ORGANOMETALLICS

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Aminotroponiminato Hafnium and Zirconium Complexes: Synthesis and Ethylene/1-Octene Copolymerization Study

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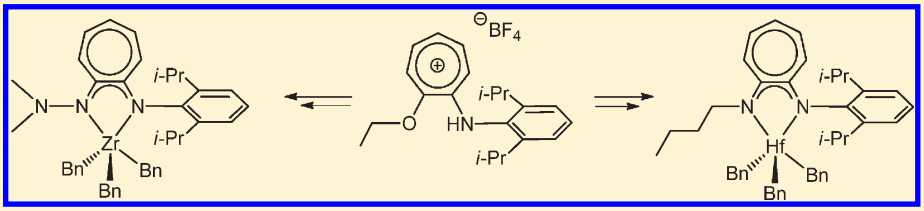
Supporting Information

ABSTRACT:



Four new aminotroponiminato hafnium and zirconium tribenzyl complexes were prepared by reacting neutral ligands with the corresponding tetrabenzyl complexes. Aminotroponimine ligands were prepared in four steps starting from tropolone. An air-stable ethoxy-amino-tropylium cation intermediate isolated during ligand synthesis was found to react directly with amines significantly faster than the neutral intermediate proposed previously. This tropylium cation represents a convenient way to prepare a large array of aminotroponimines. An ethylene/1-octene copolymerization study conducted at 120 °C demonstrated that the aminotroponiminato hafnium and zirconium complexes are catalytically active, but their activity is lower than that observed for the corresponding imino−enamido complexes. Polymer analysis data (GPC and DSC) indicated that aminotroponiminato complexes generate at least two catalytically active species under polymerization conditions.

INTRODUCTION

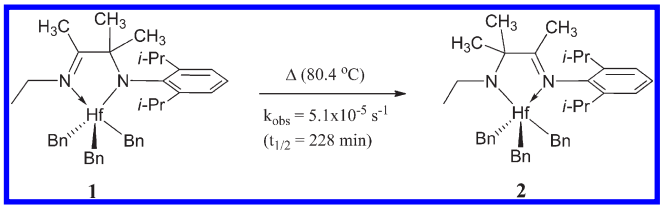
Discovery of new molecular olefin polymerization catalysts continues to attract the attention of academic and industrial chemists.[1] This research has been driven by the desire to create new polyolefin-based materials[2] and improve the current polymerization processes.[3] Recently, we[4−6] and others[7,8] reported hafnium and zirconium imino−amido complexes as useful procatalysts for olefin polymerization. These complexes exhibit good catalytic activities at temperatures above 100 °C, are capable of producing very high molecular weight ethylene-based copolymers, and have the ability to undergo reversible chain transfer with diethylzinc to produce olefin block copolymers.[5] One undesired feature of these complexes is their thermal instability at elevated temperature. For example, imino−amido complexes containing the trimethylethylidene ligand bridge (e.g., **1**) undergo 1,2-methyl shift to form isomeric complexes (e.g., **2**) which exhibit significantly lower polymerization activity than the original complexes (e.g., **1**) (Scheme 1).[6]

To address the thermal instability of imino−amido complexes, new imino−enamido complexes (e.g., **3**; Scheme 2) were prepared which have bonding features similar to those of imino−amido complexes, but their ligand framework eliminates all decomposition pathways encountered with imino−amido complexes.[9] Imino−enamido complexes are not only thermally very stable, but more importantly, exhibit higher polymerization activity, produce higher molecular weight polymers, and incorporate more 1-octene into the polymer backbone than the corresponding imino−amido complexes.[9] Very promising results obtained with imino−enamido complexes made us consider the preparation and evaluation of complexes similar to **3**, but with ligands containing different ring sizes. The ring size of imino−enamine ligands should influence the N−C−C−N geometry, thus affecting the bite angle (N−M−N), a feature that might lead to a different polymerization behavior. The direct seven-membered-ring analogue of **3** most likely cannot be prepared by the same methodology used to synthesize **3**, because such a seven-membered-ring ligand exists in the bis-imine rather than imino−enamine form, on the basis of experimental[10] and computational data.[9a] Therefore, we considered the preparation of analogues of **3**, but with aminotroponimine ligands which have a fully aromatic seven-membered-ring fragment (e.g., structures **4** and **5** in Scheme 2; only one resonance form is shown).

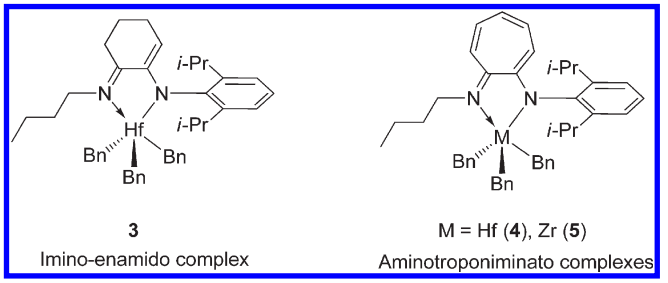
Various aminotroponiminato complexes have been described in the literature;[11] however, to our knowledge, their use as olefin polymerization catalysts has been only demonstrated by Jordan

Received: May 1, 2011
Published: August 08, 2011

Scheme 1. Thermal Rearrangement of Imino−Amido Complex 1



Scheme 2. Imino−Enamido Complex 3 and Analogous Aminotroponiminato Complexes 4 and 5



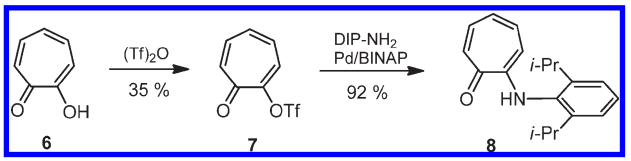
and co-workers, who showed that the cationic aluminum complexes $[\{(i\text{-Pr})_2\text{ATI}\}\text{AlR}][\text{B}(\text{C}_6\text{F}_5)_4]$ (R = Et, *i*-Bu; $(i\text{-Pr})_2$ATI = *N*,*N*′-diisopropylaminotroponiminate) are capable of polymerizing ethylene to linear polymer, albeit with low activity.[12] Additionally, the $\{(i\text{-Pr})_2\text{ATI}\}\text{AlR}^+$ (R = Et, *n*-Pr, *i*-Bu) cations catalyze the head-to-tail dimerization of *tert*-butylacetylene by an insertion/σ-bond metathesis mechanism.[13,14] Moreover, $\{(i\text{-Pr})_2\text{ATI}\}\text{AlR}^+$ cations initiate the polymerization of propylene oxide and isobutylene.[13] Aminotroponiminato zinc complexes have been studied extensively for the catalytic hydroamination of alkenes (inter- and intramolecular) and alkynes (intermolecular).[15] In addition, Roesky and co-workers described aminotroponiminato complexes of alkaline-earth and lanthanide metals as catalysts for hydroamination/cyclization reactions.[16] Dinuclear zinc aminotroponiminato complexes have been reported to catalyze the copolymerization of epoxides (propylene oxide, cyclohexene oxide, or mixtures thereof) and CO_2 to give low yields of polycarbonate products.[17]

A little over a decade ago, Lippard and co-workers developed a multicomponent system for the preparation of unsymmetrical diols from carbonyl compounds, CO, and aminotroponiminato titanium dialkyl complexes.[18] Synthesis of Hf(IV) and Zr(IV) aminotroponiminato[19] and related tropocorand[20] complexes have been described in the literature, but none of these complexes were evaluated as procatalysts for olefin polymerization. Moreover, all reported hafnium and zirconium aminotroponiminato complexes, with the exception of one dinuclear complex,[20a] contain at least two ligands per metal center, whereas our objective was to prepare and evaluate mononuclear complexes containing a single aminotroponiminato ligand. In this contribution, we describe the synthesis and full characterization of four aminotroponiminato tribenzyl hafnium and zirconium complexes and their evaluation as procatalysts for ethylene/1-octene copolymerization reactions.

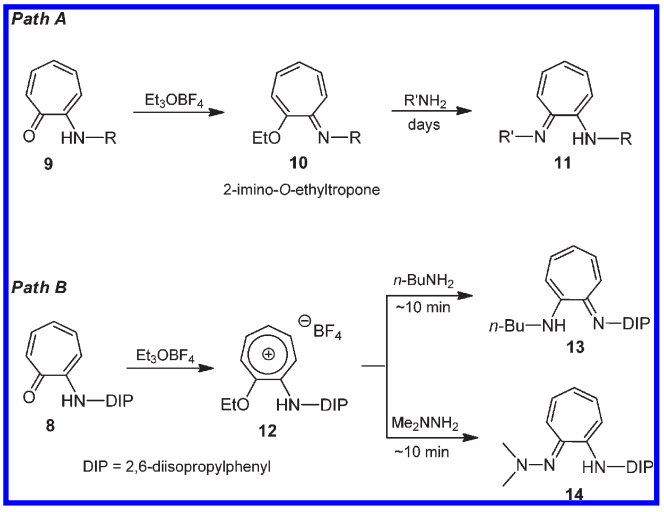
RESULTS AND DISCUSSION

Ligand Synthesis. Ligands needed for the preparation of the desired aminotroponiminato hafnium and zirconium tribenzyl

Scheme 3. Synthesis of Aminotropone 8



Scheme 4. Postulated (Path A)[21a,23] and Observed (Path B) Routes to Aminotroponimines



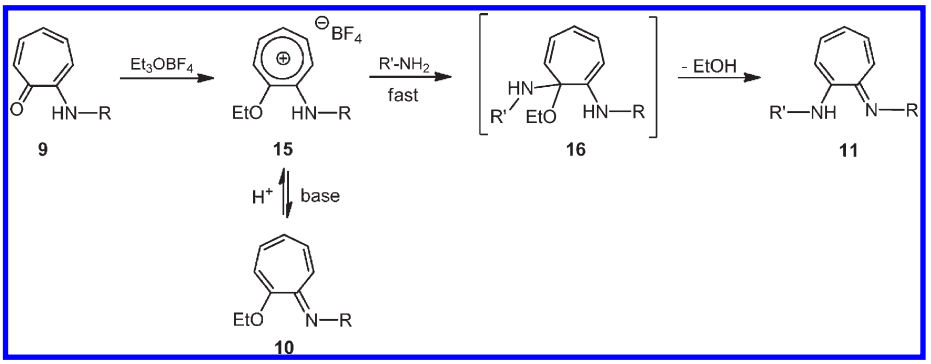
complexes contain two different substituents on the nitrogen atoms, and therefore it is necessary to introduce the amine and imine groups sequentially, a strategy that has been described previously in the literature. The first nitrogen-containing substituent was introduced in two steps starting from tropolone (**6**),[15g,21] as shown in Scheme 3. Synthesis of 2-triflatotropone (**7**)[21a] and 2-(2,6-diisopropylphenyl)aminotropone (**8**)[21b] was accomplished by following published procedures.

The second nitrogen-containing group was introduced by the reaction of aminotropones with Et_3OBF_4 and an amine. This transformation was postulated to proceed via a neutral 2-imino-*O*-ethyltropone[15g,22,23] (**10**) (Scheme 4, path A), which subsequently reacts with excess amine to form aminotroponimines (**11**).[15g,23] 2-Arylimino-*O*-ethyltropone intermediates (Ar = *p*-bromophenyl, pyrrol-1-yl) have been isolated.[23] However, they are slow to form (days), and their reaction with arylamines to form aminotroponimines takes several days at 40 °C.[23] Interestingly, reaction of **8** with Et_3OBF_4 did not produce the corresponding 2-arylimino-*O*-ethyltropone but instead generated tropylium intermediate **12** cleanly in 3 h (Scheme 4, path B) under conditions identical to those previously reported for the synthesis of aminotroponimines. This tropylium derivative (**12**) can be isolated easily by precipitation with excess diethyl ether and it is air stable. NMR tube experiments showed that **12** reacts rapidly (ca 10 min) with excess *n*-butylamine and *N*,*N*-dimethylhydrazine to give the desired aminotroponimines **13** and **14**, respectively, in high yields.

Isolation of tropylium derivative **12** and its very fast reaction with amines to form aminotroponimines, coupled with the very slow reaction of 2-imino-*O*-ethyltropones with amines to form aminotroponimines, suggest that 2-imino-*O*-ethyltropones might not be direct intermediates in these reactions. Tropylium derivatives

dx.doi.org/10.1021/om200362v |*Organometallics* 2011, 30, 4589–4597

Scheme 5. Possible Mechanism for the Formation of 11 from 9



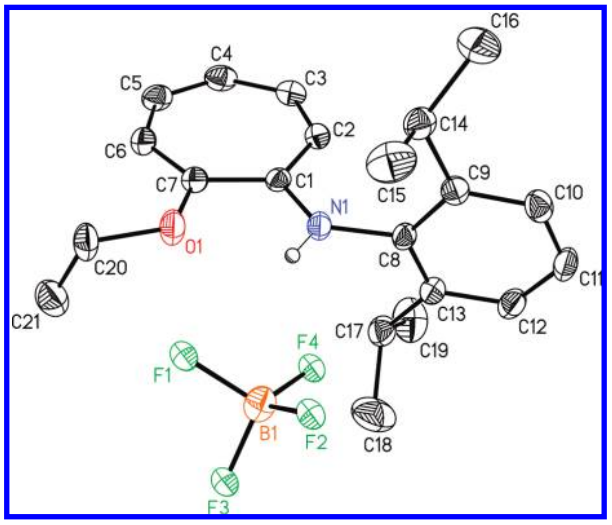


Figure 1. Molecular structure of compound **12**. Hydrogen atoms (except H1) are omitted for clarity. Thermal ellipsoids are shown at the 40% probability level. Selected bond distances (Å) and angles (deg): O1−C7 = 1.342(2), N1−C1 = 1.335(2), C1−C7 = 1.450(2), N1−H1 = 0.86(2); O1−C7−C1 = 109.39(14), C1−N1−H1 = 116.6(13).

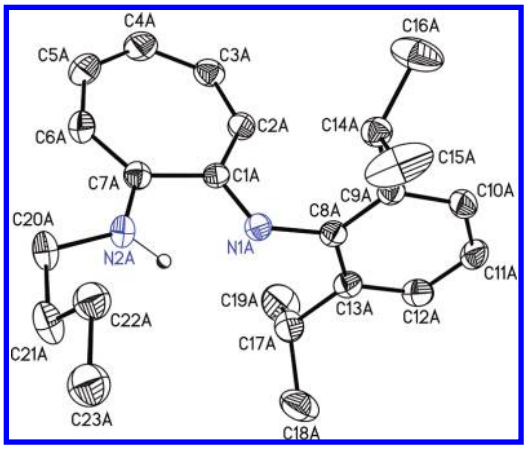


Figure 2. Molecular structure of ligand **13**. Hydrogen atoms (except H2A) are omitted for clarity. Thermal ellipsoids are shown at the 40% probability level. Selected bond distances (Å) and angles (deg): N1A−C1A = 1.299(3), N2A−C7A = 1.337(3), C1A−C7A = 1.489(3), N2A−H2A = 0.88(2); N1A−C1A−C7A = 113.5(2), C7A−N2A−H2A = 111(1).

are likely to be products of the reactions between **9** and Et_3OBF_4.[24] It is well-known that aminotropones can react with various electrophiles to form the corresponding tropylium derivatives.[24,25] However, under suitable conditions, neutral *O*-alkyl iminotropones (**10**) can be also generated.[22,23,25] In some cases the synthesis of **10** involved the reaction of aminotropone with dimethyl sulfate followed by treatment with sodium bicarbonate (e.g., R = C_6H_4-*p*-Me, CH_2Ph, C_6H_{11}),[22,25] while in other cases (R = C_6H_4-*p*-Br, pyrrol-1-yl) the neutral 2-arylimino-*O*-ethyltropones (**10**) were isolated in low to moderate yield from dichloromethane solutions of the corresponding aminotropones and Et_3OBF_4.[23] It is possible that, depending on the nature of the *N*-substituent, compound **15** (Scheme 5) may undergo slow deprotonation to form **10** during the course of the reaction. Subsequent formation of aminotroponimines from **10** is very slow,[23,26] suggesting that slow reverse protonation of **10** is necessary to regenerate tropylium **15**, which then undergoes rapid nucleophilic aromatic substitution with amines to form the cycloheptatriene derivative **16**, an intermediate leading to the final aminotroponimine **11**. Reaction of tropylium derivatives with various nucleophiles is well-documented in the literature.[24] Furthermore, the one-pot synthesis of **11** from **9** without the isolation of **10** is known to be significantly faster than from isolated **10**.[15g,23,27] On the basis of these considerations, we propose that aminotroponimines are always generated from tropylium intermediate **15**, as outlined in Scheme 5.

The ability to isolate tropylium derivatives such as **12** provides an opportunity for a more efficient and convenient way to prepare a library of aminotroponimines. Compound **12** was characterized by NMR spectroscopy, X-ray crystallography, and elemental analysis. The molecular structure of **12** is shown in Figure 1. The ^1H NMR spectrum of **12** shows the tropylium ring protons shifted significantly downfield from their positions found in neutral compounds.[6,9,28] Ring protons were assigned on the basis of 1D TOCSY and 1D NOESY NMR spectroscopy. The isopropyl methine protons appear as a single septet at 2.79 ppm, indicating identical chemical environments for the two isopropyl groups. The isopropyl methyl groups give rise to two nonequivalent doublets resonating at 1.22 and 1.12 ppm. The appearance of two separate resonances for the isopropyl methyl groups is due to restricted rotation around the N−C(ipso) bond, which makes the chemical environment for the methyl groups pointing toward and away from the tropylium ring different. This is observed commonly for compounds with the bulky 2,6-diisopropylanilino substituent.[6,9,29] NOESY experiments indicated that the methyl

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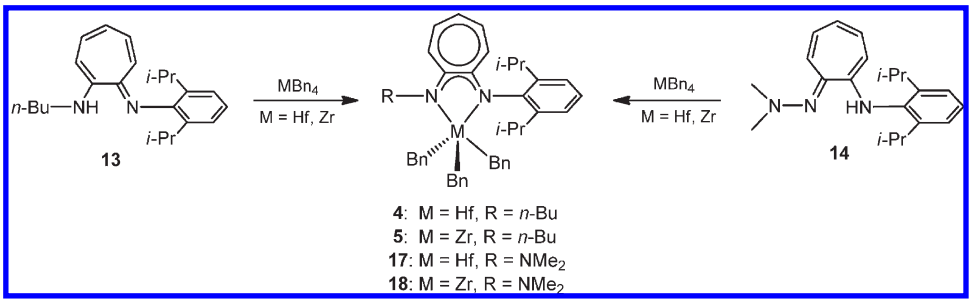
Scheme 6. Synthesis of Aminotroponiminato Hafnium and Zirconium Complexes



groups corresponding to a doublet at 1.12 ppm point toward the tropylium ring. The ^{19}F NMR spectrum of **12** shows two peaks at 152.72 and 152.77 ppm in a 1:4 ratio, which is due to the different chemical shifts of the $^{10}BF_4$ and $^{11}BF_4$ isotopomers.[30] This phenomenon has been documented previously in the literature.[31]

Preparative-scale synthesis of **13** was accomplished in 80% yield by the reaction of **8** with Et_3OBF_4 to generate compound **12** in situ, which was reacted subsequently in the same reaction vessel with *n*-butylamine. Since the product formation from **12** requires a deprotonation step, it is necessary to use excess amine for this reaction to reach high conversion.[32] Using an excess of volatile amine is a convenient way to drive the reaction to completion. The molecular structure of ligand **13** and its representative bond distances are shown in Figure 2. The C−N bond distances are consistent with the assignment of the amine and imine nitrogen atoms. The structural information obtained from NMR spectroscopy are consistent with the X-ray crystal structure data. The position of the amine hydrogen in the solution phase could not be assigned unequivocally on the basis of NOESY NMR measurements. Protons attached to the seven-membered ring of the ligand were assigned with the aid of 1D TOCSY and 1D NOESY NMR spectroscopy. Similar to the case for **12**, the isopropyl groups in **13** have the same chemical environment, as shown by the appearance of only one methine resonance at 2.98 ppm. The isopropyl methyl groups appear as two doublets at 1.20 and 1.14 ppm. The isopropyl methyl groups pointing toward the seven-membered ring resonate at 1.14 ppm on the basis of the NOESY NMR spectra.

The preparative-scale synthesis of **14** was carried out in 95% yield by the reaction of isolated tropylium derivative **12** and *N*,*N*-dimethylhydrazine at 25 °C. Ligand **14** was characterized by NMR spectroscopy and elemental analysis. Unlike in **13**, the nitrogen atom with the 2,6-diisopropylphenyl substituent in **14** is the amine nitrogen. This conclusion is based on the observation of only one doublet for the isopropyl methyl groups resonating at 1.09 ppm in the ^{1}H NMR spectrum of **14**, indicating that all isopropyl methyl groups are in the same chemical environment. A single bond between the amine nitrogen and the C1 carbon of the seven-membered ring allows for free rotation around this bond, which in turn facilitates free rotation of the N−C(ipso) bond. A similar phenomenon was observed in the case of the imino−enamine ligand of complex **3**.[9] Another indication that the hydrogen atom resides on different nitrogen atoms in **13** and **14** comes from a comparison of chemical shifts of protons H2 and H6 attached to the seven-membered ring of these ligands. In **13**, H2 resonates at higher frequency than H6 (6.50 ppm vs 5.96 ppm), a trend which is reversed in **14**, with H2 and H6 resonating at 5.87 and 7.39 ppm, respectively. If the hydrogen atom resided on the same nitrogen atom in both **13** and **14**, one would expect very similar chemical shifts, at least for H2 protons. The inversion of chemical shifts for protons H2 and H6 in **13** and **14** is consistent with inversion of the double bonds in these ligands.

Following the successful synthesis of ligands **13** and **14**, the preparation of other new ligands was explored. For example, a dimeric aminotroponimine ligand (**19**) was prepared via the reaction of **12** with 1,4-butanediamine.[33] However, the attempt to prepare an aminotroponimine with 2,6-diisopropylaniline substituents on both amine and imine nitrogen atoms failed, presumably due to steric hindrance.

Synthesis of Metal Complexes. Ligands **13** and **14** were converted to their corresponding Hf and Zr complexes via reaction with tetrabenzyl hafnium ($HfBn_4$) and tetrabenzyl zirconium ($ZrBn_4$) over ca 2 h in benzene at 25 °C (Scheme 6). All complexes were isolated in a crystalline form by slow diffusion of hexane into benzene solutions at −45 °C. NMR yields were close to quantitative; however, the isolated yields of the first crop of crystals varied between 30 and 80%.

All metal complexes were fully characterized by NMR spectroscopy and elemental analysis, and the molecular structures of **4** and **17** were determined by X-ray crystallography. Similar to imino−enamido complexes, aminotroponiminato complexes **4**, **5**, **17**, and **18** were stable at 75 °C for 18 h. The ^{1}H NMR spectrum of **4** shows a broad singlet at 2.21 ppm corresponding to the benzyl CH_2 groups and a broad signal at 6.91 ppm for the ortho CH_2*Ph* protons, suggesting a relatively fast exchange of the benzyl groups at ambient temperature. The ^{1}H NMR spectra of **5** and **17** reveal similar behavior. The molecular structures of complex **4** and **17** are shown in Figures 3 and 4, respectively, whereas comparisons among representative bond distances of **3**, **4**, and **17** are presented in Figure 5. Comparison of the C1−N1, C7−N2, N1−Hf, and N2−Hf bond distances in complexes **3** and **4** clearly shows that the imine bond is completely delocalized over the N1−C1−C7−N2 bonds in **4**. Similar to the case for **4**, the nearly identical C1−N1 and C7−N2 bond distances of **17** indicate a delocalized electron structure over the N1−C1−C7−N2 bonds. The sum of angles around N1, N2, and N3 equals 359.7, 359.6, and 341.4°, respectively. This indicates that N1 and N2 are virtually planar, whereas N3 is pyramidized. The dimethylamine fragment is perpendicular to the plane of the metallacycle. The Hf−C−C_{ipso} bond angles in complexes **4** and **17** are in the range of 108.4 and 117.2°, indicating a η^1-bonding mode for all benzyl groups.

Table 1 shows the N−Hf−N bite angles, N−C1−C7−N torsion angles, and dihedral angles of the least-squares planes defined by N−C1−C7−N and N−Hf−N atoms for complexes

dx.doi.org/10.1021/om200362v |*Organometallics* 2011, 30, 4589–4597

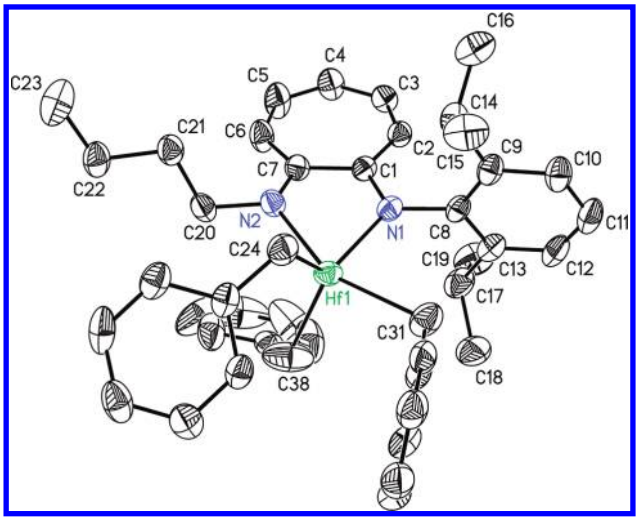


Figure 3. Molecular structure of complex **4**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 40% probability level. Selected bond distances (Å) and angles (deg): N1−C1 = 1.359(4), N2−C7 = 1.338(4), C1−C7 = 1.462(4), Hf1−N1 = 2.208(3), Hf1−N2 = 2.160(3); N2−Hf1−N1 = 69.62(10).

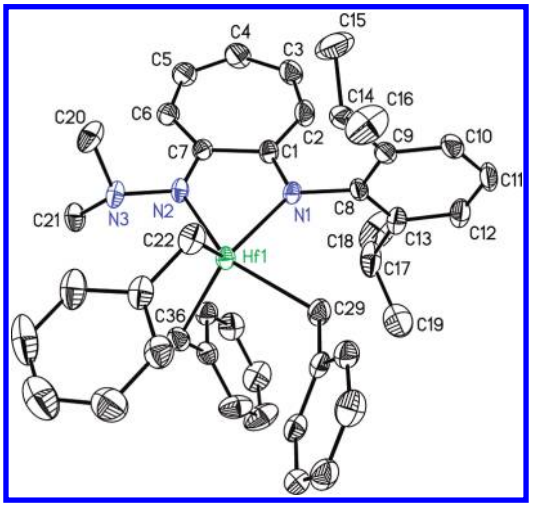


Figure 4. Molecular structure of complex **17**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 40% probability level. Selected bond distances (Å) and angles (deg): N1−C1 = 1.345(3), N2−C7 = 1.343(3), C1−C7 = 1.467(3), Hf1−N1 = 2.293(2), Hf1−N2 = 2.094(2); N2−Hf1−N1 = 67.02(8).

1, **3**, **4**, and **17**. These parameters are not significantly different between acyclic (**1**), six-membered-ring cyclic (**3**), and seven-membered-ring cyclic aromatic (**4**, **17**) backbone structures, indicating similar geometries for the core five-membered-ring metallacycle in all of these complexes.

Polymerization Results. Ethylene/1-octene copolymerization reactions were conducted in a 2 L batch reactor at 120 °C. Procatalysts were activated with 1.2 equiv (relative to procatalyst) of $\{[HNMe(C_{18}H_{37})_2][B(C_6F_5)_4]\}$ activator. All polymerization reactions were carried out for 10 min and stopped by venting the ethylene pressure. The polymeric products were characterized by differential scanning calorimetry (DSC) and gel permeation chromatography (GPC). Interestingly, polymers prepared by

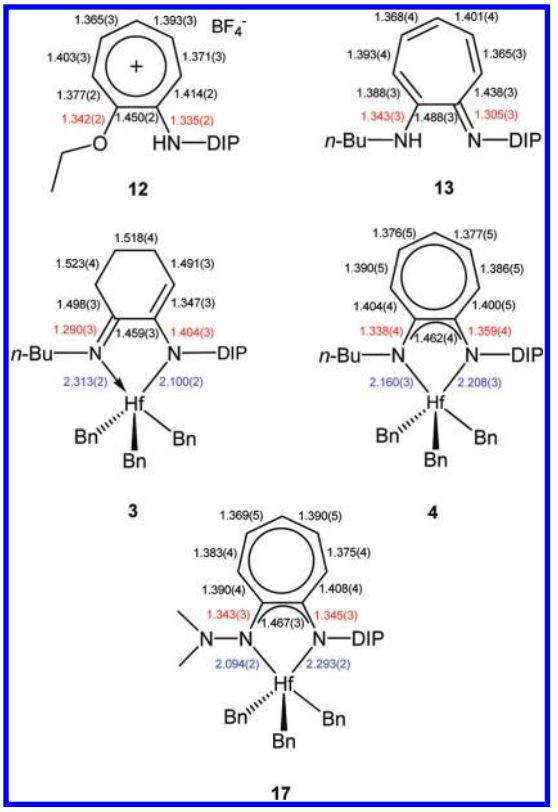


Figure 5. Comparison of important bond lengths (Å) in compounds **3**, **4**, **12**, **13**, and **17**.

Table 1. Select Structural Parameters (deg) for Complexes 1, 3, 4 and 17

	1	3	4	17
N−Hf−N angle	72.6	72.0	69.6	67.0
N−C1−C7−N torsion angle[a]	4.6	6.0	4.6	0.7
dihedral angle[b]	10.7	12.7	9.7	3.7

[a] Absolute values are shown. [b] The angle between the N1−C1−C7−N2 and N1−Hf1−N2 least-squares planes.

aminotroponiminato catalysts exhibited a pale yellow color upon isolation, which faded upon exposure to sunlight over the course of a few hours. This is mostly likely due to highly colored, highly conjugated residual organic fragments originating from ligand decomposition. A comparison of the results given in Table 2 reveals that aminotroponiminato catalysts are active for olefin polymerization, with hafnium derivatives (**4**, **17**) exhibiting higher activity than their zirconium analogues (**5**, **18**). However, even the best aminotroponiminato procatalyst identified in this work (**4**) is about 5 times less active than the analogous imino−enamido hafnium complex **3**. The DSC scans revealed bimodal melting transitions for all polymer samples prepared by aminotroponiminato procatalysts. Additionally, GPC chromatograms for polymers produced by two of the four new complexes show a bimodal molecular weight distribution. These results indicate that the aminotroponiminato catalysts are unstable under the polymerization conditions, producing more than one active catalytic species. Aminotroponiminato complexes led to lower 1-octene incorporation than imino−enamido procatalyst **3** under identical conditions. The molecular weights of polymers

dx.doi.org/10.1021/om200362v |*Organometallics* 2011, 30, 4589–4597

Table 2. Polymerization Results for 3−5, 17, and 18[a]

run no.	cat. (amt (μmol))	yield (g)	efficiency[b]	T_m (°C)	M_w (g/mol)	M_w/M_n	octene content (mol %)[c]
1	**3** (0.4)	45.3	113 250	74.0	1 280 000	1.8	8.6
2	**4** (1)	24.0	24 000	80.2/106.0	497 746	2.8	7.7
3	**5** (2)	10.3	5 150	91.4/111.3	434 983	1.8	6.3
4	**17** (1)	13.8	13 800	104.0/116.4	445 415	9.6[d]	4.2
5	**18** (2)	12.2	6 100	106.2/118.2	354 212	12.8[d]	4.1

[a] Polymerization conditions: temperature = 120 °C; 533 g of Isopar E, 250 g of 1-octene, 10 mmol of H_2, 460 psi of ethylene; 10 min run time; activator $[HNMe(C_{18}H_{37})_2][B(C_6F_5)_4]$, (1.2 equiv); MMAO-3A (10 equiv); [b] Efficiency = polymer (g)/metal (mmol). [c] Determined by IR. [d] GPC traces are bimodal.

made from aminotroponiminato procatalysts are very high (M_w values of up to 500 KDa) but are lower compared to ultra-high molecular weight polymers produced by **3**. Polymerization data indicate that aminotroponiminato complexes exhibit poorer overall performance as procatalysts for olefin polymerization in comparison to the analogous imino-enamido complexes.

CONCLUSIONS

Imino−amido complexes exhibit interesting olefin polymerization characteristics, but their thermal sensitivity can limit their application as useful procatalysts. Our recent goal has been to identify ligands/metal complexes with a bonding environment similar to that found in imino−amido complexes, but with structural features which remove thermal degradation pathways. The search for such molecules led us to the synthesis and evaluation of imino−enamido and aminotroponiminato classes of complexes. Both of these classes of procatalysts are significantly more stable than similar imino−amido complexes, a feature which is undoubtedly due to the lack of alkyl substituents in the bridges of these ligands. In this work, we showed that aminotroponiminato hafnium and zirconium complexes can be prepared easily in five steps starting from readily available tropolone. During the course of ligand synthesis, an unexpected, air-stable tropylium cation intermediate was isolated and found to react directly with amines significantly faster than the neutral intermediate proposed in the literature. Isolation of this tropylium cation opens up a more convenient way to synthesize various aminotroponimines. Newly prepared aminotroponiminato complexes contain a bulky 2,6-diisopropylphenyl substituent on one of the nitrogen atoms and a *n*-butyl or dimethylamino substituent on the other nitrogen atom. Aminotroponiminato hafnium and zirconium catalysts are active for olefin polymerization, but their activity is noticeably lower than that observed for the analogous imino−enamido complex **3**, containing a cyclohex-2-enylidene backbone. The high thermal stability of aminotroponiminato complexes does not translate into corresponding high stability under polymerization conditions. Multiple melting peaks of the polymers and broad polydispersities identified by DSC and GPC analysis respectively indicate that aminotroponiminato procatalysts undergo a structural change upon activation and/or under high-temperature polymerization conditions, leading to multiple active species.

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. 2-Triflatotropone[21a] and 2-(2,6-diisopropylanilino)tropone[21b] were prepared according to reported procedures. NMR spectra were recorded on a VNMRS-500 spectrometer. ^{1}H NMR data are reported as follows: chemical shift (multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, and m = multiplet), integration, and assignment). Chemical shifts for ^{1}H 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; CD_2Cl_2, 5.32 ppm) as references. ^{13}C NMR data were determined with ^{1}H decoupling, and the chemical shifts are reported in ppm vs tetramethylsilane (C_6D_6, 128 ppm; CD_2Cl_2, 53.80 ppm). The ^{19}F NMR data are reported in ppm relative to neat $CFCl_3$. All compounds were synthesized and stored in a Vacuum Atmospheres glovebox under a dry nitrogen atmosphere unless otherwise noted. Elemental analyses were performed at Midwest Microlab, LLC.

Preparation of *N*-[2,6-Bis(1-methylethyl)phenyl]-2-ethoxycycloheptatrienylium Tetrafluoroborate (12). Triethyloxonium tetrafluoroborate (1.28 g, 6.74 mmol) was dissolved in CH_2Cl_2 (5 mL), and a solution of 2-[[2,6-bis(1-methylethyl)phenyl]amino]-2,4,6-cycloheptatrien-1-one (1.50 g, 5.33 mmol) in CH_2Cl_2 (10 mL) was added to it dropwise at 25 °C. The solution was stirred overnight, followed by precipitation of the product with excess diethyl ether. The resulting off-white solid was purified by dissolution in a minimum quantity of CH_2Cl_2, followed by precipitation with excess Et_2O. Finally, the solid was recrystallized from a concentrated acetone solution layered with Et_2O. Large colorless block crystals formed, which were filtered, crushed, washed with Et_2O, and dried under vacuum to give an air-stable, white crystalline solid. Yield: 1.38 g, 65%. ^{1}H NMR (CD_2Cl_2, 500 MHz, 30 °C): 9.25 (br s, 1H, NH), 8.07 (td, J_{H-H} = 1.4, 10.4 Hz, 1H, H5), 7.96 (d, J_{H-H} = 10.6 Hz, 1H, H6), 7.88 (tm, J_{H-H} = 10.3 Hz, 1H, H3), 7.66 (tm, J_{H-H} = 9.5 Hz, 1H, H4), 7.55 (tm, J_{H-H} = 7.8 Hz, 1H, H11), 7.40 (d, J_{H-H} = 7.8 Hz, 2H, H10, H12), 7.19 (d, J_{H-H} = 11.6 Hz, 1H, H2), 4.74 (q, J_{H-H} = 7.0 Hz, 2H, H14), 2.79 (septet, J_{H-H} = 6.8 Hz, 2H, $CH(CH_3)_2$), 1.69 (t, J_{H-H} = 7.0 Hz, 3H, H15), 1.22 (d, J_{H-H} = 6.8 Hz, 6H, $CH(CH_3)_2$), 1.12 (d, J_{H-H} = 6.8 Hz, 6H, $CH(CH_3)_2$). ^{13}C{^{1}H} NMR (CD_2Cl_2, 125 MHz, 30 °C): 159.4 (C7), 158.9 (C1), 145.9 (C9, C13), 145.4 (C3), 141.7 (C5), 135.0 (C4), 131.1 (C11), 129.7 (C8), 125.6 (C10, C12), 124.5 (C2), 123.9 (C6), 69.4 (C14), 29.3 ($CH(CH_3)_2$), 24.1 ($CH(CH_3)_2$), 23.4 ($CH(CH_3)_2$), 14.2 (C15). ^{19}F{^{1}H} NMR (CD_2Cl_2, 470 MHz, 30 °C): −152.7, −152.8. Anal. Calcd for $C_{21}H_{28}BF_4NO$: C, 63.49; H, 7.10; N, 3.53. Found: C, 63.44; H, 6.99; N, 3.55.

Preparation of 7-[[2,6-Bis(1-methylethyl)phenyl]imino]-*N*-butyl-1,3,5-cycloheptatrien-1-amine (13). The synthesis was based on the reported general procedure for the preparation of *N*,*N*′-dialkylaminotroponimines, with modifications.[34] To a solution of triethyloxonium tetrafluoroborate (418 mg, 2.20 mmol) dissolved in CH_2Cl_2 (5 mL) was added slowly a solution of 2-[[2,6-bis(1-methylethyl)phenyl]amino]-2,4,6-cycloheptatrien-1-one (**8**; 587 mg, 2.09 mmol) in CH_2Cl_2 (15 mL). After it was stirred at 25 °C for 3 h, the solution was cooled to ∼0 °C and a precooled solution of *n*-$BuNH_2$ (1.467 g, 20 mmol) in CH_2Cl_2 (5 mL) was added. The solution was warmed to 25 °C and was stirred overnight. The solvent was removed

under vacuum, and the residue was purified by column chromatography (eluent hexane/Et_2O 3/1 containing 3 vol % Et_3N), affording 557 mg of pure product as an orange solid (80%). ^1H NMR (C_6D_6, 500 MHz, 30 °C): 7.89 (br s, 1H, NH), 7.25 (d, J_{H-H} = 7.7 Hz, 2H, H10, H12), 7.15 (tm, J_{H-H} = 7.7 Hz, 1H, H11), 6.64 (tm, J_{H-H} = 10.1 Hz, 1H, H5), 6.50 (d, J_{H-H} = 12.0 Hz, 1H, H2), 6.31 (m, 1H, H3), 6.02 (tm, J_{H-H} = 9.2 Hz, 1H, H4), 5.92 (d, J_{H-H} = 10.0 Hz, 1H, H6), 2.98 (septet, J_{H-H} = 6.8 Hz, 2H, C*H*$(CH_3)_2$), 2.86 (t, J_{H-H} = 7.0 Hz, 2H, H14), 1.30 (m, 2H, H15), 1.20 (d, J_{H-H} = 6.8 Hz, 6H, CH(C*H*$_3)_2$), 1.17 (m, 2H, H16), 1.14 (d, J_{H-H} = 6.8 Hz, 6H, CH(C*H*$_3)_2$), 0.71 (t, J_{H-H} = 7.3 Hz, 3H, H17). $^{13}C\{^1H\}$ NMR (C_6D_6, 125 MHz, 30 °C): 155.0 (C1), 151.1 (C7), 146.8 (C8), 138.3 (C9, C13), 134.0 (C5), 133.1 (C3), 123.8 (C10, C12), 123.7 (C11), 121.3 (C2), 119.3 (C4), 104.9 (C6), 42.8 (C14), 30.7 (C15), 28.8 (*C*H$(CH_3)_2$), 23.8 (CH$(CH_3)_2$), 23.6 (CH$(CH_3)_2$), 20.5 (C16), 13.7 (C17). Anal. Calcd for $C_{23}H_{32}N_2$: C, 82.09; H, 9.58; N, 8.32. Found: C, 82.36; H, 9.45; N, 8.42.

Preparation of 2-[[2,6-Bis(1-methylethyl)phenyl]amino]-2,4,6-cycloheptatrien-1-one 2,2-Dimethylhydrazone (14). *N*-[2,6-Bis(1-methylethyl)phenyl]-2-ethoxycycloheptatrienylium tetrafluoroborate (**12**; 410 mg, 1.03 mmol) was dissolved in CH_2Cl_2 (5 mL), and excess *N*,*N*-dimethylhydrazine (0.84 mL, 11 mmol) was added dropwise. The solution immediately turned from yellow to red. The reaction mixture was stirred at 25 °C for 3 h, followed by removal of volatiles under vacuum. Flash chromatography (eluent hexane/Et_2O 3/1 containing 3 vol % Et_3N) was performed, and solvents were removed under vacuum to give a dark red oil. Yield: 317 mg, 95%. ^1H NMR (C_6D_6, 500 MHz, 30 °C): 8.46 (br s, 1H, NH), 7.39 (d, J_{H-H} = 11.6 Hz, 1H, H6), 7.16 (m, 3H, H10, H11, H12), 6.52 (m, 1H, H5), 6.26 (td, J_{H-H} = 10.1, 1.1 Hz, 1H, H3), 5.92 (tm, J_{H-H} = 9.2 Hz, 1H, H4), 5.87 (d, J_{H-H} = 10.0 Hz, 1H, H2), 3.06 (septet, J_{H-H} = 6.8 Hz, 2H, C*H*$(CH_3)_2$), 2.46 (s, 6H, H14, H15), 1.09 (d, J_{H-H} = 6.8 Hz, 12H, CH(C*H*$_3)_2$). $^{13}C\{^1H\}$ NMR (C_6D_6, 125 MHz, 30 °C): 152.5 (C7), 150.7 (C1), 145.5 (C9, C13), 137.0 (C8), 132.9 (C3), 132.4 (C5), 127.5 (C11), 124.1 (C10, C12), 120.0 (C4), 118.6 (C6), 108.5 (C2), 46.9 (C14, C15), 28.9 (*C*H$(CH_3)_2$), 24.6 (CH$(CH_3)_2$), 23.3 (CH$(CH_3)_2$). Anal. Calcd for $C_{21}H_{29}N_3$: C, 77.97; H, 9.04; N, 12.99. Found: C, 78.30; H, 9.03; N, 12.67.

Preparation of [*N*-[2,6-Bis(1-methylethyl)phenyl]-7-(butylimino-κN)-1,3,5-cycloheptatrien-1-aminato-κN]tris(phenylmethyl)hafnium (4). 7-[[2,6-Bis(1-methylethyl)phenyl]imino]-*N*-butyl-1,3,5-cycloheptatrien-1-amine (**13**; 250 mg, 0.74 mmol) and $HfBn_4$ (403 mg, 0.74 mmol) were dissolved in dry C_6D_6 (3 mL), giving an orange solution which was stirred at 25 °C. Completion of the reaction was confirmed by ^1H NMR spectra taken after 90 min. The reaction mixture was concentrated under vacuum, layered with hexane, and cooled to −45 °C overnight. The resulting yellow crystals were filtered, washed with cold hexane, and dried under vacuum. Isolated yield: 557 mg, 79%. ^1H NMR (C_6D_6, 500 MHz, 30 °C): 7.21 (m, 3H, H10, H11, H12), 7.15 (tm, J_{H-H} = 7.5 Hz, 6H, meta CH_2Ph), 6.91 (dm, J_{H-H} = 6.1 Hz, 6H, ortho CH_2Ph), 6.85 (m, 3H, para CH_2Ph), 6.85 (m, 1H, H5), 6.59 (d, J_{H-H} = 11.2 Hz, 1H, H6), 6.50 (m, 1H, H2), 6.48 (m, 1H, H3), 6.25 (t, J_{H-H} = 8.8 Hz, 1H, H4), 3.18 (m, 2H, H14), 2.79 (septet, J_{H-H} = 6.8 Hz, 2H, C*H*$(CH_3)_2$), 2.21 (br s, 6H, CH_2Ph), 1.38 (m, 2H, H15), 1.26 (d, J_{H-H} = 6.8 Hz, 6H, CH(C*H*$_3)_2$), 1.14 (sextet, J_{H-H} = 7.5 Hz, 2H, H16), 0.94 (d, J_{H-H} = 6.8 Hz, 6H, CH(C*H*$_3)_2$), 0.77 (t, J_{H-H} = 7.3 Hz, 6H, H17). $^{13}C\{^1H\}$ NMR (C_6D_6, 125 MHz, 30 °C): 168.5 (C1), 162.4 (C7), 146.2 (br, CH_2Ph, quat), 146.0 (C8), 142.6 (C9, C13), 135.2 (C5), 134.9 (C3), 128.6 (meta CH_2Ph), 127.9 (ortho CH_2Ph), 127.2 (C11), 125.0 (C10, C12), 124.8 (C4), 122.3 (para CH_2Ph), 120.2 (C2), 116.7 (C6), 87.0 (br, *C*H$_2$Ph), 46.8 (C14), 29.2 (*C*H$(CH_3)_2$), 28.4 (C15), 25.8 (CH$(CH_3)_2$), 24.0 (CH$(CH_3)_2$), 20.8 (C16), 13.9 (C17). Anal. Calcd for $C_{44}H_{52}HfN_2$: C, 67.12; H, 6.66; N, 3.56. Found: C, 66.40; H, 6.60; N, 3.65.

Preparation of [*N*-[2,6-Bis(1-methylethyl)phenyl]-7-(butylimino-κN)-1,3,5-cycloheptatrien-1-aminato-κN]tris(phenylmethyl)zirconium (5). 7-[[2,6-Bis(1-methylethyl)phenyl]imino]-*N*-butyl-1,3,5-cycloheptatrien-1-amine (**13**; 250 mg, 0.74 mmol) and $ZrBn_4$ (339 mg, 0.74 mmol) were dissolved in dry C_6D_6 (3 mL). The orange solution was stirred for 4 h and then concentrated under vacuum, layered with hexane, and cooled to −45 °C overnight. The resulting yellow crystals were filtered, washed with cold hexane, and dried under vacuum. Isolated yield: 204 mg, 39%. ^1H NMR (C_6D_6, 500 MHz, 30 °C): 7.19 (m, 3H, H10, H11, H12), 7.10 (tm, J_{H-H} = 7.5 Hz, 6H, meta CH_2Ph), 6.88 (br s, 6H, ortho CH_2Ph), 6.85 (m, 3H, para CH_2Ph), 6.80 (m, 1H, H5), 6.56 (d, J_{H-H} = 11.7 Hz, 1H, H2), 6.52 (d, J_{H-H} = 11.2 Hz, 1H, H6), 6.45 (t, J_{H-H} = 8.8 Hz, 1H, H3), 6.24 (t, J_{H-H} = 9.3 Hz, 1H, H4), 3.04 (m, 2H, H14), 2.79 (septet, J_{H-H} = 6.8 Hz, 2H, C*H*$(CH_3)_2$), 2.35 (br s, 6H, CH_2Ph), 1.35 (m, 2H, H15), 1.23 (d, J_{H-H} = 6.8 Hz, 6H, CH(C*H*$_3)_2$), 1.11 (sextet, J_{H-H} = 7.5 Hz, 2H, H16), 0.93 (d, J_{H-H} = 6.8 Hz, 6H, CH(C*H*$_3)_2$), 0.75 (t, J_{H-H} = 7.3 Hz, 6H, H17). $^{13}C\{^1H\}$ NMR (C_6D_6, 125 MHz, 30 °C): 168.1 (C1), 161.3 (C7), 146.9 (C8), 145.4 (br, CH_2Ph, quat), 142.3 (C9, C13), 135.0 (C5), 134.8 (C3), 129.1 (meta CH_2Ph), 128.3 (ortho CH_2Ph), 127.0 (C11), 125.0 (C10, C12), 124.2 (C4), 122.4 (para CH_2Ph), 119.8 (C2), 115.4 (C6), 76.6 (br, *C*H$_2$Ph), 47.1 (C14), 29.1 (*C*H$(CH_3)_2$), 28.5 (C15), 25.8 (CH$(CH_3)_2$), 24.1 (CH$(CH_3)_2$), 20.7 (C16), 13.9 (C17). Anal. Calcd for $C_{44}H_{52}ZrN_2$: C, 75.48; H, 7.49; N, 4.00. Found: C, 75.15; H, 7.23; N, 7.72.

Preparation of [2-[[2,6-Bis(1-methylethyl)phenyl]amino-κN]-2,4,6-cycloheptatrien-1-one 2,2-dimethylhydrazonato-$\kappa N1$]tris(phenylmethyl)hafnium (17). 2-[[2,6-Bis(1-methylethyl)-phenyl]amino]-2,4,6-cycloheptatrien-1-one 2,2-dimethylhydrazone (**14**; 250 mg, 0.77 mmol) and $HfBn_4$ (420 mg, 0.77 mmol) were dissolved in dry C_6D_6 (3 mL), and the orange solution was stirred for 2 h. Completion of the reaction was confirmed by ^1H NMR. The reaction mixture was concentrated under vacuum, layered with hexane, and cooled to −45 °C overnight. The resulting yellow crystals were filtered, washed with cold hexane, and dried under vacuum. Isolated yield: 370 mg, 62%. ^1H NMR (C_6D_6, 500 MHz, 30 °C): 7.16 (m, 9H, H10, H11, H12, meta CH_2Ph), 6.94 (d, J_{H-H} = 7.6 Hz, 6H, ortho CH_2Ph), 6.88 (t, J_{H-H} = 7.3 Hz, 3H, para CH_2Ph), 6.76 (m, 2H, H5, H6), 6.68 (d, J_{H-H} = 11.5 Hz, 1H, H2), 6.45 (t, J_{H-H} = 10.3 Hz, 1H, H3), 6.25 (td, J_{H-H} = 2.5, 8.5 Hz, 1H, H4), 2.66 (septet, J_{H-H} = 6.8 Hz, 2H, C*H*$(CH_3)_2$), 2.61 (s, 6H, H14, H15), 2.09 (br s, 6H, CH_2Ph), 1.17 (d, J_{H-H} = 6.8 Hz, 6H, CH(C*H*$_3)_2$), 0.93 (d, J_{H-H} = 6.8 Hz, 6H, CH(C*H*$_3)_2$). $^{13}C\{^1H\}$ NMR (C_6D_6, 125 MHz, 30 °C): 167.0 (C1), 161.4 (C7), 147.0 (br, CH_2Ph, quat), 146.8 (C8), 142.0 (C9, C13), 135.4 (C3), 134.7 (C5), 128.5 (ortho CH_2Ph, meta CH_2Ph), 127.1 (C11), 125.6 (C4), 124.9 (C10, C12), 123.2 (C2), 122.1 (para CH_2Ph), 114.5 (C6), 85.5 (br, *C*H$_2$Ph), 43.3 (C14, C15), 29.3 (*C*H$(CH_3)_2$), 25.7 (CH$(CH_3)_2$), 23.8 (CH$(CH_3)_2$). Anal. Calcd for $C_{42}H_{49}HfN_3$: C, 65.15; H, 6.38; N, 5.43. Found: C, 64.68; H, 6.32; N, 5.57.

Preparation of [2-[[2,6-Bis(1-methylethyl)phenyl]amino-κN]-2,4,6-cycloheptatrien-1-one 2,2-dimethylhydrazonato-$\kappa N1$]tris(phenylmethyl)zirconium (18). 2-[[2,6-Bis(1-methylethyl)-phenyl]amino]-2,4,6-cycloheptatrien-1-one 2,2-dimethylhydrazone (**14**; 150 mg, 0.46 mmol) and $ZrBn_4$ (211 mg, 0.46 mmol) were dissolved in dry C_6D_6 (3 mL). The orange solution was stirred for 4.5 h and then concentrated under vacuum, layered with hexane, and cooled to −45 °C overnight. The resulting yellow crystals were filtered, washed with cold hexane, and dried under vacuum. Isolated yield: 100 mg, 31%. ^1H NMR (C_6D_6, 500 MHz, 30 °C): 7.20 (m, 3H, H10, H11, H12), 7.14 (tm, J_{H-H} = 7.7 Hz, 6H, meta CH_2Ph), 6.91 (m, 9H, ortho CH_2Ph, para CH_2Ph), 6.76 (d, J_{H-H} = 11.7 Hz, 1H, H2), 6.71 (t, J_{H-H} = 10.0 Hz, 1H, H5), 6.62 (d, J_{H-H} = 10.4 Hz, 1H, H6), 6.41 (tm, J_{H-H} = 10.5 Hz, 1H, H3), 6.23 (t, J_{H-H} = 9.3 Hz, 1H, H4), 2.70 (septet, J_{H-H} = 6.8 Hz, 2H, C*H*$(CH_3)_2$), 2.53 (s, 6H, H14, H15), 2.25 (br s, 6H, CH_2Ph), 1.20 (d, J_{H-H} = 6.8 Hz,

6H, $CH(CH_3)_2$), 0.97 (d, J_{H-H} = 6.8 Hz, 6H, $CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR (C_6D_6, 125 MHz, 30 °C): 166.9 (C1), 158.6 (C7), 147.1 (C8), 146.5 (br, CH_2Ph, quat), 141.7 (C9, C13), 135.5 (C3), 134.6 (C5), 128.8 (meta CH_2Ph), 128.2 (ortho CH_2Ph), 126.9 (C11), 125.3 (C4), 124.9 (C10, C12), 123.3 (C2), 122.0 (para CH_2Ph), 112.7 (C6), 75.0 (br, CH_2Ph), 43.6 (C14, C15), 29.3 ($CH(CH_3)_2$), 25.6 ($CH(CH_3)_2$), 23.8 ($CH(CH_3)_2$). Anal. Calcd for $C_{42}H_{49}ZrN_3$: C, 73.42; H, 7.19; N, 6.12. Found: C, 73.67; H, 6.97; N, 5.83.

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. Procatalyst and cocatalyst (activator) solutions were handled in the glovebox. A stirred 2 L reactor was charged with about 533 g of Isopar E (from ExxonMobil) and 250 g of 1-octene comonomer. Hydrogen was added as a molecular weight control agent by differential pressure expansion from a 75 mL addition tank at 300 psi (2070 kPa). The reactor contents were heated to the polymerization temperature of 120 °C and 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 Corp.) and 133 mg of a phosphorus stabilizer (Irgafos 168 from Ciba Geigy Corp.). 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 and crystallization temperatures of polymers were measured by differential scanning calorimetry (DSC 2910, TA Instruments, Inc.). Samples were first heated from room temperature to 180 °C at 10 °C/min. After being held at this temperature for 2−4 min, the samples were cooled to −40 °C at 10 °C/min, held for 2−4 min, and then heated to 160 °C. Weight average molecular weights (M_w) and polydispersity values (PDI) were determined by analysis on a Viscotek HT-350 gel permeation chromatograph (GPC) equipped with a low-angle/right-angle light scattering detector, a four-capillary inline viscometer, and a refractive index detector. The GPC utilized three Polymer Laboratories PLgel 10 μm MIXED-B columns (300 × 7.5 mm) at a flow rate of 1.0 mL/min in 1,2,4-trichlorobenzene at either 145 or 160 °C. To determine octene incorporation, 140 μL of each polymer solution was deposited onto a silicon wafer, heated at 140 °C until the trichlorobenzene had evaporated, and analyzed using a Nicolet Nexus 670 FTIR with 7.1 version software equipped with an AutoPro auto sampler.

Structure Determinations of 4, 12, 13, 17, and 19. X-ray intensity data were collected on a Bruker SMART diffractometer at −100 °C using Mo Kα radiation (λ = 0.710 73 Å) and an APEXII CCD area detector. Raw data frames were read by the program SAINT[35] 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 basisi 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 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. R1 is calculated to provide a reference to the conventional *R* value, but its function is not minimized. The amine hydrogens of **12**, **13**, and **19** were located in the electron difference maps, and their positions were fully refined.

■ ASSOCIATED CONTENT

Supporting Information. Synthesis of **19**, NMR spectra for all compounds, and X-ray data for **4**, **12**, **13**, **17**, and **19**. This material is available free of charge via the Internet at http://pubs.acs.org.

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