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Group 4 Metal Amido Fluorides and Chlorides: Molecular Structures and the First Comparison in Ethylene Polymerization Catalysis

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Lithium (2,6-diisopropylphenyl)(trimethylsilyl)amide ($2,6\text{-}i\mathrm{Pr_2C_6H_3N(SiMe_3)Li}$) reacts with $\mathrm{MCl_4}$ (M = Zr, Hf) in a 2:1 molar ratio to give $[\{2,6\text{-}i\mathrm{Pr_2C_6H_3N(SiMe_3)}\}_2\mathrm{MCl_2}]$ (**1a**, M = Zr; **1b**, M = Hf) and with $(\mathrm{C_5Me_5})\mathrm{MCl_3}$ (1:1) to give $[(\mathrm{C_5Me_5})\{2,6\text{-}i\mathrm{Pr_2C_6H_3N(SiMe_3)}\}\mathrm{MCl_2}]$ (**2a**, M = Zr; **2b**, M = Hf). Further reaction of the dichlorides (**1a**,**b**, **2a**,**b**) with $\mathrm{Me_3SnF}$ leads to the corresponding difluorides $[\{2,6\text{-}i\mathrm{Pr_2C_6H_3N(SiMe_3)}\}_2\mathrm{MF_2}]$ (**3a**, M = Zr; **3b**, M = Hf) and $[(\mathrm{C_5Me_5})\{2,6\text{-}i\mathrm{Pr_2C_6H_3N(SiMe_3)}\}\mathrm{MF_2}]$ (**4a**, M = Zr; **4b**, M = Hf). The compounds **1**−**4** were investigated as potential catalysts for the polymerization of olefins, in combination with methylaluminoxane (MAO). For the first time the catalytic activities, toward the polymerization of ethylene, of chlorides and the corresponding fluorides are compared under identical conditions. The solid-state structures of **1a**,**b**, **2b**, **3a**, and **4a** were determined by single-crystal X-ray diffraction.

Introduction

The utilization of group 4 metallocenes as catalysts for olefin polymerization is well established.[1−11] The use of bridged cyclopentadienyl ligands has allowed the preparation of *ansa*-metallocenes, which have proved significant in the stereospecific polymerization of propylene.[12] Recently, there has been growing interest in bridged amido−cyclopentadienyl complexes where the cyclopentadienyl group is linked via an $\mathrm{SiMe_2}$ unit to the amido ligand.[13] The first complexes of this type had scandium[14] and titanium[15] as the metal centers. More recently, further group 4 metal complexes have been developed.[16] Many such complexes have also found industrial applications as isospecific polymerization catalysts for propylene[17] and in the synthesis of linear low-density polyethylene (LLDPE).[18]

There are many examples of unbridged amido−monocyclopentadienyl group 4 complexes,[19−22] but little information is known about their catalytic activity. Unbridged bis(amido) complexes of zirconium, such as $[\{(\mathrm{Me_3Si})_2\mathrm{N}\}_2\mathrm{ZrCl_2}]$, were also found to be catalysts for the polymerization of olefins.[23]

Up to now, however, only chloro complexes of these amido systems have been investigated. The corresponding fluorides have not been studied to any great extent due to the lack of practical preparative procedures. The use of trimethyltin fluoride as a fluorinating agent for group 4 organometallic systems has recently been undertaken.[24] Mono- and dicyclopentadienyl group 4 chlorides were converted to the respective fluorides via metathesis with $\mathrm{Me_3SnF}$, under mild conditions.

In this paper, we describe the preparation of both bis(amido) group 4 chlorides and fluorides, as well as the amido−cyclopentadienyl chlorides and fluorides, with a view to testing their catalytic activity with respect to the polymerization of olefins. To our knowl-

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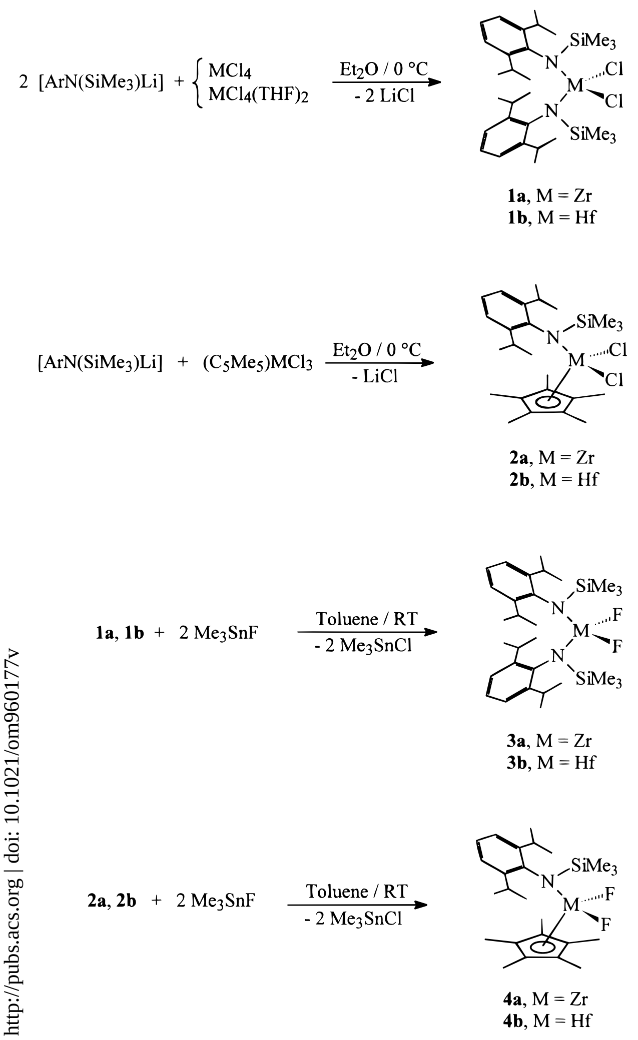
Scheme 1



edge, these represent the first structurally characterized group 4 amido fluorides and the first comparison of their catalytic properties.

Results and Discussion

The preparations of the bis(amido)zirconium and -hafnium dichlorides and difluorides (**1a**,**b**, **3a**,**b**) and the amido(pentamethylcyclopentadienyl)zirconium and -hafnium dichlorides and difluorides (**2a**,**b**, **4a**,**b**) are outlined in Scheme 1. All compounds were isolated as spectroscopically pure, crystalline materials after recrystallization from hexane. It was found that the bis(amido) dichlorides (**1a**,**b**) could be prepared from either MCl_4 or $MCl_4{\cdot}2THF$ (M = Zr, Hf). Throughout this paper Ar = 2,6-$i$$Pr_2C_6H_3$.

Work in our research group has shown that the ligand (2,6-diisopropylphenyl)(trimethylsilyl)amide provides systems with increased solubility. Use of this ligand in compounds **1**−**4** would thus ensure the complete homogeneity of catalyst solutions for the polymerization of olefins, particularly in the case of the fluorides. Despite the steric demand of the amido ligand, it was still possible to synthesize the bis(amido) compounds of zirconium and hafnium (**1a**,**b**, **3a**,**b**).

The use of the trimethylsilyl group not only provides a sterically demanding ligand but also makes it necessary to prevent the formation of imido compounds. In our group it was found that bridging imido systems are accessible by reaction of MCl_4 (M = Zr, Hf) with (tBu)NHLi, while compounds having terminal imido groups can be synthesized by heating a solution of $(C_5Me_5)Zr(NHAr)_3$.[25] Wigley and co-workers, however, prepared terminal and bridging imido chloride complexes by simple reaction of $ZrCl_4{\cdot}2THF$ or $(C_5Me_5)ZrCl_3$ with ArNHLi and treatment with Me_3SiCl. Attempts to prepare mono- or dichloro imido complexes from the appropriate stoichiometric reactions of $ZrCl_4{\cdot}2THF$ and ArNHLi did not yield tractable products.[26]

The dichlorides (**1a**,**b**, **2a**,**b**) undergo metathesis with trimethyltin fluoride to give the first group 4 bis(amido) and amido cyclopentadienyl fluorides (**3a**,**b**, **4a**,**b**). This was achieved by reaction with trimethyltin fluoride in a molar ratio of 2:1, in toluene at room temperature. The ^{19}F NMR spectra of **3a**,**b** and **4a**,**b** all contain one singlet in the region of δ 110−36, indicating that they are monomeric in solution. Interestingly, the trimethylsilyl group on the amido function is not affected by trimethyltin fluoride; i.e., an imido complex is not formed via elimination of Me_3SiF. This suggests that trimethyltin fluoride is an appropriate fluorinating agent for N-substituted group 4 systems.

The main diagnostic feature of the IR spectra of the difluorides is the appearance of two M−F bond stretching frequencies. These occur in the range 610−570 cm^{-1} and are consistent with values of known zirconium and hafnium difluorides.[27]

The crystal structure of **1a** is shown in Figure 1, with the structures of **2b** and **3a** shown in Figures 2 and 3, respectively. Relevant bond distances and angles are reported in Table 1, while crystallographic data are summarized in Table 2.

Complexes **1a** and **1b** are isostructural. The crystal structures of **1a** and **1b**, where two chlorine atoms and two (trimethylsilyl)(diisopropylphenyl)amide groups coordinate a Zr and Hf atom, respectively, do not show any significant variations in terms of internal geometrical parameters. The Cl−metal−Cl angles are 102.9(1) and 103.9(1)°, while the N−metal−N angles are 118.2(1) and 117.6(1)° in **1a** and **1b**, respectively. The average Zr−Cl distance in **1a** is 2.380(1) Å, while the average Hf−Cl bond length in **1b** is 2.347(1) Å. The difference between the mean metal−nitrogen distances in the two structures is within experimental error (2.029(2) *vs* 2.023(3) Å).

The sterically demanding pentamethylcyclopentadienyl ligand coordinating the Hf atom in **2b** causes a slight lengthening of the Hf−N distance with respect to the corresponding average bond length in the symmetrically substituted structure of **1b** (2.054(3) *vs* 2.023(3) Å). The increased bulkiness of the ring system with respect to the N-bonded ligand is also reflected by the angle N(1)−Hf(1)−X(1A), where X(1A) is the centroid of the Cp* ligand (Cp* = C_5Me_5), this being larger than the corresponding N(1)−Hf(1)−N(2) angle in **1b** (123.9(1) and 117.6(1)°, respectively).

Compound **3a** crystallizes with two independent molecules in the asymmetric unit. Each of the Zr atoms

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Table 1. Selected Bond Lengths (Å) and Angles (deg) for 1a,b, 2b, and 3a

1a	1b	2b	3a
Zr(1)−Cl(1) 2.380(1)	Hf(1)−Cl(1) 2.344(1)	Hf(1)−Cl(1) 2.364(1)	Zr(1)−F(1) 1.946(3)
Zr(1)−Cl(2) 2.380(1)	Hf(1)−Cl(2) 2.350(1)	Hf(1)−Cl(2) 2.383(1)	Zr(1)−F(2) 1.944(3)
			Zr(2)−F(3) 1.948(3)
			Zr(2)−F(4) 1.960(3)
Zr(1)−N(1) 2.029(2)	Hf(1)−N(1) 2.028(3)	Hf(1)−N(1) 2.054(3)	Zr(1)−N(1) 2.068(4)
Zr(1)−N(2) 2.030(2)	Hf(1)−N(2) 2.018(3)	Hf(1)−C(Cp*)$_{av}$ 2.495(3)	Zr(1)−N(2) 2.090(5)
		Hf(1)−X(1A) 2.182(3)	Zr(2)−N(3) 2.067(5)
			Zr(2)−N(4) 2.092(4)
Si(1)−N(1) 1.790(2)	Si(1)−N(1) 1.759(3)	Si(1)−N(1) 1.799(3)	Si(1)−N(1) 1.767(5)
Si(2)−N(2) 1.770(2)	Si(2)−N(2) 1.795(3)		Si(2)−N(2) 1.767(5)
N(1)−C(1) 1.460(3)	N(1)−C(1) 1.473(5)	N(1)−C(11) 1.462(5)	N(1)−C(1) 1.455(7)
N(2)−C(13) 1.461(3)	N(2)−C(13) 1.452(5)		N(2)−C(16) 1.451(7)
			Zr(1)···O(1) 2.250(4)
			Zr(2)···O(2) 2.241(4)
Cl(1)−Zr(1)−Cl(2) 103.0(1)	Cl(1)−Hf(1)−Cl(2) 103.9(1)	Cl(1)−Hf(1)−Cl(2) 101.9(1)	F(1)−Zr(1)−F(2) 155.0(1)
N(1)−Zr(1)−N(2) 118.2(1)	N(1)−Hf(1)−N(2) 117.6(1)	N(1)−Hf(1)−X(1A) 123.9(1)	N(1)−Zr(1)−N(2) 123.0(2)
			F(3)−Zr(2)−F(4) 156.5(1)
			N(3)−Zr(2)−N(4) 119.7(2)

Table 2. Crystal Data for 1a,b, 2b, and 3a

	1a	1b	2b	3a
formula	$C_{30}H_{52}Cl_2N_2Si_2Zr$	$C_{30}H_{52}Cl_2N_2Si_2Hf$	$C_{25}H_{41}Cl_2NSiHf$	$C_{34}H_{60}F_2N_2OSi_2Zr$
fw	659.04	746.31	633.07	698.24
cryst size (mm)	0.70 × 0.35 × 0.35	0.7 × 0.5 × 0.4	0.7 × 0.5 × 0.3	0.6 × 0.5 × 0.5
space group	$P2_1/n$	$P2_1/n$	$P2_1/c$	$C2/c$
a (Å)	11.816(2)	11.879(2)	16.842(3)	35.180(7)
b (Å)	16.305(2)	16.330(3)	9.494(2)	17.016(3)
c (Å)	18.366(2)	18.375(4)	17.048(3)	25.580(5)
α (deg)	90	90	90	90
β (deg)	94.27(1)	94.54(3)	90.61(3)	94.26(3)
γ (deg)	90	90	90	90
V (Å^3)	3529(1)	3553(1)	2726(1)	15271(5)
Z	4	4	4	8
temp (K)	153(2)	213(2)	153(2)	213(2)
ρ_c (g mm^{-3})	1.241	1.395	1.543	1.215
μ (mm^{-1})	0.551	3.174	4.079	0.387
F(000)	1392	1520	1272	5952
2θ range (deg)	5−45	7−45	7−45	7−40
no. of rflns measd	9236	9279	7042	7995
no. of unique reflns	4619	4648	3565	7036
no. of restraints	0	0	0	0
no. of refined params	348	348	278	785
R1 ($I > 2\sigma(I)$)	0.0286	0.0250	0.0203	0.0448
wR2[a] (all data)	0.0698	0.0685	0.0534	0.1199
g1; g2[b]	0.0300; 1.50	0.0404; 2.95	0.0314; 2.36	0.0533; 65.58
highest diff peak (e Å^{-3})	0.73	1.76	2.06	0.65

[a] wR2 = $\{[\sum w(F_c^2 - F_o^2)^2]/[\sum w(F_o^2)^2]\}^{1/2}$. [b] $w^{-1} = \sigma^2(F_o^2) + [(g1)P]^2 + [(g2)P]$; $P = [F_o^2 + 2F_c^2]/3$.

in this pair of isomers coordinates a THF molecule (Zr···O = 2.245(4) Å), with the oxygen lying on the plane defined by the Zr atom and the two fluorines in both molecules (deviations 0.03 and 0.06 Å). This results in the wide F−Zr−F angles observed for the two independent molecules of this species (155.1(1) and 156.5(1)°).

The X-ray crystal structure of **4a** was also determined, indicating a structure similar to that of **2b**. However, the structure could not be fully refined (R1 = 11%) and no discussion of bond distances and angles is given.[28]

All the compounds described herein show the same conformation of the N-bonded ligand, with the ring lying on a plane perpendicular to the plane defined by the Si−N−metal atoms. This conformation minimizes the steric interactions between the two isopropyl groups and the remaining atoms in the molecules.

Work in the utilization of group 4 organometallic fluorides as cataysts for the polymerization of olefins has only recently been undertaken.[29] This paper describes our initial studies of the catalytic potential of complexes **1**−**4**, with regard to ethylene polymerization. Polymerization reactions, with methylaluminoxane (MAO) as cocatalyst, were carried out at different Al:M ratios under identical conditions. Table 3 summarizes the polymerization results.

All reactions were carried out in 100 mL of toluene in a magnetically stirred 250 mL reactor at room temperature. After 30 min, the reactions were terminated by injection of ethanol. As expected, the activities of the amido cyclopentadienyl systems are much greater than those of the bis(amido) systems, with the zirconium complexes **2a** and **4a** proving to be the most active. In comparison, the activities of the hafnium analogues (**2b** and **4b**) are poor.

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(28) The compound was found to crystallize in the triclinic space group $P\bar{1}$ (a = 9.216(5) Å, b = 9.221(5) Å, c = 35.230(5) Å, α = 85.31(5)°, β = 78.87(5)°, γ = 61.22(4)°), with two independent molecules in the asymmetric unit.

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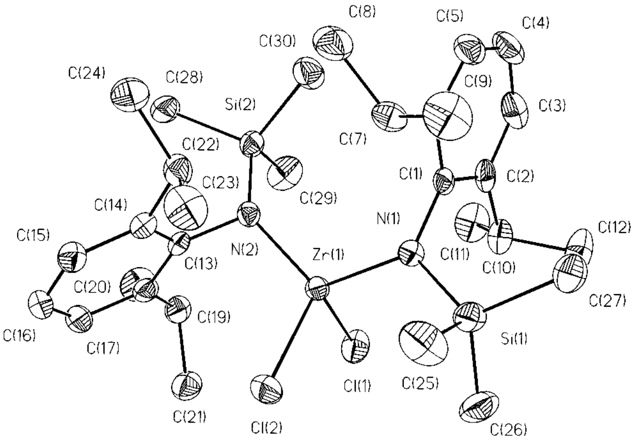

Figure 1. Crystal structure of **1a**, with anisotropic displacement parameters depicting 50% probability. All the hydrogen atoms of the molecule have been omitted for clarity.

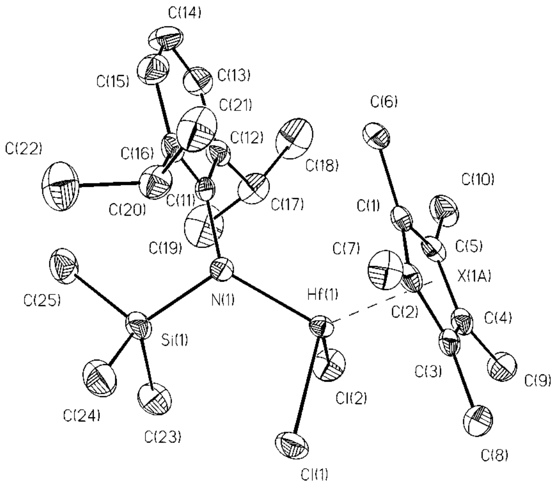

Figure 2. Crystal structure of **2b**, with anisotropic displacement parameters depicting 50% probability. All the hydrogen atoms of the molecule have been omitted for clarity.

The increase in activity of the dichloride complexes with an increase in the amount of MAO used as cocatalyst is consistent with the findings of Kaminsky,[30] Chien,[31] and Ewen.[32] Remarkably, the activity of the difluoride **4a** initially remained unchanged as the ratio Al:M was increased. For instance, there was a plateau in activity for **4a** between 1000:1 and 2000:1. As the ratio reached 3000:1, the activity once more increased as the amount of MAO increased.

Despite the visible differences in the polymerization behavior of the dichloride (**2a**) and the difluoride (**4a**), no clear trend is obvious. However, these differences led us to investigate the catalytic activities of simple metallocene difluorides compared to those of the corresponding metallocene dichlorides, using lower concentrations of MAO.[29b] More detailed studies of the influence of the concentration of MAO on catalyst performance are in progress.

Experimental Section

All reactions were carried out under a dry nitrogen atmosphere using standard Schlenk techniques. Solvents were dried and purified by known procedures and distilled from benzophenone ketyl under nitrogen prior to use. $ZrCl_4{\cdot}2THF$,[33] $HfCl_4{\cdot}2THF$,[33] $(C_5Me_5)ZrCl_3$,[34] $(C_5Me_5)HfCl_3$,[35] $[2,6\text{-}i\text{Pr}_2C_6H_3N(SiMe_3)Li]$,[36] and Me_3SnF[37] were prepared according to literature methods. $ZrCl_4$ and $HfCl_4$ were purchased (Aldrich) and used without further purification. Methylaluminoxane was obtained from Professor W. Kaminsky, Hamburg, Germany, and used as a 10% solution by weight in toluene. Ethylene (BASF AG) was polymerization grade and dried by passing through columns of P_4O_{10} prior to use.

NMR spectra were recorded on a Bruker AM 250 spectrometer. C_6D_6 was trap-to-trap distilled from CaH_2. ^1H and ^{19}F NMR data are listed in ppm downfield from TMS and $CFCl_3$, respectively. IR spectra were recorded on a Perkin-Elmer Bio-Rad Digilab FTS-7 spectrometer (Nujol mulls between CsI plates). Mass spectra were obtained on a Finnigan MAT System 8230 and a Varian MAT CH 5 mass spectrometer. Melting points (uncorrected) were obtained by using a Büchi 510 and an HWS-SG 3000 apparatus. Microanalyses were performed by Beller Laboratory (Göttingen, Germany) or in our institute.

$[\{2,6\text{-}i\text{Pr}_2C_6H_3N(SiMe_3)\}_2ZrCl_2]$ (1a). To a suspension of $ZrCl_4$ (2.47 g, 10.6 mmol) or $ZrCl_4{\cdot}2THF$ (4.00 g, 10.6 mmol) in diethyl ether (50 mL) was slowly added a solution of $[2,6\text{-}i\text{Pr}_2C_6H_3N(SiMe_3)Li]$ (5.39 g, 21.1 mmol) in diethyl ether (50 mL), at 0 °C. After the mixture was stirred for 36 h and the solvent was removed under reduced pressure, hexane (50 mL) was added and the mixture filtered, removing LiCl. The clear, pale yellow solution was concentrated to ~25 mL and stored at −25 °C overnight. A yield of 4.40 g (63%) of large, colorless crystals was obtained (mp 132 °C). MS (*m/z* (relative intensity (%), assignment)): 658 (5, M^+), 248 (100, $[2,6\text{-}i\text{Pr}_2C_6H_3N(SiMe_3)]$). IR (Nujol, cm^{-1}): 1251 s, 1163 s, 1100 m, 891 m, 839 s, 784 s, 713 s, 679 m, 528 m, 431 m, 364 m. ^1H NMR (200 MHz, C_6D_6): δ 7.09 (s, 6H, Ph), 3.65 (sept, 4H, CH_3CHCH_3, $^3J_{HH} = 6.73$ Hz), 1.44 (d, 12H, CH_3CHCH_3, $^3J_{HH} = 6.75$ Hz), 1.12 (d, 12H, CH_3CHCH_3, $^3J_{HH} = 6.68$ Hz), 0.15 (s, 18H, $SiMe_3$). Anal. Calcd for $C_{30}H_{52}Cl_2N_2Si_2Zr$: C, 54.7; H, 8.0; N, 4.3. Found: C, 54.5; H, 7.9; N, 4.1.

$[\{2,6\text{-}i\text{Pr}_2C_6H_3N(SiMe_3)\}_2HfCl_2]$ (1b). The reaction was performed by the same procedure described for the preparation of **1a**. $HfCl_4$ (3.45 g, 10.77 mmol) or $HfCl_4{\cdot}2THF$ (5.00 g, 10.76 mmol) in diethyl ether (50 mL) was treated with a solution of $[2,6\text{-}i\text{Pr}_2C_6H_3N(SiMe_3)Li]$ (5.50 g, 21.54 mmol) in diethyl ether (50 mL), at 0 °C. After removal of LiCl by filtration, the clear, colorless solution was concentrated to ~25 mL and stored at −25 °C overnight. A yield of 4.74 g (59%) of colorless crystals was obtained (mp 148 °C). MS (*m/z*): 746 (3, M^+), 73 (100, $[Me_3Si]$). IR (Nujol, cm^{-1}): 1258 m, 1251 m, 1164 m, 1104 s, 892 m, 842 s, 785 s, 717 m, 523 m, 432 m, 358 m. ^1H NMR (200 MHz, C_6D_6): δ 7.08 (s, 6H, Ph), 3.72 (sept, 4H, CH_3CHCH_3, $^3J_{HH} = 6.73$ Hz), 1.42 (d, 12H, CH_3CHCH_3, $^3J_{HH} = 6.75$ Hz), 1.15 (d, 12H, CH_3CHCH_3, $^3J_{HH} = 6.69$ Hz), 0.14 (s, 18H, $SiMe_3$). Anal. Calcd for $C_{30}H_{52}Cl_2HfN_2Si_2$: C, 48.3; H, 7.0; N, 3.8. Found: C, 47.9; H, 7.1; N, 3.9.

$[(C_5Me_5)\{2,6\text{-}i\text{Pr}_2C_6H_3N(SiMe_3)\}ZrCl_2]$ (2a). To a suspension of $(C_5Me_5)ZrCl_3$ (1.50 g, 4.51 mmol) in diethyl ether (30 mL) was slowly added a solution of $[2,6\text{-}i\text{Pr}_2C_6H_3N(SiMe_3)Li]$ (1.15 g, 4.50 mmol) in diethyl ether (30 mL), at 0 °C. After

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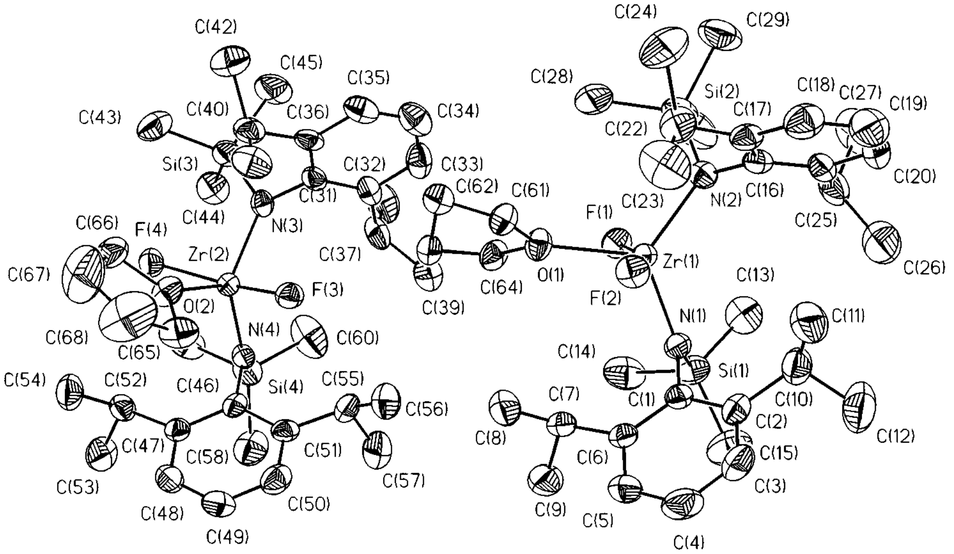

Figure 3. Crystal structure of **3a** (two independent molecules in the asymmetric unit), with anisotropic displacement parameters depicting 50% probability. All the hydrogen atoms of the two molecules have been omitted for clarity.

Table 3. Ethylene Polymerization with Compounds 1−4

catalyst	amt of catalyst (μmol)	mole ratio Al:M	yield of PE (g)	activity 10^5 g PE/(mol of M h atm)
1a	18.7	1000:1	0.122	0.13
1b	12.2	1000:1		
2a	14.7	500:1	0.237	0.32
2a	11.9	1000:1	0.889	1.49
2a	9.3	2000:1	1.113	2.38
2a	4.7	3000:1	1.134	4.76
2b	16.3	1000:1	0.051	0.06
3a	43.4	1000:1	0.186	0.09
3b	15.3	1000:1		
4a	14.4	500:1	0.197	0.27
4a	10.1	750:1	0.442	0.87
4a	11.1	1000:1	1.146	2.06
4a	7.6	1500:1	0.743	1.95
4a	11.9	2000:1	1.149	1.93
4a	9.6	3000:1	1.400	2.93
4b	20.8	1000:1	0.017	0.02

the mixture was stirred for 36 h and the solvent was removed under reduced pressure, hexane (50 mL) was added and the mixture filtered, removing LiCl. The filtrate was concentrated to ~20 mL and stored at −25 °C overnight. A yield of 1.63 g (66%) of colorless crystals was obtained (mp 168 °C). MS (*m/z*): 545 (5, M$^+$), 162 (100, [$C_9H_{12}NSi$]). IR (Nujol, cm^{-1}): 1251 s, 1163 s, 1100 m, 891 m, 839 s, 784 s, 713 s, 679 m, 528 m, 431 m, 364 m. ^{1}H NMR (200 MHz, C_6D_6): δ 7.06 (s, 3H, Ph), 3.63 (sept, 2H, $CH_3C\mathit{H}CH_3$, ${}^3J_{HH}$ = 6.71 Hz), 1.87 (s, 15H, C_5Me_5), 1.40 (d, 6H, $C\mathit{H}_3CHC\mathit{H}_3$, ${}^3J_{HH}$ = 6.72 Hz), 1.20 (d, 6H, $C\mathit{H}_3CHC\mathit{H}_3$, ${}^3J_{HH}$ = 6.65 Hz), 0.32 (s, 9H, $SiMe_3$). Anal. Calcd for $C_{25}H_{41}Cl_2NSiZr$: C, 55.0; H, 7.6; N, 2.6. Found: C, 54.8; H, 7.7; N, 2.5.

[(C_5Me_5){2,6-*i*$Pr_2C_6H_3N(SiMe_3)$}$HfCl_2$] (2b). The reaction was performed by the same method described for the preparation of **2a**, using (C_5Me_5)$HfCl_3$ (1.00 g, 2.38 mmol) and [2,6-*i*$Pr_2C_6H_3N(SiMe_3)Li$] (0.60 g, 2.35 mmol). A yield of 1.16 g (78%) of large, colorless crystals was obtained (mp 147 °C). MS (*m/z*): 633 (10, M$^+$), 248 (100, [2,6-*i*$Pr_2C_6H_3N(SiMe_3)$]). IR (Nujol, cm^{-1}): 1253 s, 1168 s, 1108 m, 1041 m, 1030 w, 888 m, 870 m, 843 s, 801 w, 780 s, 703 s, 683 m, 436 m, 357 w. ^{1}H NMR (200 MHz, C_6D_6): δ 7.07 (s, 3H, Ph), 3.57 (sept, 2H, $CH_3C\mathit{H}CH_3$, ${}^3J_{HH}$ = 6.71 Hz), 1.91 (s, 15H, C_5Me_5), 1.40 (d, 6H, $C\mathit{H}_3CHC\mathit{H}_3$, ${}^3J_{HH}$ = 6.72 Hz), 1.23 (d, 6H, $C\mathit{H}_3CHC\mathit{H}_3$, ${}^3J_{HH}$ = 6.64 Hz), 0.32 (s, 9H, $SiMe_3$). Anal. Calcd for $C_{25}H_{41}Cl_2HfNSi$: C, 47.4; H, 6.5; N, 2.2. Found: C, 47.5, H, 6.5; N, 2.0.

[{2,6-*i*$Pr_2C_6H_3N(SiMe_3)$}$_2ZrF_2$] (3a). A suspension of **1a** (1.25 g, 1.90 mmol) and Me_3SnF (0.69 g, 3.77 mmol) in toluene (50 mL) was stirred at room temperature for 5 h. All the volatiles were removed under reduced pressure to yield 1.01 g (85%) of colorless crystals after recrystallization from hexane (mp 150 °C). MS (*m/z*): 624 (80, M$^+$), 376 (100, [M − 2,6-*i*$Pr_2C_6H_3N(SiMe_3)$]). IR (Nujol, cm^{-1}): 1251 s, 1171 m, 1159 m, 1102 m, 1039 m, 930 w, 894 s, 842 s, 787 s, 752 m, 720 s, 676 m, 610 m, 600 s, 532 m, 524 m, 426 m, 355 m. ^{1}H NMR (200 MHz, C_6D_6): δ 7.06 (s, 6H, Ph), 3.62 (sept, 4H, $CH_3C\mathit{H}CH_3$, ${}^3J_{HH}$ = 6.78 Hz), 1.35 (d, 12H, $C\mathit{H}_3CHC\mathit{H}_3$, ${}^3J_{HH}$ = 6.79 Hz), 1.18 (d, 12H, $C\mathit{H}_3CHC\mathit{H}_3$, ${}^3J_{HH}$ = 6.75 Hz), 0.22 (s, 18H, $SiMe_3$). ^{19}F NMR (188 MHz, C_6D_6): δ 109.6 (s). Anal. Calcd for $C_{30}H_{52}F_2N_2Si_2Zr$: C, 57.5; H, 8.4; F, 6.1; N, 4.5. Found: C, 57.3; H, 8.5; F, 6.2; N, 4.3.

[{2,6-*i*$Pr_2C_6H_3N(SiMe_3)$}$_2HfF_2$] (3b). A mixture of **1b** (1.50 g, 2.01 mmol) and Me_3SnF (0.73 g, 3.99 mmol) was reacted in toluene (40 mL) as described for **3a** to yield 1.19 g (83%) of colorless crystals (mp 144 °C). MS (*m/z*): 714 (20, M$^+$), 73 (100, [$SiMe_3$]). IR (Nujol, cm^{-1}): 1252 s, 1172 m, 1158 m, 1102 m, 1040 m, 895 m, 844 s, 789 s, 751 m, 724 m, 611 m, 601 s, 532 m, 525 m, 426 m. ^{1}H NMR (200 MHz, C_6D_6): δ 7.06 (s, 6H, Ph), 3.64 (sept, 4H, $CH_3C\mathit{H}CH_3$, ${}^3J_{HH}$ = 6.78 Hz), 1.33 (d, 12H, $C\mathit{H}_3CHC\mathit{H}_3$, ${}^3J_{HH}$ = 6.79 Hz), 1.18 (d, 12H, $C\mathit{H}_3CHC\mathit{H}_3$, ${}^3J_{HH}$ = 6.77 Hz), 0.18 (s, 18H, $SiMe_3$). ^{19}F NMR (188 MHz, C_6D_6): δ 75.3 (s). Anal. Calcd for $C_{30}H_{52}F_2HfN_2Si_2$: C, 50.5; H, 7.4; F, 5.3; N, 3.9. Found: C, 50.3; H, 7.3; F, 5.1; N, 3.8.

[(C_5Me_5){2,6-*i*$Pr_2C_6H_3N(SiMe_3)$}ZrF_2] (4a). A mixture of **2a** (1.36 g, 2.49 mmol) and Me_3SnF (0.91 g, 4.98 mmol) was reacted in toluene (40 mL) as described for **3a** to yield 1.01 g (79%) of colorless crystals (mp 85 °C). MS (*m/z*): 511 (20, M$^+$), 248 (100, [2,6-*i*$Pr_2C_6H_3N(SiMe_3)$]). IR (Nujol, cm^{-1}): 1423 m, 1250 s, 1175 s, 1112 m, 1100 m, 874 m, 841 s, 779 m, 753 m, 711 m, 579 s, 571 m, 383 m. ^{1}H NMR (200 MHz, C_6D_6): δ 7.05 (s, 3H, Ph), 3.49 (sept, 2H, $CH_3C\mathit{HCH}_3$, ${}^3J_{HH}$ = 6.76 Hz), 1.87 (s, 15H, C_5Me_5), 1.39 (d, 6H, $C\mathit{H}_3CHC\mathit{H}_3$, ${}^3J_{HH}$ = 6.78 Hz), 1.19 (d, 6H, $C\mathit{H}_3CHC\mathit{H}_3$, ${}^3J_{HH}$ = 6.70 Hz), 0.26 (s, 9H, $SiMe_3$). ^{19}F NMR (188 MHz, C_6D_6): δ 78.2 (s). Anal. Calcd for $C_{25}H_{41}F_2NSiZr$: C, 58.5; H, 8.1; F, 7.4; N, 2.7. Found: C, 57.2; H, 7.6; F, 7.6; N, 2.9.

[(C_5Me_5){2,6-*i*$Pr_2C_6H_3N(SiMe_3)$}HfF_2] (4b). A mixture of **2b** (0.86 g, 1.36 mmol) and Me_3SnF (0.50 g, 2.73 mmol) was reacted in toluene (40 mL) as described for **3a** to yield 0.66 g (81%) of colorless crystals (mp 72 °C). MS (*m/z*): 601 (6, M$^+$), 248 (100, [2,6-*i*$Pr_2C_6H_3N(SiMe_3)$]). IR (Nujol, cm^{-1}): 1251 s, 1175 m, 1112 m, 1101 m, 891 m, 874 m, 841 s, 781 s, 755 m, 714 m, 584 s, 570 s, 358 m. ^{1}H NMR (200 MHz, C_6D_6): δ 7.06 (s, 3H, Ph), 3.53 (sept, 2H, $CH_3C\mathit{H}CH_3$, ${}^3J_{HH}$ = 6.76 Hz), 1.87 (s, 15H, C_5Me_5), 1.38 (d, 6H, $C\mathit{H}_3CHC\mathit{H}_3$, ${}^3J_{HH}$ = 6.75 Hz), 1.21

(d, 6H, CH_3CHCH_3, $^3J_{HH} = 6.70$ Hz), 0.29 (s, 9H, $SiMe_3$). ^{19}F NMR (188 MHz, C_6D_6): δ 36.3 (s). Anal. Calcd for $C_{25}H_{41}F_2HfNSi$: C, 50.0; H, 6.9; F, 6.3; N, 2.3. Found: C, 49.8; H, 6.8; F, 6.3; N, 2.2.

General Procedure for Polymerization Reactions. To solutions of complexes **1**−**4** in toluene (10 mL) were added appropriate amounts of MAO. After a prereaction time of 20 min, the catalyst solution was injected into a magnetically stirred 250 mL reactor previously charged with toluene (100 mL), into which ethylene was bubbling at a pressure of 1 atm. This pressure was maintained throughout the reaction. After 30 min, ethanol (10 mL) was injected into the reactor to terminate the reaction. The polymer produced was filtered off, washed with acidified ethanol, water, and ethanol and dried at 60 °C for 24 h. To ensure reproducibility, polymerizations were carried out twice with each complex under identical conditions.

X-ray Structure Analyses for 1a,b, 2b, 3a, and 4a. The intensities for all the structures were collected by the $\omega-2\theta$ scan method on a Siemens AED2 four-circle diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å), according to the Learnt-Profile Method.[38] All the structures were solved by direct methods (SHELXS-90)[39] and refined versus F^2 by the least-squares method with all data (SHELX-93).[40] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included in the refinement in ideal positions.

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Supporting Information Available: For compounds **1a**, **2b**, and **3a**, tables of crystal data and structure refinement details, atomic coordinates, displacement parameters, and all bond distances and angles (23 pages). Ordering information is given on any current masthead page.

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