

[ONXO]-Type Amine Bis(phenolate) Zirconium and Hafnium Complexes as Extremely Active 1-Hexene Polymerization Catalysts

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Several [ONXO]-type zirconium and hafnium dibenzyl complexes of amine bis(phenolate) ligands, where X is a heteroatom donor located on a pendant arm, were synthesized directly from the ligand precursors and the corresponding tetrabenzylmetal complexes in quantitative yields (X = N, O, S). All complexes exhibited remarkable activities in the polymerization of 1-hexene, yielding high-molecular-weight polymers, the highest activity being unprecedented under the conditions employed. An unexpected metal-dependent activity pattern was demonstrated. The high activity of the complexes is derived from the binding of the side-arm donor to the metal and is affected by its nature. The activity order of the zirconium complexes as a function of the side-arm donor was found to be OMe > NMe₂ > SMe (5:2:1). The X-ray structures of all zirconium complexes were solved and revealed very similar binding of the [ONO] ligand cores to the metal. The distances between the side-arm donor atoms and the zirconium are relatively long (Zr–O, 2.45 Å; Zr–N, 2.59 Å; Zr–S, 2.86 Å). The X-ray structures of all hafnium complexes were solved as well and found to be closely related to those of the zirconium analogues (Hf–O, 2.45 Å; Hf–N, 2.56 Å; Hf–S, 2.84 Å). However, the activity order was found to be different in the hafnium series, namely SMe > OMe > NMe₂ (3.5:1.5:0.2), the [ONSO]-type complex exhibiting the highest activity ever reported for a hafnium complex under the conditions employed. Various NMR experiments supported the notion that the side-arm donor remains attached to the metal in the reactive compounds, which exist as well-separated ion pairs.

Introduction

One of the most significant applications of group IV metal complexes is the catalytic polymerization of α -olefins. Recent attempts to find alternatives to the cyclopentadienyl-based ligand systems have resulted in the introduction of numerous “nonmetallocene” systems.¹ Substantial effort has been devoted to the development of chelating diamido ligands. Complexes derived from these ligands have been reported to lead to active polymerization catalysts;² however, the activities of most such systems are considered moderate.¹

Dialkoxo ligands, which may be considered as more “natural” ligands for the oxophilic group IV metals, have drawn a more limited attention.³ We recently introduced the amine bis(phenolate) family of ligands to group IV metal chemistry^{4–7} and found that [ONNO]-type zirconium complexes, featuring a nitrogen donor on a side arm, lead to outstanding activities in the polymerization of 1-hexene.^{6,7} The side-arm nitrogen was found to be crucial for that extreme activity,⁸ as analogous [ONO]-type zirconium complexes, lacking such a side-arm

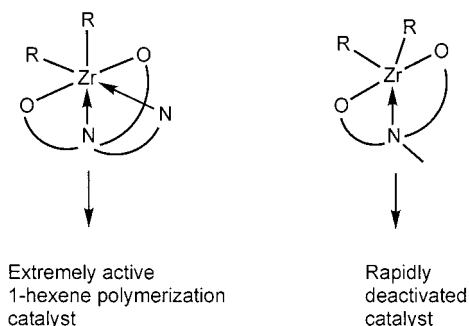
donor, were found to be practically inactive, leading only to traces of oligomeric material and rapid catalyst deactivation (Scheme 1). In the present contribution we expand both the ligand and the metal range, by introducing zirconium and hafnium complexes of [ONXO]-type ligands, in which the X-donor on the sidearm is chosen from the O, N, or S groups (Scheme 2). All complexes of these ligands demonstrated remarkable activities, and two of them have shown activity higher

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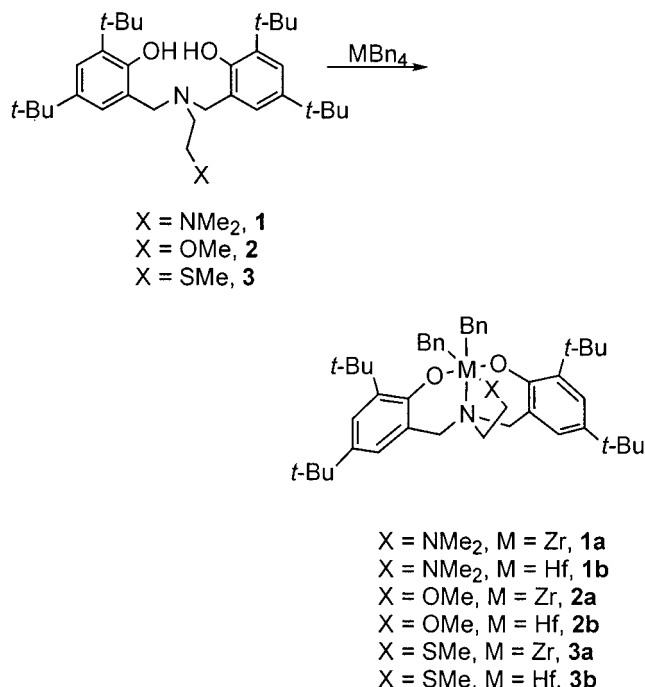
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Scheme 1



Scheme 2



than that previously demonstrated for [ONNO]-type zirconium complexes. A different activity pattern is observed when comparing zirconium and hafnium complexes of these ligands.

Results and Discussion

Ligand Design and Complex Formation. Our previous studies have shown that [ONNO]-type ligands

Table 1. Polymerization Data^a

precatalyst	solvent	activity ^b	M_w	M_w/M_n
1a	neat	21 000	35 000	3.5
1a	heptane ^c	860	170 000	2.0
1b	neat	2200	13 000	3.2
1b	heptane ^c	200	20 000	1.6
2a	neat	50 000	80 000	3.0
2a	heptane ^c	1300	160 000	1.4
2b	neat	16 500	101 000	2.2
2b	heptane ^c	700	140 000	1.8
3a	neat	9200	195 000	2.0
3a	heptane ^c	450	140 000	1.6
3b	neat	35 000	66 000	2.5
3b	heptane ^c	1600	250 000	1.4

^a The polymerization reactions are performed using 11–13 μmol of precatalyst unless otherwise stated, activated with approximately 1 equiv of $\text{B}(\text{C}_6\text{F}_5)_3$, for the polymerization of neat 1-hexene.

^b In units of $\text{g mmol cat}^{-1} \text{h}^{-1}$. ^c 1-hexene/heptane = 3/7; 6 μmol is used.

of the amine bis(phenolate) family, whose side-arm donors formed five membered chelates, led to the highest activities.⁷ We therefore aimed at ligands having two methylene units between the central and the side-arm donor. In addition, the presence of *t*-Bu groups at the positions ortho to the hydroxyl groups was found to lead to clean reactions with tetrabenzylzirconium, without reducing the activity of the resulting precatalyst.⁷ Thus, the ligand precursors described in the present study, shown in Scheme 2, were synthesized from 2,4-di-*tert*-butylphenol, formaldehyde, and the corresponding substituted primary amines. **1** is derived from *N,N*-dimethylethylenediamine,⁷ **2** is derived from 2-methoxyethylamine, and **3** is derived from 2-(methylthio)ethylamine.

The synthesis of ligand precursor **1** and the synthesis of the resulting zirconium dibenzyl complex **1a**, its X-ray structure, and its activity have been described⁷ and are given herein for comparison with the related complexes. The reactions of **2** and **3** with ZrBn_4 at 65 °C proceeded in analogy to that of **1**, giving the corresponding dibenzyl complexes **2a** and **3a**, respectively, in quantitative yields as yellow crystalline solids (Scheme 2). All complexes exhibit a C_s symmetry, as evident from their NMR spectra. Two symmetry-related phenolate rings and two different benzyl groups are consistent with the phenolate units being in a trans geometry. Most importantly, the two benzyl groups are in a cis configuration, as required for olefin polymerization catalysis.

The reactions of **1**, **2**, and **3** with HfBn_4 proceed rapidly even at room temperature, yielding the corresponding dibenzyl complexes **1b**, **2b**, and **3b**, respectively, after 2 h. The hafnium complexes are also obtained in quantitative yields, as colorless solids (Scheme 2). The spectroscopic features of the hafnium complexes are analogous to those obtained for the zirconium complexes.

Zirconium Complexes: Structure and Activity.

As previously reported, the [ONNO]- ZrBn_2 complex **1a** led to unprecedented activity in the polymerization of neat 1-hexene in the presence of $\text{B}(\text{C}_6\text{F}_5)_3$ as a cocatalyst: 21 000 $\text{g mmol cat}^{-1} \text{h}^{-1}$ (Table 1).⁷ Under these conditions, which involved considerable heat release, the polymer obtained had a molecular weight of $M_w = 35\,000$ and a broad molecular weight distribution ($\text{PDI} = 3.5$). Taming the polymerization by diluting the monomer in an inert solvent allowed the production of

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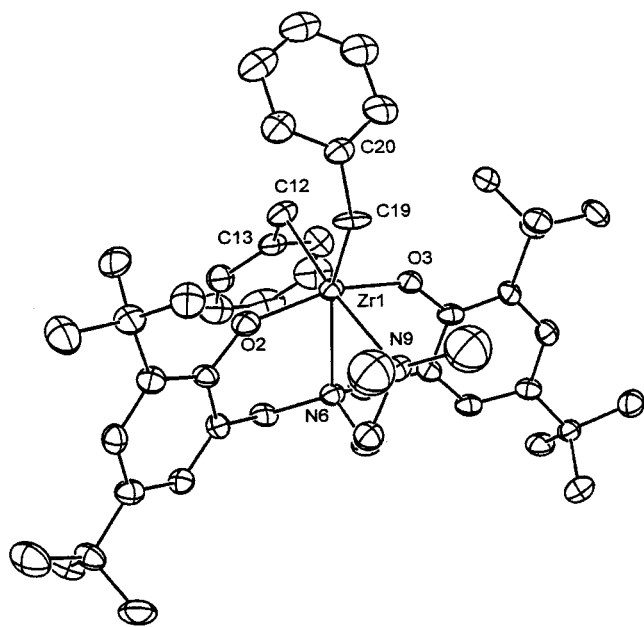


Figure 1. ORTEP drawing of the molecular structure of **1a** (50% probability ellipsoids). H atoms and atoms of the solvent of crystallization and disorder are omitted, and the methyl groups on the side-arm nitrogen are shown in reduced size for clarity. Key atoms are labeled.

Table 2. Selected Bond Distances (Å) and Angles (deg) for **1a**

Zr–O2	1.995(5)	Zr–N9	2.594(6)
Zr–O3	1.994(5)	Zr–C12	2.305(7)
Zr–N6	2.446(6)	Zr–C19	2.250(6)
O2–Zr–O3	160.3(2)	Zr–C12–C13	104.9(5)
N6–Zr–N9	69.7(2)	Zr–C19–C20	115.8(5)
C12–Zr–C19	93.7(2)		

poly(1-hexene) having high molecular weight ($M_w = 170\,000$) and narrow molecular weight distribution (PDI = 2.0) (Table 1).

The presence of a side-arm donor in the zirconium complexes was found to be essential for the extreme activity, as complexes lacking it were found to be practically inactive.^{6,7} In the crystal structure of **1a** (Figure 1, Table 2), the side-arm nitrogen was indeed found to be bound to the metal, as evident from the Zr–N distance of 2.59 Å. The cis configuration of the two benzyl groups is evident from the C–Zr–C angle of 93.7°. Both benzyl groups are bound in a η^1 fashion to the metal.

The OMe donor differs from the NMe₂ donor both sterically and electronically. The harder nature of the oxygen base, the smaller atomic radius, and the single methyl substituent may affect its binding to the metal, thus modifying activity. The activity of the [ONOO]-type zirconium complex **2a** in polymerization of 1-hexene was investigated and proved to be even higher than that of the analogous [ONNO]-type complex. Adding approximately 1 equiv of B(C₆F₅)₃ to 13 μ mol of **2a** in 80 mL of 1-hexene led to an activity of 50 000 g mmol cat^{−1} h^{−1}. The polymer obtained had a molecular weight of $M_w = 80\,000$ and a PDI of around 3.0 (Table 1). A narrower PDI (2.0) was obtained upon diluting the monomer in heptane, and the resulting molecular weight was somewhat higher: $M_w = 120\,000$.

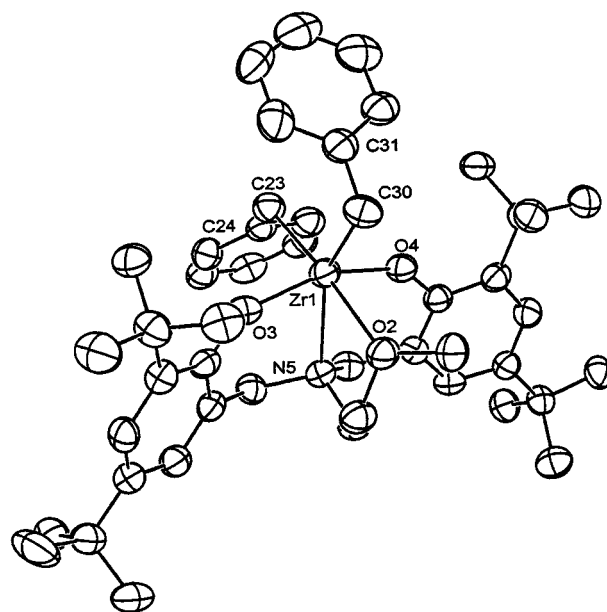


Figure 2. ORTEP drawing of the molecular structure of **2a** (50% probability ellipsoids). H atoms are omitted. Key atoms are labeled.

Table 3. Selected Bond Distances (Å) and Angles (deg) for **2a**

Zr–O3	1.994(3)	Zr–O2	2.447(3)
Zr–O4	1.983(3)	Zr–C23	2.296(5)
Zr–N	2.431(4)	Zr–C30	2.299(5)
O2–Zr–O3	158.8(1)	Zr–C23–C24	117.6(3)
N–Zr–O4	69.9(1)	Zr–C30–C31	102.2(3)
C23–Zr–C30	106.4(2)		

Single crystals of **2a** suitable for X-ray diffraction were grown from ether at −35 °C, and the structure is shown in Figure 2 (Table 3).

The structure features an octahedral complex, which closely resembles **1a**: namely, an almost superimposable [ONO] core binding to the zirconium, a coordination of the side-arm donor to the zirconium, and a similar orientation of the benzyl groups.

The sulfur donor is a softer base, and its larger radius is expected to result in a longer zirconium–side-arm donor bond. Furthermore, the longer Zr–S distance may reduce the steric effect of the single methyl substituent.

The [ONSO]-type complex **3a** exhibited activity lower than that of the [ONNO]-type complex **1a**. The highest activity resulting from activation of this precatalyst with B(C₆F₅)₃ at room temperature was found to be 9200 g mmol cat^{−1} h^{−1}, which was obtained by activation of 13 μ mol of **2a** with approximately 1 equiv of the cocatalyst in 10 mL of neat 1-hexene. The polymeric product had a high molecular weight of $M_w = 195\,000$ and a narrow PDI of around 2.0, despite the substantial heat release (Table 1).

Single crystals of **3a** were also grown from ether at −35 °C, and a molecular model is shown in Figure 3 (Table 4). The structure features another distorted-octahedral complex, which shows close similarity to those of **1a** and **2a**. The bending of the phenolate ring array toward the pendant arm and the orientations of the benzyl groups are again very similar.

The activity ratio of **1a**–**3a** is therefore approximately as follows: O–Me > N–Me₂ > S–Me (5:2:1). A different

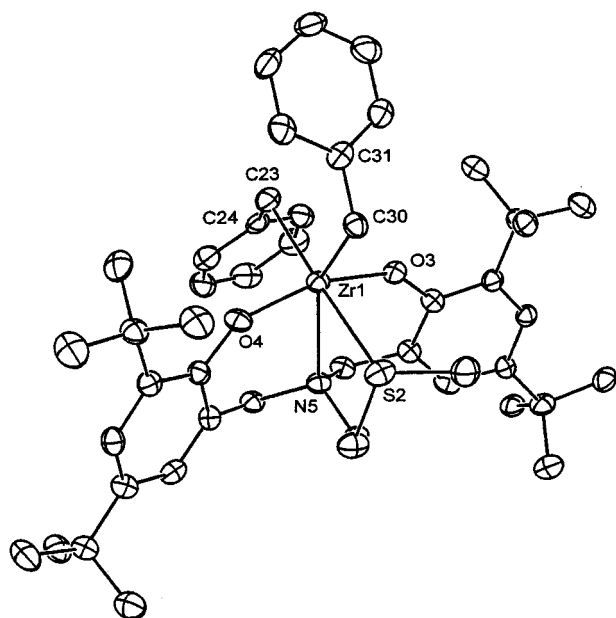


Figure 3. ORTEP drawing of the molecular structure of **3a** (50% probability ellipsoids). H atoms and atoms of the solvent of crystallization are omitted. Key atoms are labeled.

Table 4. Selected Bond Distances (Å) and Angles (deg) for 3a

Zr–O3	1.987(3)	Zr–S	2.859(1)
Zr–O4	1.973(3)	Zr–C23	2.292(5)
Zr–N	2.486(4)	Zr–C30	2.318(4)
O3–Zr–O4	159.3(1)	Zr–C23–C24	102.1(3)
N–Zr–S	71.59(9)	Zr–C30–C31	113.4(3)
C23–Zr–C30	94.9(2)		

perspective of the structures of **1a**, **2a**, and **3a**, in which several atoms have been omitted for clarity, is shown in Figure 4.

The similarity of all three structures is quite clear from the models presented in Figure 4: namely, almost superimposable [ONO] cores and only slightly different binding of the benzyl groups, oriented in the same direction. The exceptional structure is that of the most active [ONOO]-type complex, in which the "axial" benzyl group features a significantly narrower Zr–C–C angle (102°) than the corresponding angles in the [ONNO]- and [ONSO]-type complexes (116 and 113°, respectively), that may be considered to result from a partial η^2 binding. This η^2 binding "pushes" the top benzyl carbon (C30) toward the oxygen donor, thereby broadening the angle between the two benzyl groups relative to the other complexes (C–Zr–C = 106°). In contrast, the Zr–C–C angle of the other benzyl group in **2a** is much wider.

As may be expected of the nature of the donor groups, the X–Zr distances span across a relatively broad range. The largest distance (of 2.86 Å) is obtained for the methylthio donor, as sulfur has the largest covalent radius.⁹ The short O–Zr distance of 2.45 Å may be attributed to the relatively strong nature of the O–Zr coordinative bond, combined with the single methyl substituent on the oxygen, relative to the NMe₂ donor.⁷ It is noteworthy that the metal–side-arm donor dis-

Table 5. Selected Bond Distances (Å) and Angles (deg) for 1b

Hf–O3	1.980(3)	Hf–N2	2.559(4)
Hf–O4	1.976(3)	Hf–C23	2.290(5)
Hf–N5	2.424(4)	Hf–C30	2.284(5)
O3–Hf–O4	160.9(1)	Hf–C23–C24	107.9(3)
N5–Hf–N2	70.6(1)	Hf–C30–C31	112.4(3)
C23–Hf–C30	96.4(2)		

Table 6. Selected Bond Distances (Å) and Angles (deg) for 2b

Hf–O3	1.972(4)	Hf–O2	2.445(3)
Hf–O4	1.983(3)	Hf–C23	2.261(5)
Hf–N	2.438(4)	Hf–C20	2.271(4)
O3–Hf–O4	160.1(1)	Hf–C23–C24	106.1(3)
N–Hf–O2	69.8(1)	Hf–C30–C31	113.7(3)
C23–Hf–C30	97.6(2)		

Table 7. Selected Bond Distances (Å) and Angles (deg) for 3b

Hf–O4	1.976(3)	Hf–S	2.843(1)
Hf–O3	1.982(3)	Hf–C23	2.277(4)
Hf–N	2.465(3)	Hf–C30	2.283(4)
O4–Hf–O3	160.2(1)	Hf–C23–C24	105.4(3)
N–Hf–S	72.20(8)	Hf–C30–C31	113.1(3)
C30–Hf–C23	97.1(2)		

tances described herein are relatively long in comparison to analogous zirconium–donor bond distances (2.45 Å for a Zr–N bond,^{10a} 2.37 Å for a Zr–O bond,^{10b} and 2.80 Å for a Zr–S bond²¹ were found in analogous systems). It is therefore somewhat surprising that this peripheral side-arm donor has such a strong effect on the polymerization activity.^{8c}

Hafnium Complexes: Structure and Activity. The X-ray structures of [ONNO]HfBn₂ (**1b**), [ONOO]HfBn₂ (**2b**), and [ONSO]HfBn₂ (**3b**) were solved, and the structures are shown in Figures 5–7, respectively (Tables 5–7, respectively).

The structures of the hafnium complexes are closely related to those of the analogous zirconium complexes, and their [ONO] cores are even more uniform. Similar Zr–C–C angles are obtained for all complexes for the "axial" as well as "equatorial" benzyl units. The hafnium–side-arm donor bond lengths follow the same pattern as was observed in the zirconium series (Figure 8).

The [ONNO]-type hafnium complex **1b** was found to lead to a highly active 1-hexene polymerization catalyst.¹¹ Adding approximately 1 equiv of B(C₆F₅)₃ to 11 μ mol of **1b** in 10 mL of neat 1-hexene at room temperature resulted in substantial heat release and boiling of the monomer. The reaction was, however, slower than that obtained with the zirconium analogue **1a**, and the activity calculated in this case was 2200 g mmol cat^{−1} h^{−1}. Despite some reports of the opposite,¹² this finding is in accordance with the widely accepted notion that hafnium complexes are usually less active than the

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(11) Similarly to the zirconium chemistry, the extra side-arm donor is essential for high activity in 1-hexene polymerization in the hafnium complexes, as a complex lacking a side-arm donor was found to be almost inactive (Tshuva, E. Y.; Kol, M. Unpublished results).

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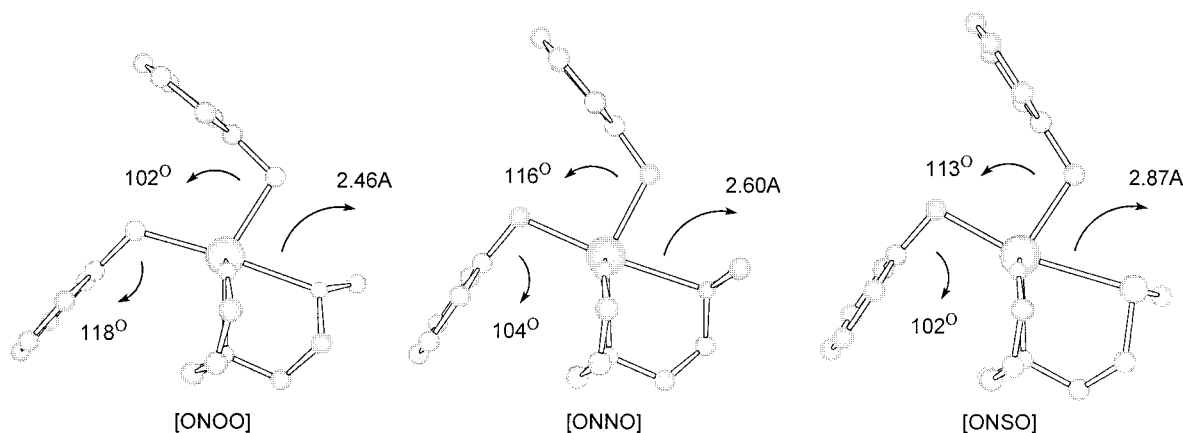


Figure 4. Side view of the structures of **1a**, **2a**, and **3a**. Some of the atoms of the phenolate rings are omitted for clarity.

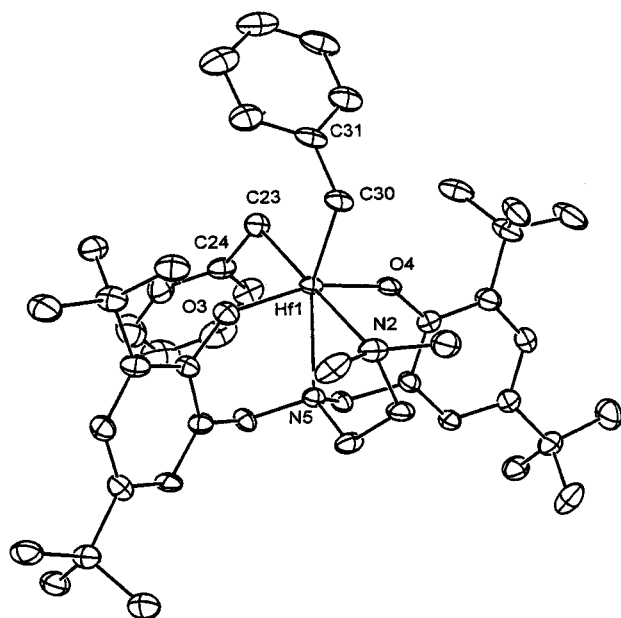


Figure 5. ORTEP drawing of the molecular structure of **1b** (50% probability ellipsoids). H atoms and atoms of the solvent of crystallization and disorder are omitted. Key atoms are labeled.

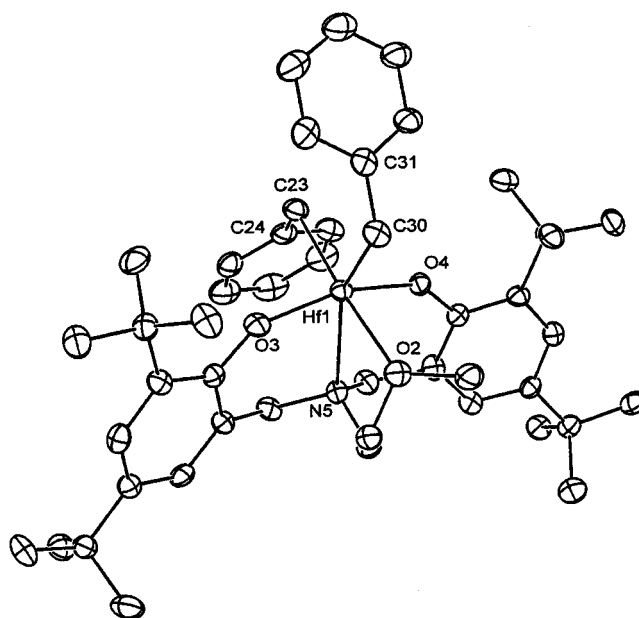


Figure 6. ORTEP drawing of the molecular structure of **2b** (50% probability ellipsoids). H atoms and atoms of the solvent of crystallization are omitted. Key atoms are labeled.

zirconium analogues.¹³ The molecular weight obtained is $M_w = 13\,000$ with a relatively broad PDI of 3.2. The molecular weight increases only slightly upon dilution of the monomer (Table 1), suggesting a relatively high termination/propagation rate ratio for this complex.

Both the [ONOO]-type hafnium complex **2b** and the [ONSO]-type hafnium complex **3b** were found to be extremely active in the polymerization of 1-hexene; however, surprisingly, the activity order was different from that obtained with the zirconium analogues. Adding approximately 1 equiv of $B(C_6F_5)_3$ to 12 μmol of **2b** in 100 mL of neat 1-hexene resulted in a rapid polymerization process, with a very high catalyst activity of $16\,500\text{ g mmol cat}^{-1}\text{ h}^{-1}$, which is higher than that obtained with the complex having the nitrogen side donor **2a**, in analogy to the zirconium results. The polymer obtained had a molecular weight of $M_w =$

101 000 and PDI of 2.2 (Table 1). Unexpectedly, adding approximately 1 equiv of $B(C_6F_5)_3$ to 11 μmol of **3b** in 100 mL of neat 1-hexene resulted in a polymer having $M_w = 66\,000$ and PDI = 2.5, with a catalyst activity of $35\,000\text{ g mmol cat}^{-1}\text{ h}^{-1}$, exceeding substantially the activity of the analogous [ONSO]-type zirconium complex.^{12,13} Thus, the ligand that showed the lowest activity in the zirconium series showed the highest activity in the hafnium series. This activity is, to the best of our knowledge, the highest activity in polymerization of neat 1-hexene ever reported for a hafnium complex activated by $B(C_6F_5)_3$. The activity ratio in the hafnium series is approximately as follows (1 being [ONSO]ZrBn₂): S-Me > O-Me > N-Me₂ (3.5:1.5:0.2).

The extreme activity of the complex exhibiting binding to a side-arm sulfur atom, which is considered a soft base, may be attributed to the softer Lewis acid nature of the hafnium atom, enabling stronger binding between the two.

Diluting the monomer in heptane had an effect similar to that observed for the previous complexes. Thus, as presented in Table 1, the activity order in

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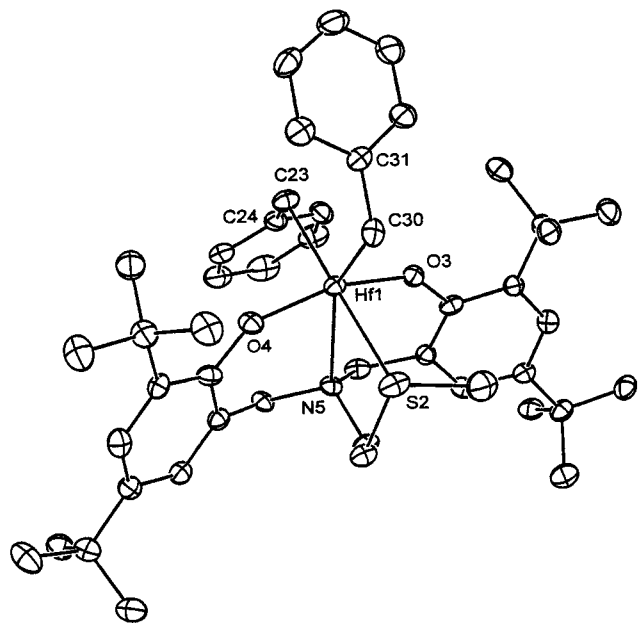


Figure 7. ORTEP drawing of the molecular structure of **3b** (50% probability ellipsoids). H atoms and atoms of the solvent of crystallization are omitted. Key atoms are labeled.

diluted monomer under a more controlled exotherm conditions is similar to that obtained in neat monomer for both the zirconium and hafnium series. In addition, the activity orders of zirconium and hafnium complexes of the same ligand are similar in neat and diluted conditions as well.

Characterization of the Reactive Species. All the structural information described above was obtained from the solid-state structures of the precatalysts. To gain insight on the structure of the reactive species in solution, we first had to correlate between the solid-state structure and the solution structure of the precatalysts. Especially, we wanted to verify the binding of the side-arm donor, which is proposed to play a significant role in the polymerization activity^{7,10} to the metal in solution. Next, we wanted to characterize the reactive species formed by addition of the cocatalyst to the precatalyst. Most importantly, since the cocatalyst could react with the side-arm donor, detaching it from the metal, we wanted to investigate whether this donor remains bound to the metal in the reactive species. In addition, we wanted to reveal whether the abstracted benzyl unit coordinates to the metal in the reactive species.

To gain this information, NMR experiments were performed. In particular, NOESY experiments were conducted to determine spatial relations between different groups in the molecules. The most significant NOESY correlations observed for the precatalyst **1a** are shown in Scheme 3 (left-hand side).

The identities of the two *tert*-butyl groups were verified by their correlation with the aromatic protons of the phenolate rings. The *ortho tert*-butyl group was found to correlate with the protons of both the “axial” and “equatorial” benzyl groups, whereas the *para tert*-butyl group correlated with neither. Most importantly, a correlation was found between the methyl groups on the side-arm nitrogen donor and both the “axial” benzyl unit and the *ortho tert*-butyl group. These correlations

indicate a close proximity of these groups, thus suggesting that the side-arm donor is indeed bound to the metal in solution. The lack of correlation between the nitrogen methyl substituents and the “equatorial” benzyl group is consistent with their spatial separation. It therefore appears that the solution structure of **1a** closely resembles its solid-state structure.

Reaction of **1a** with 1 equiv of $\text{B}(\text{C}_6\text{F}_5)_3$ in d_5 -chlorobenzene resulted in the formation of the activated compound in >90% yield, which was found to be stable for hours at room temperature and for days at -35°C . This species features a C_s symmetry similar to that of the precatalyst. ^{19}F NMR implied that a well-separated ion pair is obtained,¹⁴ a finding supported by the ^1H NMR chemical shift of one of the benzyl units, which is consistent with a noncoordinated $[\text{PhCH}_2\text{B}(\text{C}_6\text{F}_5)_3]^-$ anion. This notion was further supported by a NOESY experiment (Scheme 3, right-hand side), which revealed no correlation of the abstracted benzyl unit to any protons of the cation. The remaining benzyl unit correlates with both the *ortho tert*-butyl group and the dimethylamino arm, indicating that a monocation was formed. Moreover, addition of 5 equiv of $\text{B}(\text{C}_6\text{F}_5)_3$ did not have any influence on the ^1H NMR and the ^{19}F NMR of the product, indicating that a dicationic species¹⁵ is not formed under these conditions. The NOE correlation of the remaining benzyl unit with the dimethylamino arm supports two important structural features: (1) the side-arm donor is bound to the metal in the reactive species as well (the dimethylamino group also shows NOE correlation with the *ortho tert*-butyl unit); (2) the position of the remaining benzyl group is similar to that of the “axial” benzyl in the precatalyst, rather than to that of the “equatorial” benzyl group. This is supported by a relatively small difference in chemical shifts between the “axial” benzyl signal of the precatalyst and the benzyl group in the reactive species of 0.2 ppm. This may further suggest a relatively strong binding of the “axial” benzyl unit to the metal, although it is uncertain which of the two benzyl groups in the precatalyst was the one abstracted.

To validate these observations, similar NMR experiments were performed on several other complexes: i.e., **2a**, **1b**, **3b**, and the reactive species resulting from the addition of $\text{B}(\text{C}_6\text{F}_5)_3$ to them. For *all* complexes studied, similar features were observed, namely (1) a relatively stable reactive species is formed, which is a well-separated ion pair, in which the abstracted benzyl group is not coordinated to the metal, (2) the side-arm donor is coordinated to the metal in both the precatalyst and the reactive species, and (3) the NOE correlation between the donor substituents and the remaining benzyl group supports its location at the “axial” position in a monocationic species.

Conclusions

All the [ONXO]-type zirconium and hafnium dibenzyl complexes described in this work lead to remarkably active catalysts for the polymerization of 1-hexene. X-ray structures of all of these complexes featured

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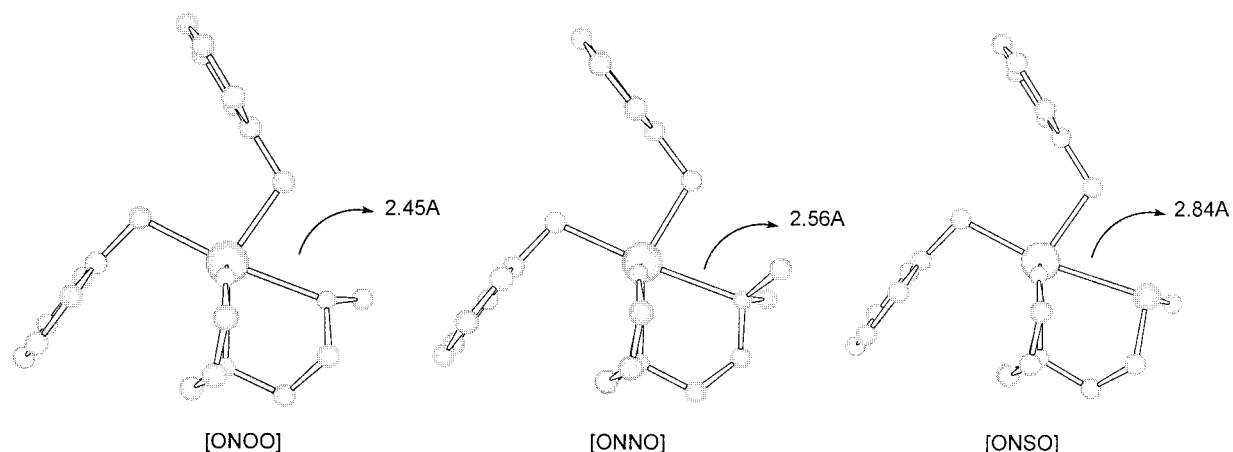
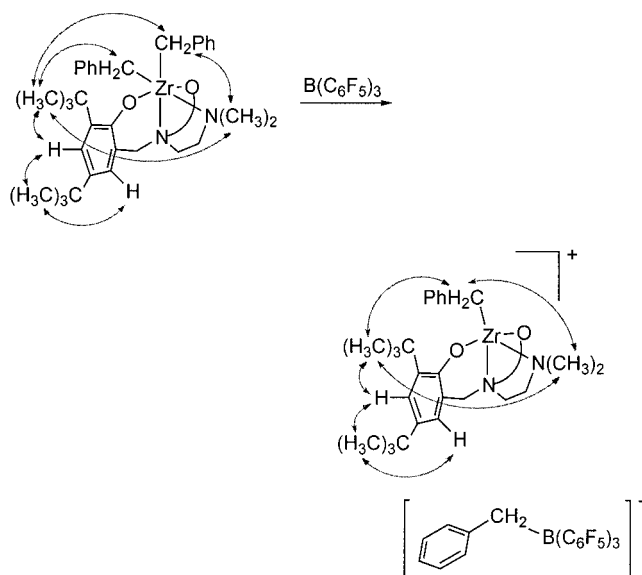


Figure 8. Side view of the structures of **1b**, **2b**, and **3b**. Some of the atoms of the phenolate rings were omitted for clarity.

Scheme 3



essentially identical [ONO] cores, as well as binding of the peripheral side-arm donors to the metal. These side-arm donors were found to be essential for the polymerization activity. NMR studies indicated that the side-arm donors remain attached to the metal in solution for both the precatalyst and the active species formed by addition of tris(pentafluorophenyl)borane. Interestingly, the order of activity in the zirconium and hafnium series was found to be different. In both series the most active complex featured a single methyl substituent, namely [ONOO]-ZrBn₂ and [ONSO]-HfBn₂, implying that steric effects may play a role in determining activity. A possible factor promoting the high activity of these complexes in the polymerization of high olefins is the formation of a well-separated ion pair in which the approach of the monomer to the active site is facilitated. We are currently studying further mechanistic aspects of these systems as well as related ones and their application in olefin polymerization catalysis.

Experimental Section

General Considerations. Starting materials for ligand precursor synthesis (**2** and **3**) were purchased from Aldrich Inc. or Fluka Inc. and used without further purification. **1** was

synthesized as previously described.^{7,16} All experiments requiring a dry atmosphere were performed under a nitrogen atmosphere in a drybox. Toluene was distilled from Na, ether was distilled from Na/benzophenone, and pentane was distilled from Na/benzophenone/tetraglyme. Anhydrous heptane was purchased from Aldrich Inc. and passed through alumina prior to use. 1-hexene was purchased from Aldrich Inc. and passed through alumina. All solvents were stored in the drybox. ZrBn₄ and HfBn₄ were prepared according to literature procedures.¹⁷ **1a** was synthesized as previously described.⁷ B(C₆F₅)₃ was purchased from Strem Chemicals Inc. and used as is. Mass spectra were determined with a GC/MS Finnigan Model 4021 spectrometer. NMR data were recorded using Bruker DMX-600, ARX-500, AVANCE-400, AMX-360, and AC-200 spectrometers. NMR solvents were sparged with argon and stored over 4 Å molecular sieves. NOESY experiments were performed on the 400 MHz spectrometer at room temperature. The X-ray diffraction measurements were carried out on a Nonius Kappa CCD diffractometer system, using Mo Kα (λ = 0.7107 Å) radiation. The analyzed crystals were embedded within a drop of viscous oil and freeze-cooled to ca. 115 K. The structures were solved by a combination of direct methods and Fourier techniques using the SIR-92 and DIRDIF-96 software¹⁸ and were refined by full-matrix least squares with SHELXL-97.¹⁹ Most of the structures contain partly disordered solvent, which affects to some extent the precision of the structure determination.

Elemental analyses of the ligand precursors **1–3** were performed in the microanalytical laboratory in the Hebrew University of Jerusalem. The elemental analysis of the zirconium and hafnium complexes was performed in these laboratories as well on the same day they were taken out of the drybox: otherwise, a consistently low carbon percentage is obtained. All gel permeation chromatography (GPC) experiments were carried out using a TSK-GEL GMH_{HR}-M column placed in a Jasco instrument equipped with a refractive index detector, relative to polystyrene standards and tetrahydrofuran as the eluting solvent. HPLC grade tetrahydrofuran was filtered under vacuum prior to use.

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Table 8. Crystal Data and Structure Refinement Parameters for 2a, 3a, 1b, and 3b

	2a	3a	1b	2b	3b
formula	C ₄₇ H ₆₅ NO ₃ Zr	C ₄₇ H ₆₅ NO ₂ SZr·C ₄ H ₁₀ O	C ₄₈ H ₆₈ N ₂ O ₂ Hf·C ₅ H ₁₂	C ₄₇ H ₆₅ NO ₃ Hf·C ₅ H ₁₂	C ₄₇ H ₆₅ NO ₂ SHf·C ₄ H ₁₀ O
fw	783.22	873.40	955.68	942.64	960.67
temp (K)	110	110	110	110	110
cryst syst	monoclinic	orthorhombic	orthorhombic	orthorhombic	orthorhombic
space group	<i>P2₁/c</i>	<i>Pbca</i>	<i>Pbca</i>	<i>Pbca</i>	<i>Pbca</i>
<i>a</i> (Å)	10.4860(6)	18.2920(4)	18.4040(2)	18.1570(3)	18.2820(3)
<i>b</i> (Å)	25.343(2)	18.6030(5)	19.1730(2)	18.6620(3)	18.6190(3)
<i>c</i> (Å)	17.348(1)	28.5410(8)	28.2250(4)	28.4990(5)	28.5240(5)
β (deg)	107.168(5)				
<i>V</i> (Å ³), <i>Z</i>	4404.8(5), 4	9712.1(4), 8	9959.5(2), 8	9656.8(3), 8	9709.4(3), 8
ρ_{calcd} (g cm ⁻³)	1.181	1.195	1.275	1.297	1.314
λ (Å)	0.71070	0.71070	0.71070	0.71070	0.71070
μ (mm ⁻¹)	0.288	0.309	2.134	2.201	2.231
no. of rflns measd	7876	7405	9063	10 989	8864
no. of indep rflns	4302	4356	6828	5760	5759
R1 (<i>I</i> > 2 σ (<i>I</i>))	0.066	0.062	0.041	0.043	0.036
wR2 (<i>I</i> > 2 σ (<i>I</i>))	0.142	0.105	0.095	0.097	0.075
R1 (all data)	0.147	0.141	0.064	0.114	0.073
wR2 (all data)	0.174	0.133	0.106	0.125	0.087
GOF (<i>F</i> ²)	0.979	1.043	0.980	0.902	1.018

Compound 2. A solution of 2,4-di-*tert*-butylphenol (5.0 g, 24.2 mmol), 2-methoxyethylamine (1.05 mL, 12.1 mmol), and 36% aqueous formaldehyde (3.0 mL, 36.0 mmol) in methanol (10 mL) was stirred and refluxed for 7 days. The mixture was cooled and the supernatant liquid decanted. The remaining oil was crystallized from methanol (25 mL), affording colorless crystals of the product (2.6 g, 42% yield). Mp: 135 °C. HRMS: *m/z* calcd 511.4026, found 511.4032. Anal. Calcd for C₃₃H₅₃NO₃: C, 77.45; H, 10.44; N, 2.74. Found: C, 77.70; H, 10.72; N, 2.79. ¹H NMR (CDCl₃): δ 7.21 (d, *J* = 2.0 Hz, 2H), 6.90 (d, *J* = 2.0 Hz, 2H), 3.75 (s, 4H, CH₂), 3.57 (t, *J* = 5.0 Hz, 2H, CH₂), 3.48 (s, 3H, OCH₃), 2.76 (t, *J* = 5.0 Hz, 2H, CH₂), 1.40 (s, 18H, C(CH₃)₃), 1.28 (s, 18H, C(CH₃)₃). ¹³C NMR (CDCl₃): δ 152.8, 140.7, 136.0, 124.9, 123.4, 121.6, 71.4 (ArCH₂), 58.9 (OCH₃), 58.0 (CH₂), 51.3 (CH₂), 35.0 (C(CH₃)₃), 34.1 (C(CH₃)₃), 31.6 (C(CH₃)₃), 30.1 (C(CH₃)₃).

Compound 3. A solution of 2,4-di-*tert*-butylphenol (4.2 g, 20.3 mmol), 2-(methylthio)ethylamine (1 mL, 10.7 mmol), and 36% aqueous formaldehyde (3.0 mL, 36.0 mmol) in methanol (10 mL) was stirred and refluxed for 48 h. The mixture was cooled and the supernatant liquid decanted. The remaining oil was crystallized from methanol, giving colorless crystals of the product (1.5 g, 28% yield). Mp: 124 °C. HRMS: *m/z* calcd 527.3797, found 527.3805. Anal. Calcd for C₃₃H₅₃NO₂S: C, 75.09; H, 10.12; N, 2.65; S, 6.07. Found: C, 74.90; H, 10.33; N, 2.81; S, 6.01. ¹H NMR (CDCl₃): δ 7.23 (s, 2H), 6.90 (s, 2H), 3.65 (s, 4H, CH₂), 2.74 (s, 4H, CH₂), 1.99 (s, 3H, SCH₃), 1.40 (s, 18H, C(CH₃)₃), 1.27 (s, 18H, C(CH₃)₃). ¹³C NMR (CDCl₃): δ 152.4, 141.3, 136.1, 125.2, 123.7, 121.2, 57.3 (ArCH₂), 51.0 (CH₂), 31.5 (CH₂), 34.9 (C(CH₃)₃), 34.1 (C(CH₃)₃), 31.6 (C(CH₃)₃), 29.6 (C(CH₃)₃), 14.78 (SCH₃).

LigZrBn₂ General Procedure. A solution of 2 or 3 (0.40 mmol) in toluene (2 mL) was added dropwise to a solution of tetrabenzylzirconium (0.40 mmol) in toluene (2 mL) at room temperature under a nitrogen atmosphere. The reaction mixture was then heated to 65 °C and stirred for 2 h. The toluene was removed under vacuum, and the dibenzyl complexes 2a and 3a were obtained quantitatively as yellow solids.

Complex 1a.⁷ Anal. Calcd for C₄₈H₆₈N₂O₂Zr: C, 72.40; H, 8.61; N, 3.52. Found: C, 72.29; H, 8.49; N, 3.70.

1a/B(C₆F₅)₃. One equivalent of B(C₆F₅)₃ was added to 1a in *d*₅-chlorobenzene. ¹H NMR (C₆D₅Cl): δ 7.63 (m, 4H), 7.29–7.01 (m, 8H), 6.89 (t, *J* = 6.2 Hz, 2H), 3.85 (d, *J* = 13.8 Hz, 2H, ArCH₂), 3.47 (br s, 2H, PhCH₂B), 3.27 (d, *J* = 13.8 Hz, 2H, ArCH₂), 3.03 (s, 2H, PhCH₂Zr), 2.62 (br, 2H, CH₂), 1.98 (s, 6H, N(CH₃)₂), 1.64 (s, 18H, C(CH₃)₃), 1.44 (s, 18H, C(CH₃)₃), 1.63–1.44 (m, 2H, CH₂). ¹⁹F NMR (C₆D₅Cl): δ -130.64 (*o*), -164.36 (*p*), -167.02 (*m*).

Complex 2a. Crystal data are presented in Table 8. Anal. Calcd for C₄₇H₆₅NO₃Zr: C, 72.07; H, 8.36; N, 1.79. Found: C,

72.25; H, 8.01; N, 2.13. ¹H NMR (C₆D₆): δ 7.74 (d, *J* = 7.4 Hz, 2H), 7.60 (d, *J* = 2.4 Hz, 2H), 7.35 (t, *J* = 7.7 Hz, 2H), 7.03 (t, *J* = 7.3 Hz, 1H), 6.90 (m, 4H), 6.76 (t, *J* = 7.6 Hz, 2H), 6.56 (t, *J* = 7.3 Hz, 1H), 3.51 (d, *J* = 13.4 Hz, 2H, ArCH₂), 2.85 (s, 2H, PhCH₂), 2.60 (d, *J* = 13.5 Hz, 2H, ArCH₂), 2.49 (s, 2H, PhCH₂), 2.48 (s, 3H, OCH₃), 2.21 (t, *J* = 5.3 Hz, 2H, CH₂), 1.90 (t, *J* = 5.3 Hz, 2H, CH₂), 1.85 (s, 18H, C(CH₃)₃), 1.36 (s, 18H, C(CH₃)₃). ¹³C NMR (C₆D₆): δ 159.0, 146.7, 141.8, 137.2, 129.9, 128.2, 125.9, 125.6, 125.3, 123.5, 121.3, 73.9 (CH₂), 68.4 (PhCH₂), 67.0 (PhCH₂), 65.2 (ArCH₂), 61.8 (OCH₃), 51.7 (CH₂), 36.2 (C(CH₃)₃), 35.1 (C(CH₃)₃), 32.6 (C(CH₃)₃), 31.0 (C(CH₃)₃).

2a/B(C₆F₅)₃. One equivalent of B(C₆F₅)₃ was added to 2a in *d*₅-chlorobenzene. ¹H NMR (C₆D₅Cl): δ 7.68 (d, *J* = 2.0 Hz, 2H), 7.63 (d, *J* = 7.2 Hz, 2H), 7.36–7.16 (m, 4H), 7.08 (t, *J* = 7.6 Hz, 4H), 6.93 (t, *J* = 7.0 Hz, 2H), 3.80 (d, *J* = 13.9 Hz, 2H, ArCH₂), 3.50 (br s, 2H, PhCH₂B), 3.38 (d, *J* = 13.9 Hz, 2H, ArCH₂), 3.31 (s, 3H, OCH₃), 3.17 (m, 2H, CH₂), 3.12 (s, 2H, PhCH₂Zr), 2.59 (m, 2H, CH₂), 1.67 (s, 18H, C(CH₃)₃), 1.47 (s, 18H, C(CH₃)₃). ¹⁹F NMR (C₆D₅Cl): δ -130.72 (*o*), -164.21 (*p*), -166.95 (*m*).

Complex 3a. Crystal data are presented in Table 8. ¹H NMR (C₆D₆): δ 7.72 (d, *J* = 7.3 Hz, 2H), 7.57 (d, *J* = 2.4 Hz, 2H), 7.34 (t, *J* = 7.7 Hz, 2H), 7.04 (t, *J* = 7.3 Hz, 1H), 6.90 (m, 4H), 6.78 (t, *J* = 7.5 Hz, 2H), 6.58 (t, *J* = 7.2 Hz, 1H), 3.58 (d, *J* = 13.4 Hz, 2H, ArCH₂), 3.08 (s, 2H, PhCH₂), 2.60 (d, *J* = 13.5 Hz, 2H, ArCH₂), 2.47 (s, 2H, PhCH₂), 2.07 (m, 2H, CH₂), 1.82 (s, 18H, C(CH₃)₃), 1.35 (s, 18H, C(CH₃)₃), 1.37–1.26 (m, 2H, CH₂), 1.00 (s, 3H, SCH₃). ¹³C NMR (C₆D₆): δ 158.9, 149.8, 146.3, 142.1, 137.5, 130.0, 129.5, 128.2, 126.5, 125.5, 125.3, 123.8, 121.4, 67.0 (PhCH₂), 65.7 (ArCH₂), 64.4 (PhCH₂), 54.7 (CH₂), 36.3 (C(CH₃)₃), 35.1 (C(CH₃)₃), 34.0 (CH₂), 32.6 (C(CH₃)₃), 31.2 (C(CH₃)₃), 15.3 (SCH₃).

LigHfBn₂ General Procedure. A solution of 1, 2, or 3 (0.40 mmol) in toluene (2 mL) was added dropwise to a solution of tetrabenzylhafnium (0.40 mmol) in toluene (2 mL) and stirred at room temperature for 2 h. The toluene was removed under vacuum, and the dibenzyl complexes 1b–3b were obtained quantitatively as colorless solids.

Complex 1b. Crystal data are presented in Table 8. Anal. Calcd for C₄₈H₆₈N₂O₂Hf: C, 65.25; H, 7.76; N, 3.17. Found: C, 65.19; H, 7.64; N, 3.35. ¹H NMR (C₆D₆): δ 7.65 (m, 4H), 7.39 (d, *J* = 7.6 Hz, 2H), 6.99 (t, *J* = 7.4 Hz, 1H), 6.92 (m, 4H), 6.76 (t, *J* = 7.7 Hz, 2H), 6.55 (t, *J* = 7.3 Hz, 1H), 3.49 (d, *J* = 13.5 Hz, 2H, ArCH₂), 2.59 (d, *J* = 13.5 Hz, 2H, ArCH₂), 2.47 (s, 2H, PhCH₂), 2.42 (s, 2H, PhCH₂), 1.84 (s, 18H, C(CH₃)₃), 1.52 (s, 6H, N(CH₃)₂), 1.52–1.30 (m, 4H, CH₂), 1.36 (s, 18H, C(CH₃)₃). ¹³C NMR (C₆D₆): δ 158.0, 141.0, 137.1, 128.6, 127.2, 125.3, 124.9, 124.6, 121.9, 120.6, 79.3 (PhCH₂), 72.9 (PhCH₂), 64.9 (ArCH₂), 60.3 (CH₂), 51.3 (N(CH₃)₂), 35.6 (C(CH₃)₃), 34.4 (C(CH₃)₃), 31.8 (C(CH₃)₃), 30.7 (C(CH₃)₃).

1b/B(C₆F₅)₃. One equivalent of B(C₆F₅)₃ was added to **1b** in *d*₅-chlorobenzene. ¹H NMR (C₆D₅Cl): δ 7.72 (d, *J* = 2.2 Hz, 2H), 7.67 (d, *J* = 7.6 Hz, 2H), 7.40–7.15 (m, 4H), 7.09 (t, *J* = 7.6 Hz, 4H), 6.94 (t, *J* = 7.2 Hz, 2H), 3.82 (d, *J* = 13.6 Hz, 2H, ArCH₂), 3.50 (br s, 2H, PhCH₂B), 3.43 (d, *J* = 13.6 Hz, 2H, ArCH₂), 2.72 (m, 2H, CH₂), 2.13 (s, 6H, N(CH₃)₂), 3.12 (s, 2H, PhCH₂Hf), 1.63 (s, 18H, C(CH₃)₃), 1.45 (s, 18H, C(CH₃)₃), 1.7–1.5 (m, 4H, CH₂). ¹⁹F NMR (C₆D₅Cl): δ –130.08 (*o*), –164.16 (*p*), –166.89 (*m*).

Complex 2b. Crystal data are presented in Table 8. Anal. Calcd for C₄₇H₆₅NO₃Hf: C, 64.85; H, 7.53; N, 1.61. Found: C, 64.97; H, 7.58; N, 1.86. ¹H NMR (C₆D₆): δ 7.65 (d, *J* = 7.6 Hz, 2H), 7.63 (d, *J* = 2.3 Hz, 2H), 7.37 (t, *J* = 7.6 Hz, 2H), 6.99 (t, *J* = 7.3 Hz, 1H), 6.92 (d, *J* = 7.6 Hz, 2H), 6.89 (d, *J* = 2.3 Hz, 2H), 6.81 (t, *J* = 7.6 Hz, 2H), 6.58 (t, *J* = 7.4 Hz, 1H), 3.55 (d, *J* = 13.4 Hz, 2H, ArCH₂), 2.61 (d, *J* = 13.5 Hz, 2H, ArCH₂), 2.58 (s, 2H, PhCH₂), 2.52 (s, 3H, OCH₃), 2.45 (s, 2H, PhCH₂), 2.20 (t, *J* = 5.4 Hz, 2H, CH₂), 1.86 (t, *J* = 5.3 Hz, 2H, CH₂), 1.83 (s, 18H, C(CH₃)₃), 1.36 (s, 18H, C(CH₃)₃). ¹³C NMR (C₆D₆): δ 158.3, 149.0, 148.3, 140.9, 137.2, 128.7, 127.5, 124.8, 124.7, 122.1, 120.9, 75.0 (PhCH₂), 73.6 (CH₂), 73.1 (PhCH₂), 65.0 (ArCH₂), 61.4 (OCH₃), 50.7 (CH₂), 35.3 (C(CH₃)₃), 34.4 (C(CH₃)₃), 32.0 (C(CH₃)₃), 30.3 (C(CH₃)₃).

Complex 3b. Crystal data are presented in Table 8. Anal. Calcd for C₄₇H₆₅NO₂HfS: C, 63.67; H, 7.39; N, 1.58. Found: C, 63.65; H, 7.43; N, 1.84. ¹H NMR (C₆D₆): δ 7.67 (d, *J* = 7.5 Hz, 2H), 7.61 (s, 2H), 7.36 (t, *J* = 7.5 Hz, 2H), 6.97 (m, 1H), 6.94 (d, *J* = 7.6 Hz, 2H), 6.89 (s, 2H), 6.81 (t, *J* = 7.5 Hz, 2H), 6.59 (t, *J* = 7.1 Hz, 1H), 3.53 (d, *J* = 13.5 Hz, 2H, ArCH₂), 2.85 (s, 2H, PhCH₂), 2.57 (d, *J* = 13.5 Hz, 2H, ArCH₂), 2.51 (s, 2H, PhCH₂), 2.07 (m, 2H, CH₂), 1.84 (s, 18H, C(CH₃)₃), 1.35 (s, 18H, C(CH₃)₃), 1.38–1.30 (m, 2H, CH₂), 0.97 (s, 3H, SCH₃). ¹³C NMR (C₆D₆): δ 158.2, 148.7, 148.4, 141.3, 137.5, 128.6, 128.3, 127.5, 125.2, 124.9, 124.6, 122.1, 121.0, 74.3 (PhCH₂), 70.4 (PhCH₂), 64.9 (ArCH₂), 54.1 (CH₂), 35.5 (CH₂), 34.4 (C(CH₃)₃), 33.1 (C(CH₃)₃), 31.9 (C(CH₃)₃), 30.5 (C(CH₃)₃), 14.4 (SCH₃).

3b/B(C₆F₅)₃. One equivalent of B(C₆F₅)₃ was added to **1a** in *d*₅-chlorobenzene. ¹H NMR (C₆D₅Cl): δ 7.69 (d, *J* = 2.0 Hz, 2H), 7.59 (d, *J* = 7.2 Hz, 2H), 7.41–7.15 (m, 4H), 7.09 (t, *J* =

7.6 Hz, 4H), 6.93 (t, *J* = 7.2 Hz, 2H), 3.89 (d, *J* = 13.8 Hz, 2H, ArCH₂), 3.52 (brs, 2H, PhCH₂B), 3.38 (d, *J* = 13.89 Hz, 2H, ArCH₂), 2.91 (s, 2H, PhCH₂Hf), 2.71 (m, 2H, CH₂), 2.07 (m, 2H, CH₂), 1.73 (s, 3H, SCH₃), 1.61 (s, 18H, C(CH₃)₃), 1.47 (s, 18H, C(CH₃)₃). ¹⁹F NMR (C₆D₅Cl): δ –130.71 (*o*), –164.21 (*p*), –166.91 (*m*).

Polymerization of Neat 1-Hexene. A solution of B(C₆F₅)₃ (ca. 0.01 mmol) in 1-hexene was added dropwise to solutions of **1a–3a** and **1b–3b** (0.01 mmol) in 1-hexene at room temperature under a nitrogen atmosphere. The reaction mixture was stirred for 2–10 min, during which time heat evolved, boiling the 1-hexene. The remaining monomer was removed under vacuum to yield atactic poly(1-hexene) as a colorless sticky oil. ¹H NMR (CDCl₃): δ 1.23 (br s, 8H, CH₂), 1.06 (br s, 1H, CH), 0.89 (t, *J* = 5.6 Hz, 3H, CH₃). ¹³C NMR (CDCl₃): δ 40.95 (br, CH₂), 35.04 (br, CH₂), 32.99 (CH), 29.39 (CH₂), 29.03 (CH₂), 24.01 (CH₂), 14.94 (CH₃).

Polymerization of 1-Hexene Diluted in Heptane. A solution of B(C₆F₅)₃ (ca. 0.006 mmol) in 1-hexene (2 mL) and heptane (3 mL) was added dropwise to solutions of **1a–3a** and **1b–3b** (0.006 mmol) in 1-hexene (1 mL) and heptane (4 mL) at room temperature under a nitrogen atmosphere. The reaction mixture was stirred for 10 min to 2 h, during which time evolution of heat was moderate. The solvents were removed under vacuum to yield poly(1-hexene) as a colorless sticky oil.

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Supporting Information Available: Tables of atomic coordinates, bond distances and angles for **2a**, **3a**, **1b**, and **3b**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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