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Synthesis of 3,3,3-Trifluoropropyl Substituted Cyclopentadienes and Their Zirconocene Derivatives: Catalytic Applications in the Polymerization of Ethylene

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The synthesis and structure of novel 3,3,3-trifluoropropyl substituted cyclopentadienes (**2**/**3**) and of their zirconocene dichloride derivatives $[Zr(\eta^5\text{-}C_5H_4C_2H_4CF_3)_2Cl_2]$ (**6**) and $[Zr\{\eta^5\text{-}C_5H_3\text{-}1,2\text{-}(C_2H_4CF_3)_2\}_2Cl_2]$ (**7**) is reported. These precatalysts have been investigated toward their properties in the methylaluminoxane (MAO) assisted polymerization of ethylene. The results can be compared to the polymerization properties of the non-fluorinated analogue $[Zr(\eta^5\text{-}C_5H_4C_2H_4CH_3)_2Cl_2]$ (**11**). Complexes **6** and **7** produce high-density polyethylene (HDPE) and are among the most active precatalysts for donor functionalized nonbridged metallocenes. An unprecedented temperature independence of the molar mass distribution is observed for the polymerization with **6**.

Introduction

Group 4 metallocene based precatalysts find a wide use in the methylaluminoxane (MAO) assisted olefin polymerization in industry.[1−3] Therefore it is of fundamental interest to gain a profound understanding of the factors which determine the properties of the resulting polymers in order to develop routes to new materials. The steric and electronic properties at the transition metal center as well as the steric and electronic effects of hemilabile functionalities have a tremendous effect on stereochemical microstructure and molecular weight distribution of the polymer or on the synthesis of copolymers.[1,2] Thus, various efforts have been made to "engineer" single-site homogeneous catalysts and to stabilize the catalytically active cationic species. Dialkylaminoethyl functionalized *ansa*-zirconocene dichlorides were the first systems yielding both high molecular polyethylene (PE) and low molecular PE depending on the polymerization temperature.[4] This effect has been explained by a coordination of the Lewis acidic cocatalyst MAO to the dialkylaminoethyl group at low temperatures. Steric repulsive interactions with the growing polymer chain avoid the planar configuration which is necessary for β-hydrogen elimination. This results consequently in polymers of higher molecular weight. At elevated temperatures the interaction of MAO with the amino group is less pronounced, yielding polymers of low molecular weight. Marks and co-workers focused on the role of metallocene−cocatalyst interaction.[5] To obtain detailed structural information on the catalytically active cation weakly coordinating borate anions instead of MAO were used as anions. The complexes derived exhibit a stabilization by Zr···F contacts between the cation and anion, such as between $[HB(C_6F_5)_3]^-$ and $[Zr(\eta^5\text{-}C_5Me_5)_2H]^+$.[5d] Intramolecular coordination of fluorine to a cationic zirconium center was realized by Erker et al. in the zwitterionic tris(cyclopentadienyl)-zirconium−betaine complex $[ZrCp_3\{C_5H_4B(C_6F_5)_3\}]$.[6] The research group of Rosenthal published a comparable zwitterionic *ansa*-zirconocene.[7] In this case the positive charge at the transition metal was also stabilized by a fluorinated anion via Zr···F contacts in addition to an agostic C−H interaction of a σ-bound alkenyl group.[7] Density functional theory (DFT) calculations reported by Fujita et al. indicate the possibility for attractive $C(sp^2)$−F···H−C interactions between a pentafluo-

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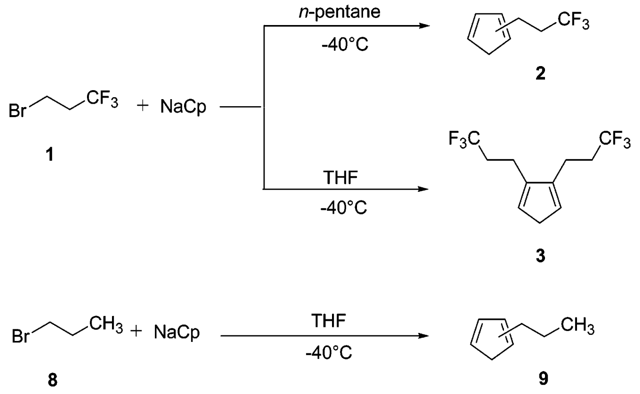
Scheme 1. Synthesis of 2, 3, and 9



rophenyl group and the β-hydrogen atom at a growing polymer chain at titanium.[8] This could depress β-hydrogen elimination, leading to higher molecular polymers. Theoretical and experimental evidence for such an attractive interaction of a CF_3 group to the α-H atoms of a benzyl ligand has been published very recently by Chan et al.[9]

In the present paper we report on the synthesis and the polymerization properties of 3,3,3-trifluoropropyl substituted zirconocene dichlorides. For comparison the polymerization properties of a non-fluorinated propyl analogue have been investigated. Unexpected features of the fluorinated zirconocenes in the MAO assisted ethylene polymerization can be attributed to the trifluoropropyl group.

Results and Discussion

Synthesis of Fluoroalkyl-substituted Cyclopentadienes. The stoichiometric reaction of 1,1,1-trifluoro-3-bromopropane (**1**) with NaCp in *n*-pentane at −40 °C produced two isomers of the fluorinated cyclopentadiene (**2**) in aliquot ratio as a colorless liquid (Scheme 1). After subsequent treatment of the mixture with KH the 3,3,3-trifluoropropylcyclopentadienid (**4**) has been obtained. Changing the solvent from *n*-pentane to the more polar THF, the reaction of **1** with NaCp leads to the 1,2-disubstituted cyclopentadiene **3**. The substitution pattern has been confirmed by ^1H NMR and ^{19}F NMR spectroscopy. Two triplets in the proton NMR spectrum with a coupling constant of 1.5 Hz at $\delta = 2.5$ and $\delta = 5.5$ of equal integral ratio can be assigned to the hydrogen atoms in the 4- and 3,5-positions, respectively. The ^{19}F NMR spectrum reveals a triplet at $\delta = -64.7$ with an F−H coupling of 11 Hz. In addition, the molecular structure of **3** was confirmed by X-ray diffraction analysis at 100 K. Suitable crystals have been obtained from a crude liquid at 277 K. The molecular structure is shown in Figure 1. Selected bond lengths and angles are summarized in Table 1. Treatment of **3** with KH yields the potassium cyclopentadienid **5**. The solvent dependent formation of either **2** or **3** can be explained by the electron withdrawing effect of the terminal trifluoromethyl group at the monosubstituted cyclopentadiene resulting in THF as solvent in a higher Brønsted acidity of the ring protons compared to the protons in CpH. Thus, another equivalent NaCp reacts readily with **2** giving CpH and the sodium salt of **2** being stabilized by the polar solvent THF. Another equivalent of **1** converts the sodium salt into **3**. Apparently, a C_2H_4 spacer unit does not completely suppress the electron withdrawing influence of the CF_3 group.[10] In the case of the non-fluorinated ligand precursor **9** we did not observe a comparable solvent dependence to give a 1,2-disubstituted cyclopentadiene (vide infra).

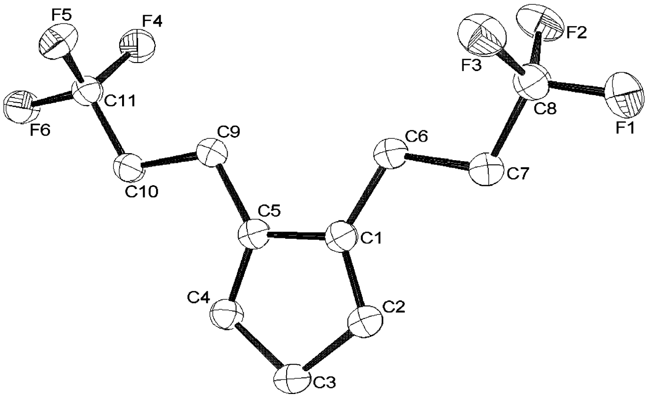


Figure 1. ORTEP diagram of **3** (ellipsoids at 50% probability level).

Table 1. Selected Bond Lengths (Å) and Angles (deg) of 3 with Standard Deviations in Parentheses

bond	length	bonds	angle
C(1)−C(2)	1.343(2)	C(2)−C(1)−C(5)	108.82(13)
C(1)−C(5)	1.479(2)	C(1)−C(2)−C(3)	109.75(13)
C(2)−C(3)	1.502(2)	C(2)−C(3)−C(4)	102.94(12)
C(3)−C(4)	1.499(2)	C(3)−C(4)−C(5)	109.60(13)
C(4)−C(5)	1.347(2)	C(4)−C(5)−C(1)	108.89(13)
F(1)−C(8)	1.3498(19)	F(1)−C(8)−F(2)	106.20(12)
F(2)−C(8)	1.3421(18)	F(1)−C(8)−F(3)	106.03(12)
F(3)−C(8)	1.3438(18)	F(2)−C(8)−F(3)	105.74(12)

Synthesis of Fluoroalkyl-substituted Zirconocene Dichlorides. The synthesis of zirconium complexes was carried out at −80 °C by adding $ZrCl_4$ to a suspension of **4** or **5** in diethyl ether. The 3,3,3-trifluoropropyl substituted dichloro compounds **6** and **7** were obtained in good yields (Scheme 2). The ^1H NMR spectrum of **6** reveals a quartet of triplets at $\delta = 1.95$ with couplings of 10.7 and 8.2 Hz, respectively. This signal can be assigned to the CH_2 protons adjacent to the terminal CF_3 group. A triplet at $\delta = 2.73$ with a coupling constant of 8.2 Hz results from the CH_2 group attached to the ring. Two additional triplets at lower field ($\delta = 5.5$ and $\delta = 5.6$) with couplings of 2.5 Hz can be assigned to the aromatic protons. As a consequence of the higher degree of fluorination, the proton NMR of compound **7** displays a more complex signal structure. A doublet and a triplet with an integral ratio of 2:1 at low field can be found for the aromatic hydrogen atoms. The spectrum shows four additional resonances due to the diastereotopic protons of the trifluoropropyl substituents. The signals at $\delta = 2.4$ and $\delta = 2.7$ consist of a doublet of doublets of doublets resulting from one geminal and two vicinal couplings. Two overlapping multiplets can be assigned for the CH_2CF_3 nuclei. The ^{19}F NMR spectrum shows a resonance with a triplet pattern at $\delta = -65.2$ arising from coupling of the fluorine nuclei with the adjacent methylene group. The molecular structure of **6** has been determined by X-ray diffraction analysis at 100 K (Figure 2). Selected bond lengths and angles are summarized in Table 2.

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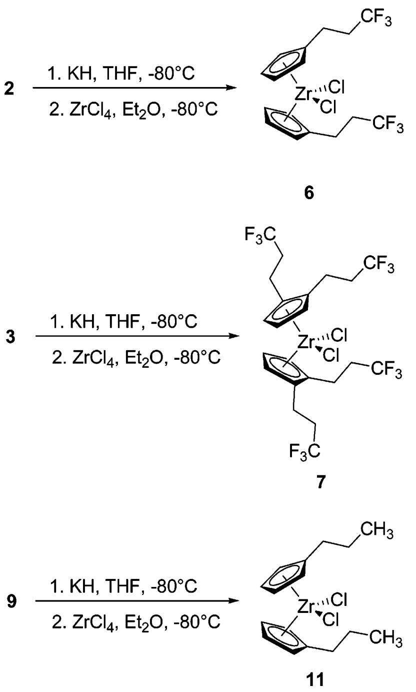
Scheme 2. Synthesis of the Zirconocene Dichlorides 6, 7, and 11



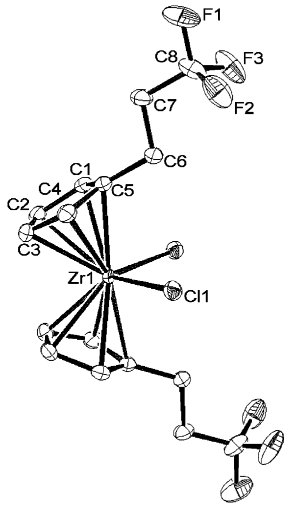


Figure 2. ORTEP diagram of **6** (ellipsoids at 50% probability level).

Table 2. Selected Bond Lengths (Å) and Angles (deg) of 6 with Standard Deviations in Parentheses

bond	length	bonds	angle
Zr(1)−Cl(1)	2.4650(3)	Cl(1)−Zr(1)−Cl(2)	95.235(15)
Zr(1)−C(1)	2.5422(10)		
Zr(1)−C(2)	2.4986(11)		
Zr(1)−C(3)	2.4949(11)		
Zr(1)−C(4)	2.5288(11)		
Zr(1)−C(5)	2.5538(10)		

Complex **6** adapts a bent-sandwich configuration with a ring centroid−Zr−ring centroid angle of 127.76(4)°. Since the angle Cl−Zr−Cl is 95.235(15)°, the coordination geometry of the zirconium atom can be viewed as distorted tetrahedral. The C(aryl)−Zr distances vary between 2.45 and 2.55 Å in accordance with an η^5-coordination of the Cp ligands. The Zr−Cl distances of approximately 2.46 Å are in the same range as comparable distances in other zirconocene dichlorides.[11]

We also prepared complex **11**, which is a non-fluorinated analogue of **6**. 1-Bromopropane (**8**) was added to a slurry of NaCp in tetrahydrofuran (THF) at −40 °C and allowed to warm to room temperature, leading to a mixture of two *n*-propyl substituted cyclopentadiene isomers (**9**) (Scheme 1). Again, after workup, treatment of **9** with KH yields the propylcyclopentadienid (**10**). The synthesis of the zirconium dichloro compound **11** was carried out at −80 °C by adding $ZrCl_4$ to a suspension of **10** in diethyl ether (Scheme 2). The analytical data of **11** are consistent with those reported in the literature.[12]

Ethylene Polymerization Experiments. Complexes **6**, **7**, and **11** have been used in the MAO activated polymerization of ethylene. Representative experimental results and polymerization details are summarized in Table 3.[13] In all cases the polymers consist of high-density polyethylene (HDPE) of low molecular weight with a broad molecular weight distribution. It is of particular interest that compounds **6** and **7** show a higher activity (456.2 and 219.7 kg mol^{-1} h^{-1} bar^{-1}, respectively) than the non-fluorinated analogue **11** (75 kg mol^{-1} h^{-1} bar^{-1}) at a polymerization temperature of $T = 50$ °C, although the effect is less dramatic at elevated temperatures. The ethylene consumption within 60 min of polymerization is consistent with the calculated activity and the amount of polyethylene obtained. To the best of our knowledge, **6** and **7** are among the most active precatalysts toward MAO assisted ethylene polymerization for donor functionalized nonbridged metallocenes.[14] This behavior can be explained with an increase of the van der Waals volume by approximately 50% on substituting the CH_3 group (13.7 cm^3 mol^{-1}) of the Cp ligand by the CF_3 group (21.3 cm^3 mol^{-1}).[15] Such an increase could eventually lead to a better cation/anion separation of the catalytically active species L_2ZrMe^+ and the CH_3MAO^- anion which in turn results in a higher activity. The sterically more demanding substitution pattern of **7** leads to a slightly decreased activity compared to the results obtained for **6**. This is in accordance with the general tendency of sterically more hindered systems, yielding lower activities.[16] Interestingly, compound **11** shows the expected increase in activity at elevated temperatures, whereas polymerization with the trifluoropropyl substituted complex **6** proceeds with comparable activities in a temperature range from 20 to 90 °C. The lower activity of **6** at $T = 70$ °C compared to the results obtained at lower or higher temperatures (entries 1−4) are compatible with different chain termination mechanisms being operative at different temperatures (see below).[13]

The molar masses of the polymers which have been obtained are mainly determined by electronic effects of the Cp ligands. Thus at $T = 50$ °C the propyl substituted compound **11** gives polyethylene of $M_w = 551\,451$ g mol^{-1}, whereas $ZrCl_2Cp_2$ (87 419 g mol^{-1}) and **6** (34 067 g mol^{-1}) yield polymers of lower molecular weight.[13] Fujita and Chang have proposed that C−F···H−C ligand−polymer interactions can stabilize a grow-

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[13] All of the data in Table 3 are reproducible within the experimental error. Thus for the M_w of **11** at 50 °C, 55.1 × 10^4 and 55.2 × 10^4 g/mol have been obtained in two independent experiments; for **6** at 70 °C M_w has been determined as $M_w = 2.1 \times 10^4$ and 1.9×10^4 g/mol.

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Table 3. Ethylene Polymerization Results[a]

entry	precatalyst	T (°C)	t (min)	yield (g)	activity[b]	M_w,[c] × 10^4	M_w/M_n [c]
1	**6**	20	60	30.7	384.1	3.29	4.85
2	**6**	50	60	36.5	456.2	3.41	5.09
3	**6**	70	60	18.6	232.5	2.11	6.56
4	**6**	90	60	35.7	445.7	2.33	3.38
5	**7**	50	60	17.6	219.7	10.1	8.39
6	**11**	50	60	6.1	75.0	55.1	9.91
7	**11**	70	60	24.3	303.8	3.99	3.97
8	**11**	90	60	28.1	351.3	2.44	3.99
9	$ZrCp_2Cl_2$	50	60			8.74	6.79

[a] [Zr] = 0.02 mmol, [Zr]/[Al] = 1/1000, in 40 mL of toluene, 4 bar ethylene feed. [b] kg(PE)/mol(cat.)·atm·h. [c] By GPC, relative to polystyrene standards. M_w in g/mol.

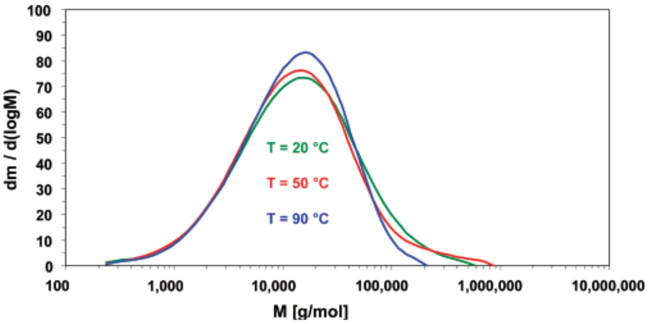

Figure 3. Molar mass distribution (GPC) of the ethylene polymerization experiments using **6**/MAO as catalyst.

ing polymer chain.[8,9] C−F···H−C interactions are generally considered to be weak, but they appear to exist in the solid state and in solution.[17−19] However, such an interaction might lead to higher molar masses of the polymer. On the other hand, F−H(α) interactions leading to β-hydrogen transfer from the growing polymer chain to the monomer have also been discussed at titanium.[20] Gladysz et al. investigated the electron withdrawing influence of perfluorinated alkyl groups at the Cp ligand of transition metal complexes, the effect being even present with a C_2H_4 spacer unit between the fluorinated group and the aromatic ring.[10b] These studies are consistent with our results regarding the generation of **3** (vide supra). We tentatively attribute the changes in M_w to the increasing electrophilicity of the transition metal center in the corresponding catalytically active cations $\mathbf{11}^+ < ZrCp_2Me^+ < \mathbf{6}^+$. This might promote chain determination by β-hydrogen elimination.[21]

Polymerization experiments at various temperatures revealed that complex **6** exhibits an unprecedented temperature independence of the molar mass distribution (Figure 3). There seems to be some compensating effect induced by the pendant trifluoropropyl groups. At lower temperatures fluorine interactions with the anion could lead to a closer proximity of the anion to the growing polymer chain, possibly resulting in chain termination steps by chain transfer to the aluminum. End group analysis supports this assumption and reveals a high degree of saturated end groups (ca. 5.6/1000 C by IR) and only a small amount of vinyl groups (ca. 0.25/1000 C by IR) for the polymerization at T = 70 °C. We also cannot exclude that intramolecular coordination of the CF_3 group to the metal center might play a certain role to depress β-hydrogen elimination steps at high temperatures. The stabilization of cationic transition metal centers in ethylene polymerization by hemilabile coordinating ligands is well-known.[22]

Conclusion

In conclusion, the differences of fluorinated zirconocene dichlorides in terms of MAO assisted ethylene polymerization compared to a non-fluorinated analogue have been reported and attributed to the properties of the fluorinated ligands. Molar masses of the polymers mainly depend on electronic effects of the Cp ligands. The precatalysts with the fluorinated Cp ligands are among the most active systems for donor functionalized nonbridged zirconocenes, possibly because of a better cation/anion separation. In addition, **6** features an unprecedented temperature independence of the molecular weight distribution.

Experimental Section

General Considerations. All solvents were purified and dried by conventional methods and distilled under argon before use. Benzene-d_6 and THF-d_8 were dried over Na/K while CD_2Cl_2 was dried by stirring over CaH_2 prior to use. 1,1,1-Trifluoro-3-bromopropane (**1**) and 1-bromopropane (**8**) were purchased from ABCR and Aldrich and distilled before use. $ZrCl_4$ and $ZrCp_2Cl_2$ were obtained from Merck as was KH in paraffin oil, which was washed with hexane. NaCp was prepared according to a literature procedure.[23] MAO (10% in toluene) was obtained from Witco GmbH (Bergkamen).

The NMR spectra were recorded at 300 K with a Bruker DRX 500 spectrometer. The ^{1}H NMR chemical shifts were referenced to residual C_6D_5H at δ 7.15, THF-d_7 at δ 3.58 and δ 1.73, and $CDHCl_2$ at δ 5.32. The ^{19}F NMR spectra were referenced to external C_6F_6 at δ −162.9. The ^{13}C NMR chemical shifts were referenced to C_6D_6 at δ 128.0, THF-d_8 at δ 25.5 and δ 67.7, and CD_2Cl_2 at δ 53.5. Mass spectra were recorded on a MS QP5050A fitted with a Shimadzu GC 17a. GPC analyses of the polymer samples were performed at Basell GmbH (Frankfurt).

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$C_5H_5CH_2CH_2CF_3$ (2). A suspension of NaCp (5.00 g, 56.8 mmol) in *n*-pentane (100 mL) was treated with a solution of **1** (9.10 g, 51.4 mmol) in *n*-pentane (30 mL) at −40 °C. The pale red reaction mixture was allowed to reach room temperature, leading to a pale suspension. The suspension was heated to reflux for an additional 3 h and then cooled to room temperature. The product and solvent were distilled together at 0 °C in vacuo to obtain a first fraction of **2**. The residue was then extracted with *n*-pentane (20 mL). The combined fractions were distilled at −30 °C under reduced pressure (27 mbar), yielding **2** as a colorless oil. Yield: 4.75 g (57%). NMR data of both isomers: ^{1}H NMR (500 MHz, C_6D_6) δ 1.81 (qt, $^3J_{F,H} = 10.7$ Hz, $^3J_{H,H} = 8.2$ Hz, 2 H, CH_2CF_3), 1.91 (qt, $^3J_{F,H} = 10.7$ Hz, $^3J_{H,H} = 8.2$ Hz, 2 H, CH_2CF_3), 2.27 (t, $^3J_{H,H} = 8.2$ Hz, 2 H, $CH_2CH_2CF_3$), 2.32 (t, $^3J_{H,H} = 8.2$ Hz, 2 H, $CH_2CH_2CF_3$), 2.38 (s, br, 2 H, CH), 2.64 (s, br, 2 H, CH), 5.66 (s, br, 1 H, CH), 5.86 (s, br, 1 H, CH), 6.12 (s, br, 1 H, CH), 6.13 (s, br, 1 H, CH), 6.22 (s, br, 1 H, CH), 6.31 (s, br, 1H, CH); ^{13}C NMR (125.7 MHz, C_6D_6) δ 14.3 (CH_2), 23.0 (CH_2), 31.9 (C_{allyl}), 33.1 (q, $^2J_{C,F} = 28.7$ Hz, CH_2CF_3), 33.6 (q, $^2J_{C,F} = 28.7$ Hz, CH_2CF_3), 41.4 (C_{allyl}), 124.7−129.2 (m, CF_3 for both isomers), 126.7 (C_{vinyl}), 127.6 (C_{vinyl}), 131.2 (C_{vinyl}), 132.4 (C_{vinyl}), 134.0 (C_{vinyl}), 134.3 (C_{vinyl}), 143.9, 145.4; ^{19}F NMR (470.4 MHz, C_6D_6) δ −65.8 (t, $^3J_{F,H} = 11$ Hz, CF_3 both isomers). MS (70 eV): *m*/*z* (%) 162 (36) [M^+], 83 (86) [$CH_2CF_3^+$], 79 (100) [$M^+ - CH_2CF_3$].

C_5H_4-1,2-$(CH_2CH_2CF_3)_2$ (4). A solution of **1** (17.0 g, 100.0 mmol) in THF (50 mL) was added to a suspension of NaCp (9.50 g, 107.9 mmol) in THF (150 mL) at −40 °C. The mixture was stirred for 18 h and then allowed to reach room temperature. A colorless solid precipitated from the pale red solution. The solvent was removed at reduced pressure (17.3 mbar) and the residue hydrolyzed with an aqueous solution of ammonium chloride (3%, 200 mL). After extraction of the resulting brown solution with *n*-pentane (3 × 130 mL), the combined pentane fractions were washed with water (4 × 100 mL) and dried over Na_2SO_4. The mixture was filtered, and then the solvent was removed from the filtrate under reduced pressure and the remaining brown oil distilled in vacuo. One fraction (75−82 °C, 13.3 mbar) consisted of a colorless liquid, from which after 2 weeks at 4 °C colorless needles precipitated. Yield: 1.14 g (9%). ^{1}H NMR (500 MHz, C_6D_6) δ 1.88−1.93 (m, 4 H, CH_2CF_3), 2.08 (t, $^3J_{H,H} = 7.8$ Hz, 4 H, CH_2), 2.49 (t, $^3J_{H,H} = 1.5$ Hz, 2 H, CH), 5.54 (t, $^3J_{H,H} = 1.5$ Hz, 2 H, CH_2(ring)); ^{13}C{^{1}H} NMR (125.7 MHz, C_6D_6) δ 20.3 ($CH_2CH_2CF_3$), 33.2 (q, $^2J_{C,F} = 28.7$ Hz, CH_2CF_3), 39.4 (C_5H_4), 127.2 (C_5H_4), 130.1 (q, $^1J_{C,F} = 310.7$ Hz, CF_3), 143.8 (C_5H_4); ^{19}F NMR (470.4 MHz, C_6D_6) δ −65.5 (t, $^3J_{F,H} = 11$ Hz, CF_3). MS (70 eV): *m*/*z* (%) 258 (75) [M^+], 175 (61) [$M^+ - CH_2CF_3$], 161 (32) [$M^+ - CH_2CH_2CF_3^+$]. Anal. Calcd for $C_{11}H_{12}F_6$: C, 51.17; H, 4.68. Found: C, 51.14; H, 4.96.

$K[C_5H_4CH_2CH_2CF_3]$ (3). To a solution of **2** (363 mg, 2.28 mmol) in THF (25 mL), a suspension of potassium hydride (91.5 mg, 2.28 mmol) in THF (20 mL) was added dropwise at −80 °C. The reaction mixture was allowed to warm to room temperature within 7 h while being stirred. All volatiles of the pale red solution were removed in vacuo. After the residue has been washed with hexane (3 × 10 mL) and dried in vacuo, a pale red solid was obtained. Yield: 380 mg (85%). ^{1}H NMR (500 MHz, THF-d_8) δ 2.37 (qt, $^3J_{F,H} = 11.5$ Hz, $^3J_{H,H} = 8.5$ Hz, 2 H, CH_2CF_3), 2.70 (t, $^3J_{H,H} = 8.5$ Hz, 2 H, $CH_2CH_2CF_3$), 5.37 (t, $^3J_{H,H} = 2.5$ Hz, 2 H, CH), 5.38 (d, $^3J_{H,H} = 2.5$ Hz, 2 H, CH); ^{13}C{^{1}H} NMR (125.7 MHz, THF-d_8) δ 23.3 (CH_2), 37.2 (q, $^2J_{C,F} = 26.1$ Hz, CH_2CF_3), 103.6 (C_5H_4), 104.4 (C_5H_4), 117.1 (C_5H_4), 128.8 (q, $^1J_{C,F} = 277.0$ Hz, CF_3); ^{19}F NMR (470.4 MHz, THF-d_8) δ −64.2 (t, $^3J_{F,H} = 11.5$ Hz, CF_3).

$K[C_5H_3$-1,2-$(CH_2CH_2CF_3)_2]$ (5). A suspension of KH (56.0 mg, 1.39 mmol) in THF (30 mL) was added dropwise to a solution of **4** (0.36 g, 1.39 mmol) in THF (20 mL) at −80 °C. The reaction mixture was allowed to warm to room temperature while being stirred for 16 h. The volatiles were removed in vacuo, and the residue was washed with pentane. The residue was dried in vacuo, giving a pale red solid. Yield: 260 mg (63%). ^{1}H NMR (500 MHz, THF-d_8) δ 2.30−2.38 (m, 4 H, CH_2CF_3), 2.70 (t, $^3J_{H,H} = 8.7$ Hz, 4 H, $CH_2CH_2CF_3$), 5.36 (d, $^3J_{H,H} = 3.1$ Hz, 2 H, CH), 5.39 (t, $^3J_{H,H} = 3.1$ Hz, 1 H, CH); ^{13}C{^{1}H} NMR (125.7 MHz, THF-d_8) δ 21.4 ($CH_2CH_2CF_3$), 37.4 (q, $^2J_{C,F} = 25.3$ Hz, CH_2CF_3), 103.1 (C_5H_3), 103.3 (C_5H_3), 114.1 (C_5H_3), 129.0 (q, $^1J_{C,F} = 276.6$ Hz, CF_3); ^{19}F NMR (470.4 MHz, THF-d_8) δ −64.7 (t, $^3J_{F,H} = 11.0$ Hz, CF_3).

$[Zr(C_5H_4CH_2CH_2CF_3)_2Cl_2]$ (6). $ZrCl_4$ (209 mg, 0.90 mmol) was added to a suspension of **3** (360 mg, 1.80 mmol) in diethyl ether (40 mL) at −80 °C. The suspension was stirred and allowed to warm to room temperature within 16 h. The solvent was removed in vacuo and the pale residue extracted with toluene (40 mL). After 24 h colorless crystals formed at −80 °C from the extract. Yield: 420 mg (97%). ^{1}H NMR (500 MHz, THF-d_8) δ 1.96 (qt, $^3J_{F,H} = 10.9$ Hz, $^3J_{H,H} = 7.9$ Hz, 4 H, CH_2CF_3), 2.73 (t, $^3J_{H,H} = 7.9$ Hz, 4 H, $CH_2CH_2CF_3$), 5.52 (t, $^3J_{H,H} = 2.5$ Hz, 4 H, CH), 5.63 (d, $^3J_{H,H} = 2.5$ Hz, 4 H, CH); ^{13}C{^{1}H} NMR (125.7 MHz, THF-d_8) δ 22.8 ($CH_2CH_2CF_3$), 33.9 (q, $^2J_{C,F} = 28.7$ Hz, CH_2CF_3), 111.5 (C_5H_4), 116.6 (C_5H_4), 128.0 (m, CF_3), 131.4 (C_5H_4); ^{19}F NMR (470.4 MHz, THF-d_8) δ −65.3 (t, $^3J_{F,H} = 10.9$ Hz, CF_3). MS (70 eV): *m*/*z* (%) 482 (7) [M^+], 399 (3) [$M^+ - CH_2CF_3$], 142 (29) [$C_5H_4(CH_2CH_2CF_2)^+$], 78 (100) [$C_5H_4(CH_2)^+$]. Anal. Calcd. for $C_{16}H_{16}Cl_2F_6Zr$: C, 39.67; H, 3.33. Found: C, 39.89; H, 3.32.

$[Zr\{C_5H_3$-1,2-$(CH_2CH_2CF_3)_2\}_2Cl_2]$ (7). A suspension of **5** (260 mg, 0.88 mmol) in diethyl ether (25 mL) was treated with $ZrCl_4$ (100 mg, 0.44 mmol) at −80 °C. The brownish red suspension was stirred and allowed to warm to room temperature within 16 h. The solvent from the yellow suspension was removed in vacuo, the pale residue extracted with toluene (50 mL), and the volume of the extract reduced to 8 mL. After 3 days yellow crystals formed at −80 °C. Yield: 140 mg (47%). ^{1}H NMR (500 MHz, THF-d_8) δ 1.86−1.93 (m, 4 H, CH_2CF_3), 1.91−1.98 (m, 4 H, CH_2CF_3), 2.38−2.44 (m, 4 H, $CH_2CH_2CF_3$), 2.62−2.68 (m, 4 H, $CH_2CH_2CF_3$), 5.29 (t, $^3J_{H,H} = 3.1$ Hz, 2 H, CH), 5.46 (d, $^3J_{H,H} = 3.1$ Hz, 4 H, CH); ^{13}C{^{1}H} NMR (125.7 MHz, THF-d_8) δ 20.6 ($CH_2CH_2CF_3$), 33.1 (q, $^2J_{C,F} = 28.7$ Hz, CH_2CF_3), 106.1 (C_5H_3), 114.1 (C_5H_3), 127.1 (q, $^1J_{C,F} = 277.0$ Hz, CF_3), 129.2 (C_5H_3); ^{19}F NMR (470.4 MHz, THF-d_8) δ −65.2 (t, $^3J_{F,H} = 11.0$ Hz, CF_3). MS (70 eV): *m*/*z* (%) 674 (33) [M^+], 639 (7) [$M^+ - Cl$], 417 (52) [$M^+ - C_5H_3(CH_2CH_2CF_3)_2$], 174 (32) [$(CH_2)C_5H_3(CH_2CH_2CF_3)^+$]. Anal. Calcd for $C_{22}H_{22}Cl_2F_{12}Zr$: C, 39.06; H, 3.28. Found: C, 38.90; H, 3.26.

$[Zr(C_5H_4CH_2CH_2CH_3)_2Cl_2]$ (11). A suspension of NaCp (4.11 g, 46.7 mmol) in THF (150 mL) was treated with 1-bromopropane (**8**) (4.5 mL, 49.4 mmol) at −40 °C. The pale red reaction mixture was allowed to reach room temperature while being stirred overnight, leading to a pale suspension. After being heated to reflux for an additional 2 h, the suspension was cooled to room temperature. The mixture was hydrolyzed with aqueous ammonium chloride solution (200 mL), and the organic fraction was separated. After washing the aqueous phase with *n*-hexane (150 mL), the combined organic fractions were dried over Na_2SO_4 and the mixture was filtered. The filtrate was distilled, yielding **9** as a yellow oil (bp: 117 °C, yield: 71%). To a solution of $C_5H_4CH_2CH_2CH_3$ (**9**) (1.08 g, 9.98 mmol) in THF (40 mL), a suspension of potassium hydride (412 mg, 10.3 mmol) in THF (20 mL) was added dropwise at −80 °C. On warming the reaction mixture to room temperature within 7 h, the color changes from pale yellow to deep red. All volatiles of the red solution were removed in vacuo. Washing the brownish residue with hexane (3 × 20 mL) and drying it in vacuo gave $K[C_5H_4CH_2CH_2CH_3]$ (**10**) as a pale brown solid. Yield: 1.49 g (98%). $ZrCl_4$ (2.33 g, 10.0 mmol) was added to a suspension of potassium (*n*-propyl)cyclopentadienid (**10**) (1.46 mg, 10.0 mmol) in diethyl ether (200 mL) at −80 °C. The suspension was stirred and allowed to reach room temperature within 16 h. After filtration of the reaction mixture all volatiles were removed in vacuo from the filtrate. The pale residue was washed with *n*-hexane (2 × 50 mL) and extracted with THF (2 × 40 mL). After 24 h colorless crystals formed at −80 °C from the THF extract. Yield: 420 mg (82%). Analytical data were consistent with the data reported in the literature.[12]

Polymerization Experiments. In a typical procedure a flame-dried argon-purged 150 mL glass reactor equipped with a stirrer was filled with toluene (18 mL) and a toluene solution of MAO (10%, 4 mL). The mixture was then stirred. After adjusting the temperature, the solution was saturated with ethylene (4 bar). The polymerization was initiated by adding a preactivated solution of the catalyst (0.02 mmol in 10 mL of toluene, preactivated with 8 mL of a MAO-toluene solution). The ethylene gas feed was then started to give a constant gas pressure (4 bar). The reaction mixture was vigorously stirred, and after 1 h the polymerization was terminated by addition of 2-propanol (5 mL). The resulting polymer suspension was treated with ethanol (100 mL), water (100 mL), and aqueous HCl (25 mL) and stirred for 16 h at room temperature. After filtration the polymer was washed several times with water and acetone and dried in air.

Crystal Structures. Crystallographic data for **3** and **6** are listed in Table 4. All diffraction data were collected on a Nonius Kappa CCD diffractometer at 100 K. The structures were solved by direct methods (SHELXTL PLUS or SIR 97) and refined with the full matrix least-squares methods on F^2 (SHELX-97).[24]

Table 4. Crystallographic Data

	compd **4**	compd **6**
cryst dimens/mm3	0.20 × 0.12 × 0.02	0.19 × 0.16 × 0.16
empirical formula	$C_{11}H_{12}F_6$	$C_{16}H_{16}Cl_2F_6Zr$
Mol mass	258.21	484.41
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$C2/c$
a/Å	4.8981(2)	20.5177(14)
b/Å	9.6292(3)	6.6645(7)
c/Å	12.5412(4)	14.6427(14)
α/deg	74.138(2)	90
β/deg	89.8490(18)	114.193(6)
γ/deg	77.1268(12)	90
V/Å^3	553.61(3)	1826.4(3)
Z	2	4
density(calcd)/(Mg m^{-3})	1.549	1.761
μ(Mo Kα)/mm^{-1}	0.160	0.948
θ range/deg	3−27.5	3−30
no. of reflns collected	13359	24163
no. of independ reflns	2552	2662
R_{int}	0.036	0.0245
no. of reflns with $I_0 > 2\sigma(I_0)$	1970	2480
completeness to max. θ/%	99.8	99.7
R_1, R_{w2} on all data	0.0574, 0.1128	0.0205, 0.0433
goodness-of-fit on F^2	1.046	1.087
R_1, R_{w2} [$I_0 > 2\sigma(I_0)$]	0.0421, 0.1043	0.0177, 0.0421
max. diff. peak hole/(e Å^{-3})	0.184 and −0.353	0.373 and −0.337
CCDC	645 098	645 099

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Supporting Information Available: Crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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