2	4b		234
3	4c	1196	288
4	4d		20
5	4f	1125	188 ^b

^a Polymerizations were conducted using $[\text{Zr}] = 2.5 \times 10^{-4}$ mol L^{-1} , Al/Zr = 500, $p = 1$ bar, and $T = 20$ °C. The reproducibility determined from two experiments was better than 10%. ^b This catalytic system is essentially deactivated after 5 min due to high viscosity.

metrically constrained $[\text{Zr}\{\eta^5\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2\}_2\text{Cl}_2]$.²⁴ The Cl–Zr–Cl bond angle is 99.48(2)° (cf. 93.7(1)° in **4f**), close to the 97° reported value in $[\text{Zr}\{\eta^5\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2\}_2\text{Cl}_2]$,²⁴ while the Cg01–Zr–Cg02 bond angle is less influenced at 127.94(4)° (cf. 129.1° in **4f**).

Polymerization Experiments. Our next concern was whether the fluorous zirconocene dichlorides **4a–d** would be at all active in ethylene polymerization using MAO as the cocatalyst.²⁵ Initial experiments were carried out at $p = 6$ bar, $T = 80$ °C, $[\text{Zr}] = 50$ μM , Al/Zr = 500, and $t = 30$ min. Under these conditions the fluorous precatalysts **4a,b** and nonfluorous **4e** were found to display similar activities, compared to the known reference systems Cp_2ZrCl_2 and $(\text{CpBu})_2\text{ZrCl}_2$ ($(1.6\text{--}2.0) \times 10^3$ kg of PE mol⁻¹ bar⁻¹ h⁻¹). The fact that **4a,e** displayed essentially equal activities indicates that the perfluoroalkyl group is effectively insulated from the cyclopentadienyl ligand by the $-\text{SiMe}_2\text{CH}_2\text{CH}_2-$ spacer functionality. Due to the high activity of these precatalysts, the reproducibility and temperature control during the polymerization runs was too poor to allow an accurate comparison of the molecular weights of the polymers obtained. We therefore studied complexes **4a–d,f** under less forcing conditions at 1 bar of ethylene pressure, room temperature, and $[\text{Zr}] = 25$ mM. The activities that were obtained are an order of magnitude lower, but the reproducibility and temperature control were significantly better, allowing comparison of the performance of the different complexes and the properties of the resulting polymers.

Table 1 compares the measured activities for **4a–d,f** in toluene. The polymerization times employed are rather long, as we were interested in the evolution of the catalytic activity over time. Remarkably, complex **4f**, which was used as the reference system, shows very high activity over the first 5 min, after which stirring became hindered, resulting in significant mass transfer limitation and a reduced activity over 30 min. Complexes **4a–c**, although less active by a factor of 2, remained active during this 30 min, resulting in higher overall productivity. The highest activity over 30 min was observed for ethylene-spaced **4a**. Substitution of the ethylene function by a tetrafluoroethylene bridge as in **4b** induced a 2-fold drop in activity. Apparently an ethylene spacer is needed to leave the delicate electronic balance on the Zr center, required for ethylene com-

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Table 2. GPC Data for the Polymer Prepared from **4a–c,f** in Toluene and FBS^a

entry	precatalyst	M_n (10^3 g mol ⁻¹) (M_w/M_n)	
		toluene	toluene/FC 72 (1/1 v/v)
1	4a ^b	119 (2.7)	n.d.
2	4a ^c	21 (8.1)	79 (3.2)
3	4b	33 (6.5)	43 (6.3)
4	4c	69 (2.7)	99 (4.3)
5	4f ^d	86 (2.2)	109 (2.7)

^a Polymerization conditions: $[Zr] = 2.5 \times 10^{-4}$ mol L⁻¹, Al/Zr = 500, $t = 30$ min, $p = 1$ bar, and $T = 20$ °C unless stated otherwise. ^b $t = 15$ min. ^c Polymerization conditions: $[Zr] = 5.8 \times 10^{-5}$ mol L⁻¹, Al/Zr = 400, $t = 30$ min, $p = 6$ bar, and $T = 40$ °C. In both cases the temperature of the reaction mixture rose to 80 °C. ^d $t = 5$ min.

plexation–insertion processes, intact.^{1a} The effectiveness of a spacer is also exemplified by **4c**, where a methylene spacer is used between the Si atom and the pentafluorophenyl ring. It is noteworthy that, measured over the first 5 min, **4c** has an activity that is essentially identical with that of **4f** (1196 and 1125 kg of PE ((mol of Zr) bar h)⁻¹, respectively). For **4d**, in which all three methyl groups are replaced by CH₂C₆F₅, the activity was poor, probably because of the steric shielding of the metal center.

GPC analyses of the polymers showed that their number-averaged molecular weight (M_n) was reasonably high and that the molecular weight distributions were broad (Table 2). Due to the long polymerization times employed, the polydispersity indexes are higher than those predicted by Flory's most probable distribution ($M_w/M_n = 2$), but they are not exceptional for metallocene catalysts and can be explained by significant heterogenization of the reaction mixtures due to the precipitating polymer (both low solubility of the PE at the low reaction temperature and the relatively long reaction time play a role) and local temperature fluctuations.²⁸

The activities measured fit well within the range of activities reported in the literature for zirconocene precatalysts.²⁶ The observation that the activities and molecular weight drop when more electron-withdrawing substituents are used parallels recent observations for pentafluorophenyl-substituted zirconocenes.²⁷

The extremely broad molecular weight distribution obtained for **4b** is remarkable, however, and closer inspection of the GPC data (Figure 5) indicated that in fact a bimodal distribution was obtained with the second molecular weight fraction located at higher average molecular weight ($M_n = 2 \times 10^6$) relative to the PE obtained for **4f** ($M_n = 86 \times 10^3$). The low-molecular-weight fraction was found to be comparable to that of **4f**. Although such a distribution could signify that the catalyst is not stable under the reaction conditions, resulting in the creation of multiple sites,²⁹ NMR

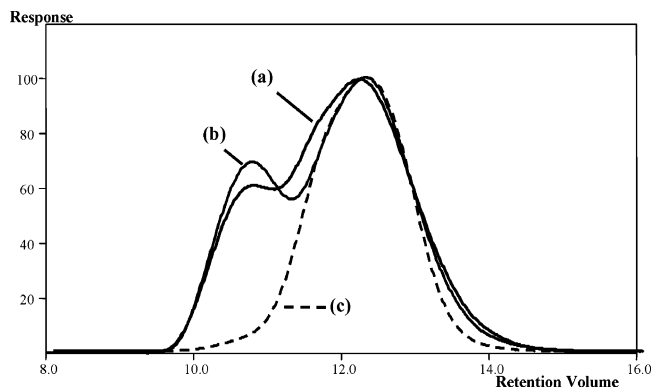


Figure 5. Differential pressure chromatograms for PE samples prepared from **4b**/MAO in toluene (a) and toluene/FC 72 (b) compared to the PE obtained from **4f**/MAO in toluene (c). Note that the low retention volume corresponds to a high-molecular-weight polymer.

investigations and pentane extractions of the quenched reaction mixtures indicate that the zirconocene moiety itself is unaffected when reacted with MAO (vide infra). Although this turned out to be hard to verify experimentally, a more likely explanation is that the hindered rotation around the Zr–Cp axis, which was already observed for the parent dichloride **4b** (vide supra), is sufficiently slow to afford species with different k_p/k_t ratios (k_p = rate constant for chain propagation, k_t = rate constant for chain termination). The steric crowding around the Zr center supplemented by the rigidity of the –C₈F₁₉ tails³⁰ may contribute to this phenomenon. Another possibility suggested by one of the reviewers of this paper, i.e. chain transfer to aluminum, appears to be less likely, as it generally leads to a lower molecular weight fraction and becomes important only at high Al/Zr ratios.^{28b,c,31} The GPC curves of the polymers obtained from the other catalysts in toluene were all unimodal.

A tempting explanation for the increased productivity of the fluorous precatalyst at longer polymerization times, which at this moment is purely speculative, is that the fluorous systems remain active after precipitation of the growing polymer chain. Precipitation normally results in liquid-to-solid mass transfer of ethylene followed by ethylene starvation and consequently chain termination.^{28a} Occlusion of the active site in the precipitated PE may well become enthalpically less favorable for the fluorous complexes compared to non-fluorous precatalysts, resulting in continued availability and activity of the active site.³²

Exploratory polymerization experiments with **4a–c,f** under FBS conditions (1:1 volumetric mixtures of toluene and FC-72 as well as of hexane and FC72) were undertaken to probe the possible effect of the fluorous

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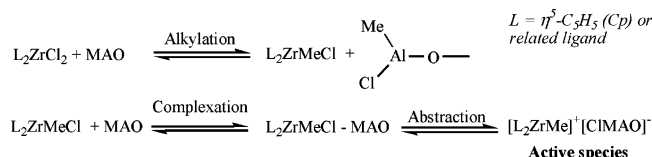
(29) For example, one could envision nucleophilic attack by MAO or AlMe₃, which is contained in MAO, on the Si atom replacing the 1*H*,1*H*,2*H*,2*H*-perfluoroalkyl group by a regular Me group.

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(32) This would be another demonstration of fluorous biphasic separation behavior in the solid state caused by the inability of the fluorous metallocene fragment to enter into enthalpically favorable interactions with the PE that could otherwise compensate for the loss of intramolecular van der Waals interactions in the partly crystalline PE. Related phase separation phenomena in the solid state have been observed in the X-ray structure of a fluorous Rh complex.²⁰

Scheme 3



biphasic conditions on the activities. It was found that the activities remained essentially unaffected, demonstrating that FC-72 is compatible with both MAO and the polymerization conditions and that the biphasic conditions did not result in problems with mass transport limitation. More importantly, under biphasic conditions the relative ranking of the activities of the fluoruous complexes and nonfluorous **4f** that was observed in toluene was essentially reproduced, suggesting that partitioning of the active species into the fluoruous phase is not yet significant at this level of fluoruous character of the metallocene precatalysts. However, when the molecular weights of the resulting polymers are compared (Table 2), a general trend toward significantly higher average molecular weight is observed under the biphasic conditions.

In trying to rationalize the effect of replacing part of the toluene solvent by FC-72, it should be noted that the ionic catalyst system is essentially insoluble in the FC-72 phase. This could be easily concluded from experiments in pure FC-72 that resulted in poor activity (<10 kg of PE (mol of Zr) bar h)⁻¹) as well as visually observable poor solubility of the catalyst components. Although the solubility of ethylene in FC-72 is ca. 20% higher than in toluene,³³ this is of relatively low importance, as the polymerization reaction takes place predominantly in the toluene phase. Some surface activity cannot be ruled out in the case of the amphiphilic fluoruous metallocene systems. However, by partial dissolution in the toluene layer (ca. 5 vol %), the main effect of the perfluorocarbon solvent is to lower the dielectric constant of the toluene phase. The latter will promote tight ion pairing of the catalytic system, which in turn may be expected to suppress the rate of β -hydrogen transfer to the metal center.³⁴ The observed increase in polymer molecular weight can thus be rationalized qualitatively.

When the shape of the GPC chromatogram for **4b** was inspected, it was found that the higher molecular weight distribution gets more pronounced under the fluoruous biphasic conditions (Figure 5), whereas the GPC curves for the other catalysts remained unimodal. Apparently the species with the highest k_p/k_t ratio is favored by the presence of the fluorocarbon solvent.

Catalyst Analysis by ¹H NMR Spectroscopy. The Lewis acid role of MAO in the formation of coordinately unsaturated cationic zirconocene alkyl species from the zirconocene dichloride precursor is now well established (Scheme 3); NMR spectroscopy has proven to be a useful technique for the characterization of these species, which are thought to be the actual catalysts for

polymerization.^{34b,35} For the Cp₂ZrMe₂-MAO systems, these are the heterodinuclear [Cp₂Zr(μ-Me)₂AlMe₂]⁺[Me-MAO]⁻ and the unsymmetrical methyl-bridged complex [Cp₂ZrMe]⁺[Me-MAO]⁻ ion pairs along with other intermediates (especially at low Al/Zr ratio) such as the neutral [Cp₂ZrMe₂][MAO] adduct or the dimeric symmetric (on the cationic part) binuclear [Cp₂ZrMe]₂(μ-Me)⁺[Me-MAO]⁻ ion pair.^{35a}

Solutions of precatalysts **4a-c** and MAO (benzene-d₆, Al/Zr = 100) were studied by ¹H NMR spectroscopy at ambient temperature (see Table 3 for NMR data and assignments). A remarkable feature for each experiment with precatalysts **4a-c** and MAO is the presence in the ¹H NMR spectrum of four broad signals for the mono-substituted-cyclopentadienyl group protons, which belong to the unsymmetrical methyl-bridged [(CpSiMe₂R_F)₂ZrMe]⁺[X-MAO]⁻ (X = Me, Cl, R_F = CH₂CH₂C₆F₁₃ (**4a**), C₈F₁₇ (**4b'**), CH₂C₆F₅ (**4c'**)) contact and separated ion pairs rather than to the heterodinuclear complex [(CpSiMe₂R_F)₂Zr(μ-Me)₂AlMe₂]⁺[X-MAO]⁻ (X = Me, Cl), for which only two Cp H signals (symmetrical cationic part) would be expected.^{35a} Nevertheless, the formation of the [(CpSiMe₂R_F)₂Zr(μ-Me)₂AlMe₂]⁺[X-MAO]⁻ (X = Me, Cl) ion pair cannot be excluded, as its NMR signals could be non-resolved from the broad [(CpSiMe₂R_F)₂ZrMe]⁺[X-MAO]⁻ (X = Me, Cl) signals at ambient temperature. It is noteworthy that species **4'** is observed in solution in equilibrium with the starting precatalyst **4** (in a 2:1 molar ratio) for complexes **4a,f**, whereas **4'** is the only species observed when **4b,c** were treated with MAO. At lower Al/Zr ratio (Al/Zr = 20), a similar pattern for the Cp protons was observed, but at lower field, which is attributed to the unsymmetrical monomethylated [(CpSiMe₂R_F)₂Zr(Me)Cl] (R_F = C₈F₁₇ (**4b''**), CH₂C₆F₅ (**4c''**)). These monomethyl complexes were observed along with unreacted precatalyst (3:1 ratio).

These observations are in accordance with previous observations for [Cp₂ZrCl₂]-MAO and **4f**-MAO^{35a,e,36} and also correlate, at least qualitatively, with recent work by Deck et al.,³⁷ where it was found that electron-withdrawing C₆F₅ groups stabilize mononuclear cationic [(CpC₆F₅)₂ZrMe]⁺[X-MAO]⁻ species. From these NMR studies no indications were obtained that precatalyst **4b** behaves differently from the other precatalysts, leaving the origin of the bimodality of the polyethylene obtained with **4b** unclear. Attempts to study solutions of complexes **4a-c,f** and MAO at low temperatures were hampered by severe line broadening.

Most remarkably, hydrolysis of the fluoruous species **4'** by aqueous alcoholic HCl regenerated the fluoruous zirconocene dichlorides (characterized by both their ¹H and ¹⁹F NMR spectra) whereas hydrolysis of a **4f**-MAO solution led to decomposition of the catalyst, free HCp-SiMe₃ being the only product observed by ¹H NMR.

(33) Derived from a plot of log x versus δ (x = mole fraction of ethylene, δ = Hildebrand parameter of the solvent): Jolley, J. E.; Hildebrand, J. H. *J. Am. Chem. Soc.* **1958**, *80*, 1050-1054.

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Moreover, pentane extraction of the quenched polymerization filtrate, from polymerization experiments with precatalysts **4a–d** and MAO, allowed, after removal of the solvent, recovery of the starting precatalyst. These results confirm the enhanced stability of the fluoros precatalyst. Also, they open up the possibility of (pre)catalyst recycling in metallocene polymerization even though there might not be a practical need for it, given the low catalyst loadings of industrial metallocene-based olefin polymerization processes.

Conclusions

In conclusion, four new crystalline, highly stable zirconocene(IV) dichlorides, substituted with one fluoros silyl group per cyclopentadienyl ring, have been prepared. They are hydrocarbon soluble and even moderately soluble in perfluorocarbons (PFC's). Three of these four fluoros complexes (**4a–c**) form active ethylene polymerization catalysts when reacted with an excess of methylaluminoxane (MAO, Al/Zr = 500) in pure toluene but also in fluoros biphasic solvent systems (e.g. toluene/perfluorohexanes). The most important observation is that these fluoros zirconocene systems display increased robustness and consequently increased productivity over prolonged polymerization times in comparison to the nonfluorous reference system [Zr(η^5 -C₅H₄SiMe₃)₂Cl₂] (**4f**). This phenomenon may well be related to phase segregation of the fluoros metallocene moiety from the polyethylene matrix and will be investigated further in future studies.

The more electron-withdrawing fluorinated hydrocarbon substituents on the cyclopentadienyl ligand result in lower initial polymerization activity and a decreased molecular weight of the polyethylene obtained, probably as a result of a decreased propagation rate. Remarkably, fluoros biphasic conditions during the polymerization reaction in general result in higher polymer molecular weight. This phenomenon was even observed for nonfluorous **4f** and is most likely caused by a suppression of the rate of β -H transfer to the metal center in these relatively nonpolar solvent combinations. For the most fluoros zirconocene complex bearing two -SiMe₂C₈F₁₇ tails (**4b**) a polyethylene with a bimodal molecular weight distribution was obtained, the higher molecular weight part of which became more pronounced under fluoros biphasic conditions. ¹H NMR experiments on benzene-*d*₆ solution of the precatalysts and MAO (Al/Zr = 100) have shown the formation of unsymmetrical [(CpSiMe₂R_F)₂ZrMe]⁺[Me-MAO]⁻ ion pairs rather than the heterodinuclear [(CpSiMe₂R_F)₂Zr(μ -Me)₂AlMe₂]⁺[MeMAO]⁻ ion pairs as the predominant species.

Experimental Section

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). ¹H (300.1 MHz), ¹³C (75.5 MHz), ²⁹Si (59.6 MHz), and ¹⁹F (282.4 MHz) NMR spectra were recorded on a Varian INOVA 300 spectrometer at 25 °C, unless otherwise stated, and were referenced internally (¹H, ¹³C) to residual solvent resonances or externally (to SiMe₄ for ²⁹Si and CFCl₃ for ¹⁹F). Melting points were measured in sealed capillaries on a Tottoli

apparatus and are uncorrected. Mass spectra (nanoES-Q-TOF-MS) were performed by C. Versluis (Department of Biomolecular Mass Spectrometry, Utrecht University, NL) using a Micromass Q-Tof hybrid tandem mass spectrometer and the MassLynx software, version 3.0. GPC analyses (against polystyrene standard in 1,2-dichlorobenzene at 140 °C) were performed by Rapra Technology Ltd (U.K.). Cyclopentadiene was obtained by cracking of dicyclopentadiene and distilled prior to use, CpLi was prepared by directly cracking dicyclopentadiene over a solution of LiBuⁿ (1.6 mol L⁻¹ in hexane). Chlorodimethyl(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)silane was prepared by following reported methods.^{11,38} All other reagents were purchased from commercial sources and used without further purification. For all the polymerization tests, a 10 wt % solution of MAO in toluene from WITCO (*d*₂₀ = 0.885, total Al content 4.8 wt %) and ethylene (3.0, >99.9%, Hoek Loos) were used as received.

Dimethyl(perfluorooctyl)silane (1b). LiBuⁿ (80 mL of a 1.6 mol L⁻¹ solution in hexane, 50 mmol) and hexane (90 mL) were added dropwise over a period of 4.5 h to a solution of C₈F₁₇I (26.52 g, 48.6 mmol) and HSiMe₂Cl (6.8 mL, 85 mmol) in Et₂O (150 mL) at -78 °C. After the mixture was warmed to ambient temperature, a white suspension had formed, and water (50 mL) and Et₂O (150 mL) were added. The layers were separated, and the ethereal layer was washed with brine (30 mL) and dried on MgSO₄. Removal of the volatiles using a rotary evaporator gave a yellow oil (19.8 g). Fractional distillation (11 mbar, 57–59 °C) using a 10 cm Vigreux column gave HSiMe₂C₈F₁₇ (**1b**) as a colorless liquid (10.14 g, 44%), which according to ¹⁹F NMR contained approximately 5% C₈F₁₇I. ¹H NMR (δ , CDCl₃): 0.38 (d, 6 H, ³J_{H,H} = 4 Hz, SiMe₂), 4.24 (br, 1 H, Si-H). ¹³C{¹⁹F} NMR (δ , CDCl₃): -7.9 (q, ¹J_{H,C} = 125 Hz, SiMe₂), 108.6, 110.5, 111.0, 111.7, 117.4 (t, ²J_{F,C} = 19 Hz, CF₃), 122.7 (CF₂Si). ¹⁹F NMR (δ , CDCl₃): -81.9 (t, 3 F, ⁴J_{F,F} = 9 Hz, CF₃), -120.8 (br s, 2 F, F²), -122.6 (br s, 2 F, F³), -122.8 (br s, 4 F, F⁴ and F⁵), -123.6 (br s, 2 F, F⁶), -127.1 (br s, 2 F, F⁷), -127.6 (d, 2 F, ³J_{H,F} = 12 Hz, F¹). ²⁹Si{¹H} NMR (δ , CDCl₃): -8.3 (tt, ²J_{F,Si} = 30 Hz, ³J_{F,Si} = 6 Hz).

(2,3,4,5,6-Pentafluorobenzyl)dimethylsilane (1c). A solution of BrCH₂C₆F₅ (10.55 g, 40.4 mmol) and HSiMe₂Cl (4.11 g, 43.4 mmol) in Et₂O (150 mL) was added over a period of 4 h to magnesium turnings (2.65 g, 109 mmol) on suspension in Et₂O (50 mL). The greenish suspension was stirred at ambient temperature for ca. 15 h and quenched with H₂O (50 mL). The aqueous layers were extracted with Et₂O (3 × 50 mL), the organic layers were washed with brine (50 mL) and dried over MgSO₄, and solvent was removed in vacuo to yield the desired product as a colorless oil (8.66 g, 89%). ¹H NMR (δ , CDCl₃): 0.17 (m, 6 H, SiMe₂), 2.20 (m, 2H, CH₂), 4.01 (m, 1 H, H-Si). ¹³C{¹H} NMR (δ , CDCl₃): -4.6 (SiMe₂), 10.1 (CH₂), 114.2 (t, ²J_{F,C} = 240 Hz, *ipso*-C₆F₅), 137.8 (dm, ¹J_{F,C} = 280 Hz, *m*-C₆F₅), 138.4 (dm, ¹J_{F,C} = 240 Hz, *p*-C₆F₅), 144.4 (dm, ¹J_{F,C} = 250 Hz, *o*-C₆F₅). ¹⁹F NMR (δ , CDCl₃): -144.5 (dd, 2 F, ³J_{F,F} = 23 Hz, ⁴J_{F,F} = 8 Hz, *o*-C₆F₅), -161.9 (dd, 2 F, ³J_{F,F} = 22 Hz, *p*-C₆F₅), -164.5 (dd, 2 F, ³J_{F,F} = 21 Hz, ⁴J_{F,F} = 9 Hz, *m*-C₆F₅). ²⁹Si{¹H} NMR (δ , CDCl₃): -11.5 (s). Anal. Calcd for C₉H₉F₅Si: C, 44.99; H, 3.78. Found: C, 45.16; H, 3.86.

Tris(2,3,4,5,6-pentafluorobenzyl)silane (1d). A solution of BrCH₂C₆F₅ (9.74 g, 37.3 mmol) and HSiCl₃ (1.2 mL, 12 mmol) in Et₂O (150 mL) was added over a period of 4.5 h to magnesium turnings (2.20 g, 90 mmol) in suspension in Et₂O (100 mL). The greenish suspension was refluxed for 1 h and then quenched with H₂O (50 mL). The aqueous layers were extracted with Et₂O (3 × 50 mL), and the organic layers were washed with brine (50 mL), dried over MgSO₄, and concentrated to dryness in vacuo to yield the title compound as a yellowish solid (5.83 g, 86%). ¹H NMR (δ , CDCl₃): 2.30 (m, 6H, CH₂), 4.06 (m, 1 H, Si-H). ¹³C{¹H} NMR (δ , CDCl₃): 7.3

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(CH₂), 111.4 (*ipso*-C₆F₅), 137.8 (dm, ¹J_{F,C} = 250 Hz, *m*-C₆F₅), 139.3 (dm, ¹J_{F,C} = 250 Hz, *p*-C₆F₅), 144.5 (dm, ¹J_{F,C} = 250 Hz, *o*-C₆F₅). ¹⁹F NMR (δ, CDCl₃): -143.2 (dd, 2 F, ³J_{F,F} = 21 Hz, ⁴J_{F,F} = 6 Hz, *o*-C₆F₅), -158.5 (t, 1 F, ³J_{F,F} = 21 Hz, *p*-C₆F₅), -162.5 (dt, 2 F, ³J_{F,F} = 21 Hz, ⁴J_{F,F} = 6 Hz, *m*-C₆F₅). ²⁹Si{¹H} NMR (δ, CDCl₃): -6.4 (s). Anal. Calcd for C₂₁H₇F₁₅Si: C, 44.07; H, 1.23. Found: C, 43.94; H, 1.30.

Bromodimethyl(perfluorooctyl)silane (2b). A mixture of HSiMe₂C₈F₁₇ (**1b**; 7.56 g, 15.8 mmol) and Br₂ (3.2 mL, 62 mmol) in CCl₄ (25 mL) was stirred for 18 h at 60 °C in a Schlenk flask which had been fitted with a condenser and a CaCl₂ tube. After removal of the volatiles in vacuo, the resulting liquid was flash-distilled to yield the title compound as a pale pink liquid (8.35 g, 95%). ¹⁹F NMR spectroscopy showed that it contained approximately 5% C₈F₁₇I and was used as such. ¹H NMR (δ, CDCl₃): 0.84 (s). ¹³C{¹⁹F} NMR (δ, CDCl₃): -0.1 (q, ¹J_{H,C} = 124 Hz, SiMe₂), 108.6 (partly resolved q, ¹J_{F,C} = 12 Hz), 110.4, 111.0 (s, 2 C), 111.6, 113.0, 117.4 (t, ²J_{F,C} = 21 Hz, CF₃), 119.3 (CF₂Si). ¹⁹F NMR (δ, CDCl₃): -82.0 (t, 3 F, ⁴J_{F,F} = 9 Hz, CF₃), -118.8 (br s, 2 F, F¹), -122.5 (br s, 2 F, F³), -122.9 (br s, 4 F, F⁴ and F⁵), -123.7 (br s, 2 F, F⁶), -127.2 (m, 4 F, F¹ and F⁷). ²⁹Si{¹H} NMR (δ, CDCl₃): 17.7 (t, ²J_{F,Si} = 35 Hz).

Bromo(2,3,4,5,6-pentafluorobenzyl)dimethylsilane (2c). A solution of HSiMe₂(CH₂C₆F₅) (**1c**; 8.66 g, 36.0 mmol) and Br₂ (3.6 mL, 70 mmol) in pentane (30 mL) was stirred at ambient temperature for a period of 3 days. The dark brown solution was concentrated to dryness to afford the desired product as a clear orange oil (11.36 g, 98%). ¹H NMR (δ, CDCl₃): 0.62 (m, 6 H, SiMe₂), 2.53 (t, 2H, ⁴J_{F,H} = 2 Hz, CH₂). ¹³C{¹H} NMR (δ, CDCl₃): 2.5 (SiMe₂), 15.5 (CH₂), 135.3, 140.2, 142.0, and 144.4 (C₆F₅). Anal. Calcd for C₉H₈BrF₅Si: C, 33.87; H, 2.53. Found (duplicate analysis): C, 34.35; H, 2.66.

Bromotris(2,3,4,5,6-pentafluorobenzyl)silane (2d). A solution of HSi(CH₂C₆F₅)₃ (**1c**; 6.97 g, 12.2 mmol) and Br₂ (1.2 mL, 23.3 mmol) in hexane (40 mL) was stirred at ambient temperature for a period of 6 days. The dark brown solution was concentrated to dryness in vacuo and the brown sticky solid extracted with pentane (50 mL); crystallization at -20 °C gave the title compound as beige microcrystals (6.0 g, 76%, first crop). ¹H NMR (δ, CDCl₃): 2.65 (m, 6H, CH₂). ¹³C{¹⁹F} NMR (δ, CDCl₃): 12.8 (t, ¹J_{C,H} = 127 Hz, CH₂), 109.8 (t, ²J_{C,H} = 7 Hz, *ipso*-C₆F₅), 138.0 (m, *m*-C₆F₅), 139.7 (m, *p*-C₆F₅), 144.6 (m, *o*-C₆F₅). ¹⁹F NMR (δ, CDCl₃): -141.9 (dd, 2 F, ³J_{F,F} = 21 Hz, ⁴J_{F,F} = 8 Hz, *o*-C₆F₅), -157.2 (t, 1 F, ³J_{F,F} = 21 Hz, *p*-C₆F₅), -162.1 (dt, 2 F, ³J_{F,F} = 21 Hz, ⁴J_{F,F} = 8 Hz, *m*-C₆F₅). ²⁹Si{¹H} NMR (δ, CDCl₃): 19.2 (s). Anal. Calcd for C₂₁H₆BrF₁₅Si: C, 38.73; H, 0.93. Found: C, 39.11; H, 1.01.

[Dimethyl(1H,1H,2H,2H-perfluorooctyl)silyl]cyclopentadiene (3a). Freshly distilled cyclopentadiene (2.40 mL, 29.1 mmol) was added to a cooled (0 °C) solution of LiBuⁿ (50 mL of a 1.6 mol L⁻¹ solution in hexane, 31.3 mmol) in hexane (100 mL). The reaction mixture was stirred for 3 h at ambient temperature. After removal of the solvent in vacuo, the solid was washed with pentane (3 × 50 mL) and dried under vacuum. The Li[C₅H₅] was dissolved in THF (100 mL) at -78 °C and the solution added dropwise by cannula over 0.5 h to a solution of C₆F₁₃C₂H₄SiMe₂Cl (**2a**; 13 g, 29.5 mmol) in THF (100 mL) at 0 °C. The reaction mixture was stirred overnight at ambient temperature. Volatiles were removed in vacuo, the solid was extracted with pentane (100 mL), and the filtrate was concentrated to dryness in vacuo to give an orange oil. The pure title compound was obtained as a colorless oil (10.94 g, 80%) by distillation (75–80 °C at 5 × 10⁻¹ mbar). The ¹H NMR spectrum is complicated by the presence of 1- and 2-silyl isomers (minor) next to the 5-silyl isomer (major, ca. 80%). ¹H NMR (δ, CDCl₃): 0.03 (s, SiMe₂, 5-(R_FSiMe₂)C₅H₅ isomer), 0.21 (s, SiMe₂, 1- and 2-(R_FSiMe₂)C₅H₅ isomers), 0.68 (m, CH₂-Si, 5-(R_FSiMe₂)C₅H₅ isomer), 0.88 (m, CH₂-Si, 1- and 2-(R_FSiMe₂)C₅H₅ isomers), 1.98 (m, CH₂-CF₂, all isomers), 3.04 (m, CH₂ of 1- and 2-(R_FSiMe₂)C₅H₅), 3.40 (m, CH₂ of 5-(R_FSiMe₂)C₅H₅

isomer), 6.63 and 6.53 (m, α- + β-*H* 5-(R_FSiMe₂)C₅H₅ isomer), 6.87 and 6.71 (m, α- + β-*H* of 1- and 2-(R_FSiMe₂)C₅H₅ isomers). Anal. Calcd for C₁₅H₁₅F₁₃Si: C, 38.30; H, 3.19; F, 52.55; Si, 5.96. Found: C, 38.08; H, 3.29; F, 52.74; Si, 5.81.

[Dimethyl(perfluorooctyl)silyl]cyclopentadiene (3b). A solution of CpLi (0.93 g, 12.9 mmol) in THF (50 mL) was added dropwise to a stirred solution of BrSiMe₂C₈F₁₇ (**2b**; 7.32 g, 13.1 mmol) in THF (50 mL) at 0 °C. The brownish solution was stirred for 1 h at ambient temperature and quenched with water (200 mL). The aqueous layer was extracted with pentane (200 mL), and the organic layer was washed with water (2 × 50 mL) and brine (30 mL) and dried over MgSO₄. Solvent was removed in vacuo using a rotary evaporator. The resulting liquid was Kugelrohr-distilled (10⁻² mbar, 100 °C) to yield the title compound as a clear yellow liquid (5.00 g, 70%). ¹H and ¹⁹F NMR analysis showed the product to be a mixture of at least two isomers (minor) with the 5-silyl isomer (major, ca. 80%) along with ca. 3% of C₈F₁₇I. ¹H NMR (δ, CDCl₃): 0.13 (s, 4.8 H, SiMe₂, major), 0.51 (s, 1.2 H, SiMe₂, minor), 3.18 (d, 0.3 H, *J* = 1.5 Hz, C₅H₅, minor), 3.7 (br, 0.7 H, C₅H₅, major), 6.4–7.2 (m, 3.5 H, C₅H₅). ¹⁹F NMR (δ, CDCl₃): -81.9 (t, 3 F, ⁴J_{F,F} = 10 Hz, C³F₃), -119.2 (br s, 2 F, C²F₂), -122.5 (br s, 2 F, C³F₂), -122.7 (br s, 4 F, C^{4,5}F₂), -123.6 (br s, 2 F, C⁶F₂), -126.8 (t, 1.5 F, ⁴J_{F,F} = 15 Hz, C¹F₂), -127.1 (m, 2 F, C⁷F₂), -127.3 (t, 0.5 F, ⁴J_{F,F} = 15 Hz, C¹F₂).

[(2,3,4,5,6-Pentafluorobenzyl)dimethylsilyl]cyclopentadiene (3c). A solution of LiCp (1.33 g, 18.46 mmol) in THF (20 mL) was added dropwise to a cooled (0 °C) solution of BrSiMe₂(CH₂C₆F₅) (**2c**; 5.78 g, 18.11 mmol) in THF (50 mL). The deep red solution was maintained at 0 °C for 30 min and then allowed to come to ambient temperature and left as such overnight. Volatiles were removed in vacuo, and the brown solid was extracted with pentane (3 × 20 mL). Filtrate was concentrated in vacuo to give the crude product as an orange oil which was Kugelrohr-distilled (120 °C, 10⁻² mbar) to yield a light yellow oil (4.72 g, 86%). ¹H and ¹³C NMR spectra in CDCl₃ were extremely complicated, due to the presence of the three isomers. ¹H NMR (δ, CDCl₃): 0.04–0.87 (3bs, 6 H, SiMe₂), 1.7–2.30 (3m, 2H, CH₂), 6.50 and 6.66 (2bs, 5H, C₅H₅). Anal. Calcd for C₁₄H₁₃F₅Si: C, 55.25; H, 4.31. Found: C, 55.20; H, 4.28.

[Tris(2,3,4,5,6-pentafluorobenzyl)silyl]cyclopentadiene (3d). A solution of LiCp (0.69 g, 9.5 mmol) in THF (10 mL) was added dropwise to a cooled (0 °C) solution of BrSi(CH₂C₆F₅)₃ (**2d**; 5.96 g, 9.15 mmol) in THF (50 mL). The deep red solution was maintained at 0 °C for 30 min and then allowed to come to ambient temperature and left as such overnight. Solvent was removed in vacuo, and pentane (50 mL) was added. The brown suspension was quenched by water (50 mL). The aqueous layer was extracted with pentane (3 × 20 mL), and the organic layers were rinsed with brine (50 mL), dried over MgSO₄, and concentrated in vacuo; the oily crude product was crystallized from pentane (15 mL) to yield orange microcrystals of the product (4.71 g, 81%). ¹H NMR (δ, CDCl₃): 1.66 (m, 6H, CH₂), 3.02 (d, 1H, ³J_{H,H} = 1 Hz, C₅H₅), 6.05 (m, 2H, C₅H₅) and 6.37 (m, 2H, C₅H₅). ¹³C{¹H} NMR (δ, CDCl₃): 7.7 (CH₂), 111.7, 130.9, 133.7, 135.2, 140.2, 141.9, and 146.8 (C₆F₅ and C(sp²) from C₅H₅). ¹⁹F NMR (δ, CDCl₃): -142.4 (bd, 2 F, *o*-C₆F₅), -158.9 (t, 1 F, ³J_{F,F} = 21 Hz, *p*-C₆F₅), -162.8 (dt, 2 F, ³J_{F,F} = 22 Hz, ⁴J_{F,F} = 7 Hz, *m*-C₆F₅). Anal. Calcd for C₂₆H₁₁F₁₅Si: C, 49.07; H, 1.74. Found: C, 48.98; H, 1.67.

[Dimethyloctylsilyl]cyclopentadiene (3e). Freshly distilled cyclopentadiene (2 mL, 24.3 mmol) was added dropwise to a stirred solution of *n*-BuLi (24.2 mmol) in *n*-hexane (100 mL) that was kept at 0 °C. The reaction mixture was stirred for 3 h at room temperature. Then, the solvent was removed and the product was washed with pentane (3 × 50 mL) and dried under vacuum. The Li(C₅H₅) was then dissolved in THF (75 mL) at -78 °C and the solution added dropwise by cannula to chlorodimethyl(octyl)silane (4.55 g, 22.0 mmol) in THF (75 mL) at 0 °C over a period of 0.5 h. The reaction mixture was

stirred overnight at room temperature. Volatiles were removed under vacuum, and the product was extracted with pentane (3 × 50 mL), filtered, and then dried under vacuum, affording 3.41 g (66%) of the pure product as a yellow liquid. GC-MS (70 eV): *m/z* 236 (M^+). As was observed for $C_5H_5SiMe_2C_6F_{13}$, this ligand appears as a mixture of three isomers in the 1H NMR spectrum, the 5-isomer being the major compound at room temperature (ca. 80%). 1H NMR (200.1 MHz, acetone- d_6): δ 6.85 and 6.65 (2 × m, CH=, 1- and 2- $[C_8H_{17}(Me)_2Si]C_5H_5$), 6.55 (m, CH=, 5- $[C_8H_{17}(Me)_2Si]C_5H_5$), 3.47 (m, 5-CH, 5- $[C_8H_{17}(Me)_2Si]C_5H_5$), 3.03 (m, 5-CH₂, 1- and 2- $[C_8H_{17}(Me)_2Si]C_5H_5$), 1.29 (m, $CH_3C_6H_{12}CH_2Si$, 1-, 2-, and 5- $[C_8H_{17}(Me)_2Si]C_5H_5$), 0.88 (m, $CH_3C_6H_{12}CH_2Si$, 1-, 2-, and 5- $[C_8H_{17}(Me)_2Si]C_5H_5$), 0.67 (m, CH_2Si , 1- and 2- $[C_8H_{17}(Me)_2Si]C_5H_5$), 0.56 (m, CH_2Si , 5- $[C_8H_{17}(Me)_2Si]C_5H_5$), 0.15 (s, $SiMe_2$, 1- and 2- $[C_8H_{17}(Me)_2Si]C_5H_5$), -0.09 (s, $SiMe_2$, 5- $[C_8H_{17}(Me)_2Si]C_5H_5$).

Bis[*dimethyl(1H,1H,2H,2H-perfluorooctyl)silyl*]-cyclopentadienyl]zirconium Dichloride (4a). LiBuⁿ (50 mL of a 1.6 mol L⁻¹ solution in hexane, 80 mmol) was added to a cooled (0 °C) solution of $C_5H_5SiMe_2C_2H_4C_6F_{13}$ (**3a**; 37 g, 78.7 mmol) in hexane (200 mL). The resulting reaction mixture was stirred for 3 h at ambient temperature. The solvent was removed, and the product was washed with pentane (3 × 50 mL) and dried in vacuo. $[Li\{C_5H_5SiMe_2C_2H_4C_6F_{13}\}]$ was dissolved in precooled (-78 °C) THF (100 mL) and was added dropwise over 0.5 h to a cooled (0 °C) solution of $ZrCl_4$ (9.08 g, 38.2 mmol) in THF (100 mL). The resulting solution was stirred for 48 h at ambient temperature. Volatiles were removed in vacuo, and the residue was extracted with boiling toluene (100 mL). The filtrate was concentrated in vacuo to afford white thin crystalline needles of pure product (31.50 g, 75%). Mp: 119–120 °C. 1H NMR (δ , C_6D_6): 0.23 (s, 6 H, $SiMe_2$), 0.91 (m, 2 H, CH_2Si), 1.96 (bm, 2 H, CH_2-CF_2), 5.78 (t, $^3J_{HH} = 2.5$ Hz, 2H, $\alpha-C_5H_4$), 6.24 (t, $^3J_{HH} = 2.5$ Hz, 2H, $\beta-C_5H_4$). 1H NMR (δ , toluene- d_8): 0.23 (s, 6 H, $SiMe_2$), 0.92 (m, 2 H, CH_2Si), 1.97 (bm, 2 H, CH_2-CF_2), 5.79 (t, $^3J_{HH} = 2.5$ Hz, 2H, $\alpha-C_5H_4$), 6.22 (t, $^3J_{HH} = 2.5$ Hz, 2H, $\beta-C_5H_4$). 1H NMR (δ , toluene- d_8 , -80 °C): 0.21 (s, 6 H, $SiMe_2$), 0.94 (vbs, 2 H, CH_2Si), 1.97 (vbs, 2 H, CH_2-CF_2), 5.65 (bs, 2H, $\alpha-C_5H_4$), 6.08 (bs, 2H, $\beta-C_5H_4$) $^{13}C\{^1H\}$ NMR (δ , acetone- d_6): -2.3 ($SiMe_2$), 6.77 (CH_2Si), 26.5 (t, $^2J_{C,F} = 23.28$ Hz, CH_2CF_2), 117.2 ($\alpha-C_5H_4$), 125.36 (ipso-C C_5H_4), 127.24 ($\beta-C_5H_4$). $^{19}F\{^1H\}$ NMR (δ , toluene- d_8): -81.2 (t, $^3J_{F,F} = 9$ Hz, CF_3), -115.6 (t, $^3J_{F,F} = 15$ Hz, $\alpha-CF_2$), -122.0 (s, $\gamma-CF_2$), -123.0 (s, $\delta-CF_2$), -123.1 (bs, $\beta-CF_2$), -126.3 (bs, $\epsilon-CF_2$). ^{29}Si NMR (acetone- d_6): δ 1.70 (s). Anal. Calcd for $C_{30}H_{28}Cl_2F_{26}Si_2Zr$: C, 32.73; H, 2.55; Cl, 6.45; F, 44.91; Si, 5.09. Found: C, 32.58; H, 2.56; Cl, 6.35; F, 44.78; Si, 5.39. MS (TOF-ES): *m/z* 1123 ($[M + Na]^+$, 100), 2223 ($[2M + Na]^+$).

Bis[*dimethyl(perfluorooctyl)silyl*]-cyclopentadienyl]zirconium Dichloride (4b). LiBuⁿ (4 mL of a 1.6 mol L⁻¹ solution in hexane, 6.4 mmol) was added to a solution of $C_5H_5SiMe_2C_8H_{17}$ (**3b**; 3.41 g, 6.3 mmol) in hexane (50 mL) at ambient temperature. The resulting reaction mixture was stirred for ca. 15 h at ambient temperature. Solvent was removed by filtration, and the beige solid was rinsed with hexane (10 mL) and dried in vacuo. The compound was then dissolved in diethyl ether (30 mL) and solid $ZrCl_4$ (0.73 g, 3.13 mmol) was added. A cloudy suspension immediately formed and was left at ambient temperature for ca. 20 h. The suspension was filtered and cooled to -20 °C to yield pale yellow needles of **4b** (1.62 g, 42%). Anal. Calcd for $C_{30}H_{20}Cl_2F_{34}Si_2Zr$: C, 28.95; H, 1.62; Cl, 5.70; Zr, 7.33; Found: C, 29.06; H, 1.54; Cl, 5.76; Zr, 7.26. Mp: 136–137 °C. 1H NMR (δ , C_6D_6): 0.62 (s, 6 H, $SiMe_2$), 5.65 (bs, 2H, $\alpha-C_5H_4$), 6.31 (s, 2 H, $\beta-C_5H_4$). 1H NMR (δ , toluene- d_8): 0.61 (s, 6 H, $SiMe_2$), 5.70 (t, $J_{FF} = 2.5$ Hz, 2H, $\alpha-C_5H_4$), 6.30 (t, $J_{FF} = 2.5$ Hz, 2 H, $\beta-C_5H_4$). 1H NMR (δ , toluene- d_8 , -80 °C): 0.64 and 0.75 (2 bs, total 6 H, $SiMe_2$), 5.46 and 5.64 (4 bs, total 2H, $\alpha-C_5H_4$), 6.15 and 6.34 (2 bs, total 2H, $\beta-C_5H_4$). $^{13}C\{^1H\}$ NMR (δ , THF- d_8): -5.2 ($SiMe_2$), 117.2, 128.5 (α , $\beta-C_5H_4$), ipso-C of C_5H_4 and C_8F_{17} signals not observed. ^{19}F NMR (δ , C_6D_6): -81.1 (t, $J_{FF} = 10$

Hz, 3 F, CF_3), -118.0 (bs, 2 F, $\alpha-CF_2$), -121.6 (br s, 2 F, $\beta-CF_2$), -121.9 (br s, 4 F, $\gamma, \delta-CF_2$), -122.8 (br s, 2 F, $\zeta-CF_2$), -126.3 (br s, 2 F, $\epsilon-CF_2$).

Bis[*(2,3,4,5,6-pentafluorobenzyl)dimethylsilyl*]-cyclopentadienyl]zirconium Dichloride (4c). LiBuⁿ (3.4 mL of 1.6 mol L⁻¹ solution in hexane, 5.44 mmol) was added to a cooled solution (0 °C) of $\{C_5H_5SiMe_2(CH_2C_6F_5)\}$ (**3c**; 1.59 g, 5.22 mmol) in hexane (20 mL). The beige suspension was left at 0 °C for 30 min and then allowed to come to ambient temperature and left for 2 h as such. The solvent was removed by filtration and the solid rinsed with pentane (20 mL) and dried in vacuo. The compound was dissolved in diethyl ether (60 mL), and solid $ZrCl_4$ (0.48 g, 2.05 mmol) was added, leading to the exothermic formation of a thick suspension, which was left at ambient temperature overnight. The suspension was filtered off and solvent removed in vacuo to yield the product as an off-white microcrystalline solid (1.53 g, 97%). Mp: 133–134 °C. 1H NMR (δ , C_6D_6): 0.33 (bs, 6 H, $SiMe_2$), 2.04 (bs, 2H, CH_2), 5.73 (t, 2H, $^3J_{HH} = 2$ Hz, $\alpha-C_5H_4$), 6.19 (t, 2H, $^3J_{HH} = 2$ Hz, $\beta-C_5H_4$). 1H NMR (δ , toluene- d_8): 0.32 (bs, 6 H, $SiMe_2$), 2.10 (bs, 2H, CH_2), 5.75 (bs, 2H, $\alpha-C_5H_4$), 6.19 (bs, 2H, $\beta-C_5H_4$). 1H NMR (δ , toluene- d_8 , -80 °C): 0.40 (bs, 6 H, $SiMe_2$), 2.10 (bs, 2H, CH_2), 5.55 (bs, 2H, $\alpha-C_5H_4$), 6.12 (bs, 2H, $\beta-C_5H_4$). ^{13}C NMR (δ , C_6D_6): -2.5 (s, $SiMe_2$), 13.3 (s, CH_2), 114.6, 126.1, 128.3, and 143.0 (C_6F_5). ^{19}F NMR (δ , C_6D_6): -143.1 (d, $^3J_{F,F} = 20$ Hz, 2F, *o*-F), -160.8 (t, $^3J_{F,F} = 20$ Hz, 1F, *p*-F), -163.9 (dt, $^3J_{F,F} = 20$ Hz, 2F, *m*-F). Anal. Calcd for $C_{28}H_{24}Cl_2F_{10}Si_2Zr$: C, 43.74; H, 3.15. Found: C, 44.02; H, 3.35

Bis[*tris(2,3,4,5,6-pentafluorobenzyl)silyl*]-cyclopentadienyl]zirconium Dichloride (4d). LiBuⁿ (2.3 mL of 1.6 mol L⁻¹ solution in hexane, 3.68 mmol) was added to a cooled solution (0 °C) of $\{C_5H_5Si(CH_2C_6F_5)_3\}$ (**3d**; 2.14 g, 3.36 mmol) in hexane (50 mL). The light beige suspension was left at 0 °C for 30 min and then allowed to come to ambient temperature and left for 2 h as such. The solvent was removed by filtration and the solid rinsed with pentane (20 mL) and dried in vacuo. The compound was dissolved in diethyl ether (40 mL), and solid $ZrCl_4$ (0.31 g, 1.33 mmol) was added, leading to the exothermic formation of a thick suspension, which was left at ambient temperature overnight. The suspension was filtered off and solvent removed in vacuo to yield the product as an off-white microcrystalline solid (1.71 g, 93%). Mp: 55–56 °C. 1H NMR (δ , C_6D_6): 2.34 (bs, 6H, CH_2), 5.36 (t, 2H, $^3J_{HH} = 3$ Hz, $\alpha-C_5H_4$), 6.13 (t, 2H, $^3J_{HH} = 3$ Hz, $\beta-C_5H_4$). ^{13}C NMR (δ , C_6D_6): 8.8 (CH_2), 111.9, 114.2, 122.4, 125.3, 140.2, 141.9, and 146.8 (C_6F_5 and C_5H_4). Anal. Calcd for $C_{52}H_{20}Cl_2F_{30}Si_2Zr$: C, 43.58; H, 1.41. Found: C, 43.45; H, 1.33

Bis[*(dimethyloctylsilyl)cyclopentadienyl*]-zirconium Dichloride (4e). To a stirred solution of LiBuⁿ (14.2 mmol, in 8.9 mL of *n*-hexane) in Et_2O (150 mL) was added $C_5H_5SiMe_2C_8H_{17}$ (3.37 g, 14.2 mmol) at -78 °C. The resulting reaction mixture was stirred for 3 h at room temperature. Volatiles were removed under vacuum. The yellow viscous liquid obtained could not be washed with pentane or hexane, because it gave a gel instead of a precipitate in these solvents. The lithiated product was dissolved in THF (75 mL) at -78 °C. A solution of $ZrCl_4$ (1.64 g, 6.90 mmol) in THF (75 mL) was prepared, and the THF solution of the lithiated ligand was added dropwise over 0.5 h at 0 °C. The mixture was stirred for 48 h at room temperature. Volatiles were removed under vacuum, and the residue was extracted with pentane (2 × 50 mL). Concentration of the orange extract under vacuum afforded a brown oil (4.43 g, 98%). 1H NMR (300.1 MHz, acetone- d_6): δ 6.76 (m, 4H, CH=), 1.31 (m, 12 H, $CH_3C_6H_{12}CH_2Si$), 0.91 (m, 3 H, $CH_3C_6H_{12}CH_2Si$), 0.80 (m, 2H, CH_2Si), 0.34 (s, 6 H, $(CH_3)_2Si$). $^{13}C\{^1H\}$ NMR (75.5 MHz, acetone- d_6): 126.85 (CH=), 126.70 (C=), 117.23 (CH=), 34.30, 32.70, 30.03 (high intensity, probably two overlapping signals), 24.56, 23.39 ($CH_3C_6H_{12}CH_2Si$), 17.43, 14.46 (2 C, $CH_3C_6H_{12}CH_2Si$), -1.78 ($Si(CH_3)_2$). ^{29}Si NMR (59.6 MHz, acetone- d_6): δ 0.37 (s, $SiMe_2$). ^{29}Si NMR (59.6 MHz, benzene- d_6): δ -4.76 (s, $SiMe_2$). Anal.

Table 3. Catalyst NMR Analysis of (4a–c,f)–MAO

compd	¹ H (δ, ppm) ^a				
	Cp	CH ₂	SiMe ₂	Zr–Me	MAO
4a	6.24 (t), 5.78 (t)	1.96 (m), 0.91 (m)	0.23 (s)		
4a + MAO ^b	6.28 (s), 6.24 (s), 5.85 (s), 5.78 (s), 5.75 (s), 5.51 (s)	2.01 (s), 1.94 (s), 0.95 (s), 0.91(s)	0.24 (s), 0.18 (s)	0.42 (bs)	–0.16 (bs)
4b	6.31 (t), 5.65 (t)		0.62 (s)		
4b + MAO ^b	6.48 (b), 5.93 (b), 5.62 (b), 5.42 (b)		0.57 (s)	0.50 (s)	–0.33 (bs)
4b + MAO ^c	6.55 (s), 5.97 (s), 5.65 (s), 5.45 (s)		0.57 (s)	0.39 (s)	–0.27 (bs), 0.49 (s)
4c	6.19 (t), 5.73 (t)	2.04 (s)	0.33 (s)		
4c + MAO ^b	6.22 (b), 5.89 (b), 5.79 (b), 5.58 (b)	2.02 (s)	0.26 (s)	0.44 (s)	–0.32 (bs), –0.56 (s)
4c + MAO ^c	6.31 (s), 5.90 (s), 5.77(s), 5.12 (s)	2.08 (s)	0.26 (s)	0.42 (s)	–0.26 (bs), –0.50 (s)
4f	6.35 (t), 5.90 (t)		0.28 (s)		
4f + MAO ^b	6.32 (b), 6.02 (s), 5.89 (s), 5.78 (s), 5.66 (s)		0.24 (s), 0.11 (s)	0.49 (s)	–0.22 (bs)

^a ¹H NMR in C₆D₆ at ca. 25 °C. ^b Al/Zr = 100. ^c Al/Zr = 20.

Calcd for C₃₀H₅₄Cl₂Si₂Zr: C, 56.88; H, 8.53; Cl, 11.22; Si, 8.85. Found: C, 56.68; H, 8.46; Cl, 11.27; Si, 8.88.

Bis[{dimethyl(1H,1H,2H,2H-perfluorooctyl)silyl]-cyclopentadienyl}zirconium Dimethyl (5a). To a stirred solution of 4a (6.39 g, 5.8 mmol) in diethyl ether (100 mL) was added a solution of LiMe (11.68 mmol) in diethyl ether at –78 °C. The solution was warmed to room temperature and stirred overnight. The volatiles were removed under vacuum, and the product was extracted with pentane (150 mL) and then dried under vacuum. The pure product (5.31 g, 86%) was obtained as a white powder and recrystallized from pentane. ¹H NMR (200.14 MHz, benzene-*d*₆): δ 5.95 and 5.84 (dt, 4H, *J*_{AX} = *J*_{AX'} = 2.45 Hz, CH=), 1.94 (m, 2H, CH₂–CF₂), 0.81 (m, 2H, CH₂–Si), 0.07 (s, 6H, Me₂Si), –0.21 (s, 3H, Me₂Zr). ¹³C{¹H} NMR (50.33 MHz, benzene-*d*₆): δ 118.42 (CH=), 117.22 (C=), 113.91 (CH=), 31.57 (Me₂Zr), 26.69 (t, ²*J*_{C,F} = 23.73 Hz, CH₂–CF₂), 7.51 (CH₂–Si), –2.50 (Si(CH₃)₂). ²⁹Si NMR (59.62 MHz, benzene-*d*₆): δ –4.71 (SiMe₂). Anal. Calcd for C₃₂H₃₄Cl₂F₂₆–Si₂Zr: C, 36.26; H, 3.21; Cl, 0.00; F, 46.65; Si, 5.29. Found: C, 36.15; H, 3.15; Cl, 0.00; F, 46.43; Si, 5.24.

NMR Analysis of Precatalyst/MAO Mixtures. In a typical experiment, ca. 5 μmol of the precatalyst was added in a Schlenk to solid MAO (0.3 mL of a 10 wt % solution in toluene evaporated to dryness in vacuo, 0.5 mmol, Al/Zr ≈ 100), solvated with C₆D₆ (ca. 0.5 mL), and transferred under nitrogen to an NMR tube, which was then capped. Hydrolysis of the catalyst was carried out with 0.1 mL of a 1:20 concentrated HCl–D₂O solution. See Table 3 for chemical shifts and assignments.

Ethylene Polymerization. In a typical polymerization experiment, a jacketed 150 mL glass reactor was fitted with a gas action stirrer (1300 rpm) and inlet/outlet for ethylene/vacuum/nitrogen. The reactor was thermostated at 20 °C using a water bath, dried and degassed in vacuo for 30 min, and then purged with nitrogen gas. The solvent was transferred via syringe, and a solution (in toluene, hexane, or FC-72) of the catalyst was added (the total volume of solvents was used for calculation of the zirconium concentration). Finally MAO (10 wt % solution in toluene or suspension in hexane) was transferred to the reaction mixture, which was stirred for 5 min under nitrogen pressure. The reactor was briefly depressurized, and ethylene was allowed at 1.1 bar pressure (at *t*₀). The reaction was quenched (at *t*_p) with 50 mL of a 1:1 mixture of EtOH and aqueous 2 M HCl and stirred for 15 min. The suspension was filtered off, and the solid was rinsed with 10% aqueous HCl and then EtOH and dried in vacuo for ca. 15 h at ambient temperature.

Determination of Partition Coefficients. The partition coefficients were determined by dissolving a known amount of complex (typically 50 μmol) in a fluorous biphasic system consisting of *c*-C₆F₁₁CF₃ (2.00 ± 0.01 mL) and toluene (2.00 ± 0.01 mL). The resulting mixture was stirred at 20 °C for 1 h, and then an aliquot of each layer was removed for ICP–AAS analysis on silicon with an accuracy of ±3 ppm. A conservative

Table 4. Crystallographic Data for 2d and 4a,c

	2d	4a	4c
empirical formula	C ₂₁ H ₆ BrF ₁₅ –Si	C ₃₀ H ₂₈ Cl ₂ F ₂₆ –Si ₂ Zr	C ₂₈ H ₂₄ Cl ₂ F ₁₀ –Si ₂ Zr
formula wt	651.26	1100.82	768.77
cryst syst	trigonal	monoclinic	triclinic
space group	R3̄ (No. 148)	C2/c (No. 15)	P1̄ (No. 2)
<i>a</i> , Å	15.9230(12)	46.3678(10)	7.8842(1)
<i>b</i> , Å	15.9230(12)	6.5983(2)	13.4155(2)
<i>c</i> , Å	29.4013(16)	14.2962(4)	15.1449(3)
α, deg	90	90	73.4706(7)
β, deg	90	106.4326(14)	80.0282(8)
γ, deg	120	90	87.9965(7)
<i>V</i> , Å ³	6455.8(8)	4195.2(2)	1512.31(4)
<i>Z</i>	12	4	2
<i>D</i> _{calcd} , g cm ^{–3}	2.010	1.743	1.688
μ(Mo Kα), mm ^{–1}	2.106	0.586	0.701
<i>F</i> (000)	3792	2176	768
no. of unique reflns, <i>R</i> _{int}	2966, 0.064	4790, 0.065	5631, 0.041
no. of rflns (<i>I</i> > 2σ(<i>I</i>))	2249	2810	4883
final <i>R</i> 1 (<i>I</i> > 2σ(<i>I</i>))	0.036	0.033	0.030
final <i>wR</i> 2	0.078	0.089	0.079
goodness of fit	1.015	0.80	1.05

estimate of the experimental error in the partition coefficient is ±1 in the last digit.

Crystallography. Colorless, X-ray-quality, single crystals of the zirconocene dichloride were grown from cooled (ca. –20 °C) concentrated Et₂O (2d), THF (4a), or Et₂O (4c) solution of the pure compound and were mounted under a flow of cold nitrogen (150 K) on an Enraf-Nonius CAD4T (2d) or a Nonius KappaCCD (4a,c) diffractometer, both equipped with a rotating anode. Crystal data and details on data collection are collected in Table 4. Data were collected using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). The structures were solved by direct methods (2d³⁹ and 4a⁴⁰) or Patterson methods (4c⁴¹) and refined with SHELXL-97⁴² against *F*² of all reflections. All geometrical calculations and illustrations were done with PLATON.⁴³

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Supporting Information Available: CIF files with atomic coordinates, bond lengths and angles, and thermal parameters for **2d** and **4a,c** and figures giving ^1H NMR spectra of solutions of **4a-c** with MAO (Al/Zr = 100) in benzene- d_6 . This material is available free of charge via the Internet at <http://pubs.acs.org>.

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