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Synthetic Optimization and Scale-Up of Imino−Amido Hafnium and Zirconium Olefin Polymerization Catalysts

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Supporting Information

ABSTRACT: Improved synthetic protocols were developed for the safe, efficient, and scalable preparation of imino−amido Hf and Zr complexes that are precatalysts for olefin polymerizations. Facile syntheses of four imino−amido complexes were achieved in high yields by direct reactions of 4 equiv of MeMgBr with mixtures of the corresponding bisimines or imine−amines and MCl_4 (M = Hf, Zr). These synthetic routes eliminate the use of the pyrophoric reagents $AlMe_3$ and *n*-BuLi used previously, avoid cryogenic conditions, and lead to significant yield improvements. Notably, competing reaction pathways between the bis-imine and MeLi were observed. This led to the discovery of the selective addition of MeMgBr to the bis-imine, which was successfully applied in the synthesis of the imine−amine ligand.

INTRODUCTION

Molecular olefin polymerization catalysts continue to attract attention among academic and industrial chemists as a result of their ability to produce improved polyolefins relative to those prepared by heterogeneous catalysts.[1] Recently we have been interested in olefin polymerization catalysts derived from complexes ligated by bidentate monoanionic ligands containing two nitrogen donors.[2−6] Within this class of complexes, we and others have examined the polymerization characteristics of imino−amido[2−4] (e.g., **1**−**3**), imino−enamido[5] (e.g., **4**) and amidoquinoline[6] (e.g., **5**) Zr and Hf complexes (Figure 1). Such catalysts exhibit several desirable features, including high catalytic activities at high temperatures, the ability to form very high molecular weight polymers, and the capability to undergo reversible chain transfer with diethylzinc to produce olefin block copolymers.[2b]

The reported syntheses of complexes **1**−**3** are reproducible[2b,7] but have some disadvantages for larger-scale preparation. We sought to improve the efficiency (higher yields) and scalability of all synthetic steps. Herein we report much improved synthetic protocols that eliminate the use of $AlMe_3$ and *n*-BuLi and afford complexes **1**−**3** in high overall yields. The effectiveness of the newly developed transformations was subsequently demonstrated by large-scale preparations of these complexes.

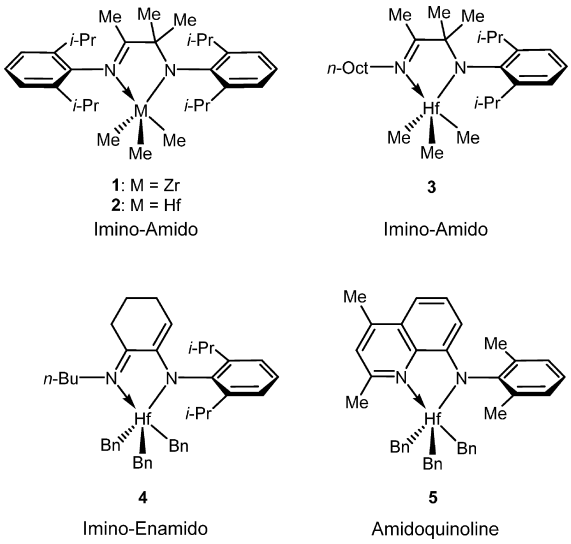

Figure 1. Imino−amido-type olefin polymerization catalysts.

RESULTS AND DISCUSSION

Imino−amido complexes **1**, **2**, and **3** were prepared previously from bis-imine **6** as outlined in Scheme 1.[2b,7] A key transformation in this reaction sequence is the preparation of ligand **7**, which involves the reaction between bis-imine **6** and $AlMe_3$ followed by hydrolysis of the resulting Al complex. While this reaction is highly selective, the transformation is not atom-economical, as only one of the three methyl groups of $AlMe_3$ is incorporated into the product. Another challenging step in this synthesis is the hydrolysis of **7** to **8**, which occurs in very low yield (29.1%). The other reactions depicted in Scheme 1 proceed in moderate yields, giving moderate overall yields (52−54%) of complexes **1** and **2** and a low overall yield (12%) of complex **3**. We sought to develop an improved synthesis of

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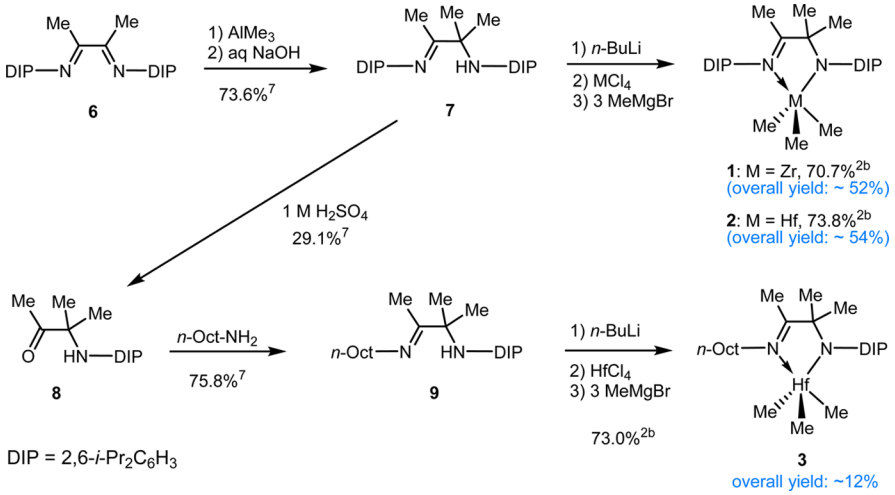
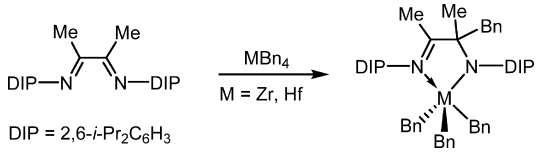
Scheme 1. Previously reported synthesis of precatalysts 1−3[2b,7]



these imino−amido complexes to facilitate their large-scale preparation.

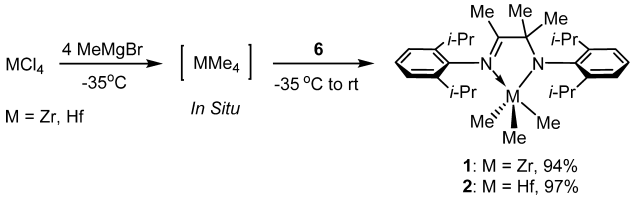
Development of New Syntheses for Imino−Amido Precatalysts 1 and 2. *Method A. Preparation of Imino−Amido Zr and Hf Complexes 1 and 2 from in Situ-Generated MMe_4 (M = Zr, Hf).* We previously reported that the reaction of bis-imine **6** with MBn_4 (M = Zr, Hf) led to the formation of imino−amido tribenzyl complexes via migratory insertion of a benzyl group into a C═N bond (Scheme 2).[2a] We

Scheme 2. Synthesis of imino−amido complexes via the reaction of a bis-imine with MBn_4 (M = Zr, Hf; Bn = benzyl)[2a]



hypothesized that an analogous reaction between bis-imine **6** and MMe_4 (M = Zr, Hf) might lead to the desired imino−amido complexes **1** and **2** (Scheme 3), which would greatly

Scheme 3. Preparation of 1 and 2 from bis-imine 6 and in situ-generated MMe_4 (M = Zr, Hf) (method A)



simplify the preparation of these complexes. Unlike the homoleptic benzyl complexes $ZrBn_4$ and $HfBn_4$, the analogous tetramethyl complexes MMe_4 are unstable at ambient temperature. $ZrMe_4$[8−10] decomposes to release methane even below −15 °C.[8] Thus, we decided not to pursue isolation of $ZrMe_4$ and $HfMe_4$ but instead to generate these species in situ and react them with **6** (Scheme 3). Addition of 4 equiv of MeMgBr (3.0 M solution in diethyl ether) to a stirred suspension of $ZrCl_4$ in anhydrous toluene at −35 °C followed by the addition of **6** gave the desired imino−amido Zr complex **1**, which was isolated as a bright-yellow solid in 94% yield. It is worth noting that when $ZrCl_4$ and MeMgBr were mixed at ambient temperature, rapid gas evolution was observed, indicative of the decomposition of $ZrMe_4$; subsequent addition of bis-imine **6** to this mixture did not produce complex **1**. The corresponding Hf complex **2** was prepared in 97% yield in a fashion analogous to that for the Zr complex. The Hf reaction proceeded more slowly, taking over 24 h at ambient temperature to reach completion, compared with the formation of **1**, which was complete by the time the reaction mixture reached ambient temperature. The reaction progress was monitored by ^{1}H NMR spectroscopy. In cases where the reaction was not fully complete, extra MeMgBr could be added to the reaction mixture to drive the reaction to completion. Typically, a slight excess of MeMgBr (4.1−4.5 equiv total) was used in order to achieve complete conversion and a high yield.

The facile reaction of bis-imine **6** with in situ-generated MMe_4 to form **1** and **2** in high yields significantly shortens the previously described synthesis from four steps to a one-pot process. However, because of the instability of the tetramethylmetal complexes (MMe_4), the reactions required cryogenic conditions (e.g., −35 °C), which is not desirable for large-scale preparations.

Method B: Preparation of Imino−Amido Zr and Hf Complexes 1 and 2 from in Situ-Generated (Bisimine)MCl_4 Complexes. It is well-known that bisimines can react with MCl_4 (M = Zr, Hf) to form (bis-imine)MCl_4 complexes.[11−13] We postulated that the reaction of in situ-formed (bis-imine)MCl_4 complexes with 4 equiv of MeMgBr might also lead to imino−amido complexes **1** and **2**.[14] Mixing of bis-imine **6** with $ZrCl_4$ in anhydrous toluene at ambient temperature for 1 h,[15] addition of MeMgBr in ether (4.0 to 4.5 equiv) at −40 °C, and warming of the reaction mixture to ambient temperature produced the desired imino−amido complex **1** in 89% isolated yield. Since this new approach most likely does not generate unstable metal alkyls, we reasoned that cryogenic conditions might not be necessary. The reaction between 4 equiv of MeMgBr and a mixture of bis-imine **6** and MCl_4 at ambient temperature indeed led to the clean and high yielding formation of **1** (86%) and **2** (98%) (Scheme 4).

Method B is a more practical approach for the large-scale preparation of **1** and **2**, as it eliminates cryogenic reaction

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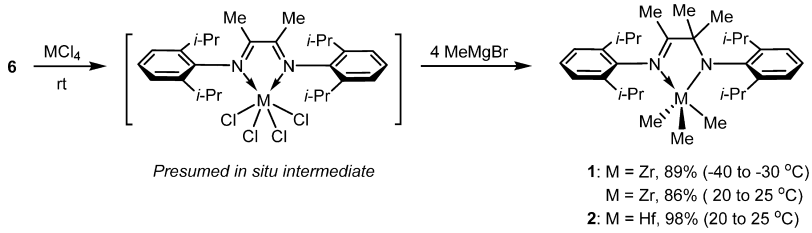
Scheme 4. Preparation of 1 and 2 from the reaction of 6, MCl_4, and MeMgBr (method B)



Scheme 5. Proposed preparation of imine−amine 7 from the reaction of bis-imine 6 and MeLi

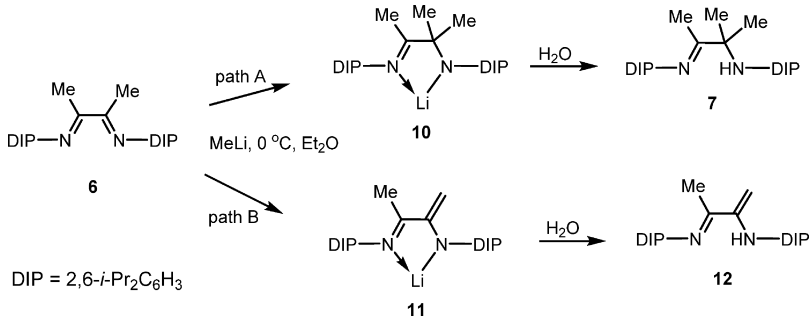
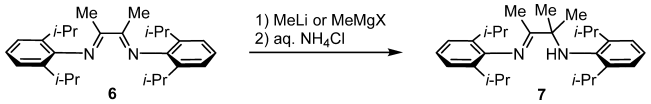


Table 1. Reactions between bis-imine 6 and MeLi or MeMgX[a]



entry	methylation reagent	solvent	temperature (°C)	time (h)	yield of **6** (%)	yield of **7** (%)[b]
1	MeLi	ether	−20 to −40	72	13	82
2	MeLi	ether	RT	5.0	12	81
3	MeMgCl	THF	RT	22	92	5.5
4	MeMgCl	toluene	RT	70	51	37
5	MeMgCl	toluene	60	21	12	86
6	MeMgCl	hexane	60	70	6.0	85
7	MeMgBr	toluene	60	3.5	<0.1	99.5 (93.3)[c]
8[d]	MeMgBr	toluene	60	7.0	<0.1	99.5 (99.5)[c]

[a]Reaction conditions: **6** (0.5 mmol), MeLi (0.55 mmol, 1.1 equiv) or MeMgX (1.0 mmol, 2 equiv), solvent (10 mL). [b]GC samples were prepared by taking one drop (10−15 mg) of the reaction mixture, adding it to 2 mL of aq. NH_4Cl, and subsequently extracting with 2 mL of EtOAc. [c]Isolated yields. [d]On a 5 mmol scale of **6** with 1.2 equiv of MeMgBr.

conditions and avoids in situ preparation of thermally unstable metal alkyls. This method was subsequently demonstrated on a 0.10 mol scale to prepare complex **2** in 97% yield. Imino−amido Zr and Hf complexes such as **1** and **2** can be now conveniently prepared in high yields from bis-imines and metal halides using this one-pot synthesis.

Preparation of Complexes 3 (M = Hf) and 15 (M = Zr). It was recently reported[16] that treatment of bis-imine **6** with MeLi in diethyl ether at ice-bath temperature generated the Li salt **10**, which was isolated in 75% yield as the ether solvate **10**·Et_2O. We were interested in generating **10** in this manner and determining whether its subsequent treatment with a proton source would produce the desired imine−amine **7** (Scheme 5, path A). If successful, such a transformation would be an attractive alternative to the previous method that used $AlMe_3$ as an alkylating agent to prepare **7**.[7]

In our hands, however, treatment of **6** with MeLi in diethyl ether (1.2 to 1.5 equiv), either under cryogenic conditions (−40 to −20 °C) or at near-ambient temperatures (0 °C to ambient temperature), followed by a water quench resulted in the formation of imine−amine **7** in 82% yield and 13% recovery of the starting bis-imine **6**, as measured by GC analysis (area %) (Table 1). To account for the observed product distribution, we hypothesized that MeLi might also act as a base and deprotonate a methyl group from **6** to form lithium salt **11** (path B), which upon a water quench could regenerate bis-imine **6**. Such reactivity between MeLi and the sterically less encumbered mesityl derivative of **6** was observed previously.[16] In fact, in that case this reaction was reported to lead to the exclusive formation of the mesityl analogue of **11**. To gain a better understanding of the outcome of this reaction, the reaction mixture of **6** and MeLi (1.2−1.5 equiv) was quenched with water at 0 °C, and the residue obtained from the organic phase was analyzed by ^{1}H NMR spectroscopy. The ^{1}H NMR spectrum (Figure 2A) showed the presence of two products in a molar ratio of about 4:1, with the major one being the desired imine−amine **7**. In addition to other resonances, the minor product of the mixture showed two characteristic vinyl resonances at 4.41 and 4.13 ppm and was assigned as imine−*N*-vinylamine **12**,[17] which is undoubtedly the protonation

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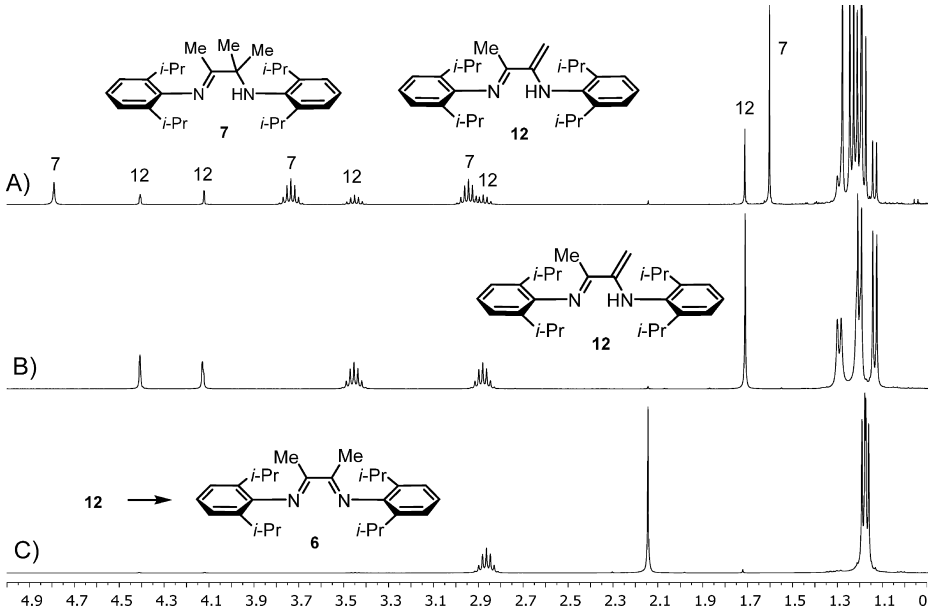
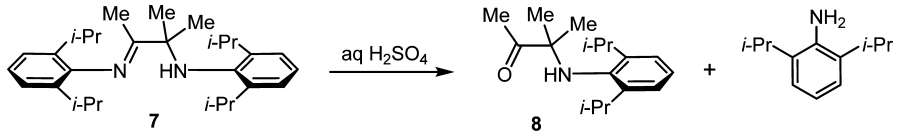


Figure 2. Fragments of ^{1}H NMR spectra (in C_6D_6) for (A) the products obtained from the reaction of **6** and MeLi quenched with H_2O, (B) compound **12** prepared from the reaction of bis-imine **6** and LDA, and (C) compound **12** isomerized to **6** after 10 days in solution at ambient temperature.

Scheme 6. Preparation of keto amine 8



product of salt **11**. There was virtually no detectable amount of bis-imine **6**, indicating complete conversion of the starting material. Thus, the presence of bis-imine **6** in the GC analysis was likely due to tautomerization of imine−*N*-vinylamine **12** to bis-imine **6** at elevated temperature on the GC column. To further confirm that the vinyl protons observed in the NMR spectrum belong to imine−*N*-vinylamine **12**, compound **12** was prepared independently by the reaction of bis-imine **6** with LDA[16] followed by a water quench. This reaction resulted in a mixture of **12** and **6** in a molar ratio of about 3:1. Trituration of the crude product with ethanol afforded pure **12** (Figure 2B), which was found to undergo complete tautomerization to bis-imine **6** after 10 days at ambient temperature (Figure 2C), indicating a very low barrier for this tautomerization. These experiments indicated that the reaction between **6** and MeLi leads to two competing pathways (Scheme 5, paths A and B) generating the two lithium salts **10** and **11**, which, when treated with water, generate compounds **7** and **12**, respectively.

To suppress the generation of salt **11** during the preparation of **7**, we considered other organometallic reagents for this transformation that are nucleophilic but less basic than MeLi (Table 1). Treatment of bis-imine **6** with 2 equiv of MeMgCl in THF at ambient temperature generated imine−amine **7** in only 5.5% yield as determined by GC analysis. The resulting mixture consisted mostly of the starting material **6** (entry 3). The yield of **7** improved to 37% in toluene at ambient temperature (entry 4) and further increased to 86% when the reaction was performed at 60 °C (entry 5). The reaction conducted in hexanes at 60 °C also gave high yields of **7**, but it was slower than the reaction carried out in toluene and some byproducts were also observed (entry 6). A significantly improved reaction was observed when MeMgBr was used in place of MeMgCl, resulting in clean conversion to **7** (99.5% yield as determined by GC analysis) with less than 0.1% **6** in toluene at 60 °C (entry 7). A high reaction yield was also obtained when a lower amount of MeMgBr (1.2 equiv) was used (entry 8). With MeMgBr as the methylation reagent, imine−amine **7** was obtained in yields of 93−99.5% with 99.5% purity on reaction scales of 0.5 to 5.0 mmol. The reaction was subsequently demonstrated on a scale of over 0.5 mol (200 g), giving **7** in 99% isolated yield. This new synthetic method not only significantly improves the yield of **7** but also leads to a much safer and scalable process.

In addition to the synthetic improvements identified for complexes **1** and **2**, we were also interested in developing an improved synthetic method for the preparation of imino−amido complexes containing different substituents on the imino and amido nitrogen atoms (e.g., **3**). Keto amine **8** is a key building block for the preparation of imine−amine ligands (via the reaction with a variety of primary amines), but it was previously prepared in low yields (29−41%)[2b,7] by hydrolysis of imine−amine **7** (Scheme 6). We found that this hydrolysis reaction cleanly gave keto amine **8** and 2,6-diisopropylaniline. The low isolated yields reported previously might have been due to the loss of product during the isolation and separation of keto amine **8** from 2,6-diisopropylaniline. We modified both the reaction conditions and the isolation procedures to increase the final yield of **8** to 91%. We performed the hydrolysis of **7** in a mixture of ethanol and water (1:1 volume ratio) in the presence of sulfuric acid at 65 °C. The amount of sulfuric acid was reduced from 4 equiv, as reported in the original synthesis,[2b,7] to 2 equiv without loss of reaction efficiency.

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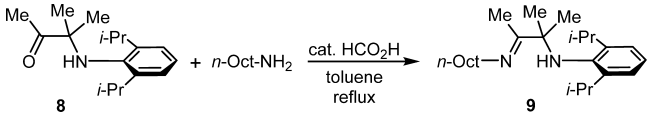
After the reaction mixture was quenched with NaOH, keto amine **8** and 2,6-diisopropylaniline were extracted with ethyl acetate (EtOAc) and thoroughly washed with water (in order to completely remove the inorganic base) before the volatiles were evaporated. Keto amine **8** and 2,6-diisopropylaniline were then separated by distillation under reduced pressure with a short-path distillation apparatus: 2,6-diisopropylaniline was effectively removed at 58−60 °C/0.8 mmHg to leave keto amine **8** in near-quantitative yield with 97% purity. The crude keto amine **8** could be further purified by crystallization from a small amount of hexane, resulting in a yield of 91% with >99% purity. The preparation of **8** using this modified procedure was demonstrated on a scale of over 0.4 mol (100 g), and the net yield improvement was from 29% to 96−99%.

The preparation of imine−amine ligand **9** was achieved by straightforward condensation of keto amine **8** with *n*-octylamine in the presence of a small amount of formic acid catalyst (*p*-toluenesulfonic acid monohydrate could also be used) in refluxing toluene (Scheme 7). Water generated in the reaction

Scheme 7. Preparation of imine−amine ligand 9



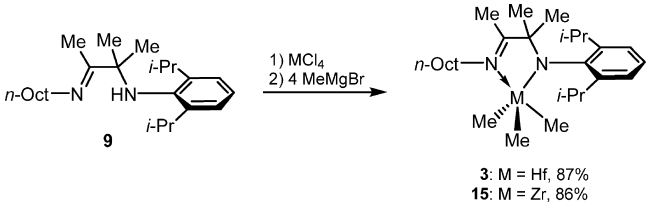
was azeotropically removed using a Dean−Stark trap. Typically, a small excess of *n*-octylamine (1.2−1.3 equiv total) was used in this reaction to facilitate the complete conversion, as a small amount of *n*-octylamine was usually lost in the Dean−Stark trap. The use of excess *n*-octylamine resulted in fast conversion to the desired product and also hindered the competitive reaction of keto amine **8** with 2,6-diisopropylaniline when **8** contaminated with a small amount of 2,6-diisopropylaniline was used in the reaction. Imine−amine ligand **9** was isolated in over 99% yield with 99% purity.

As shown in Scheme 1, imino−amido complex **3** was prepared previously by converting imine−amine ligand **9** into the corresponding lithium salt with *n*-BuLi. This salt was subsequently reacted with $HfCl_4$ to form the ligated hafnium trichloride derivative, which in turn was alkylated with 3 equiv of MeMgBr.[7] We envisioned that complex **3** and its Zr analogue (**15**) could be prepared directly by addition of ligand **9** to in situ-generated MMe_4 (M = Zr, Hf) (method A) or via the reaction of MeMgBr with a mixture of ligand **9** and MCl_4 (method B), the methods developed for the preparation of **1** and **2**.

Since method B was found previously to be more practical than method A, it was examined first for the preparation of imino−amido complexes **3** and **15**. Addition of MeMgBr (4.0−4.5 equiv) to a mixture of ligand **9** and $HfCl_4$ in toluene at 0 °C, followed by warming of the reaction mixture to ambient temperature, produced the desired complex **3**, which was isolated in 87% yield (Scheme 8). The Zr complex **15** was prepared in 86% yield following an analogous procedure. The molecular structure of **15** was determined by single-crystal X-ray analysis (Figure 3), and its metrical parameters are very similar to those of the hafnium analogue.[2b] The preparation of **3** by method B was demonstrated on a 0.10 mol scale (52 g, 87% yield).

The reaction of ligand **9** with $HfMe_4$ generated in situ from the reaction of $HfCl_4$ and MeMgBr at −35 °C also produced

Scheme 8. Preparation of imino−amido complexes 3 and 15



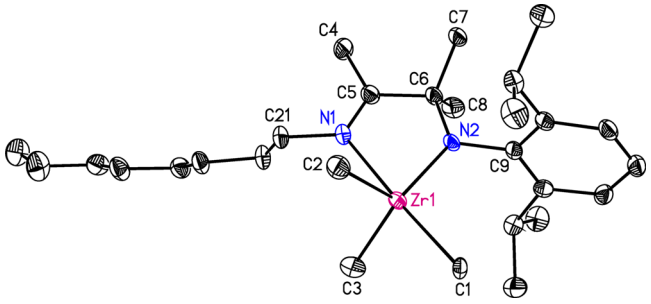


Figure 3. Molecular structure of **15**. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are shown at 50% probability. Selected bond lengths (Å) and angle (deg): Zr1−N1 = 2.385(4), Zr1−N2 = 2.062(4), N1−C5 = 1.290(6), N2−C6 = 1.485(6), Zr1−C1 = 2.366(4), Zr1−C2 = 2.259(5), Zr1−C3 = 2.245(6), N1−Zr1−N2 = 70.03(15).

complex **3** (method A, 75% yield). However, this method is less practical and robust, as it involves cryogenic reaction conditions and requires in situ preparation of thermally unstable metal alkyls.

The improved total synthesis of imino−amido complexes **3** and **15** containing different substituents on the imido and amido nitrogen atoms is summarized in Scheme 9. In comparison with the previous total synthesis of **3**, the new process described here eliminates the use of pyrophoric $AlMe_3$ and *n*-BuLi, simplifies individual procedures and product isolation, and substantially improves the overall yield from 12% to 77%.

CONCLUSIONS

Two processes were developed for the preparation of imino−amido Zr and Hf complexes **1** and **2** directly from bis-imine **6**, $ZrCl_4$ or $HfCl_4$, and MeMgBr in a one-pot synthesis. Method A involves the reaction of in situ-generated $ZrMe_4$ and $HfMe_4$ (from $ZrCl_4$ and $HfCl_4$ and MeMgBr) with bis-imine **6** to produce imino−amido complexes **1** and **2**, respectively, in near-quantitative yields. Alternatively, **1** and **2** can be conveniently prepared from the reaction of MeMgBr with a mixture of bis-imine **6** and MCl_4 (M = Zr, Hf) (method B). Method B has an advantage over method A, as it eliminates cryogenic reaction conditions and the need for in situ preparation of unstable metal alkyls.

A significantly improved method for the preparation of imino−amido complexes containing two different substituents on the imine and amine nitrogen atoms was also developed. It was discovered that very selective nucleophilic addition of MeMgBr and bis-imine **6** can be achieved, affording imine−amine **7** in 99% yield. Optimization of the hydrolysis reaction of imine−amine **7** led to a reduction in the amounts of both sulfuric acid and sodium hydroxide and a subsequent increase in the yield of keto amine **8** from 29% to 96−99%. Imino−amido complexes **3** and **15** were prepared in high yields (**3**,

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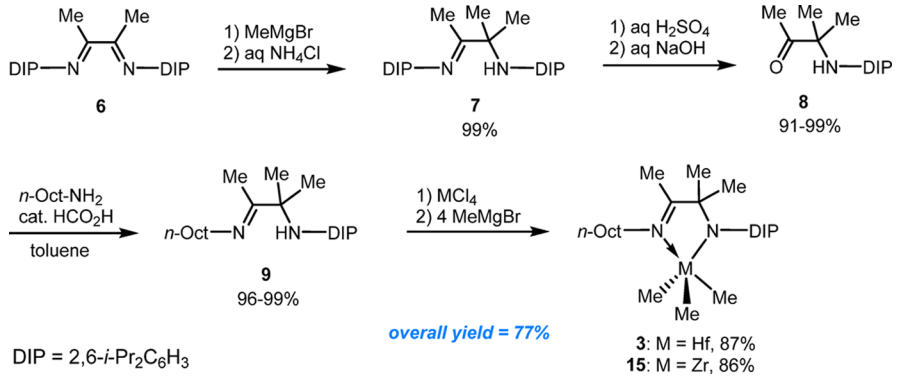
Scheme 9. Improved synthesis of imino−amido complexes 3 and 15



87%; **15**, 86%) by the reaction of MeMgBr with a mixture of imine−amine ligand **9** and MCl_4 (M = Zr, Hf). The overall yield of the improved total synthesis of **3** is 77%, which is six times higher than that of the previously reported synthesis.

EXPERIMENTAL SECTION

General Considerations. Solvents and reagents were obtained from commercial sources and used as received, unless otherwise noted. All syntheses and manipulations of air-sensitive materials were carried out under an inert atmosphere (nitrogen). Solvents (toluene, hexane, diethyl ether) were first saturated with nitrogen and then dried by passage through activated alumina and Q-5 catalyst (available from Engelhard Chemicals, Inc.) prior to use. Benzene-d_6 (C_6D_6) was dried over molecular sieves and filtered prior to use. NMR spectra were recorded on a Bruker 400 (FT 400 MHz, ^{1}H; 101 MHz, ^{13}C) spectrometer. ^{1}H NMR data are reported as follows: chemical shift (multiplicity, coupling constant, integration, assignment). Multiplicities are denoted as follows: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet, hept = heptet. Chemical shifts for ^{1}H NMR data are reported in parts per million downfield from internal tetramethylsilane (TMS, δ scale) using residual protons in the deuterated solvent (C_6D_6, 7.15 ppm) as a reference. ^{13}C NMR data were determined with ^{1}H decoupling, and the chemical shifts are reported in parts per million versus tetramethylsilane (C_6D_6, 128 ppm). Elemental analyses were performed at Midwest Microlab, LLC.

Preparation of *N,N′*-Bis(2,6-diisopropylphenyl)-1,4-diaza-2,3-dimethyl-1,3-butadiene (6). Bisimine **6** was prepared by modification of a reported procedure.[18] Into a 2 L three-neck round-bottom flask equipped with an overhead agitator, a cold water condenser, a nitrogen pad, a heating mantle, and a thermocouple were loaded 2,3-butanedione (86.09 g, 1.0 mol), 2,6-diisopropylaniline (DIPA) (354.58 g, 2.0 mol), ethanol (800 mL), and 98% formic acid (2 mL). The mixture was heated at 60−65 °C for 50 h. The resulting mixture was then allowed to cool to ambient temperature overnight. The precipitated product was filtered, rinsed with cold ethanol (4 °C, 200 mL), suction-dried, and dried under reduced pressure to give a first crop of product (310.1 g). The mother liquor/filtrate was concentrated to a black residue (102 g). Ethanol (100 mL) was added to the residue, and the resulting mixture was placed in a refrigerator overnight. The precipitate was filtered, rinsed with cold ethanol (50 mL), and dried under reduced pressure to give a second crop of product (54.5 g). The total mass of product obtained was 364.6 g, corresponding to a yield of 88.56% with over 98% purity as determined by GC analysis (with less than 2% isomers). Note: technical grade, 90% 2,6-diisopropylaniline was used. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.19−7.10 (m, 6H, Ph), 2.71 (septet, 4H, C*H*), 2.07 (s, 6H, CH_3), 1.19 (dd, 24H, CH_3).

Preparation of Imino−Amido Zr and Hf Complexes from in Situ-Generated MMe_4 (Method A). **Preparation of (*N*-(2,6-Diisopropylphenyl)-*N*-(3-(2,6-diisopropylphenyl)-imino-2-methylbutan-2-yl)amino)trimethylzirconium (1).** To a suspension of $ZrCl_4$ (2.33 g, 10.0 mmol) in anhydrous toluene (50 mL) in a 125 mL three-neck flask equipped with stir bar, a thermometer, and a nitrogen pad at −40 °C was added dropwise a solution of 3.0 M MeMgBr solution in diethyl ether (15 mL, 45 mmol) over 10 min while the temperature was maintained. The resulting mixture was stirred at −40 to −35 °C for an additional 30 min, and then a solution of *N,N′*-bis(2,6-diisopropylphenyl)-1,4-diaza-2,3-dimethyl-1,3-butadiene (**6**) (4.046 g, 10 mmol) in toluene (15 mL) was added over 10 min at −40 to −35 °C. The resulting suspension was allowed to stir at −40 to −35 °C for 1 h, and then the reaction mixture was allowed to warm to ambient temperature (25 °C) over 40 min by removal of the cooling bath, to give a dark-brown to black mixture. An aliquot (0.3 mL) was taken from the reaction mixture and filtered through a syringe filter into an NMR tube for ^{1}H NMR analysis in C_6D_6, which showed that the reaction was complete. The volatiles were removed under reduced pressure, and the residue was extracted twice with anhydrous hexane (100 mL, 50 mL). The combined hexane solution was concentrated under reduced pressure to give product **1** as a yellow solid (5.25 g, 94%). The ^{1}H and ^{13}C NMR spectra are consistent with those reported in the literature.[2b] ^{1}H NMR (400 MHz, C_6D_6) δ 7.22−7.16 (m, 3H), 7.12−7.03 (m, 3H), 3.75 (hept, J = 6.9 Hz, 2H), 2.86 (hept, J = 6.8 Hz, 2H), 1.48 (s, 3H), 1.39 (d, J = 6.8 Hz, 6H), 1.32 (d, J = 6.8 Hz, 6H), 1.30 (d, J = 6.8 Hz, 6H), 1.21 (s, 6H), 1.03 (d, J = 6.8 Hz, 6H), 0.58 (s, 9H). ^{13}C NMR (101 MHz, C_6D_6) δ 195.48, 148.99, 145.33, 142.06, 139.19, 126.83, 126.46, 124.73, 124.37, 72.91, 48.65, 29.55, 28.70, 28.62, 26.23, 25.30, 24.56, 24.20, 19.28.

Preparation of (*N*-(2,6-Diisopropylphenyl)-*N*-(3-(2,6-diisopropylphenyl)imino-2-methylbutan-2-yl)amino)-trimethylhafnium (2). $HfCl_4$ (3.203 g, 10 mmol) and anhydrous toluene (60 mL) were loaded into a 125 mL three-neck flask equipped with a stir bar and a thermometer under a nitrogen atmosphere. The suspension was cooled to −40 °C. A 3.0 M solution of MeMgBr in diethyl ether (13.7 mL, 41 mmol) was added through a syringe at such a rate to

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Org. Process Res. Dev. XXXX, XXX, XXX−XXX

maintain the reaction temperature below −35 °C. The addition took about 5 min. The resulting yellow suspension was stirred at −40 to −35 °C for 1.0 h. A solution of **6** (4.046 g, 10 mmol) in anhydrous toluene (15 mL) was added at −40 to −35 °C over 5 min. The resulting mixture was stirred at −40 to −35 °C for 2 h and then warmed to ambient temperature by removal of the cooling bath. The mixture was allowed to stir at ambient temperature (25 °C) until the conversion was complete as monitored by ^{1}H NMR spectroscopy (0.3−0.5 mL of the reaction mixture was taken and filtered through a syringe filter into an NMR tube under nitrogen for ^{1}H NMR analysis with C_6D_6 as an internal reference). Whenever the ^{1}H NMR spectrum showed that MeMgBr was completely consumed and the reaction was not complete, additional MeMgBr was added. The reaction took over 24 h, and the reaction mixture turned dark-brown to black. Upon completion of the reaction, the volatiles were removed under reduced pressure, and the residue was extracted twice with anhydrous hexane (100 mL, 50 mL). The combined hexane solution was concentrated under reduced pressure to give product **2** as a yellow solid (6.24 g, 97%). The ^{1}H and ^{13}C NMR spectra are consistent with those reported in the literature.[2b] ^{1}H NMR (400 MHz, C_6D_6) δ 7.221−7.16 (m, 3H), 7.12−7.03 (m, 3H), 3.76 (hept, J = 6.9 Hz, 2H), 2.89 (hept, J = 6.8 Hz, 2H), 1.42 (s, 3H), 1.40 (d, J = 6.8 Hz, 6H), 1.31 (d, J = 6.8 Hz, 6H), 1.28 (d, J = 6.8 Hz, 6H), 1.17 (s, 6H), 1.00 (d, J = 6.8 Hz, 6H), 0.36 (s, 9H). ^{13}C NMR (101 MHz, C_6D_6) δ 197.25, 148.59, 144.90, 143.99, 139.54, 127.07, 125.98, 124.62, 124.40, 73.38, 61.25, 29.85, 28.63, 28.59, 26.22, 25.24, 24.61, 24.32, 19.44.

Preparation of Imino−Amido Zr and Hf Complexes from in Situ-Generated Bisimine·MCl_4 (Method B). **Preparation of 1.** *Method B-1: Addition of MeMgBr at −40 to −35 °C.* To a suspension of $ZrCl_4$ (2.33 g, 10.0 mmol) in anhydrous toluene (60 mL) in a 125 mL three-neck flask equipped with a stir bar, a thermometer, and a nitrogen pad at ambient temperature (23 °C) was added **6** (4.046 g, 10.0 mmol). After 1 h of stirring at ambient temperature, the resulting mixture was cooled to −40 °C, and a 3.0 M solution of MeMgBr in diethyl ether (15 mL, 45 mmol) was slowly added at such a rate to maintain the reaction temperature below −35 °C. The addition took about 5 min. The resulting mixture was allowed to stir at −40 to −35 °C for 1 h, subsequently allowed to warm to ambient temperature (23 °C) over 2 h, and further stirred at ambient temperature (23 °C) for 1 h. A 0.3 mL aliquot of the reaction mixture was taken and filtered through a syringe filter into an NMR tube for ^{1}H NMR analysis with C_6D_6 as an internal reference, which showed that the reaction was complete. The volatiles were removed under reduced pressure, and the residue was extracted twice with anhydrous hexane (100 mL, 50 mL). The combined hexane solution was concentrated under reduced pressure to give product **1** (4.97 g, 89%). The ^{1}H and ^{13}C NMR spectra are consistent with those of the compound synthesized according to method A as well as those reported in the literature.[2b]

Method B-2: Addition of MeMgBr at Ambient Temperature. To a suspension of $ZrCl_4$ (2.33 g, 10.0 mmol) in anhydrous toluene (60 mL) in a 125 mL three-neck flask equipped with a stir bar, thermometer, and a nitrogen pad at ambient temperature (23 °C) was added **6** (4.046 g, 10.0 mmol). The resulting mixture was stirred at ambient temperature for 1 h. A 3.0 M solution of MeMgBr in diethyl ether (15 mL, 45 mmol) was added via a syringe pump at 23 to 25 °C over 1 h. The reaction mixture was allowed to stir at ambient temperature for an additional 1 h. A 0.3−0.5 mL sample of the reaction mixture was taken and filtered through a syringe filter into an NMR tube for ^{1}H NMR analysis with C_6D_6 as an external reference, which showed that the reaction was complete. The volatiles were removed under reduced pressure, and the residue was extracted twice with anhydrous hexane (100 mL, 50 mL). The combined hexane solution was concentrated under reduced pressure to give the desired product **1** (4.78 g, 86%). The ^{1}H and ^{13}C NMR spectra are consistent with those of the compound synthesized according to method A as well as those reported in the literature.[2b]

Preparation of 2. To a suspension of $HfCl_4$ (3.203 g, 10.0 mmol) in anhydrous toluene (60 mL) in a 125 mL three-neck flask equipped with a stir bar and a thermometer under a nitrogen atmosphere at ambient temperature (23 °C) was added **6** (4.046 g, 10.0 mmol). The resulting mixture was stirred at ambient temperature for 1 h. A 3.0 M solution of MeMgBr in diethyl ether (15 mL, 45 mmol) was slowly added at such a rate to maintain the reaction temperature between 23 and 40 °C. The addition took about 15 min, and the temperature rose to 36 °C. The reaction mixture was allowed to stir at ambient temperature for another 2 h. A 0.3−0.5 mL sample of the reaction mixture was taken and filtered through a syringe filter into an NMR tube for ^{1}H NMR analysis with C_6D_6 as an internal reference, which showed that the reaction was complete. The volatiles were removed under reduced pressure, and the residue was extracted twice with anhydrous hexane (100 mL, 50 mL). The combined hexane solution was concentrated under reduced pressure to give the desired product **2** (6.33 g, 98%). The ^{1}H and ^{13}C NMR spectra are consistent with those of the compound synthesized according to method A as well as those reported in the literature.[2b] The reaction was also carried out on a 0.1 mol scale, and **2** was isolated in 97% yield (62.5 g).

Preparation of *N*-(3-(2,6-Diisopropylphenylamino)-3-methylbutan-2-ylidene)-2,6-diisopropylbenzenamine (7). Into a 3 L three-neck round-bottom flask equipped with an overhead agitator, a cold water condenser, a nitrogen pad, a heating mantle, and a thermocouple were loaded **6** (202.0 g, 0.499 mol) and anhydrous toluene (800 mL). The mixture was stirred at ambient temperature to form a yellow solution. A 3.0 M solution of methylmagnesium bromide in diethyl ether (220 mL, 0.66 mol) was added slowly at ambient temperature over 30 min. A slightly exothermic reaction occurred, and the temperature rose from 18 to 22 °C. The reaction mixture was then heated and stirred at 60 °C until the reaction was complete (3 h) as monitored by GC. The resulting mixture was cooled to 0 to 5 °C with an ice−water bath. Aqueous NH_4Cl solution (20 wt %, 500 mL) was slowly added[19] over 30 min, and the reaction mixture was stirred for another 30 min. The product was extracted with ethyl acetate (250 mL × 2), and the organic phase was washed with water (500 mL). The volatiles were removed under reduced pressure by rotary evaporation, and the residue was dried in a vacuum oven at 45 °C/<1 mmHg overnight, which gave the desired product **7** (208.0 g) in 99.0% yield with over 98% purity as measured by GC area % (with less than 2% isomers as determined by GC analysis). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20−7.02 (m, 6H), 4.34 (s, 1H), 3.53 (dt, J = 13.7, 6.8 Hz, 2H), 2.81 (dt, J = 13.7, 6.9 Hz, 2H), 1.87 (s, 3H), 1.35 (s, 6H), 1.24−1.15 (m, 24H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.46, 146.59, 145.99, 140.17, 136.27, 124.51, 123.26, 123.10, 123.01, 61.74, 28.39, 27.88, 27.10, 24.20, 23.52, 23.21, 16.41.

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Org. Process Res. Dev. XXXX, XXX, XXX−XXX

Preparation of 3-(2,6-Diisopropylphenylamino)-3-methylbutan-2-one (8). Into a 3 L three-neck round-bottom flask equipped with an overhead agitator, a cold water condenser, a nitrogen pad, a heating mantle, and a thermocouple was loaded *N*-(3-(2,6-diisopropylphenylamino)-3-methylbutan-2-ylidene)-2,6-diisopropylbenzenamine (**7**) (206.0 g, 489.7 mmol) and anhydrous ethanol (800 mL). The mixture was heated with stirring to form a solution. A 2.5 N aqueous solution of H_2SO_4 (776 mL, 970 mmol) was added over 1 h at 40 °C. The mixture was subsequently heated at 65 °C until the hydrolysis was complete as monitored by GC analysis (3−4.5 h). The resulting mixture was cooled to 0 to 5 °C with an ice−water bath. A solution of 5.0 N NaOH (388 mL, 1.94 mol) was added at such a rate to remain the temperature at or below ambient temperature to adjust the pH to approximately 11. The mixture was then extracted with hexane (2 × 1 L), and the organic phase was washed with water (2 × 500 mL). Volatiles were removed under reduced pressure, and the residue (203 g) as a mixture of keto amine **8** and 2,6-diisopropylaniline was subjected to distillation at 0.8 mmHg with a short-path distillation apparatus. 2,6-Diisopropylaniline (79 g, 91%) was removed at 58−62 °C/0.8 mmHg. The crude product (123 g, 96%) remained, which was 96.5% as determined by GC analysis and pure enough for use in the next step. Further purification of the crude product was achieved by recrystallization from hexane to give 114.7 g (91%) of **8** with over 99% purity by GC analysis. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07 (s, 3H), 3.69 (s, 1H), 3.12 (hept, J = 6.9 Hz, 2H), 2.37 (s, 3H), 1.22 (s, 6H), −1.17 (d, J = 6.9 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 212.85, 145.55, 139.60, 124.72, 123.13, 63.70, 28.28, 25.42, 24.02, 23.94.

Preparation of 2,6-Diisopropyl-*N*-(2-methyl-3-(octyliminobutan-2-yl))benzenamine (9). Into a 250 mL three-neck round-bottom flask equipped with an electrical stirrer, a cold water condenser with a Dean−Stark trap attached, a nitrogen pad, a heating mantle, and a thermocouple were loaded 3-(2,6-diisopropylphenylamino)-3-methylbutan-2-one (**8**) (20.91 g, 80 mmol), *n*-octylamine (12.41 g, 96.0 mmol), toluene (100 mL), and 98% formic acid (40 mg). The mixture was heated at reflux for 2.5 h, and then additional *n*-octylamine (3.0 g, 23 mmol) was added. The mixture was heated at reflux overnight. The resulting mixture was cooled to ambient temperature and washed with water (2 × 100 mL). The volatiles were removed under reduced pressure. The residue was dried in a vacuum oven at 55−60 °C/1 mmHg overnight, which gave **9** (29.80 g, 100%) as a colorless viscous oil. ^{1}H NMR (400 MHz,, $CDCl_3$) δ 7.08−6.86 (m, 3H), 3.37 (hept, J = 6.8 Hz, 2H), 3.25 (t, J = 7.1 Hz, 2H), 1.84 (s, 3H), 1.69−1.54 (m, 2H), 1.41−1.14 (m, 10H), 1.09 (s, 6H), 1.08 (d, J = 6.9 Hz, 12H), 0.87−0.75 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.37, 145.38, 140.60, 123.02, 121.93, 59.97, 50.11, 30.89, 29.89, 28.62, 28.35, 26.86, 26.74, 25.57, 23.24, 21.66, 13.08, 12.21.

Preparation of (*N*-(1,1-Dimethyl-2-(octylimino-κ*N*)-propyl)-2,6-diisopropylbenzenaminato-κ*N*)-trimethylhafnium (3). *Method A.* $HfCl_4$ (2.127 g, 6.64 mmol) and anhydrous toluene (40 mL) were loaded into a 125 mL three-neck flask equipped with a stir bar and a thermometer under a nitrogen atmosphere. The suspension was cooled to −40 °C. A 3.0 M solution of MeMgBr in diethyl ether (9.1 mL, 27.3 mmol) was added through a syringe at such a rate to maintain the reaction temperature below −35 °C. The addition took about 5 min. The resulting slightly yellow suspension was stirred at −40 to −35 °C for 1.0 h. A solution of 2,6-diisopropyl-*N*-(2-methyl-3-(octyliminobutan-2-yl))-benzenamine (**9**) (2.474 g) in anhydrous toluene (20 mL) was added at −40 to −35 °C over 5 min. The resulting mixture was stirred at −40 to −35 °C for 2 h and then warmed to ambient temperature by removal of the cooling bath. The mixture was allowed to continue stirring at ambient temperature (25 °C) until the conversion was complete as monitored by ^{1}H NMR spectroscopy (0.3−0.5 mL of the reaction mixture was taken and filtered through a syringe filter into an NMR tube under nitrogen for ^{1}H NMR analysis with C_6D_6 as an external reference). Whenever the ^{1}H NMR spectrum showed that MeMgBr was completely consumed and the reaction was not complete, additional MeMgBr was added. The reaction took over 24 h, and the reaction mixture turned dark-brown to black. Upon completion of the reaction, the volatiles were removed under reduced pressure, and the residue was extracted with anhydrous hexane (20 mL). The wet cake was extracted with additional hexane (2 × 5 mL). The combined hexane solution was concentrated under reduced pressure to give product **3** as a slightly yellow solid (2.96 g, 75%). The ^{1}H and ^{13}C NMR spectra were consistent with those reported in the literature.[2b] ^{1}H NMR (400 MHz, C_6D_6) δ 7.28−7.15 (m, 3H), 3.68 (hept, J = 6.8 Hz, 2H), 3.44−3.35 (m, 2H), 1.55−1.44 (m, 2H), 1.41 (d, J = 7.0 Hz, 6H), 1.40 (s, 3H), 1.29 (d, J = 7.0 Hz, 6H), 1.32−1.18 (m, 10H), 0.98 (s, 6H), 0.93 (t, J = 6.9 Hz, 3H), 0.44 (s, 9H). ^{13}C NMR (101 MHz, C_6D_6) δ 189.33, 149.27, 140.68, 128.17, 127.93, 126.36, 124.78, 76.30, 56.98, 50.95, 32.18, 29.64, 28.73, 28.50, 28.01, 27.60, 26.84, 24.72, 23.09, 15.50, 14.37.

Method B. To a suspension of $HfCl_4$ (2.23 g, 7.0 mmol) in anhydrous toluene (40 mL) in a 125 mL three-neck flask equipped with a stir bar and a thermometer under a nitrogen atmosphere at ambient temperature (23 °C) was added **9** (2.474 g, 6.64 mmol). The resulting mixture was stirred at ambient temperature for 0.5 h and then cooled to 0 °C. A 3.0 M solution of MeMgBr in diethyl ether (10.5 mL, 31.5 mmol) was slowly added at such a rate to maintain the reaction temperature below 5 °C. The addition took about 5 min. The reaction mixture was allowed to stir at 0 to 5 °C for another 1 h and then slowly warmed to ambient temperature overnight. A 0.3−0.5 mL sample of the reaction mixture was taken and filtered through a syringe filter into an NMR tube for ^{1}H NMR analysis with C_6D_6 as an external reference, which showed that the reaction was complete. The volatiles were removed under reduced pressure, and the residue was extracted with anhydrous hexane (30 mL). The wet cake was extracted with additional hexane (2 × 10 mL). The combined hexane solution was concentrated under reduced pressure to give the desired product **3** (3.45 g, 87%). The ^{1}H and ^{13}C NMR spectra were consistent with those of the compound synthesized according to method A as well as those reported in the literature.[7] The reaction was also conducted on a 0.10 mol scale, which gave 51.7 g of **3** (86.9% yield).

Preparation of (*N*-(1,1,-Dimethyl-2-(octylimino-κ*N*)-propyl)-2,6-diisopropylbenzenaminato-κ*N*)-trimethylzirconium (15). Method B was used. To a suspension of $ZrCl_4$ (2.447 g, 10.5 mmol) in anhydrous toluene (40 mL) in a 125 mL three-neck flask equipped with a stir bar, a thermometer, and a nitrogen pad at ambient temperature (23 °C) was added a solution of **9** (3.726 g, 10.0 mmol) in toluene (20 mL). The resulting mixture was stirred at ambient temperature for 0.5 h and then cooled to 0 °C. A 3.0

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Org. Process Res. Dev. XXXX, XXX, XXX−XXX

M solution of MeMgBr in diethyl ether (15 mL, 45 mmol) was added via a syringe pump at 0 to 5 °C over 15 min. The reaction mixture was allowed to stir at 0 to 5 °C for an additional 1 h and then slowly warmed to ambient temperature (23 to 25 °C) overnight. A 0.3−0.5 mL sample of the reaction mixture was taken and filtered through a syringe filter into an NMR tube for ^{1}H NMR analysis with C_6D_6 as an external reference, which showed that the reaction was complete. The volatiles were removed under reduced pressure, and the residue was extracted with anhydrous hexane (90 mL). The wet cake was extracted with additional hexane (10 mL × 2). The combined hexane solution was concentrated under reduced pressure to give the desired product **15** (4.4 g, 86%). Anal. Calcd for $C_{28}H_{52}N_2Zr$: C, 66.21; H, 10.32; N, 5.51. Found: C, 66.37; H, 9.95; N, 5.30. ^{1}H NMR (400 MHz, C_6D_6) δ 7.20−7.15 (m, 3H), 3.66 (hept, J = 6.8 Hz, 2H), 3.43−3.34 (m, 2H), 1.56−1.44 (m, 2H), 1.43 (s, 3H), 1.38 (d, J = 6.7 Hz, 6H), 1.27 (d, J = 6.7 Hz, 6H), 1.34−1.13 (m, 10H), 1.00 (s, 6H), 0.92 (t, J = 6.7 Hz, 2H), 0.66 (s, 9H). ^{13}C NMR (101 MHz, C_6D_6) δ 187.87, 149.91, 138.33, 126.96, 124.92, 75.39, 51.18, 44.29, 32.18, 29.65, 28.90, 28.50, 28.03, 27.22, 26.83, 24.68, 23.09, 15.18, 14.36.

Structure Determination of 15. X-ray intensity data were collected on a Bruker SMART diffractometer using Mo Kα radiation (λ = 0.71073 Å) and an APEXII CCD area detector. Raw data frames were read by the program SAINT[20] 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 numerical absorption corrections were applied on the basis of indexed and measured faces. 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 all of the 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 was calculated to provide a reference to the conventional R value, but its function was not minimized.

Crystallographic Data for ***15****.* $C_{28}H_{52}N_2Zr$, MW = 507.93, triclinic, $P\bar{1}$, 0.23 mm × 0.16 mm × 0.16 mm), a = 9.7837(5) Å, b = 17.3161(10) Å, c = 17.4313(10) Å, α = 80.898(3)°, β = 88.203(3)°, γ = 89.242(3)°, T =100(2) K, Z = 2, V = 2914.4(3) Å^3, R_1 = 0.0683, 0.0747, wR_2 = 0.1822, 0.1860 ($I > 2\sigma(I)$, all data), GOF = 1.154.

■ ASSOCIATED CONTENT

Supporting Information

Synthetic procedures and NMR spectra of all prepared compounds. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.oprd.5b00047.

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Notes

The authors declare no competing financial interest.

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