ORGANOMETALLICS

Synthesis and Scale-up of Imino–Enamido Hafnium and Zirconium Olefin Polymerization Catalysts

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ABSTRACT: New imino-enamido hafnium and zirconium trimethyl complexes were prepared in high yield by reacting a mixture of an imino-enamine ligand and hafnium or zirconium tetrachloride with four equivalents of methylmagnesium bromide in toluene. A significantly improved imine formation reaction in the final step of the ligand synthesis was developed that involves the reaction between the keto-enamine and a reagent formed *in situ* by mixing 0.55 equivalents of titanium tetrachloride and 5.5 equivalents of *n*-butylamine. Ethylene/1-octene polymerization evaluations at 120 °C revealed that polymerization characteristics of the imino-enamido hafnium and zirconium trimethyl derivatives were very similar to those of the tribenzyl analogues. A scale-up of the hafnium trimethyl derivative, performed on a 255 g scale, was accomplished in an overall yield of 57% in four steps starting with commercially available cyclohexa-1,2-dione. Hafnium and zirconium complexes derived from two isomeric imino-enamine ligands each resulted in very high molecular weight ethylene/1-octene copolymers, which differ significantly, however, in the level of incorporated octene. These features make these new catalysts good candidates for the preparation of olefin block copolymers via chain-shuttling polymerization.

INTRODUCTION

Molecular olefin polymerization catalysts¹ have attracted a lot of attention over the last 20 years due to their ability to produce tailored polyolefins. Research in this area has been motivated by the desire to discover new catalysts for the production of new polyolefin products² and to introduce improvements in the current polymerization processes.³ Recently we⁴ investigated catalysts based on an imino-amido ligand framework^{5,6} (e.g., 1) and discovered that such catalysts exhibit several desirable features including good catalytic activities at reactor temperatures above 100 °C, the ability to form very high molecular weight polymers, and the capability to undergo reversible chain transfer with diethylzinc to produce olefin block copolymers.^{4b} One major drawback inherent to these precatalysts, however, is their thermal instability, which results in the formation of isomeric complexes (by 1,2-Me shift) that exhibit inferior polymerization characteristics.^{4c} To eliminate decomposition pathways found in imino-amido complexes, we designed and prepared imino-enamido complexes (e.g., 2, 3) that are resistant to isomerization and decomposition at elevated temperatures.⁷ Imino-enamido complexes not only are thermally robust but exhibit higher catalytic activities and

produce ethylene/1-octene copolymers with higher molecular weight and 1-octene content than the imino-amido analogues.



The reported synthesis of imino–enamido complexes 2 and 3 is reproducible and effective,⁷ but it has some disadvantages for the larger scale preparation of such complexes. Herein, we report the preparation and olefin polymerization evaluation of trimethyl hafnium and zirconium analogues of 2 and 3 using a much improved synthetic protocol, the effectiveness of which

 Received:
 March 7, 2013

 Published:
 May 10, 2013

was subsequently demonstrated by a large-scale preparation of the hafnium analogue. Additionally, the synthesis and evaluation of complexes derived from the isomeric imino– enamine ligand are also described.

RESULTS AND DISCUSSION

Development of New Synthesis for Imino–Enamido Precatalysts. The original synthetic route we developed for the synthesis of imino–enamido complexes with different substituents at the imino and amido nitrogen atoms is shown in Scheme 1.⁷ Cyclohexa-1,2-dione (4) was condensed with



morpholine to afford the morpholine-based keto-enamine 5, which was subsequently transaminated with 2,6-diisopropylaniline to produce keto-enamine 6. The imine functionality was then installed by treating 6 with the titanium reagent 7, which in turn was prepared and isolated from the reaction of tetrakis(dimethylamino)titanium ($Ti(NMe_2)_4$) and an excess of *n*-butyl amine. Titanium-mediated imine formation was found to be necessary for synthesizing 8; when organic acids such as formic acid were used instead, a complete rearrangement of 8 to its isomeric imino-enamine 9 (with double-bond transposition) occurred. The desired precatalyst 2 was then obtained from the reaction of the ligand 8 with a metal precursor, tetrabenzylhafnium (HfBn₄).

Although this method is reliable and can be used for the preparation of imino–enamido analogues, it is not very practical for the larger scale synthesis of such precatalysts. There are several issues with the above synthesis including the need to prepare and isolate the discrete titanium–imido reagent 7 from the expensive precursor $Ti(NMe_2)_4$, very long (2 days) reaction times between keto–enamine 6 and 7 to form the desired ligand 8, difficult separation of the ligand 8 away

from the titanium by products, and the need to use an expensive metal precursor $({\rm HfBn}_4)$ in the final step of the synthesis.

We desired to develop a more cost-effective and practical synthesis of these precatalysts to accelerate our discovery and scale-up efforts. The two steps in the synthesis that required the most significant improvements were the last step in the ligand synthesis (imine formation) and the preparation of the metal complex. To improve the ligand synthesis, we focused our attention on an in situ preparation of the titanium reagent and its reaction with keto-enamine 6. The synthesis and utility of TiCl₄/amine reagents have been previously described by Carlson and Nilsson in the preparation of enamines⁸ and imines⁹ from carbonyl compounds. After an optimization of key reaction parameters, the best conditions identified involved the preparation of the titanium reagent from the reaction of 0.55 equivalents of TiCl₄ and 5.5 equivalents of *n*-BuNH₂ in toluene at ambient temperature (exothermic reaction) and its subsequent reaction with one equivalent of keto-enamine 6, which provided the desired ligand 8 in 96% yield in 3 h (Scheme 2). During the workup, a solution of 8 was stirred

Scheme 2. Improved Synthesis of Ligand 8



over K_2CO_3 to ensure removal of any acidic byproducts. This procedure provided 8 together with about 1 mol % of 9, the double-bond isomer of 8. This procedure is far superior to the one outlined in Scheme 1, as it is significantly less expensive, as well as easier and faster to execute.¹⁰

With the new straightforward synthesis of ligand 8 developed, we moved our attention to improving the metalation step to provide the final precatalyst. Since complexes containing metal-methyl bonds are often used as precatalysts for olefin polymerization, and methylating reagents are less expensive than benzylating reagents, we decided to explore the preparation and evaluation of the trimethyl analogue of complex 2. It was hoped that the switch from tribenzyl to trimethyl derivatives would result in catalysts exhibiting identical or very similar polymerization behavior.¹¹ To test this hypothesis, the hafnium trimethyl derivative 11 was prepared initially by the reaction sequence shown in Scheme 3. Reaction of iodine (three equivalents) with 2 in methylene chloride gave the desired hafnium triiodo derivative 10 in 83% yield. Complex 10 exhibits C_s symmetry in solution, as shown by NMR spectroscopy.¹² In addition to 1D and 2D NMR and elemental analysis, complex 10 was also characterized by singlecrystal X-ray analysis (vide infra). Reaction of 10 with three equivalents of MeMgBr in toluene led to clean formation of the desired trimethyl complex 11 in 99% yield. The ¹H NMR

Scheme 3. Synthesis of 11 by Two Different Routes



spectrum of 11 shows the characteristic singlet at 0.50 ppm, which is assigned to the protons of the three methyl groups bound to the hafnium metal center. Additionally, the ¹H NMR spectrum of 11 shows one *i*-Pr methine signal (at 3.46 ppm) and two doublets (at 1.21 and 1.42 ppm) corresponding to the i-Pr methyl groups, indicating that both i-Pr groups have the same chemical environment. This chemical shift pattern is the same as that observed in 2 except that all the resonances of 11 are shifted downfield by about 0.1-0.2 ppm. The appearance of two separate resonances for the *i*-Pr methyl groups is due to the hindered rotation of the 2,6-diisopropylphenyl fragment along the N-C(ipso) bond, which leads to a different chemical environment of the methyl groups pointed toward and away from the cyclohex-2-envlidene bridge. 1D NOESY experiments indicated that the upfield doublet (at 1.21 ppm) corresponds to the methyl groups pointing toward the bridge of the ligand. 1D TOCSY spectroscopy is very useful in characterizing these imino-enamido complexes, as it allows for unequivocal identification of the protons associated with the two separate spin systems of the cyclohex-2-envlidene and N-n-alkyl fragments. For example, irradiation of the triplet at 0.77 ppm corresponding to the methyl group of the butyl chain in 11 clearly identified the remaining protons of the butyl group resonances at 1.08, 1.34, and 3.34 ppm. In addition to 1D and 2D NMR spectroscopy, 11 was also characterized by elemental analysis and single-crystal X-ray analysis at 200 K (vide infra).¹³

A polymerization evaluation with 11 revealed that its catalytic characteristics are very similar to those of the tribenzyl analogue 2 (vide infra). The synthesis via the hafnium triiodo derivative 10 was adequate for providing a large enough sample of 11 for polymerization evaluations, but it was not sufficient for a larger scale preparation of this precatalyst due to its length and the expense of HfBn₄. This difficulty was overcome by the successful synthesis of 11 by a much simpler route involving the addition of four equivalents of MeMgBr to a suspension of 8 and $HfCl_4$ in toluene at ambient temperature (Scheme 3). The initially formed yellow suspension changed color within minutes to black, which is typical for this type of reaction. After a short reaction time $(\sim 1 h)$ the solvent was removed under reduced pressure, the product was extracted with hexane, and the resulting suspension was filtered to remove the insoluble salts. Precatalyst 11 was obtained in 79% yield as a bright

yellow crystalline solid in very high purity, as indicated by ¹H NMR spectroscopy. This one-step procedure is analogous to the one introduced by Resconi for the preparation of bismetallocene¹⁴ and CGC¹⁵ dimethyl complexes, whereby the respective ligands and $ZrCl_4/TiCl_4$ were reacted with four equivalents of MeLi in a toluene solution.

Synthesis of Complexes 12–14. The zirconium analogue **12** was also prepared using an analogous one-step procedure as shown in Scheme 4. The reaction of a mixture of ligand 8 and

Scheme 4. Synthesis of Complex 12



ZrCl₄ in toluene with four equivalents of MeMgBr gave the desired complex **12** in 96% yield after workup. The ¹H NMR spectrum of **12** is very similar to that of **11**, except for the chemical shift of the Zr(CH₃)₃ groups, which resonate at δ 0.74 ppm, 0.24 ppm downfield relative to the Hf(CH₃)₃ peak. Interestingly, the chemical shift trend is reversed in the ¹³C{¹H} NMR spectra, with Zr(CH₃)₃ resonating at 48.60 ppm and Hf(CH₃)₃ appearing downfield at 60.40 ppm. The remaining resonances in the ¹³C{¹H} spectra of **11** and **12** are very similar to each other.

Although hafnium tribenzyl analog containing the isomerized ligand 9 resulted in lower polymerization activities,⁷ it was of interest to us to determine if the trimethyl complexes could also be prepared from ligand 9 using the one-step procedure and what their detailed polymerization characteristics would be. A mixture of ligand 9 and HfCl₄ or ZrCl₄ was reacted with four equivalents of MeMgBr, giving the desired complexes 13 and 14 in 45% and 39% yield, respectively (Scheme 5). The lower

Scheme 5. Synthesis of Complexes 13 and 14



yields for these isomers arise from the formation of a small amount ($\sim 20\%$) of a second, unidentified product,¹⁶ which needs to be separated from the desired complexes by crystallization.

The ¹H NMR spectrum of 13 shows the same number of resonances with the same splitting patterns as its isomeric hafnium complex 11, but surprisingly there are substantial chemical shift differences observed for the respective protons in these two complexes. All resonances associated with the sixmembered ring and the *n*-butyl fragments in 13 are shifted downfield relative to those found in 11. For example, the chemical shifts of the double bond and methylene (α to the imine nitrogen atom) protons in 13 are shifted downfield by 0.53 and 0.33 ppm, respectively, compared to the same

resonances in 11, which appear at 4.66 and 3.34 ppm. On the other hand, all resonances (both aromatic and aliphatic) associated with the 2,6-diisopropylphenyl group are shifted upfield in 13 compared to those in 11. This upfield chemical shift is most likely due to magnetic anisotropic shielding induced by the imine bond, which is much closer to the 2,6-diisopropylphenyl group in 13 than the distance between the carbon–carbon double bond and 2,6-diisopropylphenyl group in 11. Very similar chemical shift differences are also observed for the zirconium analogues 12 and 14. The only resonances that are very similar between isomers 11/13 and 12/14 belong to the Hf(CH_3)₃ and Zr(CH_3)₃ fragments, respectively.

Single-Crystal X-ray Structures of 10–14. Molecular structures of 10, 11, and 13 are shown in Figures 1–3,



Figure 1. Molecular structure of **10**. Hydrogen atoms were removed for clarity. Thermal ellipsoids are shown at 40% probability. Selected bonds (Å) and angles (deg): Hf–N1 = 2.244(2), Hf–N2 = 2.046(2), Hf–I1 = 2.7388(2), Hf–I2 = 2.7620(2), Hf–I3 = 2.7350(2), C1–N1 = 1.300(3), C6–N2 = 1.412(3), C1–C2 = 1.498(3), C5–C6 = 1.343(3), N2–Hf–N1 = 73.08(7), N1–Hf1–I2 = 169.75(5).



Figure 2. Molecular structure of **11**. Hydrogen atoms were removed for clarity. Thermal ellipsoids are shown at 40% probability. Selected bonds (Å) and angles (deg): Hf-N1 = 2.3194(16), Hf-N2 = 2.1196(15), Hf-C23 = 2.214(2), Hf-C24 = 2.232(2), Hf-C25 = 2.222(2), C1-N1 = 1.288(2), C6-N2 = 1.397(2), C1-C2 = 1.504(3), C5-C6 = 1.343(3), N1-Hf-N2 = 70.81(5), N1-Hf1-C25 = 161.19(8).

respectively, and selected bond lengths and angles for 10-14 are presented in Table 1.¹⁷ Metric parameters obtained for 10-14 complexes clearly confirm the identity of the individual isomers originally established by 1D NOESY experiments. For



Figure 3. Molecular structure of **13**. Hydrogen atoms were removed for clarity. Thermal ellipsoids are shown at 40% probability. Selected bonds (Å) and angles (deg): Hf-N1 = 2.0998(13), Hf-N2 = 2.3550(13), Hf-C23 = 2.2153(17), Hf-C24 = 2.2150(17), Hf-C25 = 2.2774(16), C1-N1 = 1.379(2), C6-N2 = 1.297(2), C1-C2 = 1.355(2), C5-C6 = 1.500(2), N1-Hf-N2 = 69.34(5), N1-Hf1-C25 = 151.43(5).

example, the C5-C6 bond lengths of 1.343(3) and 1.345(3) Å for 11 and 12, respectively, clearly indicate the presence of the double bond in the cyclohex-2-envlidene fragment bonded to the N-Ar fragment. On the other hand, the C5-C6 bond lengths in 13 and 14 equal 1.500(2) and 1.498(2) Å, respectively, indicating the presence of a single bond. As expected, bond lengths and angles in tribenzyl complexes 2 and 3 are very similar to those found in trimethyl analogues 11 and 12. The zirconium analogues consistently have slightly longer bond lengths around the metal center than the hafnium analogues. The difference between the M-N(imino) and M-N(enamido) bond lengths in complexes 2, 3, 10, 11, and 12 falls within a narrow range of 0.198-0.213 Å, which is noticeably smaller than those found in complexes 13 and 14 (0.255–0.273 Å) containing isomerized ligand 9. Although the difference between the Hf-N(imino) and Hf-N(enamido) bond lengths in the triiodo derivative 10 is very similar (0.198 Å) to that found in the other complexes containing ligand 8, both Hf-N(imino) and Hf-N(enamido) bond lengths are shorter by about 0.05 Å than those in 2 and 11. Also, the N1-Hf(Zr)-C25 bond angles are 161.19(8)° and 156.68(7)° for 11 and 12, respectively, noticeably smaller than the analogous angle (N1-Hf-I2) in **10** (169.75(5)°).

Polymerization Results. Ethylene/1-octene copolymerization reactions were conducted in a 2 L batch reactor under constant ethylene pressure. Precatalysts were activated with 1.2 equivalents (relative to precatalyst) of [HNMe(C₁₈H₃₇)₂][B- $(C_6F_5)_4$]. All polymerization reactions were carried out for 10 min and stopped by venting the ethylene pressure. Polymerization data are shown in Table 2. The catalytic efficiency and molecular weight (M_w) of polymers produced by 11 and 12 are very comparable to those obtained with tribenzyl analogues 2 and 3 (runs 1-4). The efficiency for the hafnium-based catalysts (2, 11) is about 4 times higher than the zirconium analogues (3, 12). Octene incorporation, as determined by IR spectroscopy, decreases from about 7-8 mol % for the hafnium analogues to 5 mol % for the zirconium analogues. As anticipated from the previous study,⁷ the efficiency of the isomeric complexes 13 and 14 is lower than that observed for 11 and 12. Similarly, octene incorporation for 13 (2.5 mol %) and 14 (1.3 mol %) is significantly lower than that observed for

Table	1.	Bond	Lengths	(Å) and	Ang	les (deg)) for	: Comp	lexes	2,	3,	and	10-	-14	1
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bond/angle	10	2 ⁷	11	3 ⁷	12	13	14
Hf(Zr)–N1	2.244(2)	2.313(2)	2.3194(16)	2.332(2)	2.3357(13)	2.0998(13)	2.1077(11)
Hf(Zr)-N2	2.046(2)	2.100(2)	2.1196(15)	2.132(2)	2.1442(12)	2.3550(13)	2.3810(10)
$Hf(Zr)-C23^{18}$		2.243(2)	2.214(2)	2.266(2)	2.2339(18)	2.2153(17)	2.2361(14)
$Hf(Zr)-C24^{18}$		2.288(2)	2.232(2)	2.303(3)	2.2577(18)	2.2150(17)	2.2372(14)
$Hf(Zr) - C25^{18}$		2.266(2)	2.222(2)	2.286(2)	2.237(2)	2.2774(16)	2.2602(13)
C1-C2	1.498(3)	1.498(3)	1.504(3)	1.508(3)	1.504(2)	1.355(2)	1.3559(18)
C2-C3	1.522(4)	1.523(4)	1.472(6)	1.517(4)	1.497(3)	1.499(2)	1.4937(19)
C3-C4	1.521(4)	1.518(4)	1.457(6)	1.517(4)	1.505(3)	1.524(2)	1.5193(18)
C4–C5	1.502(3)	1.491(3)	1.502(3)	1.487(3)	1.502(2)	1.530(2)	1.5291(18)
C5-C6	1.343(3)	1.347(3)	1.343(3)	1.349(3)	1.345(2)	1.500(2)	1.4984(17)
C1-C6	1.461(3)	1.459(3)	1.469(2)	1.460(3)	1.4713(19)	1.466(2)	1.4700(17)
N1-C1	1.300(3)	1.290(3)	1.288(2)	1.290(3)	1.2874(19)	1.379(2)	1.3803(16)
N1-C7	1.485(3)	1.486(3)	1.475(2)	1.478(3)	1.4720(18)	1.463(2)	1.4606(15)
N2-C6	1.412(3)	1.403(2)	1.397(2)	1.399(3)	1.3962(18)	1.297(2)	1.2970(16)
N2-C11	1.455(3)	1.446(2)	1.444(2)	1.447(2)	1.4396(17)	1.4470(19)	1.4444(15)
N1-Hf(Zr)-N2	73.08(7)	72.03(6)	70.81(5)	71.21(6)	70.35(4)	69.34(5)	68.61(4)
C23-Hf(Zr)-C24		101.0(1)	109.55(9)	102.6(1)	109.36(7)	107.32(7)	108.35(6)
C24-Hf(Zr)-C25 ¹⁸		120.24(8)	96.30(11)	122.38(8)	94.87(9)	97.13(6)	97.34(5)
$C23-Hf(Zr)-C25^{18}$		98.03(9)	102.37(10)	98.22(9)	105.11(8)	97.21(6)	97.65(5)

Table (2. Pol	vmerization	Data :	for	Complexes	2.	3.	11 - 14	. and	CGC ^a
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run no.	catalyst (μ mol)	polymer yield (g)	efficiency (g of polymer/ mmol of metal)	$M_{\rm w} \times 10^{-3}/{\rm PDI}$	$T_{\rm m}$ (°C)	octene content (mol %) b
1	2 (0.2)	48.8	244 000	682/3.5	80.3	8.3
2	3 (0.2)	11.1	55 500	581/2.7	95.2	5.1
3	11 (0.2)	49.6	248 000	743/3.1	83.1	7.2
4	12 (0.2)	11.8	59 000	584/2.5	93.0	5.2
5	13 (0.8)	24.8	31 000	641/3.4	114.4	2.5
6	14 (0.8)	16.5	20 625	347/2.7	118.3	1.3
7	CGC (0.3)	82.2	411 000	100/2.2	52.8	15.9

^{*a*}Polymerization conditions: 2 L batch reactor, 533 g of Isopar-E; temp = 120 °C; 250 g of 1-octene; ethylene pressure = 460 psi; precatalyst:activator = 1:1.2; activator: [HNMe($C_{18}H_{37}$)₂][B(C_6F_5)₄]; 10 μ mol of MMAO; reaction time 10 min. ^{*b*}Determined by IR; CGC = {(⁵ η - C_5Me_4)(SiMe₂-N-*t*-Bu)}TiMe₂.

11 (7.2 mol %) and 12 (5.2 mol %). It is interesting that the complexes derived from ligands 8 and 9 comprise almost identical steric environments around the metal center and yet lead to copolymers with substantial differences in octene incorporation. Since imino-enamido complexes were previously found to undergo very effective chain transfer reactions with diethyl zinc,⁷ complexes 11-14 have potential utility for the preparation of olefin block copolymers via chain shuttling polymerization with variable density splits between hard and soft segments.^{2e,4b} Important to such chemistry is the ability of the catalysts to produce very high molecular weight copolymers. Molecular weights of copolymers produced by 11–14 are very high, with $M_{\rm w}$ values ranging between 350 000 and 750 000.¹⁹ Polydispersity indexes for the polymer samples obtained from all precatalysts are somewhat larger than 2, which is indicative of multisite catalyst behavior. The identity of the active species formed under catalytic conditions is unknown at the present time.

Scale-up of 11. When assessing the industrial viability of any catalyst, critical factors to consider include the ease and cost associated with obtaining large quantities of the desired species, along with the mitigation of any potential safety hazards. Additionally, many of the laboratory techniques that are typically utilized for smaller scale reactions (e.g., column chromatography, multiple solvent washes) are often undesirable for larger scale reactions, for which the simplicity of the

reaction workup is also an important criterion. For this reason, high-yielding and robust synthetic methodologies are usually sought prior to scale-up. In the present case, we wished to evaluate our optimized synthetic methodology by applying it to the preparation of a comparatively large amount (255 g) of 11 needed for pilot plant evaluations. Generally speaking, it is desired to reduce solvent volumes in order to concentrate the reagents and thereby speed up the product-forming reactions. However, it is also important to have an appropriate amount of solvent to accommodate the heat rise associated with an exothermic reaction. For the initial transformation $(4 \rightarrow 5)$, however, the calculated exotherm is negligible, and in fact the reaction requires external heat and water removal to proceed. Ultimately, a reaction concentration of 0.84 M in 4 was chosen, which led to a convenient reaction time of 3 h (Scheme 6). Subsequent to the reaction, the solution was cooled to room temperature, and immiscible dark oil settled at the bottom of the flask. This oil, presumably a small amount of decomposed cyclohexa-1,2-dione, is easily removed from the productcontaining solution by decantation. Removal of the solvent and trituration with hexane furnished 5 as an orange-brown solid in high purity and 95% yield. The material was carried along to the next step without further purification.

The second step in the scale-up, conversion of 5 into the keto-enamine derivative 6 (the transamination reaction), was carried out on a Schlenk line in a similar fashion to the previous

Scheme 6. Summary of the Large-Scale Synthesis of 11



71%

Step 3

5 (175.0 g)



6 (185.3 g)

step with the notable exception that a mechanical stirrer was used to ensure adequate mixing of the reaction mixture. In this case, lower than reflux temperatures were used, and the formation of a large quantity of precipitate (morpholino sulfonate) resulted in a thick slurry, which proved difficult to stir with magnetic stirring. This in turn resulted in a high degree of variability in the reaction times for the various test reactions. With a mechanical stirrer, and a concentration of 0.55 M in 5, the scale-up could be readily executed with reaction times of less than 2 h. Thermodynamics of this step are not a concern, as the transamination is expected to be close to thermoneutral, with the driving force being the precipitation of morpholino sulfonate byproduct. After workup and recrystallization, the desired species was isolated in good yield (71%) and excellent purity. A net yield for 6 of 185.3 g was obtained after recrystallization. While the product of this reaction forms very cleanly, the crude residue typically contains small amounts of 2,6-diisopropylaniline, which is a solubilizing agent and reduces yields. It is worth noting that it is important to isolate 6 in high purity, as the subsequent step yields an oil that is not amenable to easy purification and so must be carried through to the final metalation in essentially crude form.

The final step of the ligand synthesis (step 3), conversion of **6** into ligand **8**, requires the greatest caution from a thermochemistry standpoint. It has been described previously⁷ that undesirable acid-catalyzed isomerization of **8** can occur and is thermodynamically favored. Reaction conditions for this step were proven to work very well on a small scale, but there was a concern related to heat transfer differences and reaction and

workup times for the scale-up of this step since even a very small amount of acid can result in the rapid and irreversible isomerization of the product. It is not trivial to quantify the thermochemistry of this complicated reaction via calculation, so we opted to determine the reaction heat by measuring it directly during a small-scale reaction in a well-insulated reactor. A heat release of 8.9 cal/g of titanium was measured for the addition of TiCl₄ to n-BuNH₂, and 2.8 cal/g of 6 was measured for the reaction of 6 with the *in situ* generated titanium reagent. Considering this energy release, a 0.2 M solution of TiCl₄ in toluene was implemented for the scale-up step. Care must be taken to avoid the high temperatures that would be expected to accelerate the isomerization reaction $(8 \rightarrow 9)$. Upon the addition of 0.31 mol of TiCl₄ to a solution of 3.07 mol of n-BuNH₂ in 1.5 L of toluene, a temperature rise up to 60 °C was observed and the solution was allowed to cool back down to 30 °C before 6 was added. The product was isolated as an oil and was stored at -20 °C until used in the final step of the scale-up. Metalation of 8 was also carried out analogously to what has been described in a small-scale preparation of 11. One practical difference that arose during this step was that the addition of the Grignard reagent took about 1 h to complete (to maintain a reaction temperature of less than 40 °C). Analysis of the product 11 by ¹H NMR showed excellent purity with less than 2% of isomer 13, for a net yield of 255 g (92%). Very good yields were obtained in each synthetic step, with an overall yield for the four steps of 57%.

CONCLUSIONS

The main objectives of this work were to identify a new version of the original imino-enamido precatalyst, develop its practical and economical synthesis, and then apply it to its macroscale preparation. Polymerization results indicate that trimethyl complexes 11 and 12 exhibit very similar behavior to their tribenzyl analogues 2 and 3. The synthesis of 11 and 12 was accomplished via a much simpler and more economical route than that used in the preparation of the original iminoenamido complexes 2 and 3. The most significant improvement in the synthesis of the trimethyl complexes came during the ligand preparation step. The new method for ligand synthesis involves the use of an *in situ* generated titanium reagent (from $TiCl_4$ and *n*-BuNH₂) rather than the application of an expensive reagent to promote the imine formation, which resulted in shortening the reaction time from 2 days to 3 h while improving the isolated yield to almost quantitative (96%). Additionally, this new procedure requires much less solvent, which further improves the efficiency of the synthesis. In the last step of the synthesis, the metalation reactions, the desired complexes were obtained by the reaction of the ligand 8 and the respective metal chlorides (HfCl₄ and ZrCl₄) with four equivalents of MeMgBr in toluene in 80-90% yields. This approach is significantly more cost-effective than the previous synthesis, which required the use of HfBn₄ and ZrBn₄ as synthetic reagents. The practicality of this new method was demonstrated by applying it successfully to the macroscale synthesis of 11, resulting in quantities suitable for pilot plant evaluations. Specifically, the scale-up resulted in the synthesis of 255 g of 11 in a good overall yield of 57%. The new synthetic method also allowed for the preparation of hafnium and zirconium complexes derived from the isomerized iminoenamine ligand 9. When activated with trialkylammonium borate, these complexes (13, 14) gave polymers with very high molecular weights and low 1-octene incorporation. On the

other hand, complexes derived from ligand 8 (11, 12) produced copolymers with noticeably higher octene incorporation. Each of the four complexes investigated (11-14) resulted in ethylene/1-octene copolymers with very high molecular weights but with different octene contents. These features coupled with the demonstrated ability of imino–enamido complexes to undergo very effective chain transfer reactions should make complexes 11-14 good candidates for the preparation of a variety of olefin block copolymers via chain-shuttling polymerization.

EXPERIMENTAL SECTION

General Considerations. All solvents and reagents were obtained from commercial sources and used as received unless otherwise noted. Toluene, hexanes, CH_2Cl_2 , and C_6D_6 were dried and degassed according to published procedures. NMR spectra were recorded on Varian VNMRS-400 and VNMRS-500 and Bruker Avance-400 spectrometers. ¹H NMR data are reported as follows: chemical shift (multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, quint. = quintet, sex. = sextet, sept. = septet and m = multiplet), integration, and assignment). Chemical shifts for ¹H NMR data are reported in ppm downfield from internal tetramethylsilane (TMS, δ scale) using residual protons in the deuterated solvent (C_6D_6 , 7.15 ppm) as references. ¹³C NMR data were determined with ¹H decoupling, and the chemical shifts are reported in ppm vs tetramethylsilane (C_6D_6 , 128 ppm). Elemental analyses were performed at Midwest Microlab, LLC.

Synthetic Details. Preparation of N-((6E)-6-(Butylimino)-1cyclohexen-1-yl)-2,6-bis(1-methylethyl)benzenamine (8). To 6.065 g (82.9 mmol) of n-BuNH₂ dissolved in 40 mL of toluene was added (within two minutes) 1.573 g (8.3 mmol) of TiCl₄ dissolved in 5 mL of toluene. The reaction mixture turned red during the addition and then orange a few minutes after the addition was complete. The temperature increased during the addition from 27 to 49 °C. After stirring for 0.5 h at ambient temperature 4.055 g (14.9 mmol) of 2-((2,6-bis(1-methylethyl)phenyl)amino)-2-cyclohexen-1-one (6) was added as a solid. The reaction mixture was stirred at ambient temperature for 3.25 h and then filtered (light yellow filtrate) into a vessel containing 2.1 g of anhydrous K2CO3. The suspension was stirred for 2 h with K₂CO₃ and then filtered to give a colorless solution $(K_2CO_3 absorbed yellow color from the solution)$. The solvent was removed under reduced pressure, leaving 4.66 g of colorless oil. Yield: 95.6%. ¹H NMR (C₆D₆, 500 MHz, 30 °C): δ 7.23-7.17 (m, 3H, *i*-Pr₂) *Ph*), 6.89 (s, 1H, NH), 4.78 (t, 1H, J = 4.6 Hz, H5), 3.39 (sept., 2H, ${}^{3}J$ = 6.9 Hz, $CH(CH_3)_2$), 3.26 (t, 2H, ³J = 6.8 Hz, H7), 2.09 (pseudo t, 2H, ${}^{3}J = 6.6$ Hz, H2), 1.96 (q, 2H, ${}^{3}J = 5.5$ Hz, H4), 1.69 (p of m, 2H, ${}^{3}J$ = 7.8 Hz, H8), 1.53 (quint., 2H, ${}^{3}J$ = 6.5 Hz, H3), 1.44 (sex. of m, 2H, ${}^{3}J$ = 7.0 Hz, H9), 1.22 (d, 12H, ${}^{3}J$ = 6.8 Hz, CH(CH₃)₂), 0.94 (t, 3H, ${}^{3}J$ = 7.3 Hz, H10) ppm. 13 C NMR (C₆D₆, 125 MHz, 30 °C): δ 160.61, 147.38, 140.90, 137.89, 126.83, 123.80, 103.26, 49.84, 33.71, 28.69, 26.80, 24.23, 23.92, 23.39, 21.03, 14.21. HSQC (C₆D₆, 500 MHz): δ (7.23-7.17, 126.83/123.80), (4.78, 103.26), (3.39, 28.69), (3.26, 49.84), (2.09, 26.80), (1.96, 23.92), (1.69, 33.71), (1.52, 23.39), (1.44, 21.03), (1.22, 24.23), (0.94, 14.21) ppm. HRMS (ESI, M + H)⁺): (m/z) calcd for C₂₂H₃₅N₂ 327.277, found 327.280.



1-yl)-2,6-bis(1-methylethyl)benzenaminato-*k*N)-tris(phenylmethyl) hafnium $(2)^7$ dissolved in 20 mL of CH₂Cl₂ at room temperature was added 1.54 g (6.07 mmol) of iodine dissolved in 60 mL of CH₂Cl₂ over a period of 20 min. After stirring for 10 min at ambient temperature, the solvent was removed under reduced pressure. To the residue was added 30 mL of hexane, and the suspension was stirred for 15 min. Yellow product was collected on the frit, washed with 15 mL of hexane, and dried under reduced pressure to give 1.47 g of product (82.7% yield). ¹H NMR (C_6D_6 , 500 MHz, 30 °C): δ 7.24 (m, 1H, ⁱPr₂para-<u>Ph</u>), 7.17 (m, 2H, ⁱPr₂-meta-<u>Ph</u>), 4.72 (t, 1H, ${}^{3}J_{H-H} = 4.9$ Hz, H5), 3.59 (m, 2H, H7), 3.56 (sept. 2H, ${}^{3}J_{H-H} = 6.8$ Hz, $CH(CH_{3})_{2}$), 1.68 (q, 2H, ${}^{3}J_{H-H} = 5.7$ Hz, H4), 1.66 (t, 2H, ${}^{3}J_{H-H} = 6.4$ Hz, H2), 1.61 (\bar{d} , 6H, ${}^{3}J_{H-H}$ = 6.9 Hz, CH(CH₃)₂), 1.58 (m, 2H, H8), 1.11 (d, $6H_{1,3}J_{H-H} = 6.8 \text{ Hz}, CH(CH_{3})_{2}$, 1.10 (sex., 2H, ${}^{3}J_{H-H} = 7.1 \text{ Hz}, H9$), 1.07 (p, 2H, ${}^{3}J_{H-H} = 6.0$ Hz, H3), 0.79 (t, 3H, ${}^{3}J_{H-H} = 7.4$ Hz, H10). ¹³C{¹H} NMR (C_6D_6 , 125 MHz, 30 °C): δ 176.25 (N=C), 149.75 (quat.), 144.81 (quat.), 143.98 (quat.), 128.20 (ⁱPr₂-para-Ph), 125.05 (ⁱPr₂-meta-<u>Ph</u>), 123.80 (C5), 52.23 (C7), 30.53 (C8), 28.95 $(CH(CH_3)_2)$, 28.70 (C2), 26.21 $(CH(CH_3)_2)$, 24.42 (C4), 24.35 (CH(CH₃)₂), 21.92 (C3), 20.98 (C9), 13.84 (C10). Anal. Calcd for C25H42N2Hfl3: C, 29.87; H, 3.76; N, 3.17. Found: C, 30.12; H, 3.62; N, 3.33.



Preparation of (N-((6E)-6-(butylimino-κN)-1-cyclohexen-1-yl)-2,6bis(1-methylethyl)benzenaminato-κN)trimethylhafnium (11). To a 30 mL toluene solution containing 0.7486 g (0.85 mmol) of (N-((6E)-6-(butylimino-κN)-1-cyclohexen-1-yl)-2,6-bis(1-methylethyl)benzenaminato-KN)triiodohafnium (10) was added 0.88 mL (2.65 mmol) of 3 M MeMgBr solution in ether at ambient temperature. The reaction mixture was stirred for 20 min followed by solvent removal under reduced pressure. The residue was extracted with 30 mL of hexane and filtered. The solvent was removed from the filtrate, leaving 0.462 g of product as a yellow crystalline solid. Yield: 99.4%. ¹H NMR $(C_6 D_{6'}, 500 \text{ MHz}, 30 \text{ °C}): \delta 7.19 - 7.24 \text{ (m, 3H, } {}^{i}\text{Pr}_2 - \underline{Ph}), 4.66 \text{ (t, 1H, })$ ${}^{3}J_{H-H} = 4.9 \text{ Hz}, \text{H5}), 3.46 \text{ (sept. 2H, } {}^{3}J_{H-H} = 7.0 \text{ Hz}, \text{CH}(\text{CH}_{3})_{2}), 3.34$ (m, 2H, H7), 1.89 (t, 2H, ${}^{3}J_{H-H} = 6.6$ Hz, H2), 1.88 (q, 2H, ${}^{3}J_{H-H} = 5.5$ Hz, H4), 1.42 (d, 6H, ${}^{3}J_{H-H} = 7.0$ Hz, CH(CH₃)₂), 1.34 (m, 2H, H8), 1.28 (p, 2H, ${}^{3}J_{H-H} = 6.2$ Hz, H3), 1.21 (d, 6H, ${}^{3}J_{H-H} = 6.9$ Hz, CH(CH₃)₂), 1.08 (sex., 2H, ${}^{3}J_{H-H} = 7.5$ Hz, H9), 0.77 (t, 3H, ${}^{3}J_{H-H} =$ 7.4 Hz, H10), 0.50 (s, 9H, Hf-CH₃). ¹³C{¹H} NMR (C₆D₆, 125 MHz, 30 °C): δ 175.30 (N=C), 152.07 (quat.), 144.98 (quat.), 144.31 (quat.), 126.07 (ⁱPr₂-para-<u>Ph</u>), 124.16 (ⁱPr₂-meta-<u>Ph</u>), 114.71 (C5), 60.40 (Hf-CH₃), 49.57 (C7), 31.00 (C8), 28.48 (CH(CH₃)₂), 28.00 (C2), 26.00 (CH(CH_3)₂), 24.69 (C4), 24.53 (CH(CH_3)₂), 23.12 (C3), 21.00 (C9), 13.82 (C10). Anal. Calcd for C₂₅H₄₂HfN₂: C, 54.68; H, 7.71; N, 5,10. Found: C, 54.94; H, 7.56; N, 5,10.

Preparation of (N-((6E)-6-(butylimino- κ N)-1-cyclohexen-1-yl)-2,6bis(1-methylethyl)benzenaminato- κ N)trimethylhafnium (11). To a toluene solution (60 mL) of N-((6E)-6-(butylimino)-1-cyclohexen-1yl)-2,6-bis(1-methylethyl)benzenamine (8) (3.03 g, 9.28 mmol) and HfCl₄ (2.97 g, 9.28 mmol) was added 12.68 mL (38.05 mmol) of a 3.0 M MeMgBr ether solution. During the addition of MeMgBr gas evolution was observed. Within minutes the reaction mixture changed color from yellow to black. The solution was stirred for 1 h, after which time the solvent was removed under reduced pressure. To the residue was added 50 mL of hexane, and the resulting yellow solution was filtered. The salts were washed with an additional 30 mL of hexane. The solvent was removed under reduced pressure, leaving 4.03 g of yellow crystalline solid. Yield: 79.1%.

Preparation of (N-((6E)-6-(Butylimino-κN)-1-cyclohexen-1-yl)-2,6bis(1-methylethyl)benzenaminato-κN)trimethylzirconium (12). Το



a toluene suspension (12 mL) containing 0.3901 g (1.19 mmol) of N-((6E)-6-(butylimino)-1-cyclohexen-1-yl)-2,6-bis(1-methylethyl)benzenamine (8) and 0.266 g (1.19 mmol) of $ZrCl_4$ was added 1.67 mL (5.02 mmol) of 3 M MeMgBr ether solution at ambient temperature. During the addition the reaction mixture changed color from yellow to black. After stirring for 2 h, 45 mL of hexane was added, and the reaction mixture was filtered. The solvent was removed from the vellow filtrate under reduced pressure to give 0.5305 g of yellow, highly crystalline product. Yield: 96.1%. ¹H NMR (C₆D₆, 500 MHz, 30 °C): δ 7.21 (s, 3H, ⁱPr₂-<u>Ph</u>), 4.70 (t, J = 5.0 Hz, 1H, H5), 3.48 (hept, 2H, J = 6.9 Hz, $CH(CH_3)_2$), 3.36–3.29 (m, 2H, H7), 1.96 $(dd, 2H, J = 7.1, 5.8 Hz, H2), 1.85 (q, 2H, J = 5.7 Hz, H4), 1.40 (d, 6H, J = 6.9 Hz, CH(CH_3)_2), 1.38-1.27 (m, 4H, H3/H8), 1.22 (d, 6H, H)$ J = 6.9 Hz, 6H, CH(CH₃)₂), 1.08 (sex, 2H, J = 7.4 Hz, H9), 0.77 (t, 3H, J = 7.4 Hz, H10), 0.74 (s, 9H, Zr-CH₃). ¹³C NMR (C₆D₆, 126 MHz, 30 °C): δ 174.54 (N=C), 151.62 (quat.), 144.89 (quat.), 144.18 (quat.), 126.13 (ⁱPr₂-para-<u>Ph</u>), 124.23 (ⁱPr₂-meta-<u>Ph</u>), 113.42 (C5), 49.91 (C7), 48.60 (Zr-CH₃), 31.21 (C8), 28.57 (CH(CH₃)₂), 27.79 (C2), 26.02 (CH(CH₃)₂), 24.77 (C4), 24.56 (CH(CH₃)₂), 23.18 (C3), 20.99 (C9), 13.84 (C10). Anal. Calcd for C₂₅H₄₂ZrN₂: C, 65.02; H, 9.17; N, 6.07. Found: C, 64.92; H, 9.08; N, 6.07.



Preparation of [N-[2-(Butylamino-κN)-2-cyclohexen-1-ylidene]-2,6-bis(1-methylethyl)benzenaminato- κ N]trimethylhafnium (13). To a toluene suspension (40 mL) of 1.0168 g (3.11 mmol) of N-[2-(butylamino)-2-cyclohexen-1-ylidene]-2,6-bis(1-methylethyl)benzenamine $(9)^7$ and 0.997 g (3.11 mmol) of HfCl₄ was added 4.25 mL (12.77 mmol) of 3 M MeMgBr ether solution. During the addition of the MeMgBr gas evolution was observed. After stirring for 2 h at ambient temperature, the solvent was removed under reduced pressure. To the residue was added 20 mL of toluene followed by 20 mL of hexane, and the yellow solution was filtered. The solvent was removed under reduced pressure, leaving a yellow crystalline solid. NMR spectroscopy showed formation of the desired product along with a small amount of impurities. The solid was dissolved in 2 mL of warm toluene followed by addition of 18 mL of hexane. The solution was filtered and put into a freezer (at -26 °C) overnight. Precipitated yellow solid was collected on a frit, washed with 3 mL of cold hexane, and dried under reduced pressure to give 433 mg of product. The solvent was removed from the filtrate, and the residue was dissolved in 15 mL of hexane and put into a freezer. After 2 days the solvent was decanted, and the large crystals that had formed were washed with 2 mL of cold hexane and dried under reduced pressure to give 333 mg of product. Combined yield: 766 mg (44.8%). ¹H NMR (500 MHz, C_6D_6): δ 7.08–7.00 (m, 3H, ⁱPr₂<u>Ph</u>), 5.19 (t, 1H, J = 5.0 Hz, H2), 3.67 (m, 2H, H7), 2.59 (hept, 2H, J = 6.8 Hz, $CH(CH_3)_2$), 2.18 (q, 2H, J =5.7 Hz, H3), 2.01 (dd, 2H, J = 7.1, 5.7 Hz, H5), 1.76 (m, 2H, H8), 1.39–1.28 (m, 4H, H4 and H9), 1.19 (d, 6H, J = 6.8 Hz, CH(CH₃)₂), 0.92 (t, 3H, J = 7.4 Hz, H10), 0.91 (d, 6H, J = 6.8 Hz, CH(CH₃)₂), 0.48 (d, 9H, J = 0.8 Hz, Hf(CH_3)₃). ¹³C NMR (126 MHz, C_6D_6): δ 183.04 (C=N), 149.37 (quat.), 145.30 (quat.), 139.37 (quat.), 126.83 (ⁱPr₂<u>Ph</u>), 123.99 (ⁱPr₂<u>Ph</u>), 111.32 (C2), 60.12 (Hf(CH₃)₃), 44.72

 $\begin{array}{l} (C7),\,31.60\;(C5),\,30.51\;(C8),\,28.97\;(CH(CH_3)_2),\,25.33\;(C3),\,24.38\\ (CH(CH_3)_2),\,23.64\;(CH(CH_3)_2),\,23.61\;(C4),\,21.43\;(C9),\,14.25\\ (C10). \mbox{ Anal. Calcd for $C_{25}H_{42}HfN_2$: C, $54.68; H, 7.71; N, $5,10$. Found: C, $54.66; H, 7.69; N, 5.07. } \end{array}$



Preparation of [N-[2-(Butylamino-κN)-2-cyclohexen-1-ylidene]-2,6-bis(1-methylethyl)benzenaminato- κN]trimethylzirconiúm (14). To a toluene solution (40 mL) of 1.2833 (3.93 mmol) of N-[2-(butylamino)-2-cyclohexen-1-ylidene]-2,6-bis(1-methylethyl)benzenamine $(9)^7$ and 0.916 g (3.93 mmol) of ZrCl₄ was added 5.4 mL (16.11 mmol) of 3 M MeMgBr ether solution at ambient temperature. During addition of the MeMgBr gas evolution was observed. Within minutes the reaction mixture changed color from yellow to black. The solution was stirred for 1 h. The solvent was removed under reduced pressure. To the residue was added 10 mL of toluene followed by 50 mL of hexane, and the yellow solution was filtered. The solvent was removed under reduced pressure to give a dark orange crystalline solid. The solid was dissolved in 2 mL of toluene and 10 mL of hexane. The solution was filtered and put into a freezer overnight. The solvent was decanted, and the large orange crystals that had formed were washed with 5 mL of cold hexane and dried under reduced pressure to give 0.693 g of product. NMR spectroscopy showed formation of clean product. Yield: 38.6%. ¹H NMR (500 MHz, $C_6 D_6$): δ 7.10–6.99 (m, 3H, ⁱPr₂<u>Ph</u>), 5.21 (t, 1H, J = 5.0 Hz, H2), 3.76 (m, 2H, H7), 2.57 (hept, 2H, J = 6.8 Hz, CH(CH₃)₂), 2.12 (q, 2H, J = 5.7 Hz, H3), 2.06 (m, 2H, H5), 1.78 (m, 2H, H8), 1.42 - 1.29 (m, 4H, H4 and H9), 1.17 (d, 6H, J = 6.8 Hz, CH(CH₃)₂), 0.92 (d, 6H, J = 6.8 Hz, CH(CH₃)₂), 0.91 (t, 2H, J = 7.4 Hz, H10), 0.71 (s, 9H, Zr(CH₃)₃). ¹³C NMR (75 MHz, C₆D₆): δ 181.71 (C=N), 148.31 (quat.), 145.59 (quat.), 138.98 (quat.), 126.61 $({}^{i}Pr_{2}\underline{Ph})$, 124.04 $({}^{i}Pr_{2}\underline{Ph})$, 109.95 (C2), 47.00 $(Zr(CH_{3})_{3})$, 45.77 (C7), 31.51 (C5), 30.71 (C8), 29.21 (CH(CH₃)₂), 25.48 (C3), 24.48 (CH(CH₃)₂), 23.75 (CH(CH₃)₂), 23.68 (C4), 21.58 (C9), 14.42 (C10). Anal. Calcd for $C_{25}H_{42}ZrN_2$: C, 65.02; H, 9.17; N, 6.07. Found: C, 64.98; H, 9.06; N, 6.01.

Scale-up of 2-(4-Morpholinyl)-2-cyclohexen-1-one (5). A 3 L, 3necked round-bottomed flask equipped with a Dean-Stark trap and a condenser was placed under nitrogen, then charged with toluene (1.60 L) and sparged with nitrogen for 30 min. Morpholine (145.8 mL, 1.672 mol) and 1,2-cyclohexanedione (150.0 g, 1.338 mol) were then added under a stream of nitrogen (caution: care must be taken to avoid prolonged exposure of 1,2-cyclohexanedione to air, as the white crystalline material quickly becomes yellow and partially liquefies in air). The mixture was then heated under reflux for 3 h, with water collecting in the Dean-Stark trap during this time. The reaction mixture was cooled to room temperature, and a dark oily residue (unwanted byproduct) separated from the solution and settled out on the bottom of the flask. The solution was isolated from the immiscible oil by decantation, and the solvent was removed under vacuum. The resulting solid residue was ground up with a spatula and then triturated with pentane, furnishing orange-brown crystalline material, which was shown by ¹H NMR to be of high purity (230.0 g, 95%). ¹H NMR $(C_6 D_{67} 300 \text{ MHz}, 30 \text{ °C}): \delta 5.35 (t, 1H, ^3J = 4.6 \text{ Hz}), 3.67-3.64 (m, 1H, ^3J = 4.6 \text{ Hz})$ 4H), 2.70-2.66 (m, 4H), 2.18-2.13 (m, 2H, H2), 1.87-1.81 (m, 2H, H4), 1.42 (quint., 2H, ${}^{3}J$ = 6.4 Hz, H3) ppm. ${}^{13}C$ NMR (C₆D₆, 75 MHz, 30 °C): δ 194.30, 147.03, 124.72, 67.32, 50.81, 40.49, 25.89, 23.63 ppm. GC/MS (CI) mass spectrum: m/z 182 (M + H)

Scale-up of 2-((2,6-Bis(1-methylethyl)phenyl)amino)-2-cyclohexen-1-one (6). A 3 L, three-necked round-bottomed flask equippedwith a mechanical stirrer was placed under a nitrogen atmosphere,then charged with toluene (1.75 L), which was sparged with nitrogen for 30 min. Molecular sieves (100 g, 4 Å) and 2-(4-morpholinyl)-2cyclohexen-1-one (5) (175.0 g, 0.9656 mol), followed by 2,6diisopropylaniline (196.1 mL, 0.9656 mol), were added under a stream of nitrogen, and the resulting mixture was heated to 70 °C. At this point, p-toluenesulfonic acid (183.7 g, 0.966 mol) was added, producing a light brown cloudy solution. The temperature was increased to 80 °C, and the solution was mechanically stirred for 1 h, at which point the solution became clear (an olive green color), and GC/MS analysis indicated complete conversion. The mixture was allowed to cool, then concentrated to dryness under vacuum. The thick residue was broken up with a large spatula, triturated with pentane to remove excess toluene, extracted in hot pentane, and filtered through a medium-porosity glass frit. The filtrate was reduced under vacuum and recrystallized at -20 °C. The white crystals (130.0 g) were harvested, the mother liquor was reduced in volume, and a second recrystallization was performed at -20 °C, furnishing an additional 55.3 g of product. The net yield was 185.3 g (71%). ¹H NMR (C₆D₆, 300 MHz): δ 7.17-7.06 (m, 3H), 6.00 (br s, 1H), 4.95 (t, 1H, J = 4.7 Hz), 3.15 (septet, 2H, J = 6.9 Hz), 2.21-2.16 (m, 2H, H2), 1.75 (q, 2H, J = 5.5 Hz, H4), 1.41 (quint., 2H, J = 6.3 Hz, H3), 1.10 (d, 12H, J = 6.9 Hz) ppm. ¹³C NMR (C₆D₆, 75 MHz): δ 194.09, 147.17, 140.82, 135.90, 127.47, 124.04, 112.08, 38.15, 28.91, 24.53, 24.36, 24.04 ppm. GC/MS (CI) mass spectrum: m/z 272 (M + H). HRMS (ESI, $(M + Na)^+$): (m/z) calcd for $C_{18}H_{25}NONa$ 294.180, found 294,183.

Scale-up of N-((6E)-6-(Butylimino)-1-cyclohexen-1-yl)-2,6-bis(1methylethyl)benzenamine (8). To a stirred solution of *n*-butylamine (303.7 mL, 3.074 mol) in toluene (1.50 L) in a 3 L round-bottomed flask in a nitrogen drybox was added TiCl₄ (33.7 mL, 0.307 mol) dropwise via addition funnel over 15 min (temperature rise from 28 °C up to 60 °C was observed due to the exothermic reaction). The resulting solution was allowed to stir for an additional 1 h, at which point the temperature decreased to 30 °C, and 2-((2,6-bis(1methylethyl)phenyl)amino)-2-cyclohexen-1-one (6) (150.1 g, 0.5532 mol) was added over $\sim 2 \min$ (causing a temperature rise up to 38 °C). The resulting brown mixture was stirred for 3 h and then filtered through a pad of Celite in a medium-porosity glass frit into a flask containing anhydrous K_2CO_3 (75 g) and stirred for 1 h. The mixture was refiltered through a fine-porosity glass fiber filter and dried under vacuum, furnishing the product as a yellow oil (166.4 g, 92%). ¹H NMR analysis revealed <2% of isomer 9.

Scale-up of (N-((6E)-6-(Butylimino-κN)-1-cyclohexen-1-yl)-2,6bis(1-methylethyl)benzenaminato-KN)trimethylhafnium (11). To a stirred solution of N-((6E)-6-(butylimino)-1-cyclohexen-1-yl)-2,6bis(1-methylethyl)benzenamine (8) (165.0 g, 0.5053 mmol) in toluene (1.60 L), in a 3 L round-bottomed flask in a nitrogen drybox, was added HfCl₄ (161.9 g, 0.5053 mol) in one portion. To the resulting tan-colored turbid solution was added MeMgBr (690.6 mL, 3 M in ether, 2.072 mol) dropwise via addition funnel over a period of \sim 1 h, to maintain the temperature below 40 °C. The reaction mixture was stirred for an additional 1 h, at which point a dark black color had developed. The solvent was removed under vacuum. The dried residue was extracted in several portions with Isopar-E and filtered through a pad of Celite in a medium-porosity glass frit. The total extraction volume was 4.4 L. A portion of the solution was analyzed by ¹H NMR to determine the purity (with <2% reverse isomer) and gravimetrically analyzed as 8.1 wt % 11 (0.106 M, net yield is calculated from this to be 92%).

Ethylene-1-octene Polymerization Procedures and Polymer Characterization. *Ethylene-1-octene Copolymerization*. A 2 L Parr reactor was used in the polymerizations. All feeds were passed through columns of alumina and Q-5 catalyst (available from Engelhard Chemicals Inc.) prior to introduction into the reactor. Precatalyst and cocatalyst (activator) solutions were handled in the glovebox. A stirred 2 L reactor was charged with about 533 g of mixed alkanes solvent and 250 g of 1-octene comonmer. The reactor contents were heated to the polymerization temperature of 120 °C, while 10 μ mol of MMAO was added to the reactor was saturated with ethylene at 460 psig (3.4 MPa). Catalysts and cocatalysts, as dilute solutions in toluene, were mixed and transferred to a catalyst addition tank and injected into the reactor. The polymerization conditions were maintained for 10 min with ethylene added on demand. Heat was continuously removed from the reaction vessel through an internal cooling coil. The resulting solution was removed from the reactor, quenched with isopropyl alcohol, and stabilized by addition of 10 mL of a toluene solution containing approximately 67 mg of a hindered phenol antioxidant (Irganox 1010 from Ciba Geigy Corporation) and 133 mg of a phosphorus stabilizer (Irgafos 168 from Ciba Geigy Corporation). Between polymerization runs, a wash cycle was conducted in which 850 g of mixed alkanes was added to the reactor and the reactor was heated to 150 °C. The reactor was then emptied of the heated solvent immediately before beginning a new polymerization run. Polymers were recovered by drying for about 12 h in a temperature-ramped vacuum oven with a final set point of 140 °C.

Polymer Characterization. Melting (T_m) and glass transition (T_a) temperatures of polymers were measured by differential scanning calorimetry (Q2000 DSC, TA Instruments, Inc.). Samples were first heated from room temperature to 200 °C using the 'Jump To' feature. After being held at this temperature for 4 min, the samples were cooled to -90 °C at 10 °C/min, held for 4 min, and then heated again to 200 °C. Molecular weight distribution (M_w, M_p) information was determined by analysis on a custom Dow-built robotic-assisted dilution high-temperature gel permeation chromatographer (RAD-GPC). Polymer samples were dissolved for 90 min at 160 °C at a concentration of 5-7 mg/mL in 1,2,4-trichlorobenzene (TCB) stabilized by 300 ppm of BHT in capped vials while stirring. They were then diluted to 1 mg/mL immediately before a 400 μ L aliquot of the sample was injected. The GPC utilized two Polymer Laboratories PLgel 10 μ m MIXED-B columns (300 mm × 10 mm) at a flow rate of 2.0 mL/min at 150 °C. Sample detection was performed using a PolyChar IR4 detector in concentration mode. A conventional calibration of narrow polystyrene (PS) standards was utilized, with apparent units adjusted to homopolyethylene (PE) using known Mark-Houwink coefficients for PS and PE in TCB at this temperature. To determine octene incorporation, 30 mg/mL solutions of each sample were dissolved at 160 °C for 120 min while covered and shaking with glass stir-bars in vials. A 90 μL amount of each polymer solution was deposited onto a silicon wafer, heated under a nitrogen purge at 145 °C until the trichlorobenzene had evaporated, and analyzed using a Nicolet Nexus 670 FTIR running Omnic (v. 7.1) software equipped with an AutoPro automated sampler.

Structure Determinations of 10–14. X-ray intensity data were collected on a Bruker SMART diffractometer using Mo K α radiation ($\lambda = 0.71073$ Å) and an APEXII CCD area detector. Raw data frames were read by the program SAINT²⁰ and integrated using 3D profiling algorithms. The resulting data were reduced to produce *hkl* reflections and their intensities and estimated standard deviations. The data were corrected for Lorentz and polarization effects, and multiscan absorption corrections were applied. The structure was solved and refined in SHELXTL6.1, using full-matrix least-squares refinement. The non-H atoms were refined with anisotropic thermal parameters, and H atoms were calculated in idealized positions and refined riding on their parent atoms. The refinement was carried out using F^2 rather than F values. R_1 is calculated to provide a reference to the conventional R value, but its function is not minimized.

Structure **10.** $C_{22}H_{33}HfI_{3}N_2$, $M_w = 884.69$, orthorhombic, *Pbca* (0.38 × 0.15 × 0.10 mm³), a = 14.8620(4) Å, b = 16.5798(5) Å, c = 21.8610(6) Å, $\beta = 94.2550(10)^{\circ}$, temp = 100(2) K, Z = 4, V = 5386.7(3) Å³, R1 = 0.0163, 0.0202, wR2 = 0.0326, 0.0336 ($I > 2\sigma(I)$, all data), GOF = 1.068.

Structure **11**. $C_{25}H_{42}HfN_2$, $M_w = 549.10$, monoclinic, P2(1)/c (0.22 × 0.22 × 0.21 mm³), a = 10.8416(2) Å, b = 17.4171(3) Å, c = 13.5117(3) Å, $\beta = 94.2550(10)^{\circ}$, temp = 200(2) K, Z = 4, V = 2544.37(9) Å³, R1 = 0.0155, 0.0183, wR2 = 0.0381, 0.0399 ($I > 2\sigma(I)$, all data), GOF = 1.035.

Structure **12**. $C_{25}H_{42}N_2Zr$, $M_w = 461.83$, monoclinic, P2(1)/c (0.38 × 0.38 × 0.36 mm³), a = 10.8529(4) Å, b = 17.0807(7) Å, c = 13.7356(5) Å, $\beta = 95.355(2)^\circ$, temp = 200(2) K, Z = 4, V = 12.7356(5)

2535.13(17) Å³, R1 = 0.0259, 0.0288, wR2 = 0.0712, 0.0746 (I > $2\sigma(I)$, all data), GOF = 1.054.

Structure **13**. $C_{25}H_{42}HfN_2$, $M_w = 549.10$, monoclinic, P2(1)/c (0.48 × 0.42 × 0.35 mm³), a = 13.5113(4) Å, b = 10.1690(3) Å, c = 19.3016(6) Å, $\beta = 110.2520(10)^\circ$, temp =100(2) K, Z = 4, V = 2488.02(13) Å³, R1 = 0.0133, 0.0144, wR2 = 0.0309, 0.0312 ($I > 2\sigma(I)$, all data), GOF = 1.167.

Structure **14**. $C_{25}H_{42}N_2Zr$, $M_w = 461.83$, monoclinic, P2(1)/c (0.45 × 0.35 × 0.30 mm³), a = 13.5205(6) Å, b = 10.1652(5) Å, c = 19.3393(11) Å, $\beta = 110.388(2)^{\circ}$, temp = 100(2) K, Z = 4, V = 2491.5(2) Å³, R1 = 0.0219, 0.0234, wR2 = 0.0598, 0.0612 ($I > 2\sigma(I)$, all data), GOF = 1.087.

ASSOCIATED CONTENT

S Supporting Information

Molecular structures of **13** and **14**. 1D and 2D NMR spectra for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(11) It is not necessarily the case that tribenzyl and trimethyl derivatives would have the same polymerization characteristics. This depends on details of the polymerization mechanism for these complexes, which is currently unknown. One important question is whether there are two polymer chains growing at the same cationic metal center or if one of the alkyl groups (Bn or Me) is a spectator ligand. If the former scenario is operating, then one could expect very similar polymerization behavior for both tribenzyl and trimethyl precatalysts.

(12) See Supporting Information for 1D and 2D spectra for all new compounds.

(13) Crystals crack below 200 K.

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(16) We were unable to isolate this side product in pure form and characterize it fully. NMR spectroscopy of this byproduct clearly indicates it has C_1 symmetry (e.g., four doublets and two heptets are observed for the *i*-Pr groups together with two distinct resonances for the methylene protons α to nitrogen atom).

(17) Molecular structures of **12** and **14** are isostructural with **11** and **13**, respectively. See Supporting Information for details.

(18) For structures 2 and 3, these values refer to bond lengths and angles between Hf and the methylene carbons of the benzyl groups.

(19) GPC data were obtained on a conventional GPC calibrated using narrow polystyrene standards. This GPC measures backbone molecular weight rather than absolute molecular weight of polymers. Previously published GPC data for 2 and 3^7 were obtained on a GPC utilizing a light-scattering detector that measures the absolute molecular weights. This is the reason that M_w data for 2 and 3 shown in Table 2 are somewhat lower than what was reported previously.

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