Hafnium Bis(phenoxyimino) Dibenzyl Complexes and Their Activation toward Olefin Polymerization

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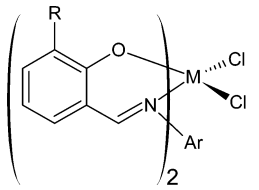
Hf bis(phenoxyimino) dibenzyl complexes bearing benzylimino and perfluorophenylimino groups were prepared by a direct reaction between the desired ligand precursors and $Hf(CH_2Ph)_4$. In the solid state, the Hf complexes adopt an octahedral configuration where imino nitrogens are in positions cis to each other and oxygens occupy apical vertices of the coordination polyhedron. According to ^1H NMR and 2D-NOESY studies, this cis-N,N configuration was also maintained in solution. In addition, the structures of Hf bis(phenoxyimino) dibenzyl complexes were studied with DFT calculations. Activation of the Hf dibenzyl complexes with $B(C_6F_5)_3$ led to the highly air-, moisture-, solvent-, and temperature-sensitive cationic bis(phenoxyimino) Hf monobenzyl species, which were further investigated by ^1H and ^{19}F NMR, $^1H-^{13}C$ heteronuclear correlation, 2D-NOESY, and ESI-MS methods. It was observed that the cationic, benzylimino-substituted Hf complexes have a propensity toward CH activation. The correlation between the stability of the cationic species toward CH activation and the catalytic behavior of the MAO-activated dibenzyl complexes was established. Accordingly, the MAO-activated Hf bis(phenoxyimino) dibenzyl complexes and their dichloro analogues, depending on the ligand substitution, have from low to very high catalytic activities (up to 14 000 kg of PE/((mol of cat.) h (bar of ethylene))) in ethylene polymerizations. In general, the produced polyethylene had a monomodal molar mass distribution with relatively narrow polydispersity. Polypropylene produced with perfluorophenyl-substituted Hf complexes had a large amount of 2,1-misinsertions in the polymer chains. To further shed light on the catalytic reaction, polymerizations of ethylene and propylene with the cationic species generated from Hf bis(phenoxyimino) dibenzyl complexes with $B(C_6F_5)_3$ were studied with ^1H NMR.

Introduction

Following the successful design of group 4 metallocenes and their application in homogeneous α-olefin polymerization,[1] in the last few decades nonmetallocene complexes of early and late transition metals have attracted growing attention as potential catalyst precursors.[2] Many organic and organometallic ligands, including, for example, amines, imines, and phosphines, have now been exploited in this area.[3] The expansion in choice of ligands means that the electronic character, geometry, and steric hindrance around the catalytically active metal center can be controlled through rational design of the ligand environment.

Recently, new and highly active group 4 polymerization catalysts based on phenoxyimine ligands (Chart 1) have been reported in a series of publications by Fujita and co-workers at Mitsui Chemicals.[4] Depending on the nature of the metal and the ligand substitution, the catalytic properties of MAO- or

Chart 1



Ar - aryl or $C_6H_{5-x}F_x$ (x=2-5) groups
M - Ti, Zr, Hf
R - H or *t*-Bu

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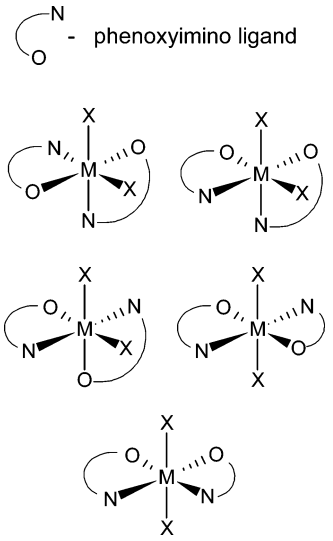
Chart 2



borane−borate/TIBA-activated Ti, Zr, and Hf bis(phenoxyimino) complexes can vary substantially in ethylene and propylene polymerization. In general, group 4 metal phenoxyimino catalysts bearing C_6F_5 imino substituents are highly active in ethylene polymerization.[5] Intriguingly, analogous MAO-activated Ti complexes, where Ar is $C_6H_{5-x}F_x$ ($x = 2, 3, 5$) (Chart 1), can cause living ethylene and propylene polymerization.[4c,6] While chain-end-controlled syndiotactic polypropylene can be obtained by MAO-activated Ti and Zr bis(salicylaldiminato) complexes having C_6F_5 groups,[7] non-fluoroaryl-substituted Zr and Hf catalysts produce atactic, low-molar-mass polypropylene.[4a,8]

Quite unexpectedly, ethylene polymerization experiments performed with Zr bis(phenoxyimino) complexes bearing phenylimino groups revealed that these catalysts were able to produce polyethylene with different modalities (molar mass distributions), depending on the applied polymerization temperature.[9] This multimodal nature of the polymers was referred to the possibility of bis(phenoxyimino) complexes to possess five different isomeric forms (Chart 2). In fact, the structural diversity of bis(phenoxyimino)-based complexes was demonstrated by ^{15}N NMR investigations[9] and X-ray crystallographic studies.[10] Similar multimodal polymerization behavior for arylimino-substituted Ti bis(phenoxyimino) catalysts was recently observed in our research group. Computational methods (on the HF/3-21G* level) were used to gain a further understanding of the dynamic nature of these catalysts in ethylene polymerization.[11]

Studies dedicated to the MAO activation of bis(phenoxyimino) group 4 metal complexes toward olefin polymerization were recently reported,[12] including a detailed investigation on the activation of the perfluorophenyl-substituted Ti bis(phenoxyimino) dichloro complex with MAO or $AlMe_3/(CPh_3)^+B(C_6F_5)_4^-$ by Bryliakov et al. As a result, cationic monomethyl complexes with a bulky Me-MAO counteranion on the outer shell were observed, and these Ti cations reacted further with ethylene to produce Ti polymeryl species.[12b]

Although cationic bis(phenoxyimino) complexes are highly preferable, studies dedicated to them are few. The general approach developed by Marks et al. to study the activation of group 4 metal alkyl derivatives with boron activators[13] has found limited use, because the alkyl derivatives of these bis(phenoxyimino) complexes have been barely accessible.[14] This is due to the fact that the corresponding alkyl derivatives are not achievable via straightforward alkylation reactions between the dichloro complexes and Li, Mg, etc. alkyls. Due to the presence of the reactive CH═N groups, these alkylation experiments led regularly to extensive side reactions.[14−16] As recently shown, this synthetic problem can be circumvented when reactions of Zr tetrabenzyl with free salicylaldimines[14b,c] or Na salicylaldiminates with Me_2TiCl_2[15] were applied. Although preliminary studies concerning the activation of alkyl bis(phenoxyimino) complexes with $B(C_6F_5)_3$ have been reported,[14c,15] more detailed investigations of this process will facilitate direct insight into the nature and structure of these highly active catalytic species. In this respect we report herein the synthesis and structure of various Hf bis(phenoxyimino) dibenzyl complexes as well as studies on their activation with $B(C_6F_5)_3$ and the reactivity of the formed cationic species with ethylene and propylene.

Results and Discussion

Preliminary Studies. An approach to bis(phenoxyimino) group 4 dialkyl complexes, developed by Scott et al., is based on the reaction of free phenoxyimino ligands with tetrabenzyl Ti or Zr.[14] A number of relatively stable Zr dibenzyl complexes were obtained by this method, although such Ti and Zr complexes had a propensity to migrate of one of the benzyl groups from the metal center to the imino function of the phenoxyimino ligands.[14,15] In our preliminary studies a similar procedure was used—the metalation of free salicylaldimino

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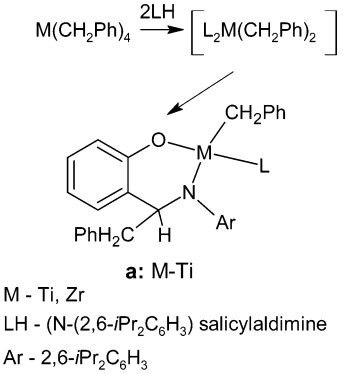
Scheme 1



ligands by metal tetraalkyls. As an example, the reaction between 2,6-diisopropylphenyl-substituted salicylaldimine and $TiMe_4$,[17] mixed at −78 °C in a 2:1 ratio, gave only a thermally unstable green $LTiMe_3$-type salicylaldiminato complex (see the Supporting Information). To further study this method, the metalation of phenoxyimino ligands with more stable Ti and Zr tetrabenzyls was investigated. ^{1}H NMR and single-crystal X-ray studies of the products showed that the obtained Ti and Zr bis(phenoxyimino) dibenzyl complexes were unstable, as one of the benzyl substituents tends to migrate from the metal to a CH═N group (Scheme 1 and Figure 1). In fact, mixtures of the desired Ti or Zr dibenzyl complexes and migration products were always obtained.

In the solid-state structure of the phenoxyimino phenoxyamino complex **a**, the Ti atom has a distorted tetragonal pyramidal configuration (Figure 1, Tables 1 and 6). As a result of the benzyl group migration, one of the phenoxyimino ligands is transformed into a phenoxyamido moiety. The difference between these two ligands is seen in the relatively short Ti−N5(amido) bond compared with the Ti−N4(imino) distance (1.923(3) vs 2.231(3) Å). The former value is typical for Ti−N(amido) bond lengths in a variety of Ti(IV) amido complexes,[18] while the latter value corresponds to typical Ti−N(imino) bond lengths in Ti bis(phenoxyimino) complexes.[19] The C11−N5 distance (1.499(4) Å) can be assigned as a single bond,[20] and it is longer than the C10−N4 double bond in the phenoxyimino ligand (1.302(5) Å). Also, the nonplanar geometry of the C11 atom suggests its sp^3 hybridization (Table 1). The Ti−C9 distance (2.161(4) Å) is in the normal

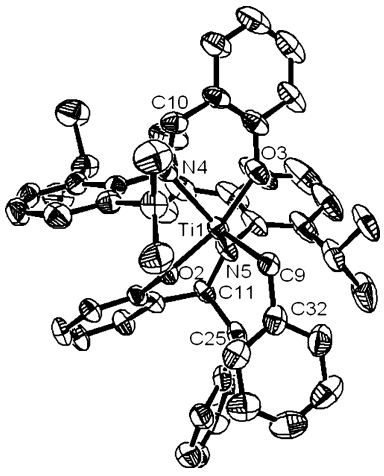


Figure 1. ORTEP plot of complex **a** with thermal ellipsoids drawn at the 50% probability level. All hydrogen atoms were omitted for clarity.

Table 1. Selected Structural Parameters for Complexes a and 10−12

	10	**11**	**12**	**a**
		Distances (Å)		
M−C	2.261(6)	2.256(5)	2.229(9)	2.161(4)
	2.313(5)		2.274(9)	
M−O	2.008(3)	2.006(3)	1.981(5)	1.838(2)
	2.031(3)		1.997(5)	1.891(3)
M−N	2.362(4)	2.417(5)	2.398(7)	2.231(3)
	2.386(4)		2.402(6)	
Ti−N(amino)				1.923(3)
C(imino)−N	1.292(6)	1.302(7)	1.294(10)	1.302(5)
	1.301(6)		1.285(10)	
C(amino)−N				1.499(4)
		Angles (deg)		
C−Hf−C	97.0(2)	94.2(3)	94.6(3)	
O−M−O	159.21(12)	157.06(19)	157.8(2)	165.65(12)
N−M−N	86.58(13)	93.3(2)	90.6(2)	129.91(13)
C_{ipso}−C−M	109.9(4)	115.2(3)	117.8(7)	119.3(2)
	116.5(4)		111.4(6)	
M−N(imino)−C	124.0(3)	126.1(4)	127.0(6)	126.1(3)
	124.7(3)		125.8(5)	
Ti−N(amino)−C				125.3(2)
C25−C11−C				111.0(3)
C25−C11−N				109.0(3)
N−C11−C				114.9(3)

range for Ti−benzyl complexes,[21] and the geometry of the Ti−CH_2Ph moiety (the Ti−C32 distance is ca. 3.164 Å, and the Ti−C9−C32 angle is 119.3(2)°) indicates η^1-benzyl coordination.

On the basis of experimental observations and theoretical conclusions, it is known that Hf−C bonds are the most stable among group 4 elements.[22] In addition, despite numerous reports on the synthesis of various Ti and Zr bis(phenoxyimino) complexes and studies of their catalytic behavior in olefin polymerization,[4−11] the synthesis and catalytic properties of Hf derivatives are still scarcely described in the scientific literature.[8] Therefore, in this respect, we found that Hf bis(phenoxyimino) dibenzyl complexes should be stable enough for their isolation and investigation. In present work we focused on the synthesis and $B(C_6F_5)_3$ activation studies of Hf bis(phenoxyimino) dibenzyl derivatives. In order to compare the catalytic behavior of Hf salicylaldiminates having different substituents at the metal atom, the corresponding Hf dichloro complexes were also synthesized and studied in ethylene and propylene polymerization reactions side by side with their Hf dibenzyl derivatives.

Synthesis of Hf Complexes. For this work, the known *tert*-butylsalicylaldimines having CH_2Ph (**1**) or C_6F_5 (**3**) imino groups and analogous new 3,5-dicumylphenoxyimines (**2**, **4**)

(17) $TiMe_4$ is highly thermally sensitive and decomposes at temperatures above −40 °C. The reagent was prepared and used in situ. See for example: (a) Thiele, K. H.; Müller, J. *J. Prakt. Chem.* **1968**, *38*, 147. (b) Kleinhenz, S.; Seppelt, K. *Chem. Eur. J.* **1999**, *5*, 3573.

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(19) In ref 10, Ti−N = 2.223(2) Å, and in ref 4c, Ti−N = 2.234(2) Å.

(20) March, J.; Smith, M. B. *Advanced Organic Chemistry: Reactions, Mechanisms, and Structure*; Wiley: New York, Chichester, Weinheim, Brisbane, Toronto, Singapore, 2001; p 20 ($C(sp^3)$−N = 1.47 Å).

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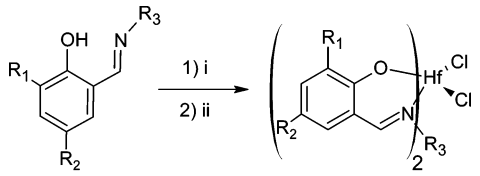
Scheme 2[a]



1-4

5: R_1 - *t*Bu, R_2 - H, R_3 - CH_2Ph

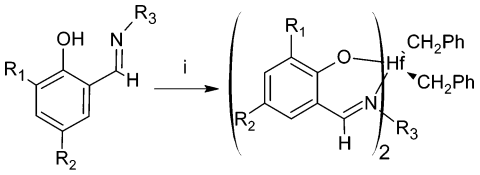
6: R_1,R_2 - cumyl, R_3 - CH_2Ph

7: R_1 - *t*Bu, R_2 - H, R_3 - C_6F_5

8: R_1,R_2 - cumyl, R_3 - C_6F_5

[a] Legend: (i) BuLi or NaH in Et_2O; (ii) $HfCl_4$ in $PhCH_3$.

Scheme 3[a]



1-4

9: R_1 - *t*Bu, R_2 - H, R_3 - CH_2Ph

10: R_1,R_2 - cumyl, R_3 - CH_2Ph

11: R_1 - *t*Bu, R_2 - H, R_3 - C_6F_5

12: R_1,R_2 - cumyl, R_3 - C_6F_5

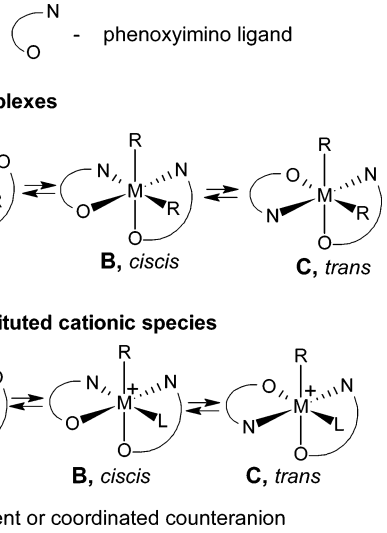
[a] Legend: (i) $Hf(CH_2Ph)_4$ in Et_2O; −78 °C.

were chosen as ligand precursors (Scheme 2). The compounds **2** and **4** were prepared via the simple reaction of the corresponding aldehyde and amine in the presence of an acid catalyst. The deprotonation of **1**−**4** with NaH or *n*-BuLi in THF and the following reaction of the Li or Na salts with $HfCl_4$ in toluene led to the desired Hf bis(phenoxyimine) dichloro complexes (**5**−**8**) with good yields (Scheme 2). For the bulky substituted aldimines **2** and **4,** the deprotonation with *n*-BuLi is preferable because the ligand deprotonation with NaH was not complete, and thus further reaction with $HfCl_4$ was not selective. Complexes **5**−**8** were obtained as yellow solid materials, and their ^1H and ^{13}C NMR spectra showed the presence of only one structural isomer in CD_2Cl_2 solution. As a curiosity, **6** and **8** having bulky cumyl substituents displayed a great affinity to make solvates with hexane.

The corresponding Hf dibenzyl complexes **9**−**12** were formed as a result of separate reactions between the ligand precursors **1**−**4** and $Hf(CH_2Ph)_4$ at −78 °C in Et_2O (Scheme 3) and were isolated as pure compounds with moderate yields. The dibenzyl complexes were obtained as orange solids, and they were thermally stable even at temperatures up to 80 °C in C_6D_5Br solution. Despite their increased resistance to elevated temperatures, the Hf bis(phenoxyimino) dibenzyl complexes were highly air- and moisture-sensitive; therefore, their isolation and further reactions were carried out in a glovebox.

The dynamic-temperature ^1H NMR analysis revealed that **9**−**12** were rigid in solution, as no isomerization of the coordination sphere in the complexes was observed, even at 80 °C. In general, the ^1H NMR spectra of **9**−**12** consist of peaks in the strong-field region corresponding to *t*-Bu (in **9**, **11**) or cumyl groups (in **10**, **12**), typical AB patterns for methylene protons of the Hf−CH_2Ph and CH═NCH_2Ph substituents, signals of aryl protons, and a single peak for the CH═N group at low field (see the Supporting Information). The diastereotopic behavior of Hf−CH_2Ph and CH═NCH_2Ph methylene protons corresponds to the cis orientation of the Hf−benzyl groups and the benzylimino substituents.[24,25]

Scheme 4



The signals of the Hf−CH_2Ph methylene protons in **9**−**12** have relatively large J_{HH} values (around 11−12 Hz), and in addition, the CH_2 and C_{ipso} signals in the ^{13}C NMR had typical shifts for η^1-bound benzyl groups. Although the J_{CH} constants were not measured for **9**−**12**, it was possible to conclude that in solution the benzyl groups coordinate to Hf in a η^1 fashion. In the case of M−η^2-CH_2Ph coordination in group 4 benzyl complexes, the signals for ortho Ph protons and CH_2 and C_{ipso} carbons should move to high field.[25,26] In addition, the J_{HH} values should be reduced (<10 Hz), and J_{CH} constants should be large (>125 Hz) for the methylene protons.[25,26]

Solid-state structures for the dibenzyl complexes **10**−**12** were determined by single-crystal X-ray diffraction methods and are illustrated in Figures 2−4, respectively. Selected bond angles and distances are given in Table 1 and crystallographic data in Table 6. In these structures, Hf adopts a distorted octahedral configuration, where the apical vertices of the coordination octahedra are occupied by oxygen atoms and the equatorial positions are taken by the imino nitrogens and the Hf−benzyl groups, both in the cis orientation. In fact, this is common for all of the solid-state structures of dialkyl group 4 metal phenoxyimino derivatives reported so far,[15] now including **10**−**12**. It can be proposed for these alkyl complexes that the cis isomeric structure (**A**; Scheme 4) presents a low local minimum of energy compared with the cis,cis and trans configurations (**B** and **C**, respectively; Scheme 4) and alkyl complexes having structures **B** and **C** might be hardly accessible.

Despite their different imino substituents, complexes **10**−**12** have similar metal−ligand distances between the central atom and the ligands: Hf−O bonds are around 2.0 Å, Hf−N(imino) distances are ca. 2.4 Å, and Hf−C bonds are between 2.23 and 2.26 Å (Table 1).[27] In the solid state (Figures 2−4), the benzyl groups in **10**−**12** coordinate to Hf in an η^1 fashion (Hf−C_{ipso} distances are in the range 3.16−3.25 Å; C_{ipso}−C−Hf angles

(24) Cuomo, C.; Strianese, M.; Cuenca, T.; Sanz, M.; Grassi, A. *Macromolecules* **2004**, *37*, 7469.

(25) Jordan, R. F.; LaPointe, R. E.; Bajgur, C. S.; Echols, S. F.; Willett, R. *J. Am. Chem. Soc.* **1987**, *109*, 4111.

(26) (a) Pelleccia, C.; Immirzi, A.; Grassi, A.; Zambelli, A. *Organometallics* **1993**, *12*, 4473. (b) Jordan, R. F.; LaPointe, R. E.; Baenziger, N.; Hinch, G. D. *Organometallics* **1990**, *9*, 1539.

(27) Compare with other Hf benzyl complexes: (a) Morgan, A. R.; Kloskowski, M.; Kalischewski, F.; Phillips, A. H.; Petersen, J. L. *Organometallics* **2005**, *24*, 5383 (Hf−C = 2.282(3) Å). (b) Scott, M. J.; Lippard, S. J. *Inorg. Chim. Acta* **1997**, *263*, 287.

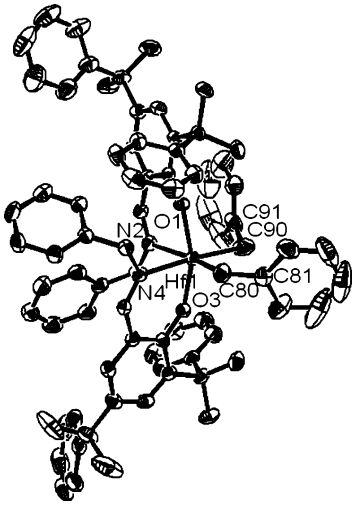


Figure 2. ORTEP plot of **10** with thermal ellipsoids drawn at the 50% probability level. All hydrogen atoms were omitted for clarity.

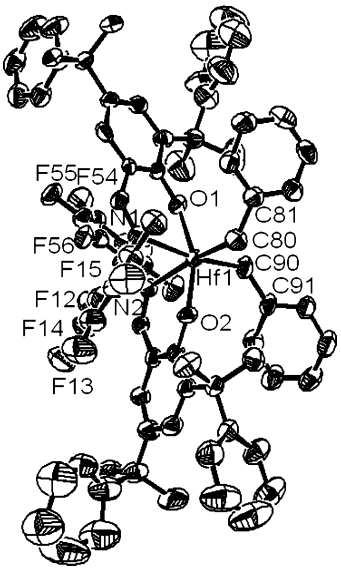


Figure 3. ORTEP plot of **12** with thermal ellipsoids drawn at the 50% probability level. All hydrogen atoms were omitted for clarity.

are between 110 and 117°), which is in good agreement with the observed ^{1}H and ^{13}C NMR spectra.

The coordination octahedron of **10** is distorted. The angle between trans oxygens (O1−Hf−O3) is reduced to 159.21(12)°, and angles for the cis-oriented imino nitrogens and the benzyl groups are 86.58(13) and 97.0(2)°, respectively. Further on, the possible molecular symmetry of the complex in the solid state is rather distorted, due to differently oriented cumyl groups. As a result, the structure of **10** is unsymmetric (Figure 2).

In complexes **11** and **12**, the Hf−benzyl groups are orientated in apical directions (parallel to Hf−O bonds in Figures 3 and 4), whereas the Hf−benzyl groups in the structure of **10** are placed so that bonds between C_{ipso} and methylene carbons (e.g., C80−C81, Figure 2) lie in the equatorial plane (defined by imino N atoms and C80 and C90 carbons) of the coordination octahedron. The reason for the apical orientation of the Hf−CH_2Ph groups in **11** and **12** can be the repulsion between the electron-rich phenyl rings of the benzyl substituents and fluorine atoms in C_6F_5 acquiring partial negative charges, as a result of strong C−F bond polarization. The angle between the Hf−CH_2Ph groups in **10** is wider than in **11** and **12** (ca. 94° in **11** and **12** vs 97° in **10**, respectively). Unlike the structures of **10** and **12**,

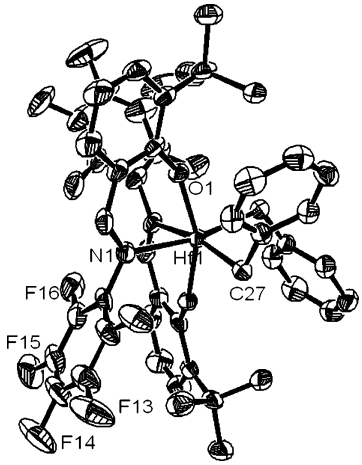


Figure 4. ORTEP plot of **11** with thermal ellipsoids drawn at the 50% probability level. Solvent molecules and all hydrogen atoms were omitted for clarity.

due to the absence of differently oriented cumyl substituents, complex **11** is centrosymmetric in the solid state (Figure 4).

In order to verify the structure of the dibenzyl complexes in solution, 2D-NOESY NMR methods were applied. As the diastereotopic behavior of the Hf−CH_2Ph methylene protons in ^{1}H NMR of **9**−**12** indicated a cis orientation of the Hf−benzyl groups (see above), isomers with an axial orientation of the Hf−CH_2Ph substituents were excluded from our considerations. The isomeric configurations which are possible for Hf bis(phenoxyimino) complexes having benzyl groups in cis positions are shown in Scheme 4. In general, the NOESY spectra of complexes **9**−**12** were similar (see the Supporting Information), showing chemical equivalence of both of the salicylaldiminato ligands in each structure. The cis,cis configuration (Scheme 4; **B**) has two chemically nonequivalent phenoxyimino ligands and can thus be excluded. In the ^{1}H NMR of **9** and **10** it can be seen that methylene protons in N−CH_2Ph groups are diastereotopic (analogous to the Hf−CH_2 substituents), which allows us to propose the cis-N,N configuration (Scheme 4; **A**) for these complexes. Due to the number of interactions of neighboring protons observed in the 2D-NOESY spectra of **9** and **11**, the presence of relatively close contacts between *t*-Bu groups and methylene (from Hf−CH_2Ph) protons was recognized. In the solid-state structure of *cis*-**11,** the shortest distance between calculated positions of *t*-Bu and methylene hydrogens was found to be ca. 2.4 Å, which corresponds to the 2D-NOESY data. In addition, the close proximity of Hf−CH_2 protons to protons of the *t*-Bu groups was observed for calculated Turbomole 5.8 structures of *cis*-**11** and *cis*-**9,** while in the calculated trans isomers of **9** and **11** such groups are placed far from each other (see the Supporting Information). On the basis of these observations, it can be proposed that the cis configuration of **9** and **11** is maintained in solution. A comparison of data obtained from 2D-NOESY, solid-state structural studies and the results of Turbomole- and ADF-based calculations led to similar conclusions for complexes **10** and **12** (see the Supporting information).

Ethylene Polymerization. Although Ti and Zr bis(phenoxyimino) complexes have been extensively studied as catalyst precursors for olefin polymerization over the past few years, only a few examples of the catalytic behavior of analogous Hf derivatives have been reported.[8] In addition, the published results were based on ethylene polymerization experiments with short reaction times, in the range of 5 min. In the present work, the long-run olefin polymerizations (up to 4 h of polymerization

Table 2. Ethylene Polymerization Data for Complexes 5−12[a]

entry	cat.	cat. concn (μmol)	reacn temp (°C)	MAO concn (M)	yield (g)	activity[b]	M_n (g/mol)	M_w (g/mol)	PDI	mp (°C)
1	**5**	2	80	2000	0.81	810	1.03×10^4	2.3×10^5	22	129
2	**5**	1	30	2000	12.9	7760[c]	6.8×10^4	4.2×10^5	6.2	138
3	**5**	0.5	30	2000	11.1	6000[d]	7.4×10^4	6.6×10^5	8.9	137
4	**6**	0.1	80	2000	1.71	34000	3.1×10^4	8.1×10^4	2.6	133
5	**6**	0.1	30	2000	0.5	10000	4.0×10^4	3.0×10^5	7.5	
6	**7**	2	80	2000	0.54	540	2.1×10^4	9.5×10^4	4.5	133
7	**7**	0.5	40	2000	6.0	24000	8.0×10^4	2.8×10^5	3.5	135
8	**8**	0.25	80	2000	1.5	12000	3.9×10^5	1.6×10^6	4.0	137
9	**8**	0.25	30	2000	4.5	36000	7.1×10^5	1.9×10^6	2.6	136
10	**9**	1	30	2000	0.05	~100				
11	**10**	0.25	30	2000	~0.03	~100	6.2×10^4	1.1×10^6	18	
12	**11**	0.5	30	2000	14	56000	7.2×10^4	2.1×10^5	2.9	
13	**12**	0.25	30	2000	3	24000	4.1×10^5	2.2×10^6	5.5	

[a] Conditions: 200 mL of toluene, pressure of ethylene 4 bar, polymerization time 30 min. [b] In units of kg of PE/((mol of cat.) h). [c] Polymerization time 100 min. [d] Polymerization time 223 min.

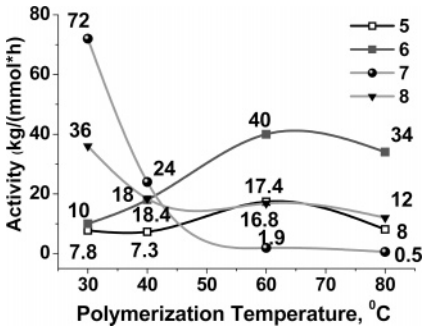


Figure 5. Catalytic activity as a function of polymerization temperature for MAO-activated complexes **5**−**8** in ethylene polymerization. The numeric values of the observed activities (in kg of PE/(mmol h)) are given for the corresponding graph points.

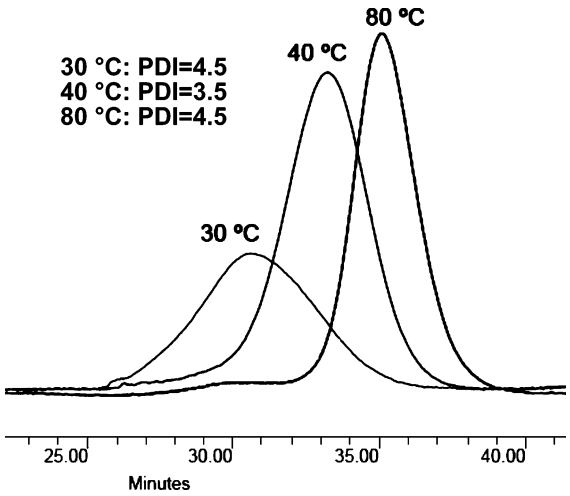


Figure 6. GPC curves of polyethylenes obtained with the catalyst **7**/MAO at different polymerization temperatures: 30, 40, and 80 °C. PDI: molar mass distribution (M_w/M_n).

time) with activated Hf bis(phenoxyimino) dichloro complexes **5**−**8** or their dibenzyl analogues **9**−**12** were investigated in detail.[28]

The MAO (methylaluminoxane)-activated hafnium dichloro salicylaldiminates showed very high activity in ethylene polymerization (Table 2), comparable to that of analogous Ti and Zr derivatives (FI catalysts)[4−8] and well-known metallocene-based catalysts.[1] The activation of the perfluorophenyl-substituted complexes **7** and **8** with MAO occurred very quickly, and initial polymerization activities with these catalysts were exceedingly high. After 5−10 min of ethylene polymerization the activity of **7**/MAO and **8**/MAO significantly decreased but then remained constant at quite a high level until the end of the polymerization run. In addition, these catalysts showed high sensitivity to increased polymerization temperature, and the maximum ethylene polymerization activity was achieved at quite low temperatures (Figure 5). In contrast, although ethylene polymerization with the benzylimino-substituted Hf catalysts **5**/MAO and **6**/MAO started immediately after addition of the complex into the reaction mixture, the complete activation of the catalyst precursors required a longer time. With **6**/MAO 5−7 min was needed to achieve the maximum ethylene consumption, while with **5**/MAO at least a few hours was required. For example, the maximum ethylene consumption with **5**/MAO at 30 °C was recorded 4 h after the initiation of polymerization. After sufficient time, the benzylimino-substituted Hf catalysts had high activity, which slightly decreased during polymerization. The catalysts **5**/MAO and **6**/MAO showed increased activity when heated from 30 °C up to 60 °C, but at higher temperatures the polymerization activity rapidly declined (Figure 5).

The properties of the polyethylene produced were investigated by GPC and DSC methods (Figure 6, Table 2, and the Supporting Information). In general, the Hf catalysts appeared to produce monomodal polyethylene with slightly broadened molar mass distribution. However, polyethylene with bimodal molar mass distribution (run 1, Table 2) was obtained at 80 °C with **5**/MAO. This is connected with the fast decline in catalytic activity during the polymerization run at 80 °C (see above), and one possible explanation is a partial decomposition of **5**/MAO in the course of polymerization. In ethylene polymerizations carried out with MAO-activated complexes **5**−**8** at different temperatures, an increase of M_w and visible shouldering of molar mass distribution curves were recognized when the polymerization temperature was decreased (Figure 6 and the Supporting Information). On the basis of these observations, it can be concluded for the investigated Hf complexes that the rate of chain termination decreases more slowly than the speed of chain propagation when the polymerization temperature is lowered. In addition, unlike the Zr and Ti bis(phenoxyimino) complexes described earlier,[9,11] these catalytic systems did not show clear dynamic behavior (changes in modality of polymer), regardless of the wide range of polymerization temperatures applied (Figure 6).

(28) TIBA/$[(PhNHMe_2)^+B(C_6F_5)_4^-]$ and TIBA/$B(C_6F_5)_3$ were used as activators, but the obtained Hf phenoxyimino catalytic systems appeared to be very sensitive to traces of air and moisture and most probably were hydrolyzed during the loading of the catalyst solution into the polymerization autoclave. In contrast, olefin polymerizations carried out in NMR tubes with Hf bis(phenoxyimino) dibenzyl complexes and $B(C_6F_5)_3$ (see text) revealed high polymerization activity.

Table 3. Propylene Polymerization Data for Complexes 5−12[a]

entry	cat.	cat. concn (μmol)	reacn temp (°C)	MAO concn (M)	yield (g)	activity[b]	M_n (g/mol)	M_w (g/mol)	PDI
1	**5**	20	30	2000	~0.1 + dimers	50[c]			
2	**5**	20	20	2000	~0.1 + dimers	40[c]			
3	**6**	20	20	2000	0.24 + dimers	120[c]			
4	**6**	20	10	2000	0.22 + dimers	300[c]			
5	**7**	20	10	2000	4.11	410	1584	4459	2.8
6	**8**	20	20	2000	1.02	102	1278	3415	2.7
7	**8**	20	10	2000	1.87	190	1272	2418	1.9
8	**9**	20	30	2000	inactive				
9	**10**	20	30	2000	inactive				
10	**11**	20	30	2000	14.0	1400	1713	4987	2.9
11	**12**	20	30	2000	0.75	75	1287	2813	2.2

[a] Conditions: 200 mL of toluene, pressure of propylene 6 bar, polymerization time 30 min. [b] In units of kg of PE/((mol of cat.) h). [c] Activity calculated on the basis of propylene consumption data.

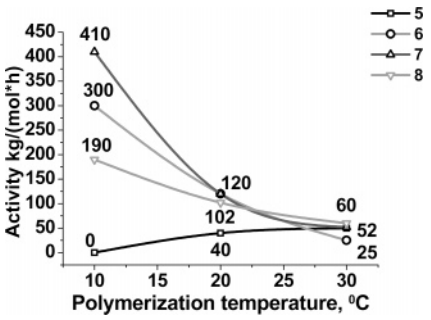


Figure 7. Catalytic activity as a function of polymerization temperature for MAO-activated complexes **5**−**8** in propylene polymerization. The numeric values of the observed activities (in kg of PE/(mol h)) are given for the corresponding graph points.

The MAO-activated dibenzyl complexes **9**−**12** were also active in ethylene polymerization. However, the catalytic activity was strongly dependent on the substitution pattern on the imino nitrogens. In the case of benzylimino-substituted catalysts **9**/MAO and **10**/MAO, the polymerization of ethylene started immediately, but ethylene consumption stayed at a very low level during polymerization, regardless of the applied polymerization time. As a result, only very small amounts of polyethylene were isolated in polymerization runs. In contrast, complexes **11**/MAO and **12**/MAO bearing perfluorophenylimino groups revealed high polymerization activities and produced polymers similar to those obtained by their MAO-activated dichloro analogues **7**/MAO and **8**/MAO (compare runs 7 and 12 and runs 8 and 13 in Table 2). On the basis of the obtained polymerization results, it can be proposed that MAO treatment of the benzylimino-substituted dibenzyl complexes **9** and **10** leads to species which are different from those produced in MAO activation of analogous dichloro complexes **5** and **6** (see below).

Propylene Polymerization. The MAO-activated Hf bis(phenoxyimino) dichloro complexes **5**−**8** were also applied to propylene polymerization with moderate activities (Table 3). The maximum polymerization activity was observed at low temperatures (Figure 7). The produced polypropylene had a low molar mass and relatively narrow molar mass distribution. Obviously, despite the presence of Hf, the rate of chain termination is high. The catalysts **5**/MAO and **6**/MAO, bearing benzylimino substituents, gave mainly mixtures of propylene dimers and trimers, and only small amounts of low-molar-mass polypropylene was obtained (Table 3 and the Supporting Information).

Similarly as in ethylene polymerization, the MAO-activated dibenzyl complexes **9** and **10**, bearing benzylimino groups, had a significantly lower polymerization activity than their dichloro analogues and were practically inactive in propylene polymerization. On the other hand, catalysts having perfluorophenylimino substituents (**11**/MAO and **12**/MAO) showed polymerization activities comparable to or even higher than and polymer properties similar to those recorded for their dichloro analogues **7**/MAO and **8**/MAO (compare runs 5 and 10 and runs 11 and 6, 7 in Table 3).

On the basis of ^{13}C NMR data recorded for the obtained polymers, the MAO-activated complexes **5**−**8**, **11**, and **12** produced different kinds of polypropylene, depending on the ligand substitution pattern. According to the ^{13}C NMR spectra of polypropylene obtained with **5**/MAO and **6**/MAO bearing benzylimino groups, the polymers are atactic, enriched with syndiotactic stereoregularity (Figure 8a).[30] Only traces of unsaturated end groups were detected, but relatively intense signals at 22.6−23.7, 25.8, and 48.4 ppm corresponding to isobutyl end groups were present (Figure 8a). On the basis of these findings, it can be concluded that the main chain termination process in propylene polymerization with **5** and **6** is the chain transfer to aluminum (Scheme 5), while the presence of a few unsaturated end groups indicates occasional β-H elimination during the polymer chain growth. Similar catalytic behavior was reported earlier for MAO-activated, perfluorophenyl-substituted Zr bis(phenoxyimino) complexes in propylene polymerization.[30] Assuming that each polypropylene macromolecule has two isobutyl end groups (resulting from a 1,2−1,2 unit sequence), the calculated average length of the polymer chain was around 50−100 monomer units, depending on the applied polymerization temperature (Table 4).

The MAO-activated dichloro and dibenzyl complexes **7**, **8**, **11**, and **12** bearing the perfluorophenylimino groups produced a similar type of polypropylene, which differs from that obtained with the benzylimino-substituted **5**/MAO and **6**/MAO (Figure 8b,c). The polymer is poorly stereoregular but has a distinct syndiotactic type structure (Table 4). The main difference between polymers produced by the benzylimino- and perfluorophenylimino-substituted catalysts is that the latter give polypropylene with a large amount of regioerrors, appearing as 2,1-threo and 2,1-erythro microstructures (Table 4, Figure 8b,c, and Scheme 6).[29c] Due to the available resolution of the ^{13}C NMR spectra the precise integration of the peaks is difficult, but the approximate calculations are presented in Table 4. For polymers produced with the catalysts **7**/MAO and **11**/MAO

(29) The analysis of ^{13}C NMR spectra of produced polypropylenes was performed on the basis of: (a) Zhongde, X.; Mays, J.; Xuexin, C.; Hadjchristidis, N.; Schilling, F. C.; Bair, H. E.; Pearson, D. S.; Fetters, L. J. *Macromolecules* **1985**, *18*, 2560 (identification of pentads). (b) Resconi, L.; Cavallo, L.; Fait, A.; Piemontezi, F. *Chem. Rev.* **2000**, *100*, 1253. (c) Busico, V.; Cipullo, R. *Prog. Polym. Sci.* **2001**, *26*, 443 (identification of end groups and regioerrors).

(30) Lamberti, M.; Gliubizzi, R.; Mazzeo, M.; Tedesco, C.; Pellecchia, C. *Macromolecules* **2004**, *37*, 276.

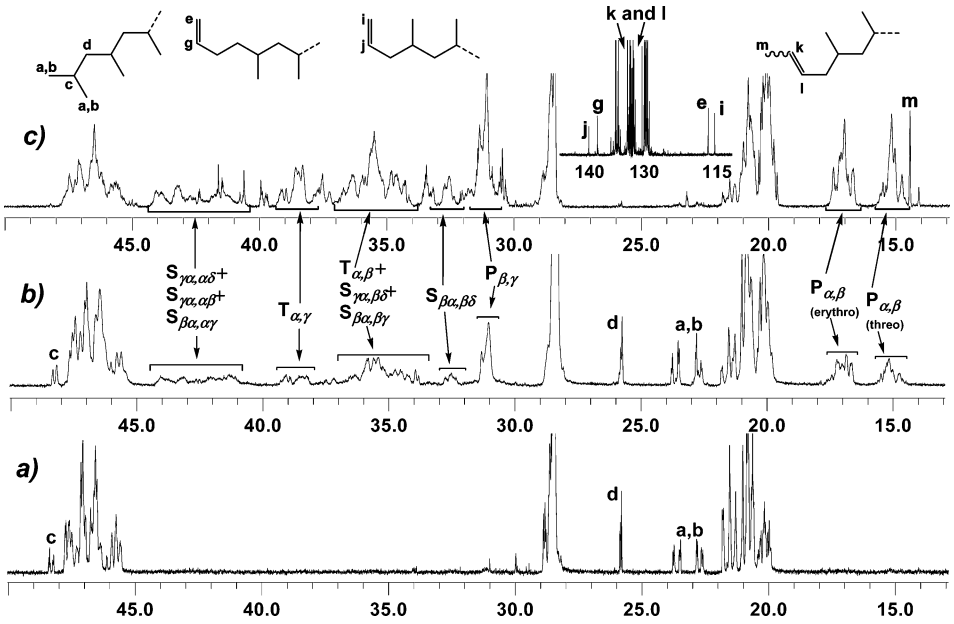
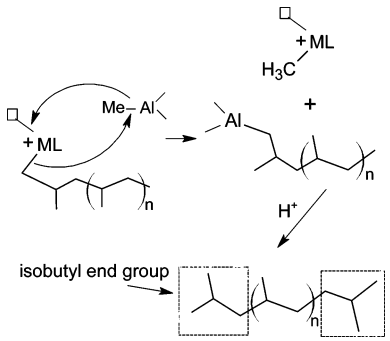


Figure 8. ^{13}C NMR spectra of polypropylenes produced by (a) **6**/MAO, (b) **7**/MAO, and c) **8**/MAO. Conditions: polymerization temperature 10 °C, propylene pressure 6 bar, MAO:Hf ratio 2000:1, 200 mL of toluene.

Scheme 5



bearing *o-tert*-butyl groups at the salicylaldiminato rings, the content of 2,1-threo and 2,1-erythro methyl groups ($P_{\alpha,\beta}$) was around 6−12%. The amount of 2,1-inserted units was significantly higher in the polypropylene chains obtained by **8** and **12**/MAO having large cumyl substituents at the phenoxy ring (up to 40%).

The dominating end groups in polymers obtained with **7**/MAO and **11**/MAO are isobutyl groups, and on the basis of the ratio of integral intensities, the calculated average polymer chain length is about 50 monomer units. The obtained average molar masses, ∼2000 g/mol, are in accordance with the molar mass values obtained with GPC measurements (compare Tables 3 and 4).

Assuming that 1,2-insertion of propylene is followed by 2,1-insertion and the chain then transfers to aluminum, the *n*-butyl end group should appear (Scheme 6). Although the peaks corresponding to the *n*-butyl end groups are difficult to assign due to the increased amount of regioerrors, presumably minor amounts of *n*-butyl groups can be present. This means that, after 2,1-insertion of propylene, the polymer chain grows further (main route), and with **7**/MAO and **11**/MAO the chain termination occurs regioselectively, mainly after 1,2-insertion of the monomer.

However, polymers produced with catalysts **8**/MAO and **12**/MAO are different, as only traces of isobutyl end groups were detected. The growing polymer chain is predominantly terminated by β-H elimination. Probably, the presence of the sterically bulky cumyl groups in the ligand frameworks prevents close coordination between the MAO^- counteranion and the catalytically active metal center, which is a prerequisite for the chain transfer to Al. The dominating chain ends in the obtained polypropylenes were allyl, 1-butenyl, and *cis*- and *trans*-2-butenyl (Figure 8c). The allyl groups result from β-H transfer in a 2,1−2,1−... sequence, while 1-butenyl and *cis*- and *trans*-2-butenyl are products of β-H eliminations in a 2,1−1,2−1,2−... polymer chain.[8a] Consequently, the chain termination with catalysts **8**/MAO and **12**/MAO takes place selectively after 2,1-insertion of the last monomer, not after 1,2-insertion, which is in agreement with previously observed results.[8a]

Generation of Cationic Species. The activation of Hf dibenzyl complexes **9**−**12** with $B(C_6F_5)_3$ was investigated by NMR methods. The activation experiments were carried out in NMR tubes in a glovebox at ambient temperature, and dry C_6D_5Br was used as a solvent. When the perfluorophenylimino-substituted Hf dibenzyl complexes **11** and **12** were mixed with $B(C_6F_5)_3$, a reaction occurred immediately. According to ^{1}H NMR and ^{1}H−^{13}C heteronuclear correlation measurements (see the Supporting Information), the abstraction of one of the benzyl groups from the Hf atom by the boron activator occurred selectively and, as a result, the "classical" cationic species **14** and **15** were formed (Scheme 7b).

In the ^{1}H NMR spectra of **14**, the signal for the methylene protons belonging to the $PhCH_2B(C_6F_5)_3^-$ anion was observed at 3.01 ppm, indicating that one of the benzyl−Hf groups was abstracted from the metal. The other Hf−CH_2Ph group remained unchanged and gave a signal at 2.84 ppm (see the Supporting Information). Unlike the spectra of the parent complexes **11** and **12,** the peaks corresponding to the methylene protons of the Hf−benzyl groups in **14** and **15** appeared as simple singlets, showing that some dynamic processes are present in solution. The resulting cationic complexes **14** and **15** were rather stable but were thermally sensitive. The visible decomposition of **14** started at 50 °C and led to another cationic Hf complex having a close interaction with the $PhCH_2B(C_6F_5)_3^-$ counteranion ($\Delta\delta$(F) = 3.9 ppm). Until the decomposition point no structural isomerization of **14** was detected. Complex **15** was even less thermally stable than **14** and decomposed readily at room

Table 4. ^{13}C NMR Analysis of Polypropylene Produced with 5−8, 11, and 12

cat.	reacn temp (°C)	[*mm*] (%) ([*rmmr*]:[*mmmr*]:[*mmmm*])	[*rm*] (%) ([*rmrm*]:[*mmrm*]:[*mmrr*])	[*rr*] (%) ([*mrrm*]:[*rrrm*]:[*rrrr*])	M^a (kg/mol)	misinsertions (%) $P_{\alpha,\beta}$(erythro)	misinsertions (%) $P_{\alpha,\beta}$(threo)
6	30	23 (1:2:1)	54 (2:3:1)	23 (1.7:2:1)	2	traces	traces
6	10	25 (1.2:1.8:1)	54 (2:3:1)	21 (2:2:1)	4.2	1.8	1.6
7	10	11 (3.4:3.1:1)	47	42	2.1	12	9
8	20	6	37	57	1.3	19	17
8	10	3	38	59	2.1	18	16
11	30	12	48	42	2.8	9	6
12	30	7	39	54	1.5	19	17

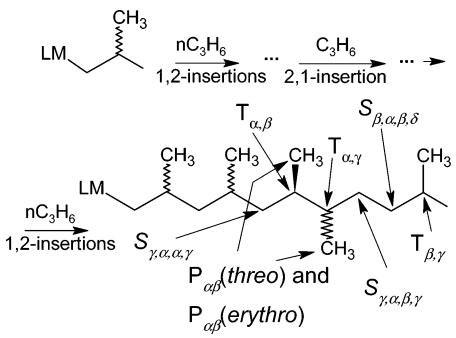
[a] Calculated average molar mass based on the ratio between intensities of signals for the chain ends and the methyl groups of the main sequence.

Table 5. Relative Energies (kJ/mol) of Isomeric Structures for Hf Bis(phenoxyimino) Dibenzyl Complexes and for the Corresponding Monobenzyl Cationic Species

complex	E_r(cis)	E_r(cis,cis)	E_r(trans)
9	−35.1	−14.0	0
	−35.0[a]	−8.7[a]	0[a]
9/B(C_6F_5)$_3$	−8.1	−7.7	0
10	−21.6	−17.2	0
10/B(C_6F_5)$_3$	−8.3	−3	0
11	−32.3	0	0
14	−34.5	−36.0	0
12	−50.9	−26.5	0
15	−19.6	0	0

[a] Calculated with the ADF2005.01 program.

Scheme 6



temperature. ^1H NMR and $^1H-^{13}C$ heteronuclear correlation experiments showed that the signals of the *o*-phenyl protons (6.8 ppm in **11** vs 6.5 ppm in **14**; 6.9 ppm in **12** vs 5.6 ppm in **15**) and the methylene carbon of the Hf−CH_2Ph groups in **14** and **15** (81 ppm in **11** vs 76 ppm in **14**; 80 ppm in **12** vs 74 ppm in **15**) are moved to high field, indicating the η^2 coordination between Hf and the benzyl group in **14** and **15**.[31] The ESI-MS studies support the efficient formation of the monobenzyl Hf cationic species **14** (M = 953.1 g/mol) and **15** (M = 1314 g/mol), as they were the main components in the solution (see the Supporting Information).

The benzylimino-substituted Hf dibenzyl complex **9** reacted rapidly with B(C_6F_5)$_3$. The reaction mixture changed from light orange to orange and then to yellow, indicating that simultaneously with the complex activation some further transformations took place. In ^1H NMR spectra, the signals of protons belonging to the $PhCH_2B(C_6F_5)_3^-$ anion, the remaining Hf−CH_2Ph group, and a peak at 2.44 ppm were found (see the Supporting Information). The signal at 2.44 ppm can be attributed to a toluene methyl group, which can appear as a result of CH activation in "classical" cationic species.[32] After 2 h, the intensity of toluene protons increased significantly, while at the same time the signal of the Hf−CH_2Ph group drastically diminished and almost disappeared. In $^1H-^{13}C$ heteronuclear correlation spectra, the peaks of the methyl group of toluene, Hf−CH_2Ph, the benzylimino substituents, and the BCH_2Ph moiety can be distinguished (Figure 9). These observations indicate that the formed cationic species derived from **9** are unstable toward CH activation processes, which can proceed by an intramolecular pathway (Scheme 7a).[33] Similarly to **14** and **15**, the peaks corresponding to methylene protons of the Hf−benzyl and benzylimino groups in **9**/B(C_6F_5)$_3$ appeared as simple singlets, showing that some dynamic processes are present in solution.

In the $^1H-^{13}C$ heteronuclear correlation spectrum the peaks corresponding to the methylene carbon (73.5 ppm for **9** vs 66.6 ppm in **9**/B(C_6F_5)$_3$) and ortho protons of the Hf−CH_2Ph group (6.9 ppm for **9** vs 6.60 ppm in **9**/B(C_6F_5)$_3$) are noticeably shifted to high field. This indicates the η^2 coordination of the remaining benzyl group to the Hf atom.[31] ESI-MS investigations of the reaction in THF confirmed the presence of CH activation processes. The main species in the solution had a molar mass of 713 g/mol, corresponding to the CH activation product from the original Hf cation (802 g/mol) (Scheme 7 and the Supporting Information).

Similar CH activations were observed for **10**, bearing the bulky cumyl groups, when treated with B(C_6F_5)$_3$. The resulting cationic complex tended to be even more unstable than **9**/B(C_6F_5)$_3$ species. Only a small amount of the Hf−CH_2Ph protons corresponding to unchanged **10**/B(C_6F_5)$_3$ was found in the ^1H NMR spectrum. The ESI-MS spectrum of **10**/B(C_6F_5)$_3$ showed the CH activation product (M = 1073 g/mol) as the main compound in solution (Scheme 7). The observed tendency of the cationic benzylimino-substituted bis(phenoxyimino) Hf monobenzyl species to undergo CH activation could be the reason for the low activity of **9**/MAO and **10**/MAO in ethylene and propylene polymerization. After MAO activation of **9** or **10,** the formed catalytic species can be instantly deactivated via the CH activation.

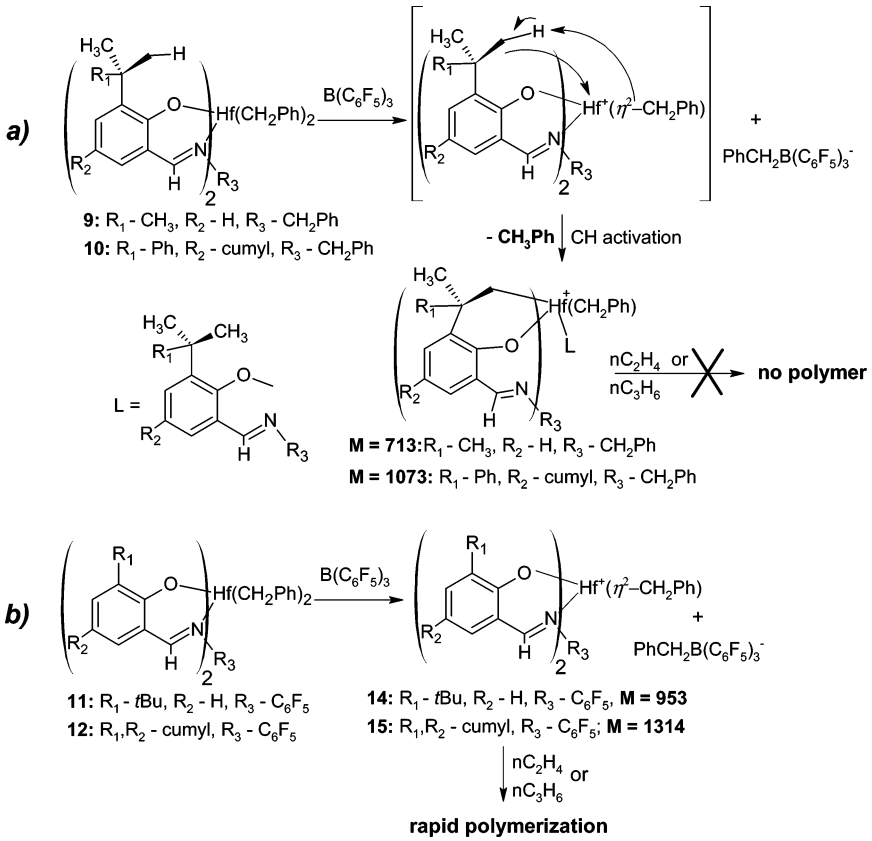
The activation process of complexes **9**−**12** was also investigated by ^{19}F NMR. In all cases, at room temperature the formed $PhCH_2B(C_6F_5)_3^-$ anions stay in the outer coordination sphere ($\Delta\delta$(F) = 2.7 ppm) and, thus, there are no direct contacts between the cationic Hf centers and the borate anions (Supporting Information). On the other hand, at low temperature (−80 °C), a weak coordination between Hf cationic species and

(31) In addition, J_{HH} values for the Hf−CH_2Ph AB pattern (measured at −80 °C in CD_2Cl_2) were 8.3 Hz for **9**/B(C_6F_5)$_3$ and 8.7 Hz for **14**, which indicates η^2 coordination of the benzyl group to the central atom.[23]

(32) The preparation of samples in a glovebox and use of dry C_6D_5Br exclude the possibility of hydrolysis of the formed cationic Hf monobenzyl species. This is supported by the fact that the similar, extremely highly sensitive to moisture and air, perfluorophenyl-substituted, cationic Hf monobenzyl complexes **14** and **15** did not show any sign of hydrolysis in NMR tubes.

(33) For the intramolecular activation of monobenzyl group 4 metal cationic species see: (a) Chen, E. Y.-X.; Marks, T. J. *Organometallics* **1997**, *16*, 3649. (b) Horton, A. D.; de With, J. *Chem. Commun.* **1996**, 1375. (c) Wright, J. M.; Landis, C. R.; Ros, M. A. M. P.; Horton, A. D. *Organometallics* **1998**, *17*, 5031. (d) Thorn, M. G.; Etheridge, Z. C.; Fanwick, P. E.; Rothwell, I. P. *J. Organomet. Chem.* **1999**, *591*, 148.

Scheme 7



borate counteranions was recognized ($\Delta\delta$(F) = 3.1 ppm). It seems that, as a consequence of the η^2 coordination of the CH_2Ph group to Hf, the positively charged metal center becomes in some extent saturated, and tight contacts with $PhCH_2B(C_6F_5)_3^-$ anion are thus prevented.

2D-NOESY methods were used to identify solution structures of the cationic Hf bis(phenoxyimino) benzyl complexes, and structural identifications were based on calculated structures. In the NOESY spectrum of **14**, it was found that protons from the *tert*-butyl substituents interact with methylene and ortho Ph protons of the Hf−CH_2Ph group (see the Supporting Information). Whereas the geometry of the calculated *cis*-**14** isomer corresponds to these observations, Hf−CH_2Ph and *t*-Bu groups in the calculated trans isomer appeared to be too far from each other (Figure 10). This excludes the possibility for the *trans*-configuration (Scheme 4, **C**). In addition, ^{1}H NMR, ^{1}H−^{13}C heteronuclear correlation, and 2D-NOESY spectra of **14** and **9**/B(C_6F_5)$_3$ showed chemical equivalence of the phenoxyimino ligands and, thus, the cis,cis isomeric structure (Scheme 4, **B**) can also be excluded from consideration. As a conclusion, the cis configuration (Scheme 4, **A**) can be proposed for cationic complex **14**.

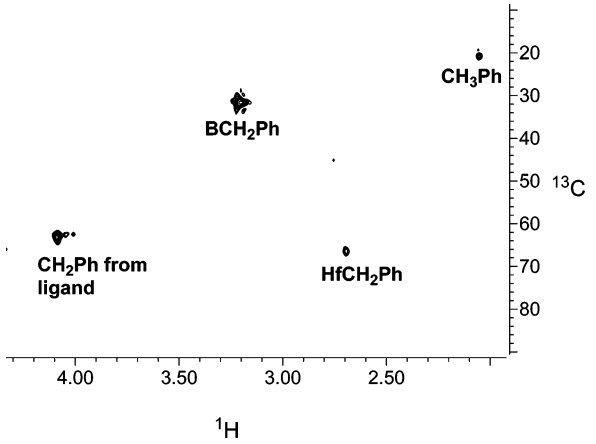


Figure 9. ^{1}H−^{13}C correlation spectrum of **9**/B(C_6F_5)$_3$ in C_6D_5Br.

In the 2D-NOESY spectrum of **9**/B(C_6F_5)$_3$, a partial CH activation of the cationic Hf complex was observed, and as a result of this, the intensities of the desired signals and, consequently, the interaction reflections for the methylene protons of the Hf−CH_2Ph groups were quite low. In any event, it was possible to distinguish the interactions between protons of the *t*-Bu substituents and the ortho Ph protons of the Hf−CH_2Ph group. On the basis of a comparison of calculated structures of cis and trans isomers these findings correspond to a cis configuration for **9**/B(C_6F_5)$_3$ in solution (see the Supporting Information). Unfortunately, 2D-NOESY spectra of **10**/B(C_6F_5)$_3$ and **15** became too complicated for interpretation due to extensive CH activation of **10**/B(C_6F_5)$_3$ or thermal decomposition of the initially formed "classical" cationic species **15**. Nevertheless, the cis-configuration can be expected for all **9**−**12**/B(C_6F_5)$_3$ species in solution. The DFT calculations, performed with Turbomole 5.8[34] and ADF 2005.01b,[35] also showed that the cis configuration is energetically favored for Hf dibenzyl phenoxyimino complexes **9**−**12**, as well as for the corresponding cationic species (see Table 5 and the Supporting Information).

(34) Ahlrichs, R.; Bär, M.; Häser, M.; Horn, H.; Kölmel, C. *Chem. Phys. Lett.* **1989**, *162*, 165. See: http://www.cosmologic.de/QuantumChemistry/main_qChemistry.html.

(35) (a) ADF2005.01b; SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands. See: http://www.scm.com. (b) te Velde, G.; Bickelhaupt, F. M.; van Gisbergen, S. J. A.; Fonseca Guerra, C.; Baerends, E. J.; Snijders, J. G.; Ziegler, T. *J. Comput. Chem.* **2001**, *22*, 931. (c) Fonseca Guerra, C.; Snijders, J. G.; te Velde, G.; Baerends, E. J. *Theor. Chem. Acc.* **1998**, *99*, 391.

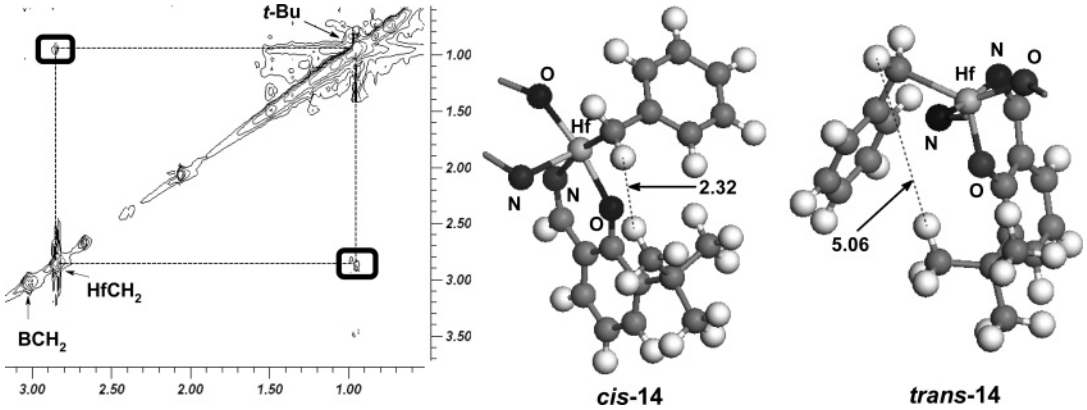


Figure 10. Calculated structures of cis and trans isomers of **14** together with a part of the measured 2D NOESY spectrum. For clarity, one of the phenoxyimino ligands is omitted from the drawn structures. For both isomers the shortest distances (in Å) between the protons of Hf−CH_2 and the *t*-Bu groups are shown.

The dynamic behavior of complexes **9**/B(C_6F_5)$_3$ and **14** was studied by low-temperature ^{1}H NMR. CD_2Cl_2 was chosen as a solvent, because the melting point of C_6D_5Br is too high (−31 °C). The cationic species for these measurements were generated at −78 °C by the addition of CD_2Cl_2 to a precooled mixture of reagents. The cationic species generated from **9** appeared to be very unstable in CD_2Cl_2, even at low temperature (−80 °C). The CH activation in **9**/B(C_6F_5)$_3$ proceeded similarly as in C_6D_5Br at room temperature. Above −10 °C, complete decomposition of the sample in CD_2Cl_2 was detected. For this reason, it was difficult to recognize the main dynamic processes within **9**/B(C_6F_5)$_3$, and the thermodynamic characteristics of these processes were calculated at an approximate level. At 27 °C and in C_6D_5Br, methylene protons of the benzylimino and the Hf−CH_2Ph substituents of **9**/B(C_6F_5)$_3$ and the Hf−CH_2Ph group of **14** appear in ^{1}H NMR spectrum as singlets, while at −80 °C the corresponding signals are seen as AB patterns (Figure 11 and the Supporting Information). In the case of **9**/B(C_6F_5)$_3$, the signals related to the methylene protons of the benzyl groups broaden at −30 °C and coalesce at −10 °C. With **14** the broadening for the AB pattern of the Hf−CH_2Ph protons started already at −70 °C and the coalescence point was recognized at −60 °C. Above −57 °C, only a singlet for the methylene protons of the Hf−CH_2Ph group was recorded (Figure 11). The measured J_{HH} value for the benzyl methylene protons in **9**/B(C_6F_5)$_3$ was 8.3 Hz, and for **14** J_{HH} was found to be 8.7 Hz.[36] Together with the shift of peaks corresponding to the methylene and the ortho protons and the carbons of the Hf−CH_2Ph groups in **9**/B(C_6F_5)$_3$ and **14** to strong field (see above), the values of J_{HH} indicate that Hf is bound to the CH_2Ph group in an η^2 fashion.

For these dynamic processes, the Gibbs energies of activation ($\Delta G^{\ddagger}$) were calculated on the basis of Eyring equations.[37] The $\Delta G^{\ddagger}$ values found for **9**/B(C_6F_5)$_3$ was ca. 14 kcal/mol, and 10.3 kcal/mol was found for **14**. There can be two explanations for the observed fluxional behavior. The isomerization process (Scheme 4) can be proposed as has been found for related Zr bis(phenoxyimino) dichloro complexes. The key feature to distinguish the structural isomerization of Zr dichloro salicylaldiminates is the dynamic behavior of CH═N protons in NMR studies.[9] However, as there are no changes in positions and shapes of signals for the CH═N protons in these low-temperature ^{1}H NMR experiments (see the Supporting Information), the structural isomerization of **9**/B(C_6F_5)$_3$ and **14** seems not to be plausible and only the cis isomer (Scheme 4, **A**) is present in solution.

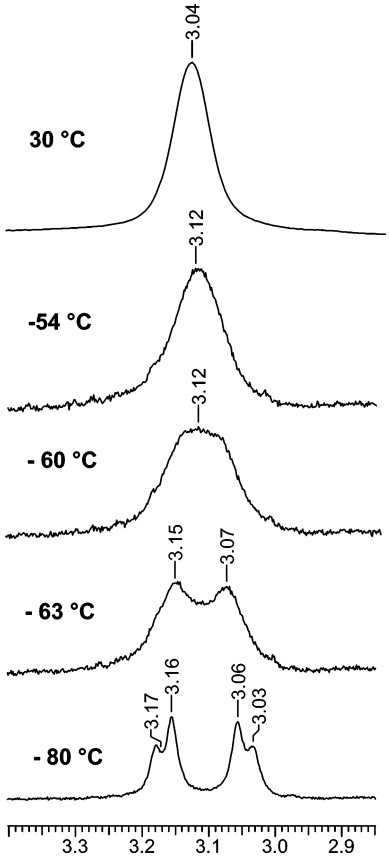
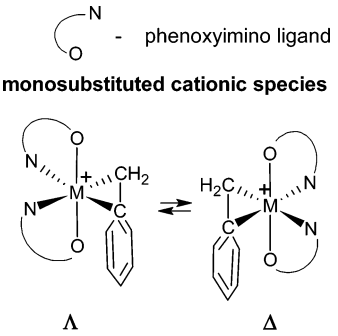


Figure 11. Dynamic behavior of the methylene protons of the $HfCH_2Ph$ group in the cationic complex **14**. The measurements were performed in CD_2Cl_2 at low temperatures and in C_6D_5Br at 30 °C.

It is well-known that six-coordinated, bis(chelate) complexes can undergo inversion of the configuration at the metal center, which leads to the interconversion between two, Δ and Λ, stereoisomers (Scheme 8).[38] Such racemization processes have been previously recognized for phenoxyimino related Zr and Hf dibenzyl bis(quinolinates).[23] For the cationic bis(phenoxyimino) Hf benzyl complexes the presence of Δ/Λ isomerization should be clearly seen in dynamic ^{1}H NMR spectra as a temperature-dependent behavior of the methylene protons of the benzyl substituents.[38a] In addition, temperature variations

(36) Solvent coordination to the metal center and dynamic exchange processes between coordinated and uncoordinated solvent can be excluded from consideration, as no changes in the shape and position of the solvent peak were detected in ^{1}H NMR spectra at temperatures between −80 and 30 °C.

Scheme 8



in ^{1}H NMR experiments should not influence the proton signals of the CH═N groups because, despite the Δ/Λ interconversion, their surroundings and relative orientations do not change markedly. Thus, the observed temperature-dependent behavior of **9**/B(C_6F_5)$_3$ and **14** supports the presence of an Δ/Λ interconversion process. On the basis of the topological and mechanistic analysis of *cis*-$(AB)_2MX_2$ systems carried out by Serpone and co-workers, it can be proposed that the Δ/Λ rearrangement of **9**/B(C_6F_5)$_3$ and **14** occurs via a bond rupture pathway trough square-pyramidal-axial intermediates.[38g] The calculated $\Delta G^{\ddagger}$ values for the Δ/Λ isomerization of **9**/B(C_6F_5)$_3$ and **14** are lower but of same order of magnitude as Δ/Λ racemization barriers found for other rigid six-coordinated group 4 metal complexes.[23,38d]

Olefin Polymerization with Cationic Hf Bis(phenoxyimino) Species. In situ generated cationic species **9**/B(C_6F_5)$_3$, **10**/B(C_6F_5)$_3$, **14**, and **15** were tested for ethylene and propylene polymerization in NMR tubes using C_6D_5Br as a solvent. Depending on the ligand substitution patterns, the activated complexes behaved differently. The benzylimino-substituted **9**/B(C_6F_5)$_3$ and **10**/B(C_6F_5)$_3$ were faintly active in ethylene polymerization, and as a result, considerable amounts (on the NMR scale) of polyethylene were detected only after 10 min of polymerization (see the Supporting Information). After 20 min of bubbling of ethylene through the reaction mixture, the solutions in NMR tubes turned to viscous sticky gels due to polymer formation.[39] The benzylimino-substituted complexes were inactive in propylene polymerization, as after 25 min of propylene bubbling only dissolved propylene and catalysts were found in the samples.

Unlike the autoclave experiments performed (see above), in NMR tubes the cationic complexes **14** and **15** bearing perfluorophenyl groups were well-protected from air and moisture traces and showed exceedingly high catalytic activity in ethylene polymerization and were also active toward propylene polymerization. The ethylene polymerization occurred quickly,[40] and the reaction solutions solidified into polymer gel in 1−1.5 min. In order to get reliable ^{1}H NMR data, ethylene was bubbled only for 30−60 s. Interestingly, ^{1}H NMR spectra of **14**/ethylene obtained for such solutions did not show significant changes (see the Supporting Information). It seems that during the first 30−60 s, only the activation of the catalyst and coordination of the monomer occurs. After this period the polymerization starts. The process is very fast, and the polymer gel forms instantaneously, which prevents further ^{1}H NMR analysis.

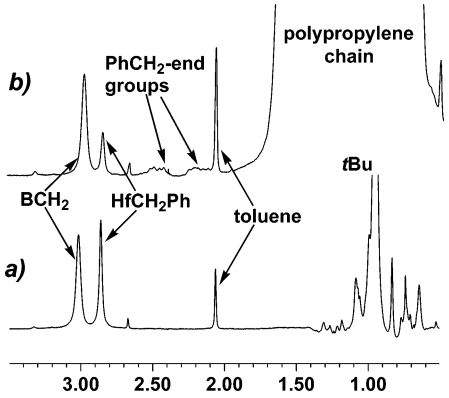


Figure 12. Propylene polymerization in a NMR tube using **14** as catalyst (a) before addition of propylene and (b) after 1 min of propylene bubbling. Conditions: C_6D_5Br, temperature 27 °C.

Propylene polymerization with **14** and **15** was significantly slower than ethylene polymerization. After 1−2 min of the initiation of propylene polymerization, the ^{1}H NMR spectra of **14**/propylene and **15**/propylene were recorded (Figure 12). The presence of polypropylene was recognized by ^{1}H NMR. It can be also noticed for **14** that the intensity of the signal at 2.85 ppm, which corresponds to methylene protons of Hf−CH_2Ph, decreased considerably and, in addition, new peaks appeared in the aliphatic region at 2.2−2.5 ppm, indicating that the benzyl group moved from Hf to the end of the formed polypropylene chain (Figure 12).

Conclusions

Hf bis(phenoxyimino) complexes activated with MAO displayed very high activity in ethylene polymerization, comparable to that of analogous Ti and Zr derivatives (FI catalysts) and well-known metallocene-based catalysts. The Hf catalysts bearing perfluorophenylimino groups were rapidly activated with MAO, and a maximum in catalytic activity is achieved during the first 5−10 min, followed by a modest decline in ethylene consumption in longer runs. In comparison, MAO activation of benzylimino-substituted Hf dichloro complexes required longer induction times, after which the formed catalytically active species were relatively stable and highly active in ethylene polymerization. In addition, MAO-activated Hf bis(phenoxyimino) complexes were also capable of polymerizing propylene with moderate activity, and atactic syndiorich polymers with low molar mass were obtained. Particularly, perfluorophenyl-substituted catalysts produced highly regioirregular polypropylene.

The synthesized Hf bis(phenoxyimino) dibenzyl complexes were thermally rather stable but decomposed rapidly in the presence of traces of water and air. The reaction of B(C_6F_5)$_3$ with dibenzyl complexes gave corresponding cationic Hf

(37) Spectral simulations were made with the help of the WinDNMR program. See: http://www.chem.wisc.edu/areas/reich/plt/windnmr.htm. For calculations the equations and methods described in ref 23 and those of Bruce et al. (Bruce, M. D.; Coates, G. W.; Hauptman, E.; Waymouth, R. M.; Ziller, J. W. *J. Am. Chem. Soc.* **1997**, *119*, 11174) were used. For **9**/B(C_6F_5)$_3$: $\Delta\nu_{AB}$ = 28.1 Hz, J_{AB} = 8.3 Hz, T_c = 283 K. For **14**: $\Delta\nu_{AB}$ = 48.6 Hz, J_{AB} = 8.7 Hz, T_c = 213 K.

(38) (a) Willem, R.; Gielen, M.; Pepermans, H.; Brocas, J.; Fastenakel, D.; Finocchiaro, P. *J. Am. Chem. Soc.* **1985**, *107*, 1146. (b) Willem, R.; Gielen, M.; Pepermans, H.; Hallenga, K.; Recca, A.; Finocchiaro, P. *J. Am. Chem. Soc.* **1985**, *107*, 1153. (c) Harrod, J. F.; Taylor, K. J. *Chem. Commun.* **1971**, 696. (d) Bickley, D. G.; Serpone, N. *Inorg. Chem.* **1979**, *18*, 2200. (e) Bickley, D. G.; Serpone, N. *Inorg. Chem.* **1976**, *15*, 948. (f) Bickley, D. G.; Serpone, N. *Inorg. Chem.* **1976**, *15*, 2577.

(39) Solutions with precipitated polymer gels gave very poor resolution in ^{1}H NMR measurements. Therefore, the polymerization time was adopted so that the reaction solutions remained transparent enough to be suitable for ^{1}H NMR experiments.

(40) During the NMR tube polymerizations the temperatures of reaction mixtures were noticeably and considerably raised, indicating the high activity of generated cationic species in ethylene polymerization.

monobenzyl species which, depending on the imino substituents, tended to be partially or completely unstable toward the CH activation. In accordance with NMR and ESI-MS studies, low activity of the MAO-activated benzylimino-substituted dibenzyl complexes **9** and **10** in olefin polymerization reflects the instability of the corresponding cationic Hf monobenzyl species toward CH activation. On the other hand, the MAO activation of Hf dichloro derivatives **5** and **6** should lead to cationic Hf monomethyl species having structures similar to those of **14** and **15**. These catalytic species, it could be suggested, are resistant toward CH activation, and in contrast to the related complexes **9** and **10**, MAO-activated **5** and **6** displayed high activity in ethylene polymerization and moderate activity in propylene polymerization. The synthesized Hf dibenzyl complexes and generated cationic species are rigid in solution at elevated temperatures (no cis/cis,cis/trans isomerization occurred under the conditions studied) and, consequently, produce polymers with monomodal molar mass distribution.

When the olefin monomer is introduced into the catalyst solution, intensities of signals assigned to the original metal−alkyl substituents decrease in the ^{1}H NMR and a new set of peaks corresponding to formed polymer chain end groups appear. This behavior can be clearly seen in propylene polymerization experiments with **14** (see above, Figure 12), proving that **14** is responsible for the polymerization. On the basis of the results above, it can be proposed that bis(phenoxyimino) group 4 metal complexes act under an analogous olefin polymerization mechanism, which is largely accepted for metallocene types of homogeneous Ziegler−Natta catalysts.[41] Activation of dialkyl bis(phenoxyimino) complexes with $B(C_6F_5)_3$ or MAO generates the monoalkylated cationic species. These complexes are responsible for olefin coordination and polymer chain propagation. According to the accepted mechanism for the chain propagation, the original metal alkyl substituents are transferred to the polymer chain end in the course of consecutive migratory monomer insertions. In fact, this was observed here.

Experimental Section

All manipulations were performed under an inert argon atmosphere using standard Schlenk techniques. The hydrocarbon and ether solvents were refluxed over sodium and benzophenone, distilled, and stored under an inert atmosphere with pieces of sodium. C_6D_6 was refluxed over sodium, and CD_2Cl_2 and C_6D_5Br were refluxed with CaH_2; these solvents were then transferred into storage flasks by evaporation−condensation under vacuum and stored in a glovebox. EI-mass spectra were measured on a JEOL SX102 spectrometer. ESI-MS and ESI-HRMS spectra were performed with a Bruker-MicroTOF spectrometer. The ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on Varian Gemini 200 MHz, Varian Gemini 300 MHz, Varian INOVA 500, and Bruker AMX 400 spectrometers. The ^{1}H and ^{13}C NMR spectra were referenced relative to $CHDCl_2$ (5.28 and 53.73 ppm, respectively), C_6D_4HBr (7.29 and 122.25 ppm, respectively), and C_6D_5H (7.24 and 128.0 ppm, respectively). Fluorine signals were referenced relative to external $B(C_6F_5)_3$ in CD_2Cl_2 (−127.8, −143.4, −160.6 ppm). Elemental analyses were performed at the Laboratory of Pharmaceutical Chemistry, Department of Pharmacy, University of Helsinki, Finland (Hf bis(phenoxyimino) dichloro complexes) and Organisch-Chemisches Institut, Wesfälische-Wilhelms Universität, Münster, Germany (Hf bis(phenoxyimino) dibenzyl complexes). High-temperature gel permeation chromatography (GPC) of polyethylene and polypropylene samples was performed in 1,2,4-trichlorobenzene at 160 °C using a Waters Alliance GPCV 2000 equipped with HMW7, 2*HMWGE, and HMW2 Waters Styrogel columns. DCS of obtained polyethylenes was performed with a Mettler Toledo Star system. Melting temperatures of PE were measured from 30 to 230 °C using a heating rate of 10 °C/min. The melting points were determined from the second heating curve. The ^{13}C NMR spectra of polypropylene samples dissolved in a mixture of 1,2,4-trichlorobenzene (90 wt %) and C_6D_6 (10 wt %) were recorded on a Varian Gemini 300 MHz at 120 °C.

2,3,4,5,6-Pentafluoroaniline, benzylamine, 2,4-bis(α,α-dimethylbenzyl)phenol, 3-*tert*-butylsalicylaldehyde, $PhCH_2MgCl$ (1 M solution in Et_2O), and MeMgBr (3 M solution in Et_2O) were purchased from Aldrich and used as received. Tris(perfluorophenyl)-borane was purchased from Strem, recrystallized from pentane, and stored in a glovebox. Methylalumoxane (MAO, 30 wt % solution in toluene) was received from Borealis Polymers Oy. 3,5-Bis(α,α-dimethylbenzyl)salicylaldehyde[10b] and $Hf(CH_2Ph)_4$[42] were prepared according to literature procedures.

Synthesis of Ligands. (a) *N*-(3-*tert*-Butylsalicylidene)benzylamine (1).[43] 3-*tert*-Butylsalicylaldehyde (2.0 g, 11.2 mmol) and benzylamine (1.2 g, 11.2 mmol), Na_2SO_4 (0.3 g) and two drops of concentrated H_2SO_4 were mixed in a 100 mL round-bottom flask. The reaction mixture was heated to 50 °C and stirred overnight. After it was cooled, the resulting material was extracted with 70 mL of hexane. The hexane extracts were filtered, and solvent was evaporated in vacuo to give the product as a yellow oil, which crystallized in 1 day to give a yellow crystalline solid (2.9 g, 97%). According to NMR analysis the crude product was pure enough and was used without additional purification. ^{1}H NMR (200 MHz, $CDCl_3$, 29 °C): δ_H 1.43 (s, 9H, *t*-Bu), 4.80 (s, 2H, C*H*$_2$Ph), 6.82 (t, J_{HH} = 7.7 Hz, 1H, 5-*H* Ar), 7.14 (dd, J_{HH} = 7.7 Hz, 1H, 4-*H* Ar), 7.30−7.42 (m, 6H, Ar *H* from CH_2Ph and 6-*H* Ph), 8.45 (s, 1H, C*H*═N), 13.68 (s, 1H, O*H*). ^{13}C{^{1}H} NMR (50.3 MHz, $CDCl_3$, 29 °C): δ_C 29.30 (s, *C*H$_3$ of *t*-Bu), 34.82 (s, *C* of *t*-Bu), 63.18 (s, *C*H$_2$Ph), 117.81 (5-*C* Ar), 123.58 (*C*−CH═N), 127.31 (*p*-*C* from CH_2Ph), 127.88 (*o*-*C* from CH_2Ph), 128.63 (*m*-*C* from CH_2Ph), 129.46 (4-*C* Ar), 129.75 (6-*C* Ar), 137.41 (*C*-*t*-Bu), 138.23 (*C*−CH$_2$ from CH_2Ph), 160.38 (*C*−OH), 166.25 (*C*H═N).

(b) *N*-[3,5-Bis(α,α-dimethylbenzyl)salicylidene]benzylamine (2). 3,5-Bis(α,α-dimethylbenzyl)salicylaldehyde (2.0 g, 5.6 mmol) and benzylamine (0.6 g, 5.6 mmol), Na_2SO_4 (0.3 g), and 2 drops of concentrated H_2SO_4 were mixed in a 100 mL round-bottom flask. A 5 mL portion of toluene was then added, and the reaction mixture was heated to 100 °C and stirred for 2 days. After it was cooled, the resulting material was extracted at elevated temperature with a mixture of hexane (60 mL) and CH_2Cl_2 (20 mL). The extracts were then filtered, and solvents were removed in vacuo to give the product as a yellow crystalline solid (2.5 g, 100%). According to NMR analysis the crude product was pure enough and was used without additional purification. ^{1}H NMR (200 MHz, $CDCl_3$, 29 °C): δ_H 1.67 (s, 6H, C*H*$_3$ of 5-α,α-dimethylbenzyl), 1.71 (s, 6H, C*H*$_3$ of 3-α,α-dimethylbenzyl), 4.65 (s, 2H, C*H*$_2$Ph), 7.03 (d, J_{HH} = 2.2 Hz, 1H, 4-*H* Ar), 7.10−7.38 (m, 16H, Ar *H*), 8.31 (t, J_{HH} = 1.1 Hz, 1H, C*H*═N), 12.13 (s, 1H, O*H*). ^{13}C{^{1}H} NMR (50.3 MHz, $CDCl_3$, 29 °C): δ_C 29.37 (s, *C*H$_3$ of 5-α,α-dimethylbenzyl), 30.93 (s, *C*H$_3$ of 3-α,α-dimethylbenzyl), 42,11 (s, *C* of 5-α,α-dimethylbenzyl), 42.42 (s, *C* of 3-α,α-dimethylbenzyl), 63.03 (s, *C*H$_2$Ph), 125.02 (6-*C* Ar), 126.04 (Ar), 126.85 (Ar), 125.55 (*p*-*C* Ph from

(41) For the mechanism of complex activation (MAO used as activator) see: (a) Sinn, H.; Kaminsky, W.; Vollmer, H. J.; Woldt, R. *Angew. Chem.* **1980**, *92*, 346. (b) Kaminsky, W.; Miri, M.; Sinn, H.; Woldt, R. *Macromol. Chem., Rapid Commun.* **1983**, *4*, 417. For the mechanism of the chain propagation step, see: (c) Cosée, P. *J. Mol. Catal.* **1964**, *3*, 80. (d) Arlman, E. J. *J. Mol. Catal.* **1964**, *3*, 89. (e) Cosée, P.; Arlman, E. J. *J. Mol. Catal.* **1964**, *3*, 99.

(42) Davies, G. R.; Jarvis, J. A. J.; Kilbourn, B. T. *Chem. Commun.* **1971**, 1511.

(43) The synthesis of ligand **1** was reported in: Matsukawa, N. Eur. Patent EP-1013674, 2000. Ethanol was used as a solvent. The reported data and our ^{1}H NMR data for **1** are identical.

3- and 5-α,α-dimethylbenzyls), 125.60 (4-*C* Ar), 126.70 (*m*-*C* Ph from CH_2Ph), 127.22 (*p*-*C* Ph from CH_2Ph), 127.75 (*o*-*C* Ph from 5-α,α-dimethylbenzyl), 127.99 (*m*-*C* Ph from 3- and 5-α,α-dimethylbenzyls), 127.95 (*C*−CH═N), 128.51 (*o*-*C* Ph from 3-α,α-dimethylbenzyl), 128.95 (3-*C* Ar), 136.08 (*C* Ph from CH_2Ph), 138.03 (*C* Ph from 3-α,α-dimethylbenzyl), 139.08 (5-*C*-Ar), 150.76 (*C* Ph from 5-α,α-dimethylbenzyl), 157.66 (*C*−OH), 166.1 (*C*H═N).

(c) *N*-(3-*tert*-Butylsalicylidene)-2,3,4,5,6-pentafluoroaniline (3).[44] 3-*tert*-Butylsalicylaldehyde (2.0 g, 11.2 mmol), 2,3,4,5,6-pentafluoroaniline (2.1 g, 11.2 mmol), Na_2SO_4 (0.3 g), and 2 drops of concentrated H_2SO_4 were mixed in a 100 mL round-bottom flask equipped with a Dean−Stark apparatus. Toluene (50 mL) was then added, and the reaction mixture was refluxed for 2 days. After the mixture was cooled, toluene was removed from the resulting material in vacuo. The yellow residue was then extracted with a mixture of hexane (50 mL) and CD_2Cl_2 (20 mL). The extracts were filtered, and solvents were evaporated in vacuo to give the product as a yellow crystalline solid (3.2 g, 84%). According to NMR analysis the crude product was pure enough and was used without additional purification. ^{1}H NMR (200 MHz, $CDCl_3$, 29 °C): δ_H 1.45 (s, 9H, *t*-Bu), 6.91 (t, J_{HH} = 7.7 Hz, 1H, 5-*H* Ar), 7.21−7.28 (m, 1H, 4-*H* Ph), 7.47 (dd, J_{HH} = 7.7 Hz, 1H, 6-H Ar), 8.81 (s, 1H, C*H*═N), 11.78 (s, 1H, O*H*). ^{13}C{^{1}H} NMR (50.3 MHz, $CDCl_3$, 29 °C): δ_C 29.26 (s, *C*H$_3$ of *t*-Bu), 34.97 (s, *C* of *t*-Bu), 118.86 (5-*C* Ar), 131.62 (6-*C* Ar), 132.22 (4-*C* Ar), 134.08 (*C*−CH═N), 135.57 (*C*−F), 136.30 (*C*−F), 138.23 (*C*(Ar)-*t*-Bu), 138.51 (*C*−F), 140.47 (*C*−F), 141.33 (*C*−F), 143.34 (*C*−F), 160.99 (*C*−OH), 171.29 (*C*H═N). ^{13}F NMR (282.2 MHz, $CDCl_3$, 27 °C): δ_F −152.6 (dd, *J* = 21.31 Hz, 2F, *o*-*F*), −159.09 (t, *J* = 21.30 Hz, 1F, *p*-*F*), −162.97 (dt, *J* = 21.30 Hz, 2F, *m*-*F*).

(d) *N*-[3,5-Bis(α,α-dimethylbenzyl)salicylidene]-2,3,4,5,6-pentafluoroaniline (4). 3,5-Bis(α,α-dimethylbenzyl)salicylaldehyde (2.0 g, 5.6 mmol), 2,3,4,5,6-pentafluoroaniline (1.0 g, 5.6 mmol), Na_2SO_4 (0.3 g), 2 drops of concentrated H_2SO_4, and toluene (50 mL) were mixed in a 100 mL round-bottom flask equipped with a Dean−Stark apparatus as described for **3**. After the mixture was cooled, toluene was removed from the resulting material in vacuo. The yellow residue was then extracted with a mixture of hexane (50 mL) and CD_2Cl_2 (20 mL). The extracts were filtered, and solvents were evaporated in vacuo to give the product as a yellow crystalline solid (2.6 g, 89%). According to NMR analysis the crude product was pure enough and was used without additional purification. ^{1}H NMR (200 MHz, $CDCl_3$, 29 °C): δ_H 1.68 (s, 6H, C*H*$_3$ of 5-α,α-dimethylbenzyl), 1.73 (s, 6H, C*H*$_3$ of 3-α,α-dimethylbenzyl), 7.15 (d, J_{HH} = 2.5 Hz, 1H, 4-*H* Ar), 7.10−7.35 (m, 10H, Ar *H*), 7.47 (d, J_{HH} = 2.5 Hz, 1H, 6-*H* Ar), 8.66 (t, J_{HH} = 1.2 Hz, 1H, C*H*═N), 12.28 (s, 1H, O*H*). ^{13}C{^{1}H} NMR (50.3 MHz, $CDCl_3$, 29 °C): δ_C 29.30 (s, *C*H$_3$ of 5-α,α-dimethylbenzyl), 30.83 (s, *C*H$_3$ of 3-α,α-dimethylbenzyl), 42,19 (s, *C* of 5-α,α-dimethylbenzyl), 42.49 (s, *C* of 3-α,α-dimethylbenzyl), 125.24 (4-*C* Ar), 125.52 (*p*-*C* Ph from 3-α,α-dimethylbenzyl), 125.58 (*m*-*C* Ph from 5-α,α-dimethylbenzyl), 125.83 (*p*-*C* Ph from 5-α,α-dimethylbenzyl), 126.64 (6-*C*-Ar), 126.67 (*o*-*C* Ph from 5-α,α-dimethylbenzyl), 127.85 (*m*-*C* Ph from 3-α,α-dimethylbenzyl), 128.13 (*o*-*C* Ph from 3-α,α-dimethylbenzyl), 131.95 (5-*C* Ar), 133.74 (*C*−CH═N), 137.08 (*C* Ph from 3-α,α-dimethylbenzyl), 140.77 (5-*C* Ar), 150.02 (*C* Ph from 5-α,α-dimethylbenzyl), 158.28 (*C*−OH), 171.4 (*C*H═N). ^{13}F NMR (282.2 MHz, $CDCl_3$, 27 °C): δ_F −152.60 (dd, *J* = 21.15 Hz, 2F, *o*-*F*), −159.26 (t, *J* = 21.36 Hz, 1F, *p*-*F*), −162.97 (dt, *J* = 21.36 Hz, 2F, *m*-*F*).

Synthesis of Hf Bis(phenoxyimino) Dichloro Complexes. (a) Bis[*N*-(3-*tert*-butylsalicylidene)benzylaminato]hafnium Dichloride (5). NaH (0.1 g, 4.2 mmol) was added at 0 °C to a stirred solution of ligand **1** (1.0 g, 3.7 mmol) in 20 mL of dry THF. The reaction mixture was stirred for 2 h at room temperature. When deprotonation of the ligand was complete, THF was removed in vacuo. The residue, the Na salt of ligand **1**, was dissolved in 20 mL of dry toluene and $HfCl_4$ (0.6 g, 1.9 mmol) was added to this solution. The reaction mixture was stirred overnight at room temperature. Toluene was evaporated in vacuo, and the residue was extracted twice with a mixture of dry hexane (15 mL) and CH_2Cl_2 (10 mL). The combined extracts were then filtered under argon, and solvents were removed in vacuo. The product was isolated as a white-yellow crystalline solid (1.0 g, 68.5%). Anal. Calcd for $C_{46}H_{44}Cl_2N_2O_2Hf$: C, 55.28; H, 5.15; N, 3.58. Found: C, 55.46; H, 5.53; N, 3.49. ^{1}H NMR (200 MHz, CD_2Cl_2, 29 °C): δ_H 1.47 (s, 18H, *t*-Bu), 4.75 (AB system, J_{HH} = 14.9 Hz, 4H, C*H*$_2$Ph), 6.76 (t, J_{HH} = 7.7 Hz, 2H, 5-*H* Ar), 6.90 (br m, 6H, Ar *H* from CH_2Ph and 4-*H* Ph), 7.05−7.18 (m, 6H, Ar *H* from CH_2Ph), 7.52 (d, J_{HH} = 7.7 Hz, 2H, 6-*H* Ar), 7.82 (s, 2H, C*H*═N). ^{13}C{^{1}H} NMR (50.3 MHz, C_6D_6, 29 °C): δ_C 29.87 (s, *C*H$_3$ of *t*-Bu), 35.28 (s, *C* of *t*-Bu), 62.17 (s, *C*H$_2$Ph), 119.62 (5-*C* Ar), 123.78 (*C*−CH═N), 128.81 (*o*-*C* from CH_2Ph), 128.90 (*m*-*C* from CH_2Ph), 133.44 (4-*C* Ar), 134.21 (6-*C* Ar), 135.84 (*C*-*t*-Bu), 140.84 (*C*-CH_2 from CH_2Ph), 160.67 (*C*−OH), 171.32 (*C*H═N). MS (ESI): *m*/*z* (intensity) 780.7 (110, M^+), 744.1 (100, M^+ − Cl).

(b) Bis{*N*-[3,5-bis(α,α-dimethylbenzyl)salicylidene]benzylaminato}hafnium Dichloride (6). BuLi (1.6 M solution in hexane, 3.5 mL, 5.6 mmol) was added at 0 °C to a stirred solution of ligand **2** (2.4 g, 5.4 mmol) in 30 mL of dry Et_2O. The reaction mixture was stirred for 2 h at room temperature. When deprotonation of the ligand was complete, Et_2O was removed in vacuo. The residue, the Li salt of the ligand **2**, was dissolved in 30 mL of dry toluene, and $HfCl_4$ (0.87 g, 2.72 mmol) was added to this solution. The reaction mixture was stirred overnight at room temperature. Toluene was evaporated in vacuo, and the residue was extracted twice with a mixture of dry hexane (20 mL) and CH_2Cl_2 (10 mL). The combined extracts were then filtered under argon, and solvents were removed in vacuo. The product was isolated as a yellow solid (3.0 g, 93%). Anal. Calcd for $C_{64}H_{64}Cl_2N_2O_2Hf\cdot{}^1/_2C_6H_{14}$: C, 67.87; H, 6.04; N, 2.36. Found: C, 67.95; H, 6.44; N, 1.96. The presence of hexane was also detected by ^{1}H and ^{13}C NMR. ^{1}H NMR (200 MHz, CD_2Cl_2, 29 °C): δ_H 1.61 (br s, 12H, C*H*$_3$ of 5-α,α-dimethylbenzyl), 1.65 (br s, 12H, C*H*$_3$ of 3-α,α-dimethylbenzyl), 3.0−4.0 (br m, 4H, C*H*$_2$Ph), 6.51−7.49 (br m, 34H, Ar *H*), 7.59 (s, 2H, C*H*═N). ^{13}C{^{1}H} NMR (50.3 MHz, CD_2Cl_2, 29 °C): δ_C 30.89 (br s, *C*H$_3$ of 5-α,α-dimethylbenzyl), 32.20 (s, *C*H$_3$ of 3-α,α-dimethylbenzyl), 42.21 (s, *C* of 5-α,α-dimethylbenzyl), 42.75 (s, *C* of 3-α,α-dimethylbenzyl), 61.32 (s, *C*H$_2$Ph), 125.7 (Ar), 126.04 (Ar); 126.85 (Ar), 126.97 (Ar), 128.04 (Ar), 128.20 (Ar), 128.36 (Ar), 129.27 (Ar), 130.13 (*C*−CH═N), 131.16 (3-*C*), 133.82 (*C* Ph from CH_2Ph), 135.61 (5-*C*), 139.2 (*C* Ph from 3-α,α-dimethylbenzyl), 141.5 (*C* Ph from 5-α,α-dimethylbenzyl), 149.6 (*C*−OH), 170.9 (*C*H═N). MS (ESI): *m*/*z* (intensity) 1140 (260, M^+), 1128 (100, M^+ − Me), 1113 (100, M^+ − 2Me), 1106 (540, M^+ − Cl), 1089 (200, M^+ − Cl−Me), 1069 (M^+ − 2Cl).

(c) Bis[*N*-(3-*tert*-butylsalicylidene)-2,3,4,5,6-pentafluoroanilinato]hafnium Dichloride (7).[45] Ligand **3** (1.0 g, 2.9 mmol) in Et_2O (20 mL) was treated with BuLi in hexane (1.6 M, 1.9 mL, 3.1 mmol), as described for **6**. The reaction of the resulting Li salt of **3** with $HfCl_4$ (0.5 g; 1.6 mmol) in toluene (20 mL) and the separation of the product was carried out as reported for complex **6**. The complex **7** was isolated as a yellow solid (0.84 g; 58%). ^{1}H NMR (200 MHz, CD_2Cl_2, 29 °C): δ_H 1.24 (s, 18H, *t*-Bu), 6.95 (t, J_{HH} = 7.7 Hz, 2H, 5-*H* Ar), 7.27 (dd, J_{HH} = 1.8 Hz, 2H, 4-*H* Ph), 7.70 (dd, J_{HH} = 1.8 Hz, 2H, 6-H Ar), 8.30 (s, 2H, C*H*═N). ^{13}C{^{1}H} NMR (50.3 MHz, $CDCl_3$, 29 °C): δ_C 29.07 (s, *C*H$_3$ of *t*-Bu), 35.13 (s, *C* of *t*-Bu), 121.16 (5-*C* Ar), 134.99 (6-*C* Ar), 137.48 (4-*C* Ar), 138.82 (*C*−CH═N), 140.59 (*C*(Ar)-*t*-Bu), 161.42

(44) The synthesis of ligand **3** was reported in: Matsukawa, N. Patent WO-2001055231, 2001. Toluene was used as a solvent. The reported data and our ^{1}H NMR data for **3** are identical.

(45) The complex **7** was first reported in ref 8.

(*C*−OH), 177.88 (*C*H═N). ^{13}F NMR (282.2 MHz, C_6D_6, 27 °C): δ_F −145.0 (dd; J = 23.00 Hz, 2F, *o-F*), −146.6 (br, 2F, *o-F*), −158.2 (t, J = 21.75 Hz, 2F, *p-F*), −161.07 (t, J = 22.3 Hz, 2F, *m-F*), −164.14 (br, 2F, *m-F*). MS (ESI): *m/z* (intensity) 932.3 (3300, M^+), 916.3 (500, M^+ − F), 893.1 (7100, M^+ − 2F), 862 (100, M^+ − 2Cl).

(d) Bis{*N*-[3,5-bis(α,α-dimethylbenzyl)salicylidene]-2,3,4,5,6-pentafluoroanilinato}hafnium Dichloride (8). Ligand **4** (2.63 g, 5.02 mmol) in Et_2O (30 mL) was treated with BuLi in hexane (1.6 M, 3.2 mL, 5.2 mmol), as described for **6**. The reaction of the resulting Li salt of **4** with $HfCl_4$ (0.8 g, 2.5 mmol) in toluene (30 mL) and the separation of the product was carried out as reported for complex **6**. The complex **8** was isolated as a yellow solid (3.0 g; 81.5%). Anal. Calcd for $C_{52}H_{46}Cl_2F_{10}N_2O_2Hf\cdot 2C_6H_{14}$: C, 61.06; H, 5.53; N, 1.87. Found: C, 60.94; H, 5.31; N, 1.91. The presence of hexane was also detected by ^{1}H and ^{13}C NMR. ^{1}H NMR (200 MHz, CD_2Cl_2, 29 °C): δ_H 1.59 (br s, 24H, C*H*$_3$ of 3- and 5-α,α-dimethylbenzyl), 7.10−7.40 (m, 24H, Ar *H*), 8.14 (s, 2H, C*H*═N). ^{13}C{^{1}H} NMR (50.3 MHz, CD_2Cl_2, 29 °C): δ_C 30.48 (br s, *C*H$_3$ of 5-α,α-dimethylbenzyl), 32.20 (s, *C*H$_3$ of 3-α,α-dimethylbenzyl), 42,53 (s, *C* of 5-α,α-dimethylbenzyl), 42.70 (s, *C* of 3-α,α-dimethylbenzyl), 125.76 (*p-C* Ph from 3-α,α-dimethylbenzyl), 125.88 (4-*C* Ar), 126.19 (*p-C* Ph from 5-α,α-dimethylbenzyl), 126.39 (*m-C* Ph from 5-α,α-dimethylbenzyl), 126.81 (6-*C* Ar), 126.89 (*m-C* Ph from 3-α,α-dimethylbenzyl), 128.15 (*o-C* Ph from 5-α,α-dimethylbenzyl), 128.45 (*o-C* Ph from 3-α,α-dimethylbenzyl), 138.48 (3-*C* Ar), 139.86 (*C* Ph from 3-α,α-dimethylbenzyl), 143.12 (*C*−CH═N), 148.69 (5-*C* Ar), 149.94 (*C* Ph from 5-α,α-dimethylbenzyl), 159.36 (*C*−OH), 177.65 (*C*H═N). ^{13}F NMR (282.2 MHz, C_6D_6, 27 °C): δ_F −144.24 (dd; J = 24 Hz, 2F, *o-F*), −146.1 (br, 2F, *o-F*), −157.8 (t, J = 22.3 Hz, 2F, *p-F*), −160.7 (t, J = 22.0 Hz, 2F, *m-F*), −164.4 (br, 2F, *m-F*). MS (ESI): *m/z* (intensity) 1292.5 (1400, M^+), 1255.4 (5200, M^+ − Cl).

Synthesis of Hf Bis(phenoxyimino) Dibenzyl Complexes. (a) Bis[*N*-(3-*tert*-butylsalicylidene)benzylaminato]hafnium Dibenzyl (9). A cooled (−20 °C) solution of ligand **1** (1.0 g, 3.7 mmol) in Et_2O (25 mL) was added slowly with a syringe to the cooled (−78 °C) solution of $Hf(CH_2Ph)_4$ (1.0 g, 1.8 mmol) and Et_2O (5 mL). The reaction mixture was stirred at −78 °C for 20 min and then placed into a freezer and kept overnight at −20 °C. The solvent was removed in vacuo, and the residue was extracted twice with dry hexane (15 × 2 mL). The combined extracts were then filtered in a glovebox through a syringe PTFE filter. Hexane was evaporated in vacuo. The product was isolated as an orange solid (1.0 g, 61%). Anal. Calcd for $C_{50}H_{54}N_2O_2Hf$: C, 67.21; H, 6.09; N, 3.14. Found: C, 67.14; H, 5.85; N, 3.22. ^{1}H NMR (200 MHz, C_6D_6, 29 °C): δ_H 1.78 (s, 18H, *t*-Bu), 2.77 (AB system, J_{HH} = 10.7 Hz, 4H, Hf−C*H*$_2$Ph), 4.45 (AB system, J_{HH} = 15.2 Hz, 4H, C*H*$_2$Ph), 6.46 (dd, J_{HH} = 1.7 Hz, 2H, 6-*H* Ar), 6.63 (t, J_{HH} = 6.9 Hz, 2H, 5-*H* Ar), 6.80−7.10 (m, 20H, Ar *H* from CH_2Ph), 7.33 (s, 2H, C*H*═N), 7.48 (dd, J_{HH} = 1.7 Hz, 2H, 4-*H* Ar). ^{13}C{^{1}H} NMR (50.3 MHz, C_6D_6, 29 °C): δ_C 30.10 (s, *C*H$_3$ of *t*-Bu), 35.34 (s, *C* of *t*-Bu), 61.87 (s, *C*H$_2$Ph), 73.50 (s, Hf−*C*H$_2$Ph), 118.83 (5-*C* Ar), 120.41 (Ph from Hf−CH_2Ph), 125.64 (*C*−CH═N), 126.82 (*o-C* from CH_2Ph), 127.89 (Ph from Hf−CH_2Ph), 129.40 (*m-C* from CH_2Ph), 133.06 (4-*C* Ar), 133.77 (6-*C* Ar), 135.41 (*C*-*t*-Bu), 141.14 (*C*-CH_2 from CH_2Ph), 148.67 (*ipso-C* from Hf−CH_2Ph), 160.59 (*C*−OH), 168.92 (*C*H═N). MS (ESI): *m/z* (intensity) 894.6 (100, M^+), 729.3 (500, L_2HfCH_2), 713.5 (300, M^+ − 2CH_2Ph).

(b) Bis{*N*-[3,5-bis(α,α-dimethylbenzyl)salicylidene]benzylaminato}hafnium Dibenzyl (10). Ligand **2** (1.65 g, 3.68 mmol) in Et_2O (25 mL) was treated with $Hf(CH_2Ph)_4$ (1.00 g, 1.84 mmol) in Et_2O (5 mL), as described for **9**. The isolation of the product was carried out as reported for complex **9**. The complex **10** was isolated as an orange solid (1.35 g; 58%). Anal. Calcd for $C_{78}H_{78}N_2O_2Hf$: C, 74.71; H, 6.27; N, 2.23. Found: C, 74.16; H, 5.94; N, 2.81. ^{1}H NMR (500 MHz, C_6D_5Br, 27 °C): δ_H 1.44 (s, 12H, C*H*$_3$ of 5-α,α-dimethylbenzyl), 1.53 (s, 6H, C*H*$_3$ of 3-α,α-dimethylbenzyl), 1.91 (s, 6H, C*H*$_3$ of 3-α,α-dimethylbenzyl), 2.00 (AB system, J_{HH} = 11 Hz, 4H, Hf−C*H*$_2$Ph), 3.69 (AB system, J_{HH} = 16 Hz, 4H, C*H*$_2$Ph), 6.33 (d, J_{HH} = 7.15 Hz, 4H, *H* Ph from cumyl), 6.51 (d, J_{HH} = 7.2 Hz, 4H, *H* Ph from cumyl), 6.56 (d, J_{HH} = 2.4 Hz, 2H, 4-*H* Ar), 6.76 (t, J_{HH} = 7.65 Hz, 2H, *p-H* Ph from Hf−CH_2Ph), 6.81 (dd, J_{HH} = 6.5 Hz, 4H, *o-H* Ph from Hf−CH_2Ph), 6.87 (dd, J_{HH} = 7.3 Hz, 4H, *m-H* Ph from Hf−CH_2Ph), 7.0 (t, J_{HH} = 7.6 Hz, 5H, *H* Ar and *H* Ph from cumyl), 7.13 (m, 10H, *H* Ph from CH═NCH_2Ph), 7.25 (d, J_{HH} = 7.7 Hz, 4H, *H* Ph from cumyl), 7.42 (d, 4H, 7.42 (d, J_{HH} = 2.5 Hz, 2H, C*H*═N). ^{13}C{^{1}H} NMR (50.3 MHz, C_6D_6, 29 °C): δ_C = 30.9 (d, *C*H$_3$ of 5-α,α-dimethylbenzyl), 32.78 (br s, *C*H$_3$ of 3-α,α-dimethylbenzyl), 42,46 (s, *C* of 5-α,α-dimethylbenzyl), 42.74 (s, *C* of 3-α,α-dimethylbenzyl), 61.38 (s, *C*H$_2$Ph), 74.75 (s, Hf−*C*H$_2$Ph), 124.0 (Ph from Hf−CH_2Ph), 125.82 (*C*−CH═N), 126.08 (*m-C* Ph from CH_2Ph), 126.57 (*o-C* Ph from CH_2Ph), 126.60 (*o-C* Ph from Hf−CH_2Ph), 127.03 (*m-C* Ph from Hf−CH_2Ph), 128.27 (*o-C* Ph from 5-α,α-dimethylbenzyl), 128.33 (*o-C* Ph from 3-α,α-dimethylbenzyl), 129.83 (*p-C* Ph from 3- and 5-α,α-dimethylbenzyl), 131.28 (3-*C*), 133.19 (*C* Ph from CH_2Ph), 135.76 (5-*C*), 138.60 (*C* Ph from 3-α,α-dimethylbenzyl), 149.33 (*ipso-C* from Hf−CH_2Ph), 150.10 (*C* Ph from 5-α,α-dimethylbenzyl), 158.46 (*C*−OH), 169.0 (*C*H═N). MS (ESI): *m/z* (intensity) 1255.4 (200, M^+), 1179.5 (250, M^+ − Ph), 1113 (1600, $L_2MCH_2^+$), 1071.5 (1800, M^+ − 2CH_2Ph).

(c) Bis[*N*-(3-*tert*-butylsalicylidene)-2,3,4,5,6-pentafluoroanilinato]hafnium Dibenzyl (11). Ligand **3** (1.26 g, 3.68 mmol) in Et_2O (25 mL) was treated with $Hf(CH_2Ph)_4$ (1.00 g, 1.84 mmol) in Et_2O (5 mL), as described for **9**. The isolation of the product was carried out as reported for complex **9**. The resulting complex is sparingly soluble in hexane, and 20 mL portions of hexane (with 1 mL of Et_2O added) were used for complex extraction. The complex **11** was isolated as an orange-yellow solid (0.79 g; 41%). Anal. Calcd for $C_{48}H_{40}F_{10}N_2O_2Hf$: C, 55.15; H, 3.86; N, 2.68. Found: C, 55.56; H, 3.84; N, 2.22. ^{1}H NMR (500 MHz, C_6D_5Br, 25 °C): δ_H 1.2 (s, 18H, *t*-Bu), 2.39 (AB system, J_{HH} = 12.3 Hz, 4H, Hf−C*H*$_2$Ph), 6.79 (t, J_{HH} = 7.0 Hz, 2H, *p-H* Ph from Hf−CH_2Ph), 6.94 (t, J_{HH} = 7.7 Hz, 2H, 5-*H* Ar), 7.19 (m, 4H, *H* Ph from Hf−CH_2Ph), 7.21 (d, J_{HH} = 7.7 Hz, 2H, 6-*H* Ph), 7.60 (d, J_{HH} = 7.7 Hz, 2H, 4-H Ar), 8.33 (s, 2H, C*H*═N). ^{13}C{^{1}H} NMR (50.3 MHz, C_6D_6, 29 °C): δ_C 29.06 (s, *C*H$_3$ of *t*-Bu), 34.87 (s, *C* of *t*-Bu), 80.75 (s, Hf−*C*H$_2$Ph), 119.90 (5-*C* Ar), 121.36 (Ph from Hf−CH_2Ph), 126.68 (Ph from Hf−CH_2Ph), 132.48 (*C*−CH═N), 134.79 (6-*C* Ar), 136.18 (4-*C* Ar), 140.55 (*C*(Ar)-*t*-Bu), 148.57 (*ipso-C* from Hf−CH_2Ph), 161.75 (*C*-OH), 177.39 (*C*H═N). ^{13}F NMR (282.2 MHz, C_6D_6, 27 °C): δ_F −146.3 (br s, 2F, *o-F*), −148.4 (br s, 2F, *o-F*), −159.2 (t, J = 21.9 Hz, 2F, *p-F*), −161.7 (br s, 2F, *m-F*), −164.0 (dt, J = 21.6 Hz, 2F, *m-F*). MS (ESI): *m/z* (intensity) 1042.3 (300, M^+), 1026.2 (100, M^+ − F), 971.2 (240, M^+ − Ph).

(d) Bis{*N*-[3,5-bis(α,α-dimethylbenzyl)salicylidene]-2,3,4,5,6-pentafluoroanilinato}hafnium Dibenzyl (12). Ligand **4** (1.74 g, 3.31 mmol) in Et_2O (25 mL) was treated with $Hf(CH_2Ph)_4$ (0.90 g, 1.66 mmol) in Et_2O (5 mL), as described for **9**. The isolation of the product was carried out as reported for complex **9**. The resulting complex is sparingly soluble in hexane, and 20 mL portions of hexane (with 8 mL of Et_2O added) were used for complex extraction. After solvent evaporation, the residue was washed with hexane to remove the unreacted ligand and $Hf(CH_2Ph)_4$. The complex **12** was isolated as a yellow solid (1.51 g; 65%). Anal. Calcd for $C_{76}H_{64}F_{10}N_2O_2Hf$: C, 66.97; H, 5.88; N, 1.78. Found: C, 66.92; H, 5.38; N, 1.30. ^{1}H NMR (500 MHz, C_6D_5Br, 30 °C): δ_H 1.32 (s, 12H, C*H*$_3$ of 5-α,α-dimethylbenzyl), 1.37 (d, 12H, C*H*$_3$ of 3-α,α-dimethylbenzyl), 1.97 (AB system, J_{HH} = 11.8 Hz, 4H, Hf−C*H*$_2$Ph), 6.72 (d, J_{HH} = 6.7 Hz, 2H, *p-H* Ph from Hf−CH_2Ph), 6.90−7.30 (m, 28H, Ar *H*), 7.94 (s, 2H, C*H*═N). ^{13}C{^{1}H} NMR (75 MHz, C_6D_5Br, 27 °C): δ_C 28.05 (s, *C*H$_3$ of

5-α,α-dimethylbenzyl), 29.06 (s, *C*H_3 of 5-α,α-dimethylbenzyl), 30.60 (s, *C*H_3 of 3-α,α-dimethylbenzyl), 42,50 (s, *C* of 5-α,α-dimethylbenzyl), 43.70 (s, *C* of 3-α,α-dimethylbenzyl), 80.23 (s, Hf−*C*H_2Ph), 121.21 (Ph from Hf−CH_2Ph), 123.18 (*4-C* Ar), 126.17 (*p-C* Ph from 3-α,α-dimethylbenzyl), 126.38 (*p-C* Ph from 5-α,α-dimethylbenzyl), 126.82 (*m-C* Ph from 5-α,α-dimethylbenzyl), 126.96 (*o-C* Ph from 5-α,α-dimethylbenzyl), 127.01 (*m-C* Ph from 3-α,α-dimethylbenzyl), 128.50 (Ph from Hf−CH_2Ph), 128.54 (Ph from Hf−CH_2Ph), 131.94 (*C*−F), 131.95 (5-*C* Ar), 132.56 (4-*C* Ar), 136.32 (*C*−F), 137.08 (*C* Ph from 3-α,α-dimethylbenzyl), 137.80 (*C*−F), 139.28 (6-*C* Ar), 139.66 (*C*−F), 140.18 (*C*−CH═N), 142.00 (5-*C* Ar), 143.10 (*C*−F), 148.70 (Ph from Hf−CH_2Ph), 150.28 (*C* Ph from 5-α,α-dimethylbenzyl), 159.90 (*C*−OH), 177.32 (*C*H═N). ^{13}F NMR (282.2 MHz, $CDCl_3$, 27 °C): δ_F −145.82 (br s, 2F, *o-F*), −158.99 (t, J = 22 Hz, 1F, *p-F*), −163.42 (br s, 2F, *m-F*). MS (ESI): *m*/*z* (intensity) 1401.7 (50, M^+), 1223.3 (150, $M^+ - 2CH_2Ph$).

Generation of Cationic Species. (a) Reaction of Bis[*N*-(3-*tert*-butylsalicylidene)benzylaminato]hafnium Dibenzyl (9) with $B(C_6F_5)_3$. In a glovebox a NMR tube was charged with dibenzylbis-[*N*-(3-*tert*-butylsalicylidene)benzylaminato]hafnium (**9**; 36 mg, 40 μmol), after which 0.4 mL of C_6D_5Br was added via a syringe at room temperature. $B(C_6F_5)_3$ (20 mg, 40 μmol) was added to the solution of the complex in the NMR tube, and the mixture was vigorously shaken. The color of the solution changed quickly from orange to yellow. Owing to its high thermal instability and very high air and moisture sensitivity, this substance could not be isolated, and the resulting yellow solution was investigated only by ^{1}H and ^{19}F NMR methods. ^{1}H NMR (200 MHz, C_6D_5Br, 29 °C, mixture of generated monobenzyl cation and product of CH activation): δ_H 1.81 (s, 18H, *t*-Bu), 2.44 (s, C*H*$_3$ from toluene), 3.08 (s, Hf−C*H*$_2$Ph), 3.64 (s, 2H, C*H*$_2$ from $PhCH_2B$), 4.45 (s, 4H, C*H*$_2$Ph), 6.62 (d, J_{HH} = 7.3 Hz, 2H, *o*-H Ph from Hf−CH_2Ph), 7.1−7.44 (Ar *H*), 7.55 (d, J_{HH} = 7.7 Hz, 2H, 4-*H* Ar), 7.78 (s, 2H, C*H*═N). ^{19}F NMR (282 MHz, C_6D_5Br, 29 °C, mixture of generated monobenzyl cation and product of CH activation): δ_F −127.7 (m, $B(C_6F_5)_3$), −130.52 (d, J = 22.7 Hz, 2F, *o-F*), −142.20 (m, $B(C_6F_5)_3$), −159.7 (m, $B(C_6F_5)_3$), −163.82 (br s, 1F, *p-F*), −166.62 (t, 2F, *m-F*). MS (ESI): *m*/*z* (intensity) 713.2 (3.2×10^5, L_2MH^+).

(b) Reaction of Bis{*N*-[3,5-bis(α,α-dimethylbenzyl)salicylidene]-benzylaminato}hafnium Dibenzyl (10) with $B(C_6F_5)_3$. Dibenzylbis-{*N*-[3,5-bis(α,α-dimethylbenzyl)salicylidene]benzylaminato}-hafnium (**10**; 52 mg, 40 μmol) was activated with $B(C_6F_5)_3$ (20 mg, 40 μmol) in C_6D_5Br (0.4 mL) in the same way as described for the reaction of **9** with $B(C_6F_5)_3$. Upon addition of $B(C_6F_5)_3$, the reaction mixture turned from orange to yellow. Owing to its high thermal instability and very high air and moisture sensitivity, this substance could not be isolated, and the resulting yellow solution was investigated only by ^{1}H and ^{19}F NMR methods. ^{1}H NMR (200 MHz, C_6D_5Br, 29 °C, product of CH activation): δ_H 1.90 (s, 12H, C*H*$_3$ of 5-α,α-dimethylbenzyl), 2.01 (m, 12H, C*H*$_3$ of 3-α,α-dimethylbenzyl), 2.47 (s, 3H, C*H*$_3$ from toluene), 3.08 (s, traces, Hf−C*H*$_2$Ph), 3.64 (s, 2H, C*H*$_2$ from $PhCH_2B$), 3.75−5.00 (m, 4H, C*H*$_2$Ph), 6.18 (d, traces, *H* Ph from $HfCH_2Ph$), 6.45 (d, J_{HH} = 7.7 Hz, 2H, C*H*$_2$ from BCH_2Ph), 6.80−7.9 (m, 38H, Ar *H* and *H* Ph from Hf−CH_2Ph), 8.09 (m, 2H, C*H*═N). ^{19}F NMR (282 MHz, C_6D_5Br, 29 °C, product of CH activation): δ_F −127.7 (m, $B(C_6F_5)_3$), −130.52 (d, J = 22.8 Hz, 2F, *o-F*), −142.20 (m, $B(C_6F_5)_3$), −159.7 (m, $B(C_6F_5)_3$), −163.82 (br s, 1F, *p-F*), −166.62 (t, 2F, *m-F*). MS (ESI): *m*/*z* (intensity) 1071.5 (2×10^5, L_2MH^+), 1014.5 (3.2×10^5, $L_2M^+ - 4Me$), 999.4 (4.6×10^5, $L_2M^+ - Ph$).

(c) Reaction of Bis[*N*-(3-*tert*-butylsalicylidene)-2,3,4,5,6-pentafluoroanilinato]hafnium dibenzyl (11) with $B(C_6F_5)_3$. Dibenzylbis[*N*-(3-*tert*-butylsalicylidene)-2,3,4,5,6-pentafluoroanilinato]-hafnium (**11**; 41 mg, 40 μmol) was activated with $B(C_6F_5)_3$ (20 mg, 40 μmol) in C_6D_5Br (0.4 mL) in the same way as described for the reaction of **9** with $B(C_6F_5)_3$. Owing to its high thermal instability and very high air and moisture sensitivity, this substance could not be isolated, and the resulting orange solution was investigated only by ^{1}H and ^{19}F NMR methods. ^{1}H NMR (200 MHz, C_6D_5Br, 29 °C): δ_H 0.94 (s, 18H, *t*-Bu), 2.84 (s, 2H, Hf−C*H*$_2$Ph), 3.01 (s, 2H, C*H*$_2$ from $PhCH_2B$), 6.50 (d, J_{HH} = 7.2 Hz, 2H, *o*-H Ph from Hf−CH_2Ph), 6.7 (d, 1H, BCH_2Ph), 6.7 (2H, 5-*H* Ar), 6.75 (m, 2H, *H* Ph from Hf−CH_2Ph), 6.8 (d, J_{HH} = 7.8 Hz, 2H, *H* Ph from BCH_2Ph), 6.9 (d, J_{HH} = 7.0 Hz, 3H, *H* Ph from Hf−CH_2Ph), 7.0 (d, J_{HH} = 7.6 Hz, 2H, 4-*H* Ph), 7.4 (d, J_{HH} = 7.6 Hz, 2H, 6-H Ar), 8.1 (s, 2H, C*H*═N). ^{19}F NMR (282 MHz, C_6D_5Br, 29 °C): δ_F −127.7 (m, $B(C_6F_5)_3$), −130.97 (d, J = 22.6 Hz, 6F, *o-F*), −142.30 (m, $B(C_6F_5)_3$), −148.7 (d, J = 20.6 Hz, 4F, *o-F*), −152.11 (t, J = 22.2 Hz, 2F, *p-F*), −158.7 (t, J = 20.70 Hz, 4F, *m-F*), −159.75 (m, $B(C_6F_5)_3$), −164.23 (t, J = 21.0 Hz, 3F, *p-F*), −167.08 (t, J = 20.4 Hz, 6F, *m-F*). MS (ESI): *m*/*z* (intensity) 953.1 (1.2×10^6, $L_2MCH_2Ph^+$), 933.1 (2.5×10^5, $L_2MCH_2Ph^+$-F), 914.2 (2.0×10^5, $L_2MCH_2Ph^+ - 2F$), 897.0 (1.5×10^5, $L_2MCH_2Ph^+ - 3F$), 880.1 (7.5×10^5, $L_2MCH_2Ph^+ - 4F$).

(d) Reaction of Bis{*N*-[3,5-bis(α,α-dimethylbenzyl)salicylidene]-2,3,4,5,6-pentafluoroanilinato}hafnium Dibenzyl (12) with $B(C_6F_5)_3$. Dibenzylbis{*N*-[3,5-bis(α,α-dimethylbenzyl)salicylidene]-2,3,4,5,6-pentafluoroanilinato}hafnium (**12**; 56 mg, 40 μmol) was activated with $B(C_6F_5)_3$ (20 mg, 40 μmol) in C_6D_5Br (0.4 mL) in the same way as described for the reaction of **9** with $B(C_6F_5)_3$. Owing to its high thermal instability and very high air and moisture sensitivity, this substance could not be isolated, and the resulting orange solution was investigated only by ^{1}H and ^{19}F NMR methods. ^{1}H NMR (500 MHz, C_6D_5Br, 30 °C): δ_H 1.33 (s, 12H, C*H*$_3$ of 5-α,α-dimethylbenzyl), 1.69 (d, 12H, C*H*$_3$ of 3-α,α-dimethylbenzyl), 2.25 (s, 2H, Hf−C*H*$_2$Ph), 3.27 (s, 2H, C*H*$_2$ from $PhCH_2B$), 5.69 (d, J_{HH} = 5.8 Hz, 2H, *H* Ph from Hf−CH_2Ph), 6.5−6.9 (m, 4H, *H* Ph from BCH_2Ph), 6.9−7.4 (m, 20H, *H* Ph from ligand, *H* Ph from BCH_2Ph, *H* Ph from Hf−CH_2Ph), 7.47 (s, 2H, 6-*H* Ar), 7.87 (s, 2H, 6-*H* Ar), 8.37 (s, 2H, C*H*═N). ^{13}F NMR (282.2 MHz, $CDCl_3$, 27 °C): δ_C −127.75 (m, $B(C_6F_5)_3$), −130.97 (d, J = 20.0 Hz, 6F, *o-F*), −142.30 (m, $B(C_6F_5)_3$), −148.33 (d, J = 14.6 Hz, 4F, *o-F*), −151.86 (t, J = 22.6 Hz, 2F, *p-F*), −158.4 (t, J = 20.0 Hz, 4F, *m-F*), −159.7 (m, $B(C_6F_5)_3$), −164.20 (t, J = 20.6 Hz, 3F, *p-F*), −167.0 (t, J = 19.9 Hz, 6F, *m-F*). MS (ESI): *m*/*z* (intensity) 1314.3 (2.5×10^4, $L_2MCH_2Ph^+$), 1294.3 (1.5×10^5, $L_2MCH_2Ph^+ - F$), 1274.3 (8.0×10^4, $L_2MCH_2Ph^+ - 2F$).

Polymerization Experiments. A 1 L Büchi glass autoclave was charged with 200 mL of toluene and MAO, thermostated at the required temperature, and saturated with ethylene, after which the desired amount of complex solution was added. The $B(C_6F_5)_3$-activated benzyl complexes exhibited extremely high air and moisture sensitivity and thermal instability, and even in the presence of TIBA, used as a scavenger, only very low or no activity was observed in the corresponding experiments. The preparation of stock solutions of the complexes was performed in a glovebox. The catalyst solution was introduced into the autoclave under argon pressure. The monomer pressure (±50 mbar) and reaction temperature (±0.5 °C) were kept constant during each polymerization run. The monomer consumption, polymerization temperature, and pressure were controlled by real-time monitoring. The polymerizations were quenched by pouring the resulting reaction mixture into 400 mL of methanol acidified with aqueous hydrochloric acid. After precipitation, the polymers were washed several times with methanol and water and then dried at 60 °C overnight.

The olefin polymerizations in NMR tubes were carried out with freshly prepared solutions of $B(C_6F_5)_3$-activated Hf dibenzyl complexes. The appropriate amounts of complex, C_6D_5Br, and activator ($B(C_6F_5)_3$) were placed into a NMR tube equipped with a rubber septum (see Generation of Cationic Species). In a glovebox, the NMR tube with catalyst solution was placed into a Schlenk flask equipped with a rubber septum. The olefin was bubbled via

Table 6. Crystallographic Data for Complexes 10−12 and a

	10	11	12	a
formula	$C_{78}H_{78}N_2O_2Hf$	$C_{48}H_{40}F_{10}N_2O_2Hf\cdot 1.5C_4H_{10}O$	$C_{76}H_{64}F_{10}N_2O_2Hf$	$C_{52}H_{58}N_2O_2Ti$
fw	1253.91	1156.49	1405.78	790.90
space group	*P*1̄	*Pbcn*	*C*2/*c*	$P2_1/c$
a (Å)	14.608(2)	25.253(2)	30.721(6)	20.734(1)
b (Å)	15.646(2)	9.4870(10)	19.795(4)	12.020(1)
c (Å)	15.844(2)	22.630(2)	22.751(5)	20.224(1)
α (deg)	89.03(1)	90.00	90.00	90.00
β (deg)	65.96(1)	90.00	95.02(3)	117.80(1)
γ (deg)	73.39(1)	90.00	90.00	90.00
V (Å^3)	3148.6(8)	5421.6(9)	13782.5(5)	4458.5(5)
d_{calcd} (g cm^{-3})	1.323	1.417	1.355	1.178
Z	2	4	8	4
μ (mm^{-1})	1.71	2.00	1.59	0.233
λ (Å)	0.710 73	0.710 73	0.710 73	0.710 73
T (K)	173(2)	173(2)	173(2)	173(2)
R^a	0.0839	0.0720	0.1199	0.1464
$R_w{}^b$	0.1165	0.1093	0.1919	0.1589

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$ for observed reflections ($I > 2\sigma(I)$). [b] $R_w = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$ for all data.

a long needle through the catalyst solution. The pressure inside the NMR tube was normalized by a short needle introduced inside the NMR tube with an open connection to the outside atmosphere. The polymerization process was followed by ^{1}H NMR.

Single-Crystal X-ray Diffraction Studies. Crystal data of compounds **10**−**12** were collected with a Nonius KappaCCD area-detector diffractometer at 173(2) K using Mo Kα radiation (graphite monochromator, 0.710 73 Å). Software used: data reduction, COLLECT;[46] absorption correction, SADABS;[47] structure solution, SHELX-97[48a] or SIR 2002,[48b] direct methods; refinement, SHELX-97;[48a] graphics, SHELXTL.[49]All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined on calculated positions.

In the structure of **11**, Et_2O solvent molecules are heavily disordered, and their site occupation factors are 0.25 and 0.50. Both Et_2O molecules were refined with common isotropic atomic displacement parameters. Hydrogen atoms were placed on calculated positions, which is one reason for the short contacts. No other procedure to locate H atoms of the solvent molecules from the data set was successful.

The crystals of **12** were extremely fragile and broke instantaneously into smaller crystallites due to very loose van der Waals connections between molecules, indicating voids and loose connections between molecules inside the crystal structure. The final residual maximum in **12** implies disorder due to a partially cracked crystal.

Crystallographic data for complexes **10**−**12** and **a** are given in Table 6.

Calculation Details. Turbomole 5.8[34] and ADF 2005.01[35] quantum chemistry programs were used. All calculations were performed on a Sipeli supercomputer at the Finnish IT Center for Science (CSC).[50] The Turbomole computations were made at the B-P (B-P86) level.[51] The SVP basis sets were used for all atoms to calculate the optimized geometries. For the computations with the Amsterdam density functional program (ADF), triple-ζ STO basis sets (TVZ) were used for all atoms, and calculations were performed at the BLYP level. In addition, the scalar relativistic correction on ZORA formalism[52] was applied.

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Supporting Information Available: CIF files giving crystallographic data for **10**−**12** and **a** and figures giving ^{1}H and ^{19}F NMR, LT NMR, HETCOR 2D COSY, 2D NOESY, and ESI-MS spectra of bis(phenoxyimino) Hf dibenzyl complexes and products of their activation with $B(C_6F_5)_3$ and results of GPC studies of produced polyethylene and polypropylene. This material is available free of charge via the Internet at http://www.pubs.acs.org.

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