Controlled Benzylation of α-Diimine Ligands Bound to Zirconium and Hafnium: An Alternative Method for Preparing Mono- and Bis(amido)M(CH_2Ph)$_n$ (n = 2, 3) Complexes as Catalyst Precursors for Isospecific Polymerization of α-Olefins

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Reactions of M(CH_2Ph)$_4$ (M = Zr, Hf) with various α-diimine ligands afforded amido-imino or diamido complexes through intramolecular benzylation of the C═N bonds of the ligands. Selective benzylation of α-diimine ligands, i.e., single- and double-benzylation, was accomplished by varying the substituent on the nitrogen atom of the imine moiety or the ligand backbone. Kinetic analysis of the second benzylation step indicated that the benzyl group migrated from the metal center to the C═N moiety via an ordered four-center transition state ($\Delta S^{\ddagger} = -3(4)$ eu for **3a**; $-5(9)$ eu for **5b**). Upon activation with B(C_6F_5)$_3$ or [Ph_3C][B(C_6F_5)$_4$], amido-imino (**3**, **6**) and diamido (**2**, **4**) complexes became active catalysts for 1-hexene polymerization, and the resulting poly(1-hexene)s had moderate isotacticity ([*mmmm*], up to 90%). Polymerization of vinylcyclohexane was also catalyzed with moderate activity to give highly isotactic poly(vinylcyclohexane) ([*mmmm*] > 95%) via a chain-end control mechanism.

Introduction

Recent progress in homogeneous α-olefin polymerization catalysts has been focused on the development of nonmetallocene-type catalysts with flexibly tunable multidentate ligands.[1] Because the catalytic activity as well as the regio- and stereoselectivity of the polymerization reaction can be controlled by modifying the ligand architecture, the simple preparation of various precatalysts is desirable. Among the wide variety of ligand types, amido- or imine-based ligands have attracted much interest because precise steric and electronic control is possible by changing the substituents at the nitrogen atoms of the ligands.[2] The high-throughput screening method developed by Dow and Symyx for screening polymerization precatalysts uses mainly an amine elimination reaction: the reaction of group 4 metal-amide complexes with various amine ligands, which produce amido metal complexes, has been applied to finely optimize pyridyl-amide-based group 4 metal catalysts with unprecedented unique polymerization behavior.[3] Another promising methodology for convenient synthesis of the catalysts is an alkylation reaction of the C═N bond of ligand precursors, such as commercially available carbodiimides or imine-based compounds easily designed by the condensation of amines and aldehydes. The alkylation approach is controlled by selective alkylation of the C═N bond of the ligands to give amido-metal or imino-metal species. Sita et al. demonstrated one-pot syntheses of Cp(amidinate)MR_2 (M = group 4 metal) complexes by treating $CpMR_3$ with appropriate carbodiimides via the insertion of metal-alkyl into the C═N bond of carbodiimides.[4] We investigated a selective alkylation reaction of the C═N bond in a pyrrole-imine ligand motif and found that benzylation of the C═N bond of the ligand could be controlled by varying the scaffold of the pyrrole-imine ligand (bidentate or tridentate) or the steric bulkiness on the nitrogen atom of the imine moiety. This method allowed us to isolate a variety of group 4 metal dibenzyl complexes having pyrrolyl-imine, pyrrolyl-amido, and pyrrolyl-amido-imine ligands in a one-pot procedure.[5,6] Controlled alkylation of the C═N bond in a ligand motif by alkylmetal complexes is one rational method to access a variety of catalyst precursors supported by amido or imine moieties, and such a controlled alkylation was reported for pyridine-bis(imine), tetradentate phenol-imine, and bi/terpyridine ligand systems of early transition metals, lanthanides, and main group metals.[7]

Recently, we and the group at Dow Chemical independently reported that the reaction of M(CH_2Ph)$_4$ (M = Zr, Hf) with neutral α-diimine ligands produces various tribenzyl complexes supported by monoanionic amido-imino ligands (types **A** and **B** in Chart 1), in which one C═N bond of the α-diimine ligand

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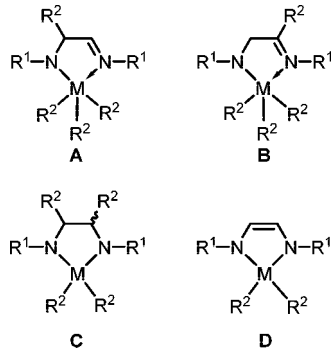
Chart 1



is selectively benzylated.[8,9] The research group at Dow Chemical also reported that thermolysis of the tribenzyl complexes having 2,6-disubstituted aromatic substituents on the nitrogen atom results in the formation of dibenzyl complexes with ene-diamido dianionic ligands (type **D**),[8] which is a typical coordination mode of α-diimine ligands to early transition metals.[10] Although several transformations of neutral α-diimine ligands to monoanionic amido-imino or dianionic ene-diamido ligands were accomplished, double alkylation of both C═N bonds to form a diamido ligand (type **C**) has not been reported. In the course of our studies on controlling alkylation of the C═N bond of α-diimine ligands, leading to various α-olefin polymerization catalyst precursors, we found that a rational modification of substituents on the nitrogen atom of α-diimine ligands led to the selective formation of monobenzylated products **A** and **B**, as well as double-benzylated product **C**. In this contribution, we report the selective transformation of various α-diimine ligands and $M(CH_2Ph)_4$ (M = Zr and Hf) to give amido-imino and bis(amido) complexes of zirconium and hafnium, and a kinetic study for estimating thermodynamic parameters in the second benzylation step of the double-benzylation reaction. The mono- and double-benzylated complexes are capable of catalyzing isospecific polymerization of 1-hexene and vinylcyclohexane and copolymerization of ethylene and 1-hexene.

Results and Discussion

Synthesis and Characterization of Zirconium and Hafnium Complexes. Treatment of the α-di(aldimine) ligand **1a** with $Zr(CH_2Ph)_4$ produced the double-benzylated bis(amido) complex **2a** in moderate isolated yield (eq 1). The ^{1}H NMR spectrum of **2a** in benzene-d_6 had a symmetric pattern with two sets of benzyl methylene protons: one was observed as an AB-type resonance due to the benzyl groups bound to the zirconium at δ 2.26 and 2.35 with a coupling constant of 10.2 Hz, and the other was displayed as mutually coupled methylene protons at δ 2.99 and 3.14 due to the benzyl groups that migrated into the two imine moieties of **1a**. A doublet of doublets centered at δ 4.47, coupled with the methylene protons of the benzyl group, was assigned to the methine proton adjacent to the nitrogen atom.[6,7] The $^1J_{C-H}$ value (129 Hz) of Zr*C*H_2Ph of **2a** indicated that the benzyl group coordinated to the zirconium atom of **2a** in an η^2-configuration in solution.[11]

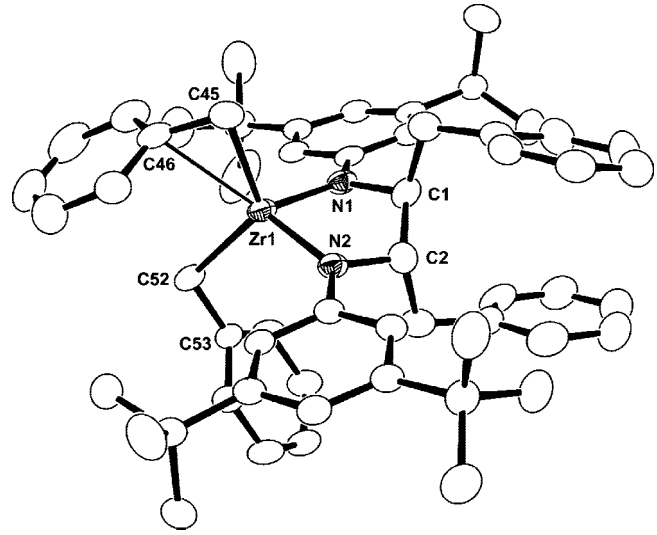


Figure 1. ORTEP drawing of the molecular structure of **2a**. All hydrogen atoms are omitted for clarity.

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

Zr−N1	2.044(2)	Zr−N2	2.037(2)
Zr−C45	2.275(3)	Zr−C46	2.585(3)
Zr−C52	2.289(3)	N1−C1	1.498(3)
N2−C2	1.488(3)	C1−C2	1.516(4)
N1−Zr−N2	88.43(8)	N1−Zr−C45	109.20(9)
N1−Zr−C52	109.48(10)	N2−Zr−C45	105.53(10)
N2−Zr−C52	113.64(9)	C45−Zr−C52	124.58(9)
Zr−C45−C46	84.76(16)	Zr−C52−C53	108.00(16)

The molecular structure of **2a** was clarified by X-ray crystallographic analysis (Figure 1), confirming the formation of a dianionic bis(amido) ligand by the double benzylation of both imine moieties of **1a** with an *anti*-stereochemistry. The zirconium atom adopted a pseudo-tetrahedral geometry. Although the two benzyl groups bound to zirconium are magnetically equal on the NMR time scale, an interaction between the *ipso* carbon of one benzyl group and the zirconium atom (Zr−C46, 2.585(3) Å; Zr−C45−C46, 84.76(16)°) was observed in the solid state.[5,6,12] The N1−C1 (1.498(3) Å) and N2−C2 (1.488(3) Å) bonds were in the normal range for a single bond, and the Zr−N(amido) bonds Zr−N1 (2.044(2) Å) and Zr−N2

(7) An alkylation of the C═N bond of a ligand backbone was reported in several cases. The use of pyridine-bis(imine) ligands: (a) Bruce, M.; Gibson, V. C.; Redshaw, C.; Solan, G. A.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **1998**, 2523. The use of tetradentate phenol-imine ligands: (b) Woodman, P. R.; Alcock, N. W.; Munslow, I. J.; Sanders, C. J.; Scott, P. *J. Chem. Soc., Dalton Trans.* **2000**, 3340. (c) Knight, P. D.; Clarke, A. J.; Kimberley, B. S.; Jackson, R. A.; Scott, P. *Chem. Commun.* **2002**, 352. (d) Knight, P. D.; O'Shaughnessy, P. N.; Munslow, I. J.; Kimberley, B. S.; Scott, P. *J. Organomet. Chem.* **2003**, *683*, 103. (e) Knight, P. D.; Clarkson, G.; Hammond, M. L.; Kimberley, B. S.; Scott, P. *J. Organomet. Chem.* **2005**, *690*, 5125. The use of bi-/terpyridine ligands: (f) Jantunen, K. C.; Scott, B. L.; Hay, P. J.; Gordon, J. C.; Kiplinger, J. L. *J. Am. Chem. Soc.* **2006**, *128*, 6322. (g) Masuda, J. D.; Jantunen, K. C.; Scott, B. L.; Kiplinger, J. L. *Organometallics* **2008**, *27*, 803. (h) Masuda, J. D.; Jantunen, K. C.; Scott, B. L.; Kiplinger, J. L. *Organometallics* **2008**, *27*, 1299.

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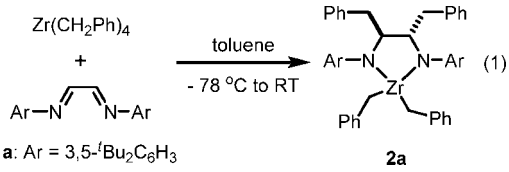
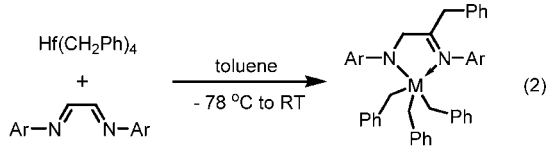
(2.037(2) Å) were within the range observed for zirconium−nitrogen single bonds.[13] Both amido nitrogen atoms (the sum of angles around the amido nitrogen atoms = 359.91° and 359.93°) were planar, thus resulting in the formation of a planar five-membered metallacyclic ring.



1a: Ar = 3,5-^{t}Bu$_2$C$_6$H$_3$ **2a**

In contrast to the reaction of $Zr(CH_2Ph)_4$, $Hf(CH_2Ph)_4$ reacted with the same ligand **1a** in toluene at −78 °C to give the corresponding monobenzylated complex **3a**, which was a product of the monobenzylation of one of two C=N bonds followed by intramolecular hydrogen transfer, the same as that observed for the reactions of $M(CH_2Ph)_4$ (M = Zr, Hf) with α-di(aldimine) ligands having a 2,6-disubstituted aryl ring.[8,9] Complex **3a** was thermally stable at room temperature, and no further benzylation reaction proceeded under mild conditions. Complex **3a** was characterized on the basis of its spectral data and combustion analysis. The ^{1}H NMR spectrum of **3a** in benzene-d_6 displayed rather simple singlet signals due to two benzyl methylene protons at δ 2.46 and 3.12, respectively, assignable to the benzyl groups bound to the hafnium atom and the benzyl group bound to the ligand in a 3:1 integral ratio. The resonance of methylene protons between the amido nitrogen and imine moiety was observed as a singlet at δ 4.52 with two-proton intensity.



1a: Ar = 3,5-^{t}Bu$_2$C$_6$H$_3$ **3a**

When the hexane solution of **3a** was heated to 110 °C for 5 h in a sealed tube, further benzylation of the other imine moiety of the ligand proceeded to afford bis(amido)hafnium complex **4a**. In the ^{1}H NMR spectrum, the resonances due to methylene protons bound to hafnium were observed at δ 2.08 and 2.18 as a typical AB*q* signal, whereas the methylene protons of the two benzyl groups inserted into the imine moiety were observed as a doublet of doublets centered at δ 2.87 ($^2J_{H-H}$ = 14.0 Hz and $^3J_{H-H}$ = 10.7 Hz) and 3.15 ($^2J_{H-H}$ = 14.0 Hz and $^3J_{H-H}$ = 3.6 Hz). The similarity of the ^{1}H NMR spectrum of **4a** to that of **2a** suggested that **4a** was a doubly benzylated bis(amido) complex. This result is in sharp contrast to that reported by Dow Chemical Company: thermolysis of a similar hafnium tribenzyl complex bearing 2,6-diisopropylphenyl groups at the nitrogen atoms afforded an ene-diamido complex (type **D** in Chart 1) via the elimination of two benzyl groups.[10] The mechanism for the conversion of **3a** to **4a** might involve pre-equilibrium of the 1,2-hydrogen shift before the second benzylation (Scheme 1). The differences between the two reaction patterns observed by us and the Dow Chemical group may be due to the steric bulkiness around the imine moiety; the less bulky aromatic ring of **1a** allowed for the second benzylation of the imine group of **3a**.

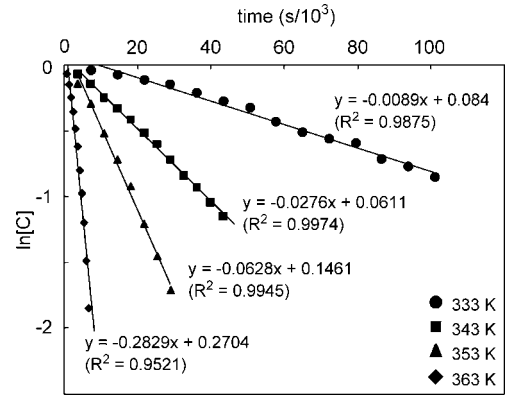


Figure 2. First-order thermal decomposition of **3a** at 333, 343, 353, and 363 K.

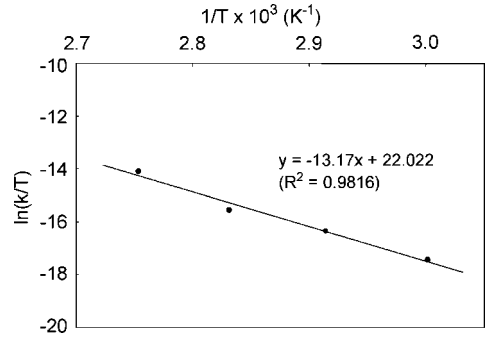
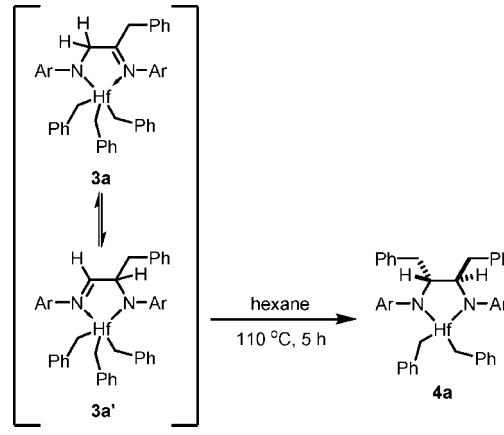


Figure 3. Eyring plot of the first-order thermal decomposition of **3a**.

Scheme 1



The intramolecular benzylation process from **3a** to **4a** obeyed first-order kinetics at 333, 343, 353, and 363 K (Figure 2), as determined by ^{1}H NMR spectroscopy. The corresponding Eyring plot afforded the thermodynamic parameters $\Delta H^{\ddagger}$ = 26(2) kcal mol^{-1} and $\Delta S^{\ddagger}$ = −3(4) eu (Figure 3). Scott et al. investigated the kinetics of thermolysis of dibenzylzirconium complexes containing a tetradentate phenoxyimine ligand, revealing that a simple insertion reaction of a benzyl group bound to zirconium into the imino moiety obeyed first-order kinetics with a negative $\Delta S^{\ddagger}$ value (Figure 4).[7d,14] A radical mechanism was accordingly

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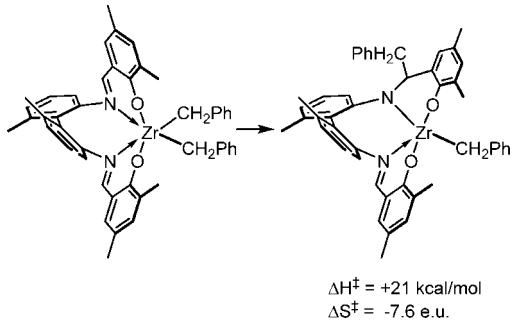
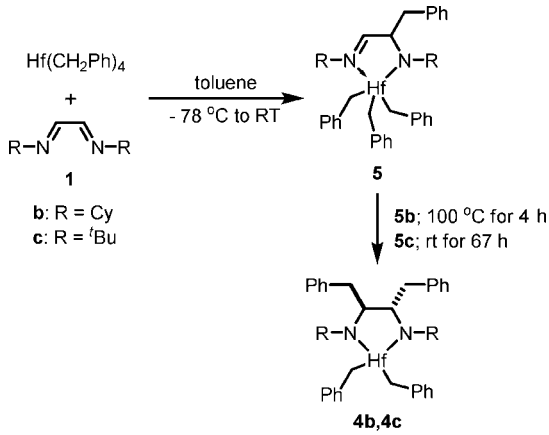


Figure 4. Thermal decomposition of dibenzylzirconium complexes having a tetradentate phenoxyimine ligand (from refs 7b−e).

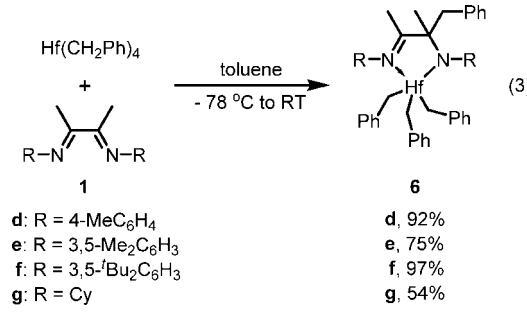
Scheme 2



ruled out because it had a positive $\Delta S^{\ddagger}$ value together with less selective formation of many products. Thus, the negative activation entropy observed in our case suggested that a concerted four-membered cyclic transition state occurred during the second benzylation of the nascent product **3a′**.

We previously reported that alkyl-substituted α-di(aldimine) ligands such as **1b** and **1c** react with $Hf(CH_2Ph)_4$ at −78 °C to give the corresponding monobenzylated complexes **5b** and **5c**.[8] We anticipated that the remaining C═N bond of **5b** and **5c** could react further with Hf-CH_2Ph. In fact, this reaction occurred under a high reaction temperature or a prolonged reaction time to give the corresponding double-benzylated complexes **4b** and **4c** (Scheme 2), which were spectroscopically characterized to have the same ligand backbone and benzyl groups as **2a** and **4a**, respectively. Kinetic analysis of the transformation from **5b** to **4b** was perfomed at 358, 363, 368, and 373 K, and similar to **3a**, the first-order rate constant was obtained for each temperature (Figure S1 in the Supporting Information), giving the activation parameters $\Delta H^{\ddagger} = 26(3)$ kcal/mol and $\Delta S^{\ddagger} = -5(9)$ eu (Figure S2 in the Supporting Information). Thus, benzyl migration from **5b** to **4b** also proceeded through an ordered cyclic transition state.

When the α-di(ketimine) ligands **1d**−**g** were used, monobenzylation proceeded smoothly to give the corresponding complexes **6d**−**g** in moderate to excellent yield (eq 3). In contrast to the reaction of α-di(aldimine) ligands, neither methyl migration nor double benzylation occur even upon heating the solution of **6f** at 100 °C overnight, being consistent with the fact that β-methyl elimination rarely proceeds via a C−C bond cleavage in early transition metal complexes.[15,16]



α-Olefin Polymerization Behavior of Zirconium and Hafnium Complexes. Zirconium and hafnium dibenzyl complexes **2** and **4** having C_2-symmetric chiral diamido ligands may act as isospecific catalyst precursors. This hypothesis was tested using these complexes as catalyst precursors for 1-hexene polymerization and combining them with $B(C_6F_5)_3$ or $[Ph_3C][B(C_6F_5)_4]$ as cocatalysts (Table 2). It is noteworthy that these dibenzyl complexes activated by cocatalysts catalyzed the polymerization of 1-hexene to afford isotactic-rich poly(1-hexene) (up to [*mmmm*] = 70% as determined by the ^{13}C NMR spectra of the polymers).[17] In the ^1H NMR spectra of the resulting polymer having a bimodal distribution, signals characteristic of the disubstituted vinylidene (around δ 4.7; arising from a β-hydrogen elimination after a 1,2-insertion) and the vinylene (around δ 5.4; arising from a β-hydrogen elimination after a 2,1-insertion) end groups were observed as main unsaturated end groups (Table 2, entry 5).[18] The ^1H NMR spectra of poly(1-hexene)s with a unimolecular weight distribution displayed the resonance (around δ 5.4) corresponding to the vinylene end groups (see the Supporting Information for the ^1H NMR spectrum of poly(1-hexene)s). The broadened polydispersity and the higher molecular weight compared to the calculated value based on the ratio of the catalyst and 1-hexene implied the polymerization occurred in an uncontrolled manner, which was presumably due to the rapid decomposition of the catalytically active cationic species or slow initiation compared to the propagation. Selection of the cocatalyst remarkably affected the polymerization activity of this catalyst system. The combination of dibenzyl complexes **2a** and **4a**−**c** with $B(C_6F_5)_3$ resulted in very low yield (up to 4% yield of poly(1-hexene), entries 1−5), whereas the combination of $[Ph_3C][B(C_6F_5)_4]$ with **4a** and **4b** afforded poly(1-hexene)s in moderate to good yields (entries 10−12). The tendency of the benzyl[tris(pentafluorophenyl)]borate anion to bind to a naked cationic metal center through η^6-coordination of the benzyl group[12c] dramatically retards the catalytic activity. When dibenzyl complexes were treated with $[Ph_3C][B(C_6F_5)_4]$ in the absence of 1-hexene, the cationic species was thermally sensitive and rapidly decomposed. In contrast, treatment of **2a** or **4a** with $B(C_6F_5)_3$ resulted in the formation of rather stable zwitterionic benzyl complexes in which coordination of the benzylborate anion to the metal center was confirmed by the $\Delta(m,p\text{-F})$ in the ^{19}F NMR spectra (eq 4).[19]

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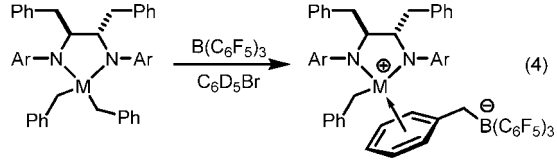
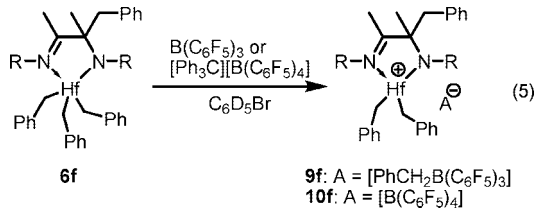
Table 2. 1-Hexene Polymerization Behavior of C_2-Symmetric Zirconium and Hafnium Complexes Activated with $B(C_6F_5)_3$ or $[Ph_3C][B(C_6F_5)_4]$[a]

entry	cat./cocat.[b]	temp (°C)	yield (%)	M_w ($\times 10^3$)[c]	M_w/M_n[c]	[*mmmm*] (%)[d]
1	**2a**/*B*	rt	3	bimodal	nd	nd
2	**4a**/*B*	rt	4	190	1.5	55
3	**4b**/*B*	rt	tr	nd	nd	nd
4	**4c**/*B*	rt	tr	nd	nd	nd
5	**2a**/*TB*	rt	28	bimodal	nd	nd
6[e]	**2a**/*TB*	−10	11	314	1.5	70
7	**4a**/*TB*	rt	37	365	1.5	45
8[e]	**4a**/*TB*	−10	54	451	1.5	55
9	**4b**/*TB*	rt	89	239	1.9	atactic
10[e]	**4b**/*TB*	−10	6	nd	nd	atactic
11	**4c**/*TB*	rt	20	245	1.6	55
12[e]	**4c**/*TB*	−10	23	361	1.3	50

[a] Conditions: [cat.]:[cocat.]:[1-hexene] = 0.01:0.01:5.0 (in mmol) in C_6H_5Cl for 6 h. Total volume is 2 mL. [b] *B* = $B(C_6F_5)_3$, *TB* = $[Ph_3C][B(C_6F_5)_4]$. [c] Determined by GPC. [d] Determined by ^{13}C NMR (ref 17). [e] Polymerization for 24 h.



Unexpectedly, C_s-symmetric hafnium tribenzyl complexes **6e**−**h** were much better precatalysts for the polymerization of 1-hexene (Table 3). The polymers obtained by **6**/$B(C_6F_5)_3$ or **6**/$[Ph_3C][B(C_6F_5)_4]$ had moderate to excellent isotacticity (up to [*mmmm*] = 90%), despite the broad molecular weight distribution. In the ^{13}C NMR of the poly(1-hexene), the signal of the C3 carbon derived from [*mrrm*]-pentad was not observed, and lowering the polymerization temperature to −20 °C increased the isotacticity, suggesting that stereoregularity resulted from the chain-end control. In contrast to the dibenzyl complexes **2a** and **4a**, both $B(C_6F_5)_3$ and $[Ph_3C][B(C_6F_5)_4]$ effectively activated complexes **6**, except for **6g**, to give poly(1-hexene) in excellent yield. As described in eq 5, the reactions of **6f** with these cocatalysts gave the corresponding ionic pairs **9f** and **10f**. In this case, the benzylborate anion of **9f** was separated from the metal center as confirmed by its ^{19}F NMR spectrum.



The molecular structure of **2a** suggested that the coordination environment around the metal atoms in complexes **2**−**6** was spacious enough to polymerize bulky monomers. We thus studied the polymerization of vinylcyclohexane (VCH), which is a monomer that is difficult to polymerize by homogeneous[20] and heterogeneous[21] catalysts due to the bulky cyclohexyl substituent next to the vinyl moiety. Among the runs shown in Table 4, the activity of tribenzyl complexes **3a** and **6f** was relatively high to give polymerized VCH (PVCH) in good yield. Measuring $^{13}C\{^1H\}$ NMR spectra of PVCHs, only six sharp peaks due to six different carbons of the highly isotactic polymer were observed (Figure S14 in the Supporting Information).[22] Recently, Sita et al. demonstrated living isospecific polymerization of VCH by half-sandwich zirconium acetamidinate catalysts, and Kol disclosed that the non-Cp-type zirconium complexes with amine-bis(phenolate) ligands catalyzed isospecific VCH polymerization with ultrahigh activity.[23] In all cases, the achiral C_s-symmetric precatalysts afford highly isotactic PVCHs, but the stereochemistry control mechanism is still not clear due to the absence of the peaks corresponding to the stereoerrors. Hafnium complexes **3a** and **6f**/$[Ph_3C][B(C_6F_5)_4]$ were found to be active catalysts for the copolymerization of ethylene/1-hexene (Table S1 in the Supporting Information), and there was relatively high 1-hexene incorporation (39%, determined by ^1H NMR[24]) in the catalyst system using **3a**.

Table 3. 1-Hexene Polymerization Behavior of Hafnium Tribenzyl Complexes Activated with $B(C_6F_5)_3$ or $[Ph_3C][B(C_6F_5)_4]$[a]

entry	cat./cocat.[b]	temp (°C)	yield (%)	M_w (10^3)[c]	M_w/M_n[c]	[*mmmm*] (%)[d]
1	**6d**/*B*	rt	88	45	2.3	65
2[e]	**6d**/*B*	−20	86	375	1.7	75
3	**6e**/*B*	rt	91	46	2.1	60
4[e]	**6e**/*B*	−20	86	187	6.5	80
5	**6f**/*B*	rt	91	24	2.3	60
6[e]	**6f**/*B*	−20	86	138	2.3	90
7	**6g**/*B*	rt	tr	nd	nd	nd
8	**6d**/*TB*	rt	88	102	4.0	30
9[e]	**6d**/*TB*	−20	90	385	2.3	80
10	**6e**/*TB*	rt	91	100	5.6	40
11[e]	**6e**/*TB*	−20	90	225	7.2	80
12	**6f**/*TB*	rt	92	30	2.4	60
13[e]	**6f**/*TB*	−20	92	179	1.7	90
14	**6g**/*TB*	rt	3	318	5.5	40

[a] Conditions: [cat.]:[cocat.]:[1-hexene] = 0.01:0.01:5.0 (in mmol) in C_6H_5Cl for 6 h. Total volume is 2 mL. [b] *B* = $B(C_6F_5)_3$, *TB* = $[Ph_3C][B(C_6F_5)_4]$. [c] Determined by GPC. [d] Determined by ^{13}C NMR (ref 17). [e] Polymerization for 24 h.

Table 4. Vinylcyclohexane Polymerization Behavior of Zirconium and Hafnium Complexes Activated with $[Ph_3C][B(C_6F_5)_4]$[a]

entry	cat.	temp (°C)	yield (%)	T_m (°C)[c]	[*mmmm*] (%)[d]
1	**2a**	rt	8		>95
2	**3a**	rt	64	339	>95
3	**4a**	rt	20		>95
4	**6f**	rt	87	347	>95

[a] Conditions: [cat.]:[cocat.]:[1-hexene] = 0.01:0.01:5.0 (in mmol) in C_6H_5Cl for 6 h. Total volume is 2 mL. [b] Determined by GPC. [c] Determined by DSC. [d] Determined by ^{13}C NMR (ref 22).

Conclusion

We demonstrated that the substituents on the nitrogen atoms of the α-diimine ligands significantly affected the following reaction pattern: (1) single benzylation of diaryl or dialkyl α-di(aldimine) ligands or diaryl α-di(ketimine) ligands, giving amido-imino complexes **3a**, **5**, and **6**, and (2) double benzylation

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of the bis(3,5-di(*tert*-butyl)phenyl)-α-di(aldimine) or dialkyl-α-di(aldimine) ligands, giving bis(amido) complexes **2** and **4**. Some of these complexes serve as catalyst precursors for isospecific polymerizations of 1-hexene and VCH and copolymerization of ethylene and 1-hexene polymerization upon activation by the appropriate cocatalysts. Thus, in addition to salt-, amine-, and alkane-eliminations, alkylation of the C═N bonds of neutral ligands by starting alkyl complexes is a convenient alternative method for preparing a wide variety of early transition metal complexes, due to the easy alkylation of polarized unsaturated C═N bonds bound to early transition metals.

Experimental Section

General Procedures. All manipulations involving air- and moisture-sensitive organometallic compounds were carried out under argon using the standard Schlenk technique or an argon-filled glovebox. $B(C_6F_5)_3$ was purchased and used as received. Compounds $[Ph_3C][B(C_6F_5)_4]$,[25] $Zr(CH_2Ph)_4$, and $Hf(CH_2Ph)_4$[26,27] and 1,4-diaza-1,3-butadiene ligands[28] were prepared according to the literature. Hexane and toluene were dried and deoxygenated by distillation over sodium benzophenone ketyl under argon. 1-Hexene and vinylcyclohexane were distilled from sodium benzophenone ketyl and then distilled over CaH_2 by trap-to-trap distillation, stored in glovebox. Chlorobenzene was distilled over CaH_2 by trap-to-trap distillation, stored in glovebox. Benzene-d_6, bromobenzene-d_5, and toluene-d_8 were distilled from P_2O_5 and thoroughly degassed by trap-to-trap distillation before use.

^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were measured on a Varian-Unity-Inova-300 spectrometer. Assignments for ^{1}H and ^{13}C NMR peaks for all complexes were aided by 2D ^{1}H−^{1}H COSY and 2D ^{1}H−^{13}C HETCOR spectra, respectively. The gel permeation chromatographic analyses were carried out at 40 °C by using a Shimadzu LC-10A liquid chromatograph system and a RID 10A refractive index detector, equipped with a Shodex KF-806 L column, which was calibrated versus commercially available polystyrene standards (Showa Denko). Thermal analyses of the polymers were made on a Seiko DSC 6200 under an N_2 atmosphere. The samples were heated to 400 °C. The DSC curves were recorded at a heating rate of 10 °C min^{-1}.

Preparation of (3,5-^{t}Bu$_2$Ph-DAB-(CH$_2$Ph)$_2$)Zr(CH$_2$Ph)$_2$ (2a). To a solution of $Zr(Ch_2Ph)_4$ (542 mg, 1.19 mmol) in toluene (10 mL) cooled to − 78 °C was added a solution of ligand **1a** (514 mg, 1.19 mmol) in toluene (10 mL). The reaction mixture was allowed to warm to room temperature and then stirred overnight. The color of the solution turned to red-orange. After removal of insoluble products by centrifugation, all volatiles were removed in vacuo. The resulting red-orange solid was dissolved in hexane (7 mL) and stored in a freezer (−30 °C). Orange microcrystals were formed and dried under vacuum to give **2a** (614 mg, 0.691 mmol, 58% yield), mp 125−130 °C. ^{1}H NMR (300 MHz, C_6D_6, 35 °C): δ 1.26 (s, 36H, C(CH$_3$)$_3$), 2.26 (d, 2H, ^2J = 10.2 Hz, ZrCHHPh), 2.35 (d, 2H, ^2J = 10.2 Hz, ZrCHHPh), 2.99 (dd, 2H, ^2J = 13.7 Hz, ^3J = 10.2 Hz, CHHPh), 3.14 (dd, 2H, ^2J = 13.7 Hz, ^3J = 4.1 Hz, CHHPh), 4.47 (dd, 2H, ^3J = 4.1, 10.2 Hz, NCH), 6.80 (d, 4H, ^4J = 1.6 Hz, NC$_6$H$_3$^{t}Bu$_2$-m), 6.81−7.18 (m, 20H, aromatics), 7.24 (t, 2H, ^4J = 1.6 Hz, NC$_6$H$_3$^{t}Bu$_2$-p). ^{13}C NMR (75 MHz, C_6D_6, 35 °C): δ 31.8 (CH$_3$), 35.3 (C(CH$_3$)$_3$), 42.9 (CH$_2$Ph), 63.7 (t, $^1J_{C-H}$ = 129 Hz, ZrCH$_2$Ph), 65.5 (d, $^1J_{C-H}$ = 136 Hz, NCH), 111.0, 116.4, 123.0, 126.2, 126.4, 128.5, 129.6, 131.2, 139.9, 143.2, 149.6, 153.1. Anal. Calcd for $C_{58}H_{72}N_2Zr$: C, 78.41; H, 8.17; N, 3.15. Found: C, 78.07; H, 7.90; N, 3.25.

Preparation of (3,5-^{t}Bu$_2$Ph-DAB-CH$_2$Ph)Hf(CH$_2$Ph)$_3$ (3a). In a Schlenk tube, $Hf(CH_2Ph)_4$ (1.10 g, 2.02 mmol) was dissolved in toluene (10 mL) at room temperature. The solution was cooled to −78 °C, and a solution of ligand **1a** (873 mg, 2.02 mmol) in toluene (5 mL) was added. The reaction mixture was allowed to warm to room temperature and then stirred overnight. The color of the solution turned orange. After removal of insoluble products by centrifugation, all volatiles were removed in vacuo. The resulting orange oil was dissolved in hexane (3 mL) and stored in a freezer (−30 °C). Yellow microcrystals were formed and dried under vacuum to give **3a** (1.16 g, 1.19 mmol, 59% yield), mp 133−140 °C. ^{1}H NMR (300 MHz, C_6D_6, 35 °C): δ 1.31 (s, 18H, C(CH$_3$)$_3$), 1.45 (s, 18H, C(CH$_3$)$_3$), 2.46 (s, 6H, HfC*H*$_2$Ph), 3.12 (s, 2H, C*H*$_2$Ph), 4.52 (s, 2H, NCH$_2$), 6.58−6.63 (m, 2H, aromatics), 6.67 (d, 2H, ^4J = 1.6 Hz, NC$_6$*H*$_3$^{t}Bu$_2$-*o*), 6.86−7.01 (m, 11H, aromatics), 7.14 (m, 9H, aromatics), 7.29 (br t, 1H, NC$_6$*H*$_3$^{t}Bu$_2$-*p*), 7.39 (br t, 1H, NC$_6$*H*$_3$^{t}Bu$_2$-*p*). ^{13}C NMR (75 MHz, C_6D_6, 35 °C): δ 31.6 (CH$_3$), 32.0 (CH$_3$), 35.4 (*C*(CH$_3$)$_3$), 35.5 (*C*(CH$_3$)$_3$), 39.0 (*C*H$_2$Ph), 64.3 (NCH$_2$), 84.7 (Hf*C*H$_2$Ph), 112.0, 114.9, 122.1, 127.4, 127.9, 128.1, 128.2, 128.5, 128.6, 128.7, 128.9, 129.0, 143.1, 145.1, 151.5, 152.5, 189.8 (N═*C*). Anal. Calcd for $C_{58}H_{72}N_2Hf$: C, 71.40; H, 7.44; N, 2.87. Found: C, 71.49; H, 7.38; N, 2.95.

Preparation of (3,5-^{t}Bu$_2$Ph-DAB-(CH$_2$Ph)$_2$)Hf(CH$_2$Ph)$_2$ (4a). In a sealed Schlenk tube, **3a** (100 mg, 0.102 mmol) was dissolved in hexane (3 mL) at room temperature. The solution was stirred for 5 h at 110 °C. The color of the solution turned orange. After removal of insoluble products by centrifugation, all volatiles were removed in vacuo to give **4a** as a yellow-orange powder (89.5 mg, 91.7 μmol, 90% yield), mp 148−150 °C. ^{1}H NMR (300 MHz, C_6D_6, 35 °C): δ 1.46 (s, 36H, C(CH$_3$)$_3$), 2.08 (d, 2H, ^2J = 11.5 Hz, HfC*H*HPh), 2.18 (d, 2H, ^2J = 11.5 Hz, HfCH*H*Ph), 2.87 (dd, 2H, ^2J = 14.0 Hz, ^3J = 10.7 Hz, C*H*HPh), 3.15 (dd, 2H, ^2J = 14.0 Hz, ^3J = 3.6, CH*H*Ph), 4.55 (dd, 2H, ^3J = 3.6, 10.7 Hz, NC*H*), 6.80−7.24 (m, 26H, aromatics). ^{13}C NMR (75 MHz, C_6D_6, 35 °C): δ 31.8 (CH$_3$), 35.3 (*C*(CH$_3$)$_3$), 42.7 (*C*H$_2$Ph), 60.8 (d, $^1J_{C-H}$ = 138 Hz, NC*H*), 72.0 (t, $^1J_{C-H}$ = 126 Hz, Hf*C*H$_2$Ph), 111.0, 115.9, 123.7, 126.2, 127.2, 127.8, 128.6, 129.4, 130.8, 139.9, 150.2, 152.6.

Compounds **5b** and **5c** were prepared as described in the procedure for **3a**.

Preparation of (Cy-DAB-CH$_2$Ph)Hf(CH$_2$Ph)$_3$ (5b). Yield: 76%, mp 162−164 °C (dec). ^{1}H NMR (300 MHz, C_6D_6, 35 °C): δ 0.43−1.97 (m, 20H, cyclohexyl), 2.01 (d, 3H, ^2J = 12.1 Hz, HfCH*H*Ph), 2.06 (d, 3H, ^2J = 12.1 Hz, HfC*H*HPh), 2.54 (dd, 1H, ^2J = 13.5 Hz, ^3J = 7.4 Hz, CH*H*Ph), 2.85 (dd, 1H, ^2J = 13.5 Hz, ^3J = 3.8 Hz, C*H*HPh), 3.45 (m, 1H, cyclohexyl), 3.82 (m, 1H, cyclohexyl), 4.43 (ddd, 1H, ^3J = 1.7, 3.8, 7.4 Hz, NCH), 6.90−6.97 (m, 5H, aromatics), 7.05 (d, 6H, J = 7.1 Hz, *o*-Ph of HfCH$_2$*Ph*), 7.11−7.22 (m, 3H, aromatics), 7.28 (t, 6H, ^3J = 7.7 Hz, *m*-Ph of HfCH$_2$*Ph*), 7.71 (d, 1H, J = 1.7 Hz, N═CH). ^{13}C NMR (75 MHz, C_6D_6, 35 °C): δ 25.5 (CH$_2$), 25.6 (CH$_2$), 26.0 (CH$_2$), 26.3 (CH$_2$), 27.1 (CH$_2$), 27.2 (CH$_2$), 33.3 (CH$_2$), 34.3 (CH$_2$), 35.0 (CH$_2$), 35.8 (CH$_2$), 43.7 (*C*H$_2$Ph), 56.2, 61.8, 68.3 (N*C*H), 82.5 (Hf(*C*H$_2$Ph)), 121.7, 127.3, 127.4, 128.6, 128.8, 130.5, 137.1, 147.9, 178.2 (N═CH). Anal. Calcd for $C_{42}H_{52}N_2Hf$: C, 66.08; H, 6.87; N, 3.67. Found: C, 65.99; H, 7.15; N, 3.74.

Preparation of (^{t}Bu-DAB-CH$_2$Ph)Hf(CH$_2$Ph)$_3$ (5c). Yield: 41%, mp 90−92 °C (dec). ^{1}H NMR (300 MHz, C_6D_6, 35 °C): δ 1.01 (s, 9H, C(CH$_3$)$_3$), 1.13 (s, 9H, C(CH$_3$)$_3$), 2.39 (br, 6H, HfC*H*$_2$Ph), 2.67 (dd, 1H, ^2J = 13.2 Hz, ^3J = 11.3 Hz, CH*H*Ph), 3.09 (dd, 1H, ^2J = 13.2 Hz, ^3J = 5.5 Hz, C*H*HPh), 3.93 (ddd, 1H, ^3J = 2.7, 5.5, 11.3 Hz, NC*H*), 6.88−7.23 (m, 14H, aromatics), 7.28 (t, 6H, J = 7.4 Hz, HfCH$_2$C$_6$*H*$_5$-*m*), 7.83 (d, 1H, ^3J = 2.7 Hz, N═C*H*). ^{13}C NMR (75 MHz, C_6D_6, 35 °C): δ 30.0 (C(*C*H$_3$)$_3$), 31.0

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($C(CH_3)_3$), 46.6 (CH_2Ph), 57.7 ($C(CH_3)_3$), 59.9 ($C(CH_3)_3$), 63.9 ($Hf(CH_2Ph)$), 121.9, 122.0, 127.0, 127.7, 128.4, 129.0, 129.1, 138.9, 176.4 (N=C). Anal. Calcd for $C_{38}H_{48}N_2Hf$: C, 64.17; H, 6.80; N, 3.94. Found: C, 64.46; H, 7.11; N, 4.60.

Preparation of (Cy-DAB-$(CH_2Ph)_2$)Hf$(CH_2Ph)_2$ (4b). In a Schlenk tube, $Hf(Ch_2Ph)_4$ (309 mg, 0.551 mmol) was dissolved in toluene (5 mL) at room temperature. The solution was cooled to −78 °C, and a solution of Cy-DAB (125 mg, 0.551 mmol) in toluene (7 mL) was added. The reaction mixture was allowed to warm to room temperature and stirred overnight. Then the mixture was stirred for 4 h at 100 °C. After removal of insoluble products by centrifugation, all volatiles were evaporated to give **4b** as an orange powder (162 mg, 0.212 mmol, 39% yield), mp 162 °C (dec). ^{1}H NMR (300 MHz, C_6D_6, 35 °C): δ 0.76−2.09 (m, 20H, cyclohexyl), 2.06 (br, 4H, HfCH_2Ph), 2.82 (m, 2H, cyclohexyl), 2.91 (dd, 2H, ^2J = 13.7 Hz, ^3J = 9.9 Hz, C*H*HPh), 3.01 (dd, 2H, ^2J = 13.7 Hz, ^3J = 3.8 Hz, CH*H*Ph), 3.66 (dd, 2H, ^3J = 3.8, 9.9 Hz, NC*H*), 6.77−7.34 (m, 20H, aromatics). ^{13}C NMR (75 MHz, C_6D_6, 35 °C): δ 25.3 (CH_2), 26.0 (CH_2), 26.2 (CH_2), 33.7 (CH_2), 34.7 (CH_2), 43.7 (CH_2Ph), 60.0, 60.7 (N*C*H), 69.8 (Hf*C*H_2Ph), 109.7, 122.3, 126.0, 127.7, 128.5, 129.2, 129.5, 140.5, 145.2. Anal. Calcd for $C_{42}H_{52}N_2Hf$: C, 66.08; H, 6.87; N, 3.67. Found: C, 66.54; H, 7.01; N, 3.25.

Preparation of (^{t}Bu-DAB-$(CH_2Ph)_2$)Hf$(CH_2Ph)_2$ (4c). To a suspension of $Hf(Ch_2Ph)_4$ (581 mg, 1.07 mmol) in hexane (20 mL) cooled to −78 °C was added a solution of ^{t}Bu-DAB (180 mg, 1.07 mmol) in hexane (5 mL). The reaction mixture was allowed to warm to room temperature and then stirred for 67 h. The color of the solution turned yellow. After removal of insoluble products by centrifugation, all volatiles were removed under vacuum to give **4c** as a yellow powder (717 mg, 1.01 mmol, 94% yield), mp 82 °C (dec). ^{1}H NMR (300 MHz, C_6D_6, 35 °C): δ 1.13 (s, 18H, C(CH_3)$_3$), 1.89 (d, 2H, ^2J = 11.5 Hz, HfC*H*HPh), 2.17 (d, 2H, ^2J = 11.5 Hz, HfCH*H*Ph), 2.92 (dd, 2H, ^2J = 14.8 Hz, ^3J = 10.4 Hz, C*H*HPh), 3.00 (dd, 2H, ^2J = 14.8 Hz, ^3J = 3.3 Hz, CH*H*Ph), 3.58 (dd, 2H, ^3J = 3.3, 10.4 Hz, NC*H*), 6.87−7.31 (m, 20H, aromatics). ^{13}C NMR (75 MHz, C_6D_6, 35 °C): δ 29.8 (CH_3), 45.3 (CH_2Ph), 56.7 (N*C*H), 58.6 ($C(CH_3)_3$), 69.9 (Hf*C*H_2Ph), 122.2, 126.0, 127.6, 128.5, 129.0, 129.3, 140.5, 145.2. Anal. Calcd for $C_{38}H_{48}N_2Hf$: C, 64.17; H, 6.80; N, 3.94. Found: C, 64.18; H, 7.14; N, 4.48.

Preparation of (4-MeC_6H_4-^{Me}DAB-CH_2Ph)Hf$(CH_2Ph)_3$ (6d). In a Schlenk tube, $Hf(Ch_2Ph)_4$ (292 mg, 0.537 mmol) was dissolved in toluene (5 mL) at room temperature. The solution was cooled to −78 °C, and a solution of 4-MeC_6H_4-^{Me}DAB (299 mg, 0.649 mmol) in toluene (5 mL) was added. The reaction mixture was allowed to warm to room temperature and then stirred overnight. After removal of insoluble products by centrifugation, all volatiles were removed in vacuo. The resulting orange solid was washed with hexane to give **6e** as pale yellow microcrystals (397 mg, 0.492 mmol, 92% yield), mp 95 °C (dec). ^{1}H NMR (300 MHz, C_6D_6, 35 °C): δ 1.00 (s, 3H, N=CCH_3), 1.35 (s, 3H, NCCH_3), 1.92 (d, 3H, ^2J = 11.8 Hz, HfC*H*HPh), 2.05 (s, 3H, CH_3), 2.06 (d, 3H, ^2J = 11.8 Hz, HfCH*H*Ph), 2.27 (s, 3H, CH_3), 2.40 (d, 1H, ^2J = 14.3 Hz, C*H*HPh), 3.27 (d, 1H, ^2J = 14.3 Hz, CH*H*Ph), 6.00 (d, 2H, ^3J = 8.0 Hz, $NC_6H_4CH_3$), 6.60 (d, 6H, ^3J = 7.1 Hz, *o*-Ph of HfCH_2*Ph*), 6.82 (d, 2H, ^3J = 8.0 Hz, $NC_6H_4CH_3$), 6.92 (t, 3H, ^3J = 7.1 Hz, *p*-Ph of HfCH_2*Ph*), 6.99−7.36 (m, 9H, aromatics), 7.19 (t, 6H, ^3J = 7.1 Hz, *m*-Ph of HfCH_2*Ph*). ^{13}C NMR (75 MHz, C_6D_6, 35 °C): δ 19.7 (*C*H_3), 20.7 (*C*H_3), 20.9 (*C*H_3), 25.5 (*C*H_3), 44.5 (*C*H_2Ph), 79.1 (N*C*), 85.2 (Hf(*C*H_2Ph)), 121.7, 122.7, 127.7, 127.9, 128.4, 129.3, 129.5, 130.1, 130.5, 131.4, 135.3, 136.0, 137.7, 144.8, 145.6, 147.5, 194.0 (N=*C*). Anal. Calcd for $C_{46}H_{48}N_2Hf$: C, 68.43; H, 5.99; N, 3.47. Found: C, 67.98; H, 6.25; N, 3.51.

Compounds **6e**−**g** were prepared as described in the procedure for **6d**.

Preparation of (3,5-$Me_2C_6H_3$-^{Me}DAB-CH_2Ph)Hf$(CH_2Ph)_3$ (6e). Yield: 75%, mp 108 °C (dec). ^{1}H NMR (300 MHz, C_6D_6, 35 °C): δ 1.08 (s, 3H, N=CCH_3), 1.39 (s, 3H, NCCH_3), 1.96 (d, 3H, ^2J = 11.8 Hz, HfC*H*HPh), 2.06 (s, 6H, CH_3), 2.12 (d, 3H, ^2J = 11.8 Hz, HfCH*H*Ph), 2.27 (s, 6H, CH_3), 2.43 (d, 1H, ^2J = 14.0 Hz, C*H*HPh), 3.45 (d, 1H, ^2J = 14.0 Hz, CH*H*Ph), 5.80 (br, 2H, aromatics), 6.63 (d, 6H, ^3J = 7.1 Hz, *o*-Ph of HfCH_2*Ph*), 6.63 (2H, aromatics overlapped with other resonance), 6.88 (s, 1H, $NC_6H_3Me_2$-*p*), 6.90 (t, 3H, ^3J = 7.1 Hz, *p*-Ph of HfCH_2*Ph*), 7.01 (s, 2H, $NC_6H_3Me_2$-*o*), 7.18 (t, 6H, ^3J = 7.1 Hz, *m*-Ph of HfCH_2*Ph*), 7.23−7.43 (m, 4H, aromatics). ^{13}C NMR (75 MHz, C_6D_6, 35 °C): δ 19.7 (CH_3), 21.1 (CH_3), 21.6 (CH_3), 25.5 (CH_3), 44.6 (*C*H_2Ph), 79.0 (NC), 85.1 (Hf(*C*H_2Ph)), 121.7, 127.9, 128.3, 129.0, 129.3, 129.5, 137.8, 139.3, 147.5, 147.7, 148.1, 193.6 (N=*C*). Anal. Calcd for $C_{48}H_{52}N_2Hf$: C, 69.01; H, 6.27; N, 3.35. Found: C, 68.64; H, 6.64; N, 3.39.

Preparation of (3,5-^{t}$Bu_2C_6H_3$-^{Me}DAB-CH_2Ph)Hf$(CH_2Ph)_3$ (6f). Yield: 97%, mp 193 °C (dec). ^{1}H NMR (300 MHz, C_6D_6, 35 °C): δ 1.17 (s, 3H, N=CCH_3), 1.26 (s, 18H, C(CH_3)$_3$), 1.42 (s, 18H, C(CH_3)$_3$), 1.56 (s, 3H, NCCH_3), 2.01 (d, 3H, ^2J = 12.4 Hz, HfC*H*HPh), 2.10 (d, 3H, ^2J = 12.4 Hz, HfCH*H*Ph), 2.51 (d, 1H, ^2J = 14.5 Hz, C*H*HPh), 3.52 (d, 1H, ^2J = 14.5 Hz, CH*H*Ph), 6.57 (d, 6H, ^3J = 7.4 Hz, *o*-Ph of HfCH_2*Ph*), 6.90 (t, 3H, ^3J = 7.4 Hz, *p*-Ph of HfCH_2*Ph*), 7.14−7.58 (m, 11H, aromatics), 7.17 (t, 6H, ^3J = 7.4 Hz, *m*-Ph of HfCH_2*Ph*). ^{13}C NMR (75 MHz, C_6D_6, 35 °C): δ 19.8 (CH_3), 26.0 (CH_3), 31.4 (C(*C*H_3)$_3$), 31.7 (C(*C*H_3)$_3$), 35.1 ($C(CH_3)_3$), 35.2 ($C(CH_3)_3$), 44.2 (*C*H_2Ph), 79.1 (NC), 85.2 (Hf(*C*H_2Ph)), 119.7, 120.0, 121.8, 126.3, 127.4, 127.8, 127.9, 128.4, 129.4, 129.5, 137.9, 147.2, 147.5, 147.7, 152.1, 152.8, 193.0 (N=C). Anal. Calcd for $C_{60}H_{76}N_2Hf$: C, 71.80; H, 7.63; N, 2.79. Found: C, 71.27; H, 8.18; N, 2.78.

Preparation of (Cy-^{Me}DAB-CH_2Ph)Hf$(CH_2Ph)_3$ (6g). Yield: 54%, mp 200 °C (dec). ^{1}H NMR (300 MHz, C_6D_6, 35 °C): δ 0.80−2.13 (m, 20H, cyclohexyl), 1.03 (s, 3H, N=CCH_3), 1.36 (s, 3H, NCCH_3), 2.21 (d, 3H, ^2J = 11.8 Hz, HfCH*H*Ph), 2.28 (d, 3H, ^2J = 11.8 Hz, HfC*H*HPh), 2.61 (d, 1H, ^2J = 14.3 Hz, CH*H*Ph), 2.82 (d, 1H, ^2J = 14.3 Hz, C*H*HPh), 3.28−3.46 (m, 2H, cyclohexyl), 6.91 (t, 3H, ^3J = 7.4 Hz, *p*-Ph of HfCH_2*Ph*), 7.02−7.22 (m, 5H, aromatics), 7.09 (d, 6H, ^3J = 7.4 Hz, *o*-Ph of HfCH_2*Ph*), 7.26 (t, 6H, ^3J = 7.4 Hz, *m*-Ph of HfCH_2*Ph*). ^{13}C NMR (75 MHz, C_6D_6, 35 °C): δ 19.7 (CH_3), 20.7 (CH_3), 20.9 (CH_3), 25.5 (CH_3), 44.5 (*C*H_2Ph), 79.1 (N*C*), 85.2 (Hf(*C*H_2Ph)), 121.7, 122.7, 127.7, 127.9, 128.4, 129.3, 129.5, 130.1, 130.5, 131.4, 135.3, 136.0, 137.7, 144.8, 145.6, 147.5, 194.0 (N=*C*). Anal. Calcd for $C_{44}H_{56}N_2Hf$: C, 66.78; H, 7.13; N, 3.54. Found: C, 66.64; H, 7.38; N, 3.56.

Observation of [(3,5-^{t}Bu_2Ph-DAB-$(CH_2Ph)_2$)Zr(CH_2Ph)]-[$PhCH_2B(C_6F_5)_3$] (7a). In a glovebox, to a solid mixture of **2a** (10 mg, 11 μmol) and $B(C_6F_5)_3$ (5.7 mg, 11 μmol) was added C_6D_5Br (0.60 mL) at −30 °C, and the solution was transferred to a J-Young NMR tube. The color of the solution gradually turned orange. The ^{1}H and ^{19}F NMR spectra of the solution at 25 °C revealed the quantitative formation of [(3,5-^{t}Bu_2Ph-DAB-$(CH_2Ph)_2$)-Zr(CH_2Ph)][$PhCH_2B(C_6F_5)_3$] (**7a**). ^{1}H NMR (300 MHz, C_6D_5Br, 25 °C): δ 1.29 (s, 18H, C(CH_3)$_3$), 1.30 (s, 18H, C(CH_3)$_3$), 2.35 (d, 1H, ^2J = 11.6 Hz, ZrC*H*HPh), 2.57 (d, 1H, ^2J = 11.6 Hz, ZrC*H*HPh), 2.73−2.90 (m, 2H, CH_2Ph), 2.95−3.15 (m, 2H, CH_2Ph), 3.57 (br, 2H, BCH_2Ph), 4.33−4.43 (m, 2H, NCH), 6.39−7.24 (aromatic protons). ^{19}F NMR (282 MHz, C_6D_5Br, 25 °C): δ −130.5 (d, 6F, J = 21.1 Hz, *ortho*), −160.7 (t, 3F, J = 21.1 Hz, *para*), −164.6 (m, 6F, *meta*).

Observation of [(3,5-^{t}Bu_2Ph-DAB-$(CH_2Ph)_2$)Hf(CH_2Ph)]-[$PhCH_2B(C_6F_5)_3$] (8a). In a glovebox, to a solid mixture of **4a** (10 mg, 11 μmol) and $B(C_6F_5)_3$ (5.7 mg, 11 μmol) was added C_6D_5Br (0.60 mL) at −30 °C, and the solution was transferred to a J-Young NMR tube. The color of the solution gradually turned orange. The ^{1}H and ^{19}F NMR spectra of the solution at 25 °C revealed the quantitative formation of [(3,5-^{t}Bu_2Ph-DAB-$(CH_2Ph)_2$)Hf-

$(CH_2Ph)][PhCH_2B(C_6F_5)_3]$ (**8a**). ^{1}H NMR (300 MHz, C_6D_5Br, 25 °C): δ 1.31 (s, 18H, $C(CH_3)_3$), 1.32 (s, 18H, $C(CH_3)_3$), 2.26 (d, 1H, ^2J = 12.6 Hz, HfC*H*HPh), 2.45 (d, 1H, ^2J = 12.6 Hz, ZrC*H*HPh), 2.54−2.75 (m, 2H, CH_2Ph), 2.85−3.20 (m, 2H, CH_2Ph), 3.65 (br, 2H, BCH_2Ph), 4.39−4.51 (dd, 1H, ^3J = 3.8, 11.0 Hz, NC*H*), 6.31−7.24 (aromatic protons). ^{19}F NMR (282 MHz, C_6D_5Br, 25 °C): δ −131.8 (d, 6F, *J* = 22.0 Hz, *ortho*), −161.8 (t, 3F, *J* = 21.4 Hz, *para*), −165.7 (m, 6F, *meta*).

Observation of [(3,5-^{t}Bu$_2$Ph-^{Me}DAB-CH$_2$Ph)Hf(CH$_2$Ph)$_2$]-[PhCH$_2$B(C$_6$F$_5$)$_3$] (9f). In a glovebox, to a solid mixture of **6f** (10 mg, 10 μmol) and $B(C_6F_5)_3$ (5.1 mg, 10 μmol) was added C_6D_5Br (0.60 mL) at −30 °C, and the solution was transferred to a J-Young NMR tube. The color of the solution gradually turned red. The ^{1}H and ^{19}F NMR spectra of the solution at 25 °C revealed the quantitative formation of [(3,5-^{t}Bu$_2$Ph-^{Me}DAB-CH$_2$Ph)Hf-(CH$_2$Ph)$_2$][PhCH$_2$B(C$_6$F$_5$)$_3$] (**9f**). ^{1}H NMR (300 MHz, C_6D_5Br, 25 °C): δ 1.29 (s, 18H, $C(CH_3)_3$), 1.32 (s, 18H, $C(CH_3)_3$), 1.40 (br, 1H, HfC*H*HPh), 1.54 (s, 3H, NCCH_3), 1.66 (br d, 1H, ^2J = 11.1 Hz, HfCH*H*Ph), 1.77 (br d, 1H, ^2J = 9.0 Hz, HfC*H*HPh), 1.99 (s, 3H, NCCH_3), 2.35 (br d, 1H, ^2J = 9.0 Hz, HfCH*H*Ph), 2.81 (d, 1H, ^2J = 15.0 Hz, C*H*HPh), 2.93 (d, 1H, ^2J = 15.0 Hz, CH*H*Ph), 3.36 (br, 2H, BCH_2Ph), 5.73 (br d, 2H, ^3J = 4.9 Hz, *o*-Ph of HfCH$_2$*Ph*), 5.89 (br d, 2H, ^3J = 6.5 Hz, *o*-Ph of HfCH$_2$*Ph*), 6.46−7.50 (aromatic protons). ^{19}F NMR (282 MHz, C_6D_5Br, 25 °C): δ −130.4 (d, 6F, *J* = 22.4 Hz, *ortho*), −164.3 (t, 3F, *J* = 21.2 Hz, *para*), −166.9 (m, 6F, *meta*).

Observation of [(3,5-^{t}Bu$_2$Ph-^{Me}DAB-CH$_2$Ph)Hf(CH$_2$Ph)$_2$]-[B(C$_6$F$_5$)$_4$] (10f). In glovebox, to a solid mixture of **6f** (10 mg, 10 μmol) and $[Ph_3C][B(C_6F_5)_4]$ (9.2 mg, 10 μmol) was added C_6D_5Br (0.60 mL) at − 30 °C, and the solution was transferred to a J-Young NMR tube. The color of the solution gradually turned yellow. The ^{1}H and ^{19}F NMR spectra of the solution at 25 °C revealed the quantitative formation of [(3,5-^{t}Bu$_2$Ph-^{Me}DAB-CH$_2$Ph)Hf-(CH$_2$Ph)$_2$][B(C$_6$F$_5$)$_4$] (**10f**) and Ph_3CCH_2Ph. ^{1}H NMR (300 MHz, C_6D_5Br, 25 °C): δ 1.40 (s, 18H, $C(CH_3)_3$), 1.43 (s, 18H, $C(CH_3)_3$), 1.54 (d, 1H, ^2J = 11.2 Hz, HfCH*H*Ph), 1.66 (s, 3H, N=CCH_3), 1.80 (d, 1H, ^2J = 11.2 Hz, HfCH*H*Ph), 1.89 (d, 1H, ^2J = 10.2 Hz, HfCH*H*Ph), 2.12 (s, 3H, NCCH_3), 2.45 (d, 1H, ^2J = 10.2 Hz, HfCH*H*Ph), 2.94 (d, 1H, ^2J = 14.9 Hz, C*H*HPh), 3.06 (d, 1H, ^2J = 14.9 Hz, C*H*HPh), 5.57 (br d, 2H, ^2J = 7.0 Hz, *o*-Ph of HfCH$_2$*Ph*), 6.01 (br d, 2H, ^2J = 5.7 Hz, *o*-Ph of HfCH$_2$*Ph*), 6.72−7.00 (aromatic protons). ^{19}F NMR (282 MHz, C_6D_5Br, 25 °C): δ −132.1 (d, 6F, *J* = 22.4 Hz, *ortho*), −162.8 (t, 3F, *J* = 21.2 Hz, *para*), −166.5 (m, 6F, *meta*).

Kinetic Study for the Thermal Decomposition. Complex **3a** (20.0 mg, 20.5 μmol) and Cp_2Fe (1.7 mg as an internal standard) were placed in a J-Young NMR tube, and toluene-d_8 (ca. 0.6 mL) was added. The tube was heated in an oil-bath at appropriate temperature (temperature regulated in the range of 1 K), and the ^{1}H NMR spectra were measured at 308 K. The initial concentrations were calculated with respect to the internal standard, and the disappearance of **3a** was monitored over 1−2 half-lives. Kinetic experiments were conducted at four different temperatures (333, 343, 353, and 363 K) to obtain separate reaction rates. First-order kinetics plots were generated by ploting time versus −ln(relative concentration). An Eyring plot was generated by plotting ln(rate constant/*T*) versus (1000/*T*). The activation energy and transition-state thermodynamic values were determined in the standard fashion. Observation of the thermal decomposition of **5b** was carried out at 358, 363, 368, and 373 K as described in the procedure for **3a**.

Polymerization of 1-Hexene. In a glovebox, a solution of precatalyst (10 μmol) in C_6H_5Cl (0.50 mL) was added to a solution of $B(C_6F_5)_3$ or $[Ph_3C][B(C_6F_5)_4]$ (10 mmol) and 1-hexene (0.62 mL) in C_6H_5Cl (0.88 mL). The reaction mixture was stirred for the appropriate temperature and time outside of a glovebox. The reaction was quenched by adding MeOH. The polymer was extracted with hexane, and the extract was purified by passing through silica gel. Polymer was obtained by evaporating hexane and dried at 60 °C. The isotacticity of the poly(1-hexene) was determined by the ^{13}C NMR measurement.[17]

Polymerization of Vinylcyclohexane. In a glovebox, a solution of precatalyst (10 μmol) in C_6H_5Cl (0.50 mL) was added to a solution of $[Ph_3C][B(C_6F_5)_4]$ (10 mmol) and vinylcyclohexane (0.68 mL) in C_6H_5Cl (0.82 mL). The reaction mixture was stirred for the appropriate temperature and time outside of a glovebox. The reaction was quenched by adding MeOH. After filtering and removal of the volatiles in vacuo, the crude product was dissolved in toluene. The solution was poured into a large excess of MeOH, and then white precipitates were collected by filtration and dried at 60 °C. The isotacticity of the poly(vinylcyclohexane) was determined by the ^{13}C NMR measurement.[22]

Copolymerization of Ethylene/1-Hexene. Under ethylene atmosphere (1 atm), a solution of precatalyst (10 μmol) in toluene (0.88 mL) was added to a solution of $[Ph_3C][B(C_6F_5)_4]$ and 1-hexene (0.62 mL) in toluene (8.5 mL). The reaction was quenched by adding MeOH, and then white precipitates were collected by filtration and dried at 60 °C. The 1-hexene content of the copolymer was determined by ^{1}H NMR measurement.[24]

X-ray Crystallographic Analysis. Single crystals were grown from a solution of hexane under argon atmosphere at ambient temperature. A yellow platelet crystal of $C_{58}H_{72}N_2Zr$ having approximate dimensions of 0.60 × 0.25 × 0.20 mm was mounted on a CryoLoop (Hampton Research Corp.) with a layer of light mineral oil and placed in a nitrogen stream at 120(1) K. All measurements were made on a Rigaku RAXIS RAPID imaging plate area detector with graphite-monochromated Mo Kα (0.71075 Å) radiation. Crystal data and structure refinement parameters are summarized in Table S2 (see Supporting Information).

The structure was solved by direct methods (SIR2004)[29] and refined on F^2 by full-matrix least-squares methods, using SHELXL-97.[30] Non-hydrogen atoms of $C_{58}H_{72}N_2Zr$ were anisotropically refined. H-atoms were included in the refinement on calculated positions riding on their carrier atoms. The function minimized was $[\sum w(F_o^2 - F_c^2)^2]$ ($w = 1/[\sigma^2(F_o^2) + (0.0548P)^2 + 0.0000P]$), where $P = (\mathrm{Max}(F_o^{2,0}) + 2F_c^2)/3$ with $\sigma^2(F_o^2)$ from counting statistics. The functions R1 and wR2 were $(\sum||F_o| - |F_c||)/\sum|F_o|$ and $[\sum w(F_o^2 - F_c^2)^2/\sum(wF_o^4)]^{1/2}$, respectively. The ORTEP-3 program[31] was used to draw the molecule.

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Supporting Information Available: Kinetic profile for **5b**, ^{1}H and ^{19}F NMR spectra of cationic species, ^{13}C NMR spectra of poly(1-hexene) and poly(vinylcyclohexane), table of ethylene/1-hexene copolymerization, ^{1}H NMR spectra of copolymer, and X-ray crystallographic file for **2a** in CIF format are included. These materials are available free of charge via the Internet at http://pubs.acs.org.

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