Synthesis, Characterization, and Polymerization Behavior of Zirconium and Hafnium Complexes that Contain Asymmetric Diamido-N-Donor Ligands

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Two new "NNN" (diamido-N-donor) ligands have been synthesized that contain ethylene/*o*-phenylene "arms" and a phenyl-substituted amine donor in the central position, [Mesityl-NH-*o*-C_6H_4N(Ph)CH_2CH_2NHMesityl] (H_2**1**) and [*t*-Bu_{d6}-NH-*o*-C_6H_4N(Ph)CH_2CH_2NHMesityl] (H_2**2**). The Zr and Hf complexes that have been isolated include [**1**]MX_2 (M = Zr or Hf, X = NMe_2, Cl, or Me) and [**2**]MX_2 (M = Zr or Hf, X = NMe_2, Cl, Me). The structures of [**1**]$ZrMe_2$, [**2**]$ZrMe_2$, and a dimeric species with the formula [MesitylN-*o*-$C_6H_4NCH_2CH_2$NMesityl]Zr_2-$(NMe_2)_5$ have been determined in X-ray crystallographic studies. Abstraction of a methyl group in [**1**]MMe_2 (M = Zr or Hf) with [Ph_3C][$B(C_6F_5)_4$] gives rise to cationic complexes that are active initiators for the polymerization of 1-hexene. Similar activation of [**2**]MMe_2 (M = Zr or Hf) gives rise to dimeric monocations that eventually break up and react further to yield cationic monomethyl species. In all cases the poly[1-hexene] produced in the presence of the monometallic cations was found to be atactic.

Introduction

Recent activity in the area of terminal olefin polymerization has centered on the development of well-behaved, nonmetallocene systems for the polymerization of ethylene or ordinary α-olefins.[1−6] Advances have been made rapidly in the area of stereospecific polymerization of terminal olefins, living polymerizations, and in rare cases both.[5−21] We have focused our attention on zirconium and hafnium complexes that contain diamido/donor ligands in which the donor is a nitrogen, oxygen, or sulfur, e.g., those labeled **A** in Scheme 1 (where, for example, Ar = mesityl or 2,6-$Cl_2C_6H_3$).[22−28] Several of the monoalkyl cations derived from diamido/donor complexes of this type are relatively well-behaved catalysts for the living polymerization of 1-hexene.[22,24,29] For some time we have been aware of the possibility of preparing asymmetric monoalkyl cations in the category of living catalysts that in theory also would promote the stereospecific polymerization of simple olefins. Asymmetry could result from the fact that the diamido/donor ligand has different "arms" and perhaps different substituents on the two different amido nitrogens. If (ideally) the resulting enantiomeric metal complexes *do not invert configuration* at the metal during the polymerization reaction, then an isotactic olefin polymerization would be possible. Although some complexes that

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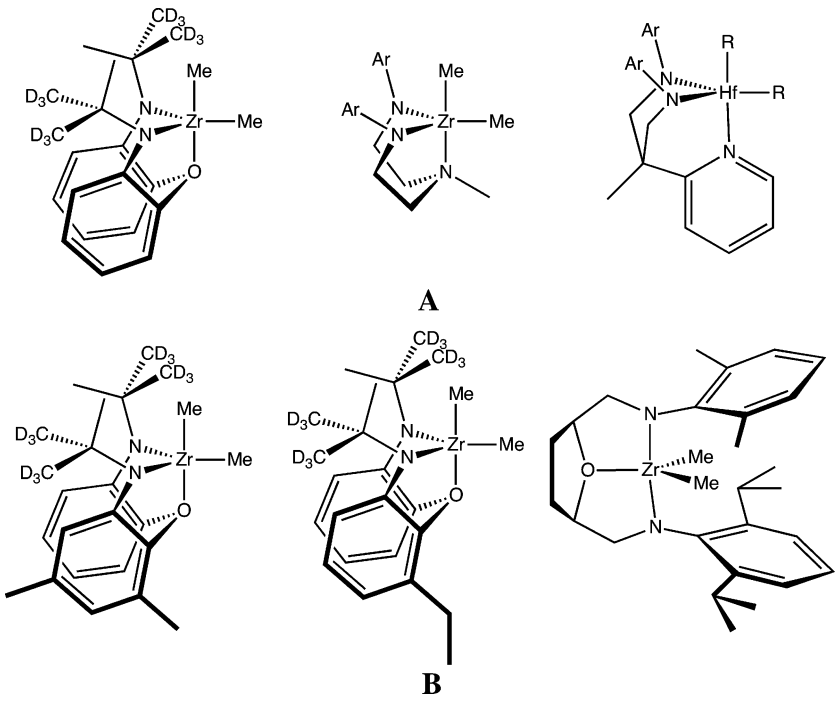
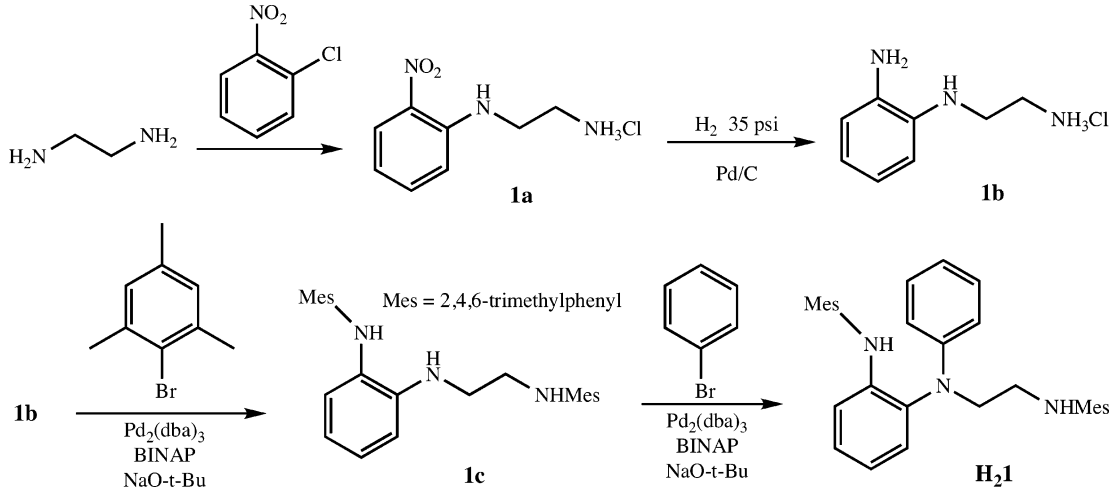
Scheme 1



Scheme 2. Synthesis of $H_2$1



contain asymmetric diamido/donor ligands have been prepared in our group (**B** in Scheme 1),[22,23] no stereochemical control with a catalyst of this type has been observed in the few experiments that have been carried out. To maximize the potential asymmetry of a diamido/donor ligand, we have prepared two new C_1-symmetric diamido/donor ligands. Here we report their preparation, activation of zirconium and hafnium dialkyl complexes to yield cationic monoalkyl complexes, and polymerization of 1-hexene by the cationic monoalkyl complexes.

Results and Discussion

Ligand Synthesis. We chose to prepare diamido/donor ligands in which one of the two "arms" contains a phenylene ring while the other contains an ethylene linkage. The amido substituents can be identical (H_2**1**, Scheme 2) or different (H_2**2**, Scheme 3). In the synthesis of H_2**1**, ethylenediamine was added to *o*-chloronitrobenzene to generate the previously reported[30] hydrochloride salt **1a** in 60% yield after recrystallization. This reaction can be scaled up to 100 g without difficulty. Reduction of the nitro group in **1a** with Pd/C under 35 psi of H_2 afforded the hydrochloride salt **1b** in satisfactory yield (70%, 20 g scale) after recrystallization from methanol. Compound **1b** was then arylated using conditions reported by Buchwald[31] to generate the dimesityl-substituted triamine (**1c**), which was isolated in 65% yield after purification by column chromatography and crystallization from hexane. We had hoped to attach a methyl group to the central donor nitrogen of **1c**, but could not find a suitable method to do so. For example, complex mixtures of products formed when MeI was employed in acetonitrile in the presence of potassium carbonate, presumably as a consequence of competing

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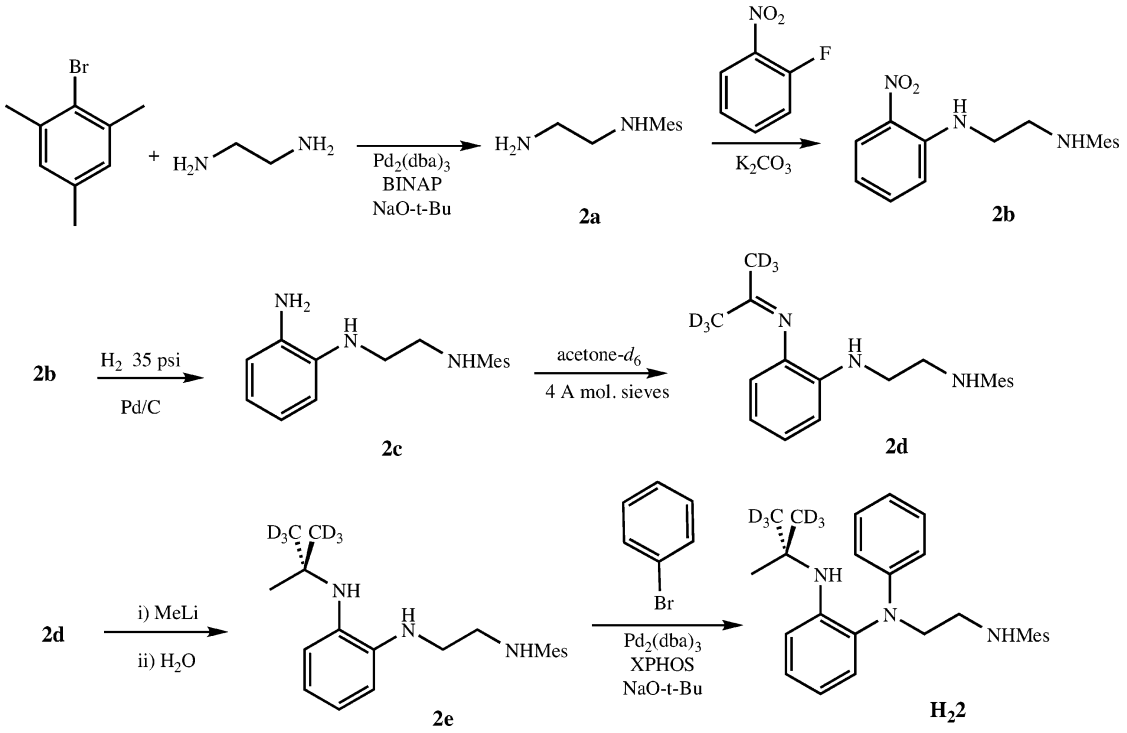
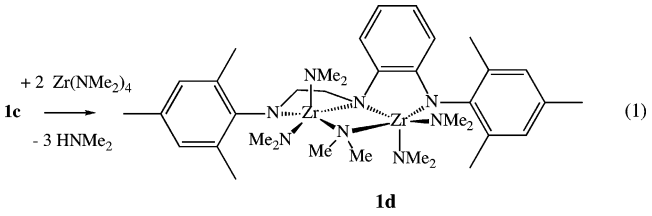
Scheme 3. Synthesis of $H_2$2



methylation at any of the three amine nitrogens. One potential way to overcome this difficulty is to prepare a bisdimethylamido zirconium complex first employing **1c**, remove the central proton with a lithium reagent, and then add methyl iodide, a method that was successful for preparing a complex that contained the [(Mesityl-$NCH_2CH_2)_2NMe]^{2-}$ ligand.[32] However, **1c** reacted with $Zr(NMe_2)_4$ to give **1d** (eq 1), as elucidated in an X-ray



(1)

study (Figure 1, Table 1); effectively **1c** is triply deprotonated and bound to two zirconium centers through two bridging amido nitrogens. The $Zr-N_{amido}$ bond lengths are normal (all close to 2.05 Å), while the $Zr-N_{bridging}$ distances are much longer, characteristic of Zr−N single bonds (2.275(2)−2.453(2) Å; see caption to Figure 1). The longest $Zr-N_{bridging}$ bonds (2.333(2) and 2.453(2) Å) are to the central nitrogen in the ligand, as might be expected due to steric contraints. Further details of the structure can be found in the Supporting Information. In the complex proton NMR spectrum of **1d**, two of the five dimethylamido groups are rotating readily on the NMR time scale at room temperature, while the remaining three (including the bridging dimethylamido group) do not, as judged by the presence of broad resonances for them. (See Experimental Section.) A variable-temperature spectrum between 5 and 75 °C did not clarify the nature of the fluxional process or processes in this molecule, and since **1d** is not central to this investigation, we did not study it further.

Substitution of the central nitrogen in **1c** with a phenyl group can be achieved through a palladium/phosphine-catalyzed *N*-aryl coupling reaction with bro-

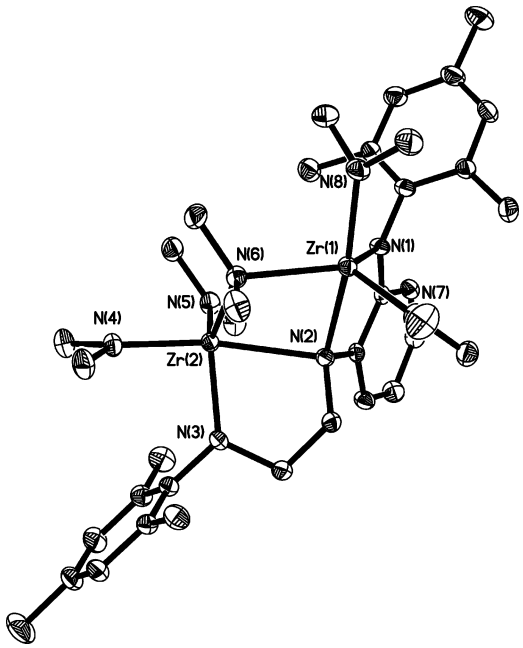


Figure 1. Thermal ellipsoid plot of [MesitylN-*o*-C_6H_4-NCH_2CH_2NMesityl]$Zr_2(NMe_2)_5$ (**1d**; 35% probability). Selected bond distances (Å) and angles (deg): Zr(1)−N(1) = 2.112(2); Zr(1)−N(2) = 2.333(2); Zr(1)−N(6) = 2.295(2); Zr(1)−N(7) = 2.030(2); Zr(1)−N(8) = 2.064(2); Zr(2)−N(3) = 2.082(2); Zr(2)−N(2) = 2.453(2); Zr(2)−N(4) = 2.068(2); Zr(2)−N(5) = 2.039(2); Zr(2)−N(6) = 2.275(2); Zr(1)−N(2)−Zr(2) = 95.59(6); Zr(1)−N(6)−Zr(2) = 101.75(7); N(2)−Zr(1)−N(6) = 79.89(6); N(2)−Zr(2)−N(6) = 77.78(6); N(1)−Zr(1)−N(6) = 120.43(6); N(3)−Zr(2)−N(6) = 117.75(7).

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Table 1. Crystallographic Data, Collection Parameters, and Refinement Parameters for [MesitylN-*o*-$C_6H_4NCH_2CH_2$NMesityl]$Zr_2(NMe_2)_5$ (1d), [1]$ZrMe_2$ (3c), and [2]$ZrMe_2$ (5c)[a]

	1d	3c[b]	5c
empirical formula	$C_{36}H_{60}N_8Zr_2$	$C_{34}H_{41}N_3Zr$	$C_{29}H_{39}N_3Zr$
fw	787.36	582.93	520.85
temperature	193(2) K	183(2) K	193(2) K
cryst syst	triclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
unit cell dimens	$a = 10.5468(4)$ Å	$a = 11.1743(8)$ Å	$a = 10.3983(9)$ Å
	$b = 13.1591(5)$ Å	$b = 19.3928(14)$ Å	$b = 15.5014(14)$ Å
	$c = 14.4106(5)$ Å	$c = 16.5054(12)$ Å	$c = 18.4205(17)$ Å
	$\alpha = 94.063(1)°$	$\alpha = 90°$	$\alpha = 89.535(2)°$
	$\beta = 104.604(1)°$	$\beta = 91.664(1)°$	$\beta = 83.932(2)°$
	$\gamma = 92.716(1)°$	$\gamma = 90°$	$\gamma = 71.647(2)°$
volume (Å^3)	1926.10(12)	3575.2(4)	2801.4(4)
Z	2	4	4
density (calcd, g/cm^3)	1.358	1.202	1.235
abs coeff (mm^{-1})	0.576	0.338	0.412
$F(000)$	824	1352	1096
cryst size (mm)	0.18 × 0.13 × 0.08	0.3 × 0.15 × 0.15	0.27 × 0.21 × 0.15
θ range for data collection	1.47 to 25.00°	2.41 to 23.29°	1.11 to 24.00°
index ranges	$-12 \le h \le 12$	$-12 \le h \le 8$	$-10 \le h \le 11$
	$-15 \le k \le 13$	$-21 \le k \le 21$	$-15 \le k \le 17$
	$-14 \le l \le 17$	$-17 \le l \le 18$	$-21 \le l \le 21$
no. of reflns collected	10 226	14 215	13 921
no. of indep reflns	6707 [$R_{int} = 0.0356$]	5143 [$R_{int} = 0.0394$]	8770 [$R_{int} = 0.0340$]
abs corr	none	empirical	empirical
no. of data/restraints/params	6707/0/431	5143/0/369	8770/0/618
goodness-of-fit on F^2	1.022	1.062	1.075
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0291$	$R_1 = 0.0561$	$R_1 = 0.0658$
	$wR_2 = 0.0788$	$wR_2 = 0.1489$	$wR_2 = 0.1510$
R indices (all data)	$R_1 = 0.0326$	$R_1 = 0.0711$	$R_1 = 0.0874$
	$wR_2 = 0.0804$	$wR_2 = 0.1568$	$wR_2 = 0.1604$
largest diff peak and hole (e·Å^{-3})	0.393 and −0.446	1.469 and −0.436	0.904 and −0.681

[a] Wavelength = 0.71073 Å; refinement was by full matrix least squares on F^2. [b] One molecule of diethyl ether was present per zirconium.

mobenzene.[33] Selective addition of the phenyl group to the central nitrogen proceeded in high yield to give H_2**1**. Compound H_2**1** was purified by column chromatography and isolated in 55% yield as a yellow-brown resin. Difficulties with chromatographic separation limited the scale at which the reaction could be performed. The highest isolated yields were realized when the phenylation was conducted on a 4−5 g scale of **1c**.

The synthesis of H_2**2** began with arylation of ethylenediamine with bromomesitylene. A large excess of ethylenediamine allowed **2a** to be isolated on a large scale (>20 g) in good yield (65%) after vacuum distillation. Compound **2a** was then added to *o*-fluoronitrobenzene to generate **2b**, which was subsequently reduced with Pd/C under 35 psi of H_2 to afford **2c**. Compound **2c** was treated with acetone-d_6 to give the imine **2d**, which upon treatment with MeLi gave the triamine **2e**.[22] Synthesis of precursors **2b**−**2e** all proceeded without any required chromatographic purification in good yields (≥70%) on scales of roughly 20 g. Unlike H_2**1**, the final phenylation of **2e** with bromobenzene was found to give only 50% conversion (by NMR) using the traditional *rac*-BINAP (racemic-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl) cocatalyst. Use of the XPHOS (dicyclohexyl-(2′,4′,6′-triisopropylbiphenyl-2-yl)-phosphine) ligand[34] resulted in a near quantitative conversion of **2e** to ligand H_2**2**. Compound H_2**2** was purified by column chromatography and isolated in 50% yield as a yellow-brown resin.

Synthesis of Zr and Hf Complexes. Bisdimethylamido zirconium and hafnium complexes were prepared as white or off-white, air- and moisture-sensitive crystalline solids in good yield through reaction of H_2**1** or H_2**2** with $Zr(NMe_2)_4$ or $Hf(NMe_2)_4$ (Scheme 4). NMR spectra of the resulting bisdimethylamido species are complicated, but several features are worth pointing out, some of which are characteristic of other species discussed later. In general, spectra of all analogous zirconium and hafnium complexes were identical except for some minor differences in chemical shift. In the compounds that contain [**1**]$^{2-}$ (**3a** and **4a**) it is clear that the mesityl rings do not rotate readily on the NMR time scale, although not all six mesityl methyl resonances are visible due to overlap with dimethylamido methyl resonances. Ortho and meta proton resonances for the central phenyl ring can be discerned (in **3a** at 7.07 ppm for H_o and 7.00 ppm H_m), consistent with a readily rotating phenyl ring on the central nitrogen donor. Three phenylene ring protons can also be clearly observed (in **3a** at 6.54, 6.44, and 6.20 ppm) along with four backbone protons (in **3a** at 4.30, 3.70, 3.62, and 3.02 ppm). The two dimethylamido ligand resonances are sharp, characteristic of dimethylamido ligands that rotate readily about the Zr−N bond and that do not interconvert readily on the NMR time scale. Therefore, we can conclude that the central nitrogen donor does not dissociate from the metal, invert at nitrogen, and reassociate on the NMR time scale (∼1−100 s^{-1}), since one might predict that the two amido ligands would exchange in such a process.

In all compounds that contain the [**2**]$^{2-}$ ligand, the "*t*-Bu_{d6}" proton resonance contains a small upfield shoulder as a consequence of some pentadeutero *tert*-butyl group (primarily) being formed during the syn-

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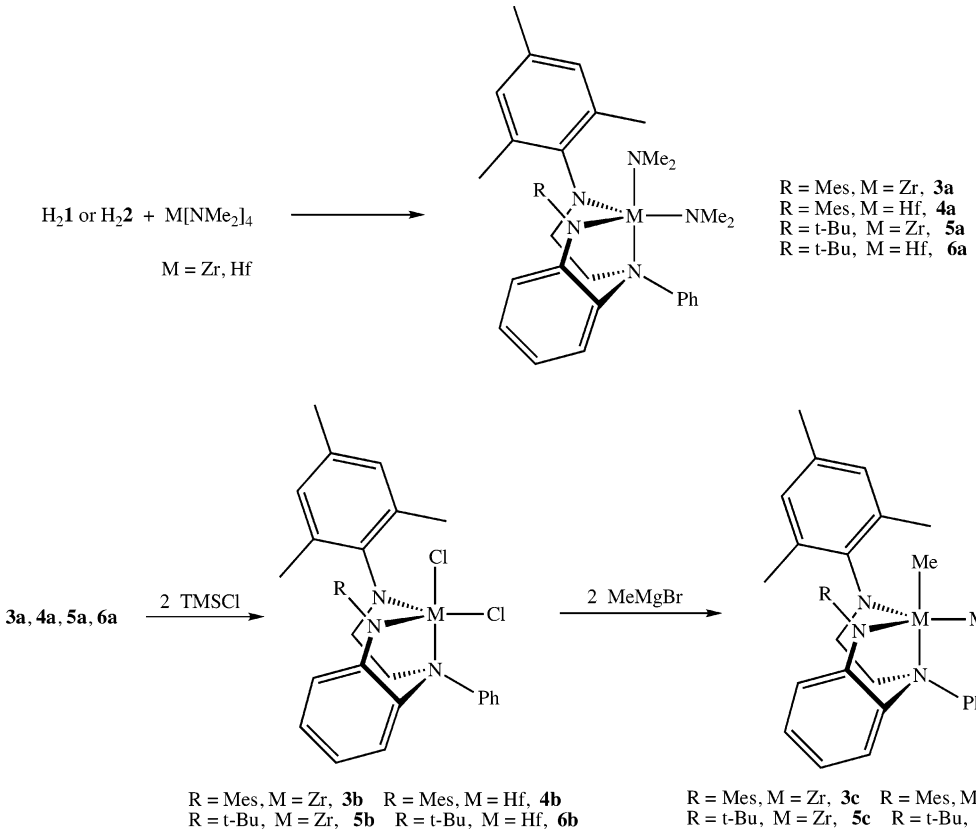
Scheme 4



thesis of H_2**2**,[22] a fact that contributes to a total integral for the *t*-Bu_{d6} group of between 3.1 and 3.2 protons. In **5a** and **6a** some slowing down of rotation of one of the two dimethylamido groups is apparent in the form of broadening of one of the dimethylamido resonances at room temperature. We assume that complexes that contain the [**2**]$^{2-}$ ligand are more crowded than those that contain the [**1**]$^{2-}$ ligand and that an increase in steric congestion is responsible for hindered rotation of one of the dimethylamido groups.

Treatment of the bisdimethylamido complexes with 2 equiv of TMSCl yielded the dichloride derivatives **3b**−**6b** (Scheme 4). In these species, distinct mesityl methyl resonances are clearly discernible (e.g., at 2.57, 2.48, 2.45, 2.19, 2.04, and 2.02 ppm in **3b**), along with others characteristic of asymmetric species and a rotating central phenyl ring. The dichloride complexes are not soluble in pentane or diethyl ether, which raises the possibility that they are dimeric in the solid state, as has been observed for other dichloride compounds in this general family of diamido/donor complexes whose structure has been determined.[22]

Treatment of the dichloride complexes with 2 equiv of MeMgBr yielded the dimethyl derivatives **3c**−**6c** (Scheme 4). The most distinguishing features of the dimethyl complexes are sharp singlet resonances for two inequivalent methyl groups bound to the metal near 0 ppm (e.g., at 0.22 and 0.11 in **4c**). Compound **6c** was also prepared using $^{13}CH_3MgI$ in ether. In the carbon NMR spectrum, the methyl group resonances were found at 58.93 ppm (J_{CH} = 111 Hz, J_{CC} = 2.9 Hz) and 57.17 ppm (J_{CH} = 112 Hz, J_{CC} = 2.9 Hz) in bromobenzene-d_5.

The solid state structure of **3c** was determined by X-ray crystallography (Figure 2 and Tables 1 and 2). The geometry of **3c** can be viewed as a distorted square pyramid or distorted trigonal bipyramid with N(2)−Zr−C(1) = 141.69(17)° and N(2)−Zr−C(2) = 122.49(17)°. The sum of the angles around N(1) and N(3) is close to 360° (359.5° and 360.0°, respectively), as expected for π-donating disubstituted amido ligands bound to Zr. The amide and carbon bond lengths around Zr in **3c** are within the range commonly encountered for complexes of this type, although the Zr−N(1) bond is slightly longer (0.06 Å) than the Zr−N(3) bond. This difference is likely to be the consequence of weaker π-donation to Zr by the less basic diaryl amido nitrogen N(1). The Zr−N(2) bond length of 2.463(4) Å is one of the longest metal-donor bonds reported for alkyl complexes of Zr-containing

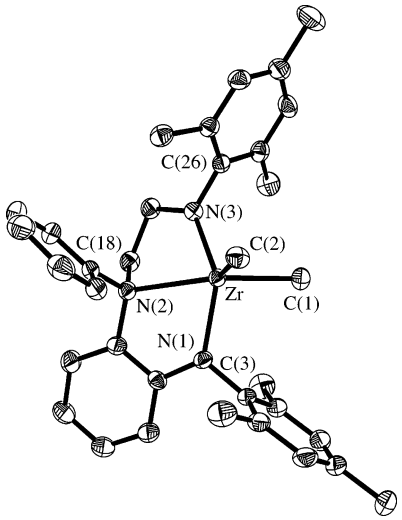


Figure 2. Thermal ellipsoid plot of [**1**]$ZrMe_2$ (**3c**; 35% probability).

Table 2. Selected Bond Lengths (Å) and Angles (deg) for [1]$ZrMe_2$ (3c) and [2]$ZrMe_2$ (5c)[a]

	3c	5c
Zr−N(1)	2.123(4)	2.070(4)
Zr−N(3)	2.061(4)	2.062(4)
Zr−N(2)	2.463(4)	2.510(4)
Zr−C(1)	2.238(5)	2.238(6)
Zr−C(2)	2.257(5)	2.239(6)
N(1)−Zr−N(3)	134.17(15)	116.18(17)
N(1)−Zr−N(2)	70.51(14)	71.44(15)
N(3)−Zr−N(2)	71.30(14)	72.50(14)
N(1)−Zr−C(1)	96.26(18)	107.2(2)
N(1)−Zr−C(2)	111.76(18)	117.6(2)
N(3)−Zr−C(1)	98.22(18)	95.97(19)
N(3)−Zr−C(2)	109.68(17)	115.2(2)
N(2)−Zr−C(1)	141.69(17)	165.32(19)
N(2)−Zr−C(2)	122.49(17)	93.2(2)
C(1)−Zr−C(2)	95.8(2)	100.1(3)

[a] One of two molecules in the asymmetric unit.

diamido/donor ligands of this general type.[22,23,25,28,35,36] This longer bond is consistent with the weaker donor ability of the diaryl/alkylamine donor (as compared to donors shown in Scheme 1) and perhaps also the greater steric requirements of the phenylated central amine.

Compound **5c** crystallized in the triclinic space group $P\bar{1}$ with two independent molecules in the asymmetric unit, only one of which is shown in Figure 3. (See also Tables 1 and 2.) The geometry of **5c** more closely approaches that of a TPB structure with C(1) and N(2) in axial positions. For example, the C(1)−Zr−N(2) angle (165.32(19)°) is much closer to 180° than the C(1)−Zr−N(2) angle in **3c**, and the N(1)−Zr−N(3) angle is 116.18(17)° (vs 134.17(15)° in **3c**). The Zr−N_{amido} and Zr−C bond lengths are similar to those found for **3c**. As expected, there is no significant difference in the Zr−N_{amido} bond lengths in **5c** because both N(1) and N(3) are alkyl/aryl-substituted amides. The Zr−N(2) bond length (2.510(4) Å) is even longer than that in **3c**, possibly as a consequence of the larger steric demands of the *tert*-butyl substituent on N(1).

Activation of Dimethyl Species and Formation of Cations. Activation of the dimethyl complexes **3c** and **4c** in bromobenzene at 0 or −10 °C with 1 equiv of $[Ph_3C][B(C_6F_5)_4]$ led to formation of Ph_3CCH_3 and generation of the methyl cations **3d** and **4d** (eq 2). No

$$\mathbf{3c}, \mathbf{4c} + [Ph_3C][B(C_6F_5)_4] \xrightarrow[-Ph_3CCH_3]{C_6H_5Br \text{ or } C_6D_5Br} \{[\mathbf{1}]M(Me)\}\{B(C_6F_5)_4\} \quad (2)$$

$$M = Zr\ (\mathbf{3d}) \text{ or } Hf\ (\mathbf{4d})$$

four-coordinate cation (as a $[B(C_6F_5)_4]^-$ salt) in the general category of diamido/donor complexes has ever been isolated. Therefore these cations, like others, could be explored only through NMR studies. In each case, the methyl resonance is found near 0 ppm (at −0.05 ppm in **3d** and −0.14 ppm in **4d**). *One* of the mesityl rings is beginning to rotate on the NMR time scale, as judged by some broadening of the ortho-methyl group and meta aryl proton resonances. (Note that these spectra were recorded at −10 °C (**3d**) and 0 °C (**4d**), where ring rotations would be slower relative to the rate at room temperature.) We attribute the greater ease of rotation of the mesityl rings in these cations to their more open, pseudo-tetrahedral nature, whereas all

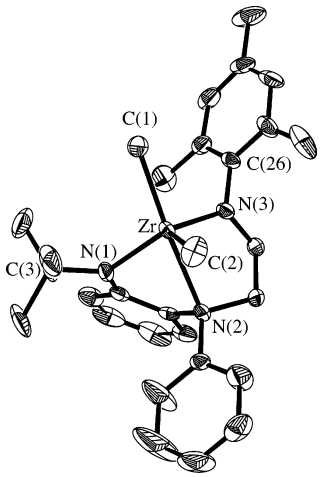


Figure 3. Thermal ellipsoid plot of [**2**]$ZrMe_2$ (**5c**; 35% probability).

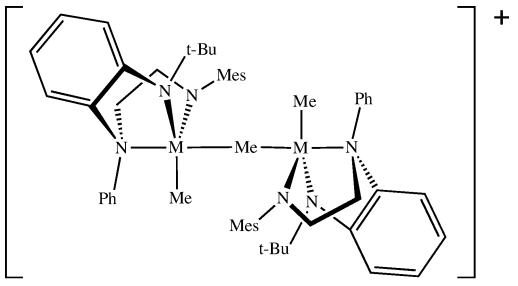
neutral compounds discussed so far have been five-coordinate. We have no information concerning the degree of association of the anion or bromobenzene with the cation, i.e., the degree of "solvation" of the ion pair.

In contrast to activation of **3c** and **4c**, activation of **5c** and **6c** in bromobenzene at 0 or −10 °C with 1 equiv of $[Ph_3C][B(C_6F_5)_4]$ first led to formation of Ph_3CCH_3 and generation of the dimeric monocations **5e** and **6e** (eq 3). These cations are relatively long-lived when only

$$\mathbf{5c}, \mathbf{6c} + 0.5\ [Ph_3C][B(C_6F_5)_4] \xrightarrow[-0.5\ Ph_3CCH_3]{C_6D_5Br} \{[\mathbf{2}]_2M_2Me_3\}\{B(C_6F_5)_4\} \quad (3)$$

$$M = Zr, \mathbf{5e}; M = Hf, \mathbf{6e}$$

0.5 equiv of $[Ph_3C][B(C_6F_5)_4]$ is employed. They react further with $[Ph_3C][B(C_6F_5)_4]$ as described below. In **5e** and **6e** only two types of methyl groups are observed (at 0.27 (area 6) and 0.01 ppm (area 3) in **5e** and 0.13 (area 3) and 0.06 ppm (area 6) in **6e**). Dimeric monocations that contain diamido/donor ligands have been observed in other systems, and one has been crystallographically characterized that contains one bridging methyl group and two terminal methyl groups.[25] In another system it has been proposed that the bimetallic monocation contains three bridging methyl groups.[29] In ^{13}C-labeled **6e**, the labeled methyl resonances are found at 64.78 ppm (for two methyl groups) and 50.20 ppm with J_{CH} values of 113.6 and 132.6 Hz, respectively. Therefore we propose that two terminal methyl groups (with resonances at 64.78 ppm) and one bridging methyl group (with a resonance at 50.20 ppm) are present in **6e**, and presumably also in **5e**. One possible structure



C

Table 3. Data for the Polymerization of 1-Hexene by 3d or 4d in C_6H_5Br

entry		[cat.] (mM)	1-hex (equiv)	T (°C)	10^3M_n (theory)	10^3M_n (found)	PDI (M_w/M_n)
1	**3d**	10	100	0	8.4	10.0	1.68
2	**3d**	10	200	0	16.8	16.9	2.20
3	**3d**	10	300	0	25.2	26.6	2.43
4	**3d**	10	400	0	33.6	35.2	2.33
5	**3d**	5.0	290	−25	24.4	40.8	4.04
6	**4d**	10	200	0	16.8	14.4	2.54
7	**4d**	9.9	300	0	25.2	16.8	4.01
8	**4d**	9.9	200	−25	16.8	19.2	2.69

that is attractive for steric reasons is the heterochiral species **C**, shown below, in which the two terminal methyl groups are related by a center of symmetry. In a homochiral version the two terminal methyl groups would be related by a C_2 axis.

In the presence of $[Ph_3C][B(C_6F_5)_4]$, the dimeric monocations **5e** and **6e** slowly react further to yield the monomeric cations shown in eq 4. Compound **5e** appeared to react in less than 5 min at 0 °C, while **6e** required close to 45 min at 0 °C at the concentrations employed (∼0.1 M). On the basis of studies involving previous diamido/donor ligands,[22,24,25,29] the dimeric monocations are believed to be in equilibrium with the monomethyl monocation and the neutral dimethyl species. The neutral dimethyl species then reacts further with $[Ph_3C][B(C_6F_5)_4]$ to yield monomethylmonocations, as shown in eq 2 for species that contain the $[\mathbf{1}]^{2-}$ ligands. In ^{13}C-labeled **6d** the methyl resonance is found at 66.27 ppm with $J_{CH} = 113.5$ Hz.

$$\mathbf{5e}, \mathbf{6e} + 0.5\ [Ph_3C][B(C_6F_5)_4] \xrightarrow[-0.5\ Ph_3CCH_3]{C_6D_5Br} \{[\mathbf{2}]M(Me)\}\{B(C_6F_5)_4\} \quad (4)$$

$$M = Zr\ (\mathbf{5d})\ \text{or}\ M = Hf\ (\mathbf{6d})$$

Attempts to observe bimetallic cations through reaction of **3c** or **4c** with 0.5 equiv of $[Ph_3C][B(C_6F_5)_4]$ were not successful; the activator was consumed but an unidentifiable mixture of products was produced, which did not evolve to a single product over a period of several days, according to ^{1}H NMR spectra. It is not clear to us why **3c** and **4c** do not yield methyl-bridged dimers analogous to **5e** and **6e**, especially since complexes that contain ligand $[\mathbf{1}]^{2-}$ should be less sterically crowded than those that contain ligand $[\mathbf{2}]^{2-}$.

Polymerization of 1-Hexene. Complexes **3d** and **4d** proved to be effective initiators for the polymerization of 1-hexene. Polymerization of 100 equiv of 1-hexene by **3d** was complete in less than 5 min at 0 °C according to ^{1}H NMR studies. Results from a series of bulk polymerization experiments are summarized in Table 3. The poly[1-hexene] produced in each case was essentially atactic, according to ^{13}C NMR spectra.[37] In all runs, the poly[1-hexene] formed had modest polydispersity indices and molecular weight distributions that tended to become bimodal with increasing molecular weight (monomer added). The bimodal nature of these molecular weight distributions for higher monomer equivalents suggests that some chain termination occurs during polymerization. Decomposition of the active catalyst by β-H elimination from 1,2 or 2,1 insertion products did not appear to be taking place with initiators **3d** and **4d**; that is, no olefinic resonances were observed in the ^{1}H NMR spectra of the poly[1-hexene]. Carrying out the polymerization experiments at −25 °C instead of 0 °C did not significantly alter the molecular weights and polydispersities of the poly[1-hexene], nor did any tacticity become evident. These results are analogous to those obtained for poly[1-hexene] prepared with zirconium cations that contain the $[(Mesityl\text{-}NCH_2CH_2)_2NMe]^{2-}$ ligand system, where it was determined that CH activation in a mesityl methyl group led to catalyst deactivation.[25,38]

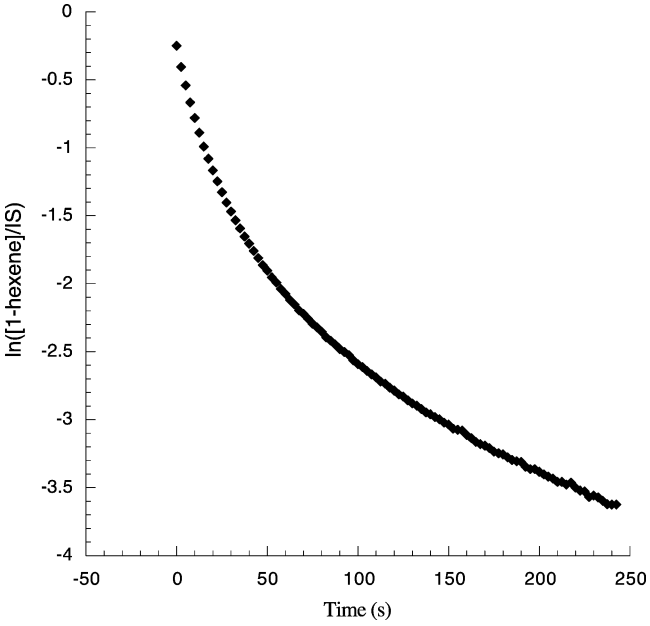


Figure 4. Consumption of 90 equiv of 1-hexene by {[**2**]-ZrMe}$\{B(C_6F_5)_4\}$ (**5d**, 20.0 mM) in C_6D_5Br (internal standard = diphenylmethane).

Polymerization of 1-hexene with **5d** was much slower than polymerization with either **3d** or **4d**. Consumption of 100 equiv of 1-hexene at 0 °C required 6 h, as judged by ^{1}H NMR. The slower rate of monomer consumption by **5d** allowed the polymerization to be followed by ^{1}H NMR. The consumption of 90 equiv of 1-hexene at 0 °C is shown in Figure 4 in the form of a plot of the natural log of relative concentration versus time. The plot should be linear for a living polymerization in which the catalyst concentration remains constant. The curved plot suggests that the active catalyst derived from **5d** decomposes during polymerization. The results from a series of bulk polymerization experiments are summarized in Table 4. The M_n values obtained for the poly[1-hexene] in these experiments are much lower than those found for polymers produced by **3d** and **4d**, which suggests that some form of more substantial catalyst decomposition is taking place. Lowering the reaction temperature to −25 °C increased the M_n values of the

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Table 4. Data for the Polymerization of 1-Hexene by 5d in C_6H_5Br or C_6D_5Br

entry	[cat.] (mM)	1-hex (equiv)	T (°C)	10^3M_n (theory)	10^3M_n (found)	PDI (M_w/M_n)
1	4.7	100	0	8.4	4.9	1.60
2	4.4	200	0	16.8	5.3	2.24
3	4.0	300	0	25.2	6.6	2.43
4	4.2	450	0	37.8	8.1	2.21
5	8.8	100	−25	8.4	8.7	1.29
6	8.2	200	−25	16.8	12.3	1.60

poly[1-hexene], possibly as a result of a slowing of decomposition pathways relative to the rate of polymerization. Analysis of the poly[1-hexene] by ^{13}C NMR and ^1H NMR showed them to be atactic, and olefinic resonances indicative of β-H elimination from a 1,2 insertion product were present as broad multiplets between 5.34 and 5.43 ppm. Catalyst decomposition after β-hydride elimination would account for the observations shown in Figure 4. Results obtained with initiator **5d** and the slow activation of precatalyst **6c** led us to forego examination of initiator **6d**.

It is clear from the polymerization results that polymerization of 1-hexene with **3d**−**5d** is not living, and furthermore the process is not stereoselective to any significant degree.

Conclusions

Cationic zirconium and hafnium complexes described here that contain two new asymmetric diamido-N-donor ligands are initiators for the polymerization of 1-hexene at or below 0 °C in bromobenzene, but the polymerizations are not living and the resulting poly[1-hexene] is atactic. Since chirality at the metal is established only if the central, diphenylalkylamine-like donor remains bound *throughout* a polymerization reaction (i.e., for seconds to minutes, or longer), we suspect that the central donor most likely dissociates too readily during polymerization, thereby interconverting chirality at the metal center and dramatically reducing the possibility of stereocontrol. However, it is still possible that the central donor remains firmly bound, but the asymmetry that has been introduced is simply insufficient in controlling the stereochemistry of 1-hexene insertion. In any case future efforts will involve complexes in which a group with a fixed chirality is present, or in which interconversion of enantiomers is unlikely or not possible.

Experimental Section

General Procedures. All manipulations other than those involving the synthesis of ligands H_2**1** and H_2**2** were performed in a nitrogen-filled Vacuum Atmospheres drybox or using standard Schlenk techniques. All precatalysts were activated in a glovebox free of ether, THF, and other coordinating solvents. Toluene, pentane, and diethyl ether were sparged with nitrogen and passed through activated alumina prior to use. Bromobenzene and 1-hexene were stored over and distilled from calcium hydride. Benzene-d_6 and bromobenzene-d_5 were purchased from Cambridge Isotope Laboratories and dried/distilled from sodium benzophenone ketyl and calcium hydride, respectively. Organic reagents were purchased from Aldrich or Acros Organics and used as received. MeMgBr was purchased from Aldrich and titrated prior to use. $ZrCl_4$, $HfCl_4$, $Pd_2(dba)_3$, and all phosphines were purchased from Strem Chemicals and used without further purification. $Zr(NMe_2)_4$ and $Hf(NMe_2)_4$ were synthesized according to published procedures.[39] $[Ph_3C][B(C_6F_5)_4]$ was obtained as a gift from the Exxon Mobil Corporation. ^1H and ^{13}C NMR spectra were recorded on a Varian spectrometer operating at either 300 or 500 MHz (^1H). ^1H NMR chemical shifts are given in ppm versus residual protons in the deuterated solvents as follows: δ 7.16 C_6D_6, δ 7.29 C_6D_5Br (most downfield resonance), δ 2.50 DMSO-d_6, δ 7.27 $CDCl_3$. ^{13}C NMR chemical shifts are reported in ppm versus ^{13}C shifts of the solvent as follows: δ 128.39 C_6D_6, δ 125.45 (ipso carbon). Mass spectra were recorded by the Department of Chemistry Instrument Facility staff at MIT. Combustion analyses were performed by H. Kolbe Microanalytics Laboratory, Mülheim an der Ruhr, Germany.

GPC analyses were carried out on a system equipped with two Jordi-Gel DVB mixed bed columns (250 mm length × 10 mm inner diameter) in series. HPLC grade THF was supplied at a flow rate of 1.0 mL/min with a Knauer 64 HPLC pump. A Wyatt Technology mini Dawn light-scattering detector coupled with a Knauer differential refractometer was employed. Data analysis was carried out using Astrette 1.2 software (Wyatt Technology). M_n and M_w values for poly[1-hexene] were obtained using $dn/dc = 0.076$ mL/g (Wyatt Technology), and the auxiliary constant of the apparatus (5.9×10^{-4}) was calibrated using a polystyrene standard ($M_n = 2.2 \times 10^5$).

2-(2-Nitrophenylamino)ethylammonium Chloride (1a). *o*-Chloronitrobenzene (100 g, 0.635 mol) was refluxed with excess ethylenediamine (340 mL, 5.089 mol) and water (184 mL, 10.2 mol) at 120 °C for 2 h. The unreacted ethylenediamine was removed in vacuo, and the resulting residue was dissolved in hot, dilute HCl (pH = 3−4). The solution was filtered and cooled to −20 °C, at which point brilliant orange needle-shaped crystals formed. The remaining solution was acidified and cooled to yield more crystals; total yield 85.87 g (60%). ^1H NMR (300 MHz, DMSO-d_6): δ 8.17 (br t, 1H), 8.07 (d, 1H), 8.01 (br s, 3H), 7.55 (t, 1H), 7.15 (d, 1H), 6.73 (t, 1H), 3.67 (q, 2H), 3.00 (t, 2H).

2-(2-Aminophenylamino)ethylammonium Chloride (1b). A Fischer−Porter bottle was charged with 22.31 g (0.103 mol) of **1a**, and 1 L of methanol was added. The bottle was sealed with a septum, and the orange solution was sparged with nitrogen for 15 min. Once the solution was degassed, 1.1 g of Pd/C (3% Pd) was added, and the system flushed with hydrogen. The reaction vessel was pressured to 35 psi of hydrogen, and the reaction was stirred for 12 h at 60 °C. The reaction mixture was filtered through Celite, and the pale brown filtrate was concentrated to half its volume in vacuo and stored at −20 °C. The product crystallized as pale pink needles over the course of 1−2 days. The mother liquor was concentrated to obtain a second crop of crystals; total yield was 14.0 g (73%). ^1H NMR (300 MHz, DMSO-d_6): δ 8.20 (br s, 3H), 6.50 (m, 4H), 4.69 (br s, 2H), 3.24 (t, 2H), 3.04 (t, 2H).

***N*-(2,4,6-Trimethylphenyl)-*N*′-[2-(2,4,6-trimethylphenylamino)ethyl]benzene-1,2-diamine (1c).** Under an inert atmosphere, 0.7480 g (1.5 mol %) of $Pd_2(dba)_3$ and 1.5203 g (4.5 mol %) of BINAP[31] were dissolved in toluene, and the solution was stirred and heated gently for 20 min. The mixture was filtered through Celite into a flask containing 10.169 g (0.0542 mol) of **1b** and 20.5 g (0.213 mol) of NaO-*t*-Bu. To the mixture was added 300 mL of toluene and 17.5 mL (0.114 mol) of 2-bromomesitylene. The reaction vessel was sealed with a septum and the red-brown mixture allowed to stir at 100 °C for 65 h. The reaction mixture was extracted into 300 mL of diethyl ether, and the solution was washed three times with 250 mL of water and twice with 250 mL of a saturated NaCl solution. The organic layer was separated, dried over $MgSO_4$, and filtered through Celite to give a dark red-brown filtrate. The volatiles were removed in vacuo, and the resulting dark

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brown oil was purified by flash chromatography (SiO_2, 1:1 ether/hexanes). The pooled fractions were concentrated to ~20 mL and stored at −20 °C for 24 h. Compound **1c** precipitated as a pale yellow crystalline powder (12.06 g, 57%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.94 (s, 2H), 6.84 (s, 2H), 6.79 (dd, 2H), 6.65 (t, 1H), 6.27 (d, 1H), 4.72 (s, 1H), 4.09 (br t, 1H), 3.41 (t, 2H), 3.32 (t, 2H), 3.25 (br s, 1H), 2.32 (s, 3H), 2.31 (s, 6H), 2.22 (s, 3H), 2.12 (s, 6H). ^{13}C{^{1}H} (75 MHz, $CDCl_3$): δ 142.84, 137.93, 137.03, 134.43, 133.73, 133.05, 131.77, 129.88, 129.58, 129.31, 120.57, 118.88, 114.45, 111.46, 48.12, 44.89, 21.09, 20.79, 18.67, 18.33. HRMS: calcd $[M + H]^+$ 388.2747, found $[M + H]^+$ 388.2747.

Synthesis of Complex 1d. A reaction vessel was charged with 1.00 g (2.58 mmol) of **1c** and 1.424 g (5.33 mmol) of $Zr(NMe_2)_4$ and made homogeneous through addition of 100 mL of diethyl ether. The amber solution was allowed to stir for 16 h at room temperature, during which time compound **1d** precipitated from solution as a pale yellow powder (1.49 g, 70%). Crystals suitable for X-ray diffraction were grown by vapor diffusion of pentane into benzene. ^{1}H NMR (500 MHz, C_6D_6): δ 7.71 (d, 1H), 7.04 (s, 1H), 7.01 (s, 1H), 6.97 (s, 1H), 6.96 (s, 1H), 6.90 (t, 1H), 6.79 (t, 1H), 6.13 (d, 1H), 4.56 (td, 1H), 4.40 (td, 1H), 4.01 (dd, 1H), 3.21 (dd, 1H), 2.85 (s, 6H and br s, 3H), 2.63 (v br s, 15H), 2.55 (s, 3H), 2.51 (s, 3H), 2.31 (s, 3H), 2.27 (s, 3H), 2.26 (s, 3H), 2.21 (s, 3H). Anal. Calcd for $C_{36}H_{60}N_8Zr_2$: C, 54.92; H, 7.68; N, 14.23. Found: C, 55.11; H, 7.59; N, 14.28.

***N*-Phenyl-*N*′-(2,4,6-trimethylphenyl)-*N*-[2-(2,4,6-trimethylphenylamino)ethyl]benzene-1,2-diamine ($H_2$1).** Compound H_2**1** was prepared in a manner analogous to **1c** through a $Pd_2(dba)_3$/BINAP-catalyzed *N*-aryl coupling that employed 3.998 g (0.0103 mol) of **1c** and 1.4 mL (0.013 mol) of bromobenzene. After the aqueous workup, the crude product was purified by flash chromatography (SiO_2, 5% EtOAc in hexanes) to give 2.69 g (56%) of H_2**1** as an extremely viscous brown-yellow oil that was used without further purification. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.20 (t, 2H), 7.12 (d, 1H), 7.03 (t, 1H), 6.90 (s, 2H), 6.80 (s, 2H), 6.74 (m, 4H), 6.23 (d, 1H), 5.76 (s, 1H), 3.88 (t, 2H), 3.34 (t, 2H), 3.11 (br s, 1H), 2.30 (s, 3H), 2.23 (s, 3H), 2.19 (s, 6H), 2.07 (s, 6H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 148.25, 143.75, 143.09, 136.26, 135.64, 135.03, 132.20, 131.67, 129.94, 129.66, 129.57, 129.43, 129.34, 127.85, 118.34, 118.03, 114.39, 112.26, 51.55, 46.43, 21.10, 20.74, 18.44, 18.41. HRMS: calcd $[M + H]^+$ 464.3060, found $[M + H]^+$ 464.3040.

***N*′-(2,4,6-Trimethylphenyl)ethane-1,2-diamine (2a).** Compound **2a** was prepared by a $Pd_2(dba)_3$/BINAP (1.5 mol %/4.5 mol %)-catalyzed *N*-aryl coupling between 23 mL (0.15 mol) of bromomesitylene and 40 mL (0.59 mol) of ethylenediamine in the same manner as compounds **1c** and H_2**1**. After the aqueous workup, crude **2a** was purified by vacuum distillation (85 °C, 10 mTorr), yielding 17.46 g (65%) of a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.86 (s, 2H), 3.00 (t, 2H), 2.92 (t, 2H), 2.31 (s, 6H), 2.27 (s, 3H), 2.01 (br s, 2H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 143.61, 131.29, 129.83, 129.50, 51.33, 42.65, 20.64, 18.45. HRMS: calcd $[M]^+$ 178.1465, found $[M]^+$ 178.1468.

***N*-(2-Nitrophenyl)-*N*′-(2,4,6-trimethylphenyl)ethane-1,2-diamine (2b).** A reaction vessel was charged with 12.36 g (0.0693 mol) of **2a**, 7.7 mL (0.073 mol) of 2-nitrofluorobenzene, 19.7 g (0.143 mol) of K_2CO_3, and 250 mL of acetonitrile. The reaction mixture was degassed with N_2 for 10 min and then heated at 80 °C for 18 h. During this time the reaction changed from yellow to bright orange. The acetonitrile was removed in vacuo, and the residue was extracted into 300 mL of Et_2O. The ether extract was washed once with 200 mL of water and twice with 200 mL of a saturated NaCl solution. The organic layer was then dried over $MgSO_4$ and filtered through Celite. The ether was removed in vacuo to yield 18.496 g (89%) of **2b** as bright orange crystals. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.35 (br t, 1H), 8.21 (d, 1H), 7.45 (t, 1H), 6.88 (d, 1H), 6.85 (s, 2H), 6.68 (t, 1H), 3.52 (q, 2H), 3.29 (t, 2H), 3.04 (br s, 1H), 2.29 (s, 6H), 2.25 (s, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 145.38, 142.24, 136.26, 132.19, 132.08, 130.48, 129.58, 126.94, 115.54, 113.79, 47.18, 43.53, 20.80, 18.42. HRMS: calcd $[M + H]^+$ 300.1707, found $[M + H]^+$ 300.1705.

***N*-[2-(2,4,6-Trimethylphenylamino)ethyl]benzene-1,2-diamine (2c).** A Fischer−Porter bottle was charged with 18.496 g (0.0628 mol) of **2b** and 500 mL of methyl alcohol. The orange solution was degassed with N_2 for 15 min, and 1.74 g of Pd/C (3% Pd) was added subsequently. The system was flushed with hydrogen, the vessel was pressurized to 35 psi, and the reaction was stirred at 60 °C for 3.5 h. The reaction mixture was then filtered through Celite, and the volatiles were removed in vacuo to give ~16 g (~95%) of **2c** as a crude dark red oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.86 (s, 2H), 6.84 (t, 1H), 6.73 (m, 3H), 3.66 (br s, 2H), 3.37 (t, 2H), 3.28 (t, 2H), 2.31 (s, 6H), 2.26 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 142.49, 137.51, 134.77, 132.32, 130.27, 129.77, 120.74, 119.18, 116.64, 112.04, 48.22, 44.63, 20.77, 18.53. HRMS: calcd $[M + H]^+$ 270.1970, found $[M + H]^+$ 270.1963.

***N*-Isopropylidene-d_6-*N*′-[2-(2,4,6-trimethylphenylamino)ethyl]benzene-1,2-diamine (2d).** Crude **2c** was dissolved in 50 g of acetone-d_6, and 30 g of 4 Å molecular sieves were added. The reaction vessel was sealed with a septum and flushed with N_2. The reaction was allowed to stand at room temperature for 5 days. The dark red solution was filtered through Celite, and the volatiles were removed in vacuo. Compound **2d** was isolated as 16.68 g (86% from **2b**) of a yellow-red oil, which was immediately carried on to the next step in the synthesis. ^{1}H NMR (300 MHz, acetone-d_6): δ 6.79 (s, 2H), 6.53 (t, 1H), 6.46 (t, 1H), 6.40 (d, 1H), 6.31 (d, 1H), 4.81 (br s, 1H), 3.54 (v br s, 1H), 3.30 (t, 2H), 3.15 (t, 2H), 2.26 (s, 6H), 2.21 (s, 3H).

***N*-*tert*-Butyl-d_6-*N*′-[2-(2,4,6-trimethylphenylamino)-ethyl]benzene-1,2-diamine (2e).** Methyllithium (200 mL, 0.32 mol) was transferred under nitrogen into a Schlenk flask equipped with a pressure-equalizing addition funnel. The funnel was capped with a septum, and into it was transferred a solution of 16.68 g (0.0527 mol) of **2d** in 125 mL of diethyl ether. The solution of methyllithium in the base of the flask was chilled to −78 °C, and the solution of **2d** added dropwise over 24 h. The reaction was then heated for 2 days, during which time any precipitate dissolved. The reaction was allowed to cool to room temperature, and the contents were poured over 150 mL of ice. The ether layer was separated and washed three times with 250 mL of distilled water. The solution was then dried over $MgSO_4$ and filtered through Celite and alumina to yield an amber solution that was dried in vacuo to give 13.37 g (76%) of a viscous amber oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.93 (app t, 2H), 6.85 (s, 2H), 6.70 (m, 2H), 4.60 (br s, 1H), 3.31 (app t, 2H), 3.21 (app t, 2H), 2.97 (br s, 2H), 2.29 (s, 6H), 2.25 (s, 3H), 1.28 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 143.47, 143.36, 133.40, 131.90, 130.36, 129.66, 122.93, 122.88, 117.66, 111.56, 52.31, 48.21, 45.14, 29.93, 20.78, 15.51. HRMS: calcd $[M + H]^+$ 332.2967, found $[M + H]^+$ 332.2970.

***N*-*tert*-Butyl-d_6-*N*′-phenyl-*N*′-[2-(2,4,6-trimethylphenylamino)ethyl]benzene-1,2-diamine ($H_2$2).** Compound H_2**2** was prepared through a $Pd_2(dba)_3$/XPHOS (XPHOS = dicyclohexyl-(2′,4′,6′-triisopropylbiphen-2-yl)phosphine) (1.1 mol %/4.2 mol %)-catalyzed *N*-aryl coupling between 4.253 g (0.0128 mol) of **2e** and 1.62 mL (0.0154 mol) of bromobenzene in the same manner as compounds **1c**, H_2**1**, and **2a**. After aqueous workup, the crude compound was purified by column chromatography on silica gel eluting with 5% ethyl acetate in hexanes. The purified product was dried in vacuo at 70 °C for several hours to give 2.582 g (50%) of an amber oil. ^{1}H NMR (500 MHz, C_6D_6): δ 7.09 (m, 4H), 6.98 (m, 2H), 6.76 (s, 2H) 6.74 (app t, 2H), 6.69 (t, 1H), 4.68 (s, 1H), 3.56 (t, 2H), 3.11 (q, 2H), 2.92 (br t, 1H), 2.15 (s, 3H), 2.11 (s, 6H), 1.11 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 148.54, 144.98, 143.26,

133.41, 131.56, 129.94, 129.64, 129.34, 129.26, 127.45, 118.24, 117.08, 114.43, 114.37, 51.82, 50.48, 46.17, 29.98, 20.75, 18.51. HRMS: calcd $[M + H]^+$ 408.3282, found $[M + H]^+$ 408.3264.

[1]Zr(NMe$_2$)$_2$ (3a). To a cold solution (−25 °C) of 1.386 g (2.98 mmol) of **1** in 8 mL of pentane was added dropwise a cold solution of 0.810 g of $Zr(NMe_2)_4$ in 8 mL of pentane. A slight darkening of the solution occurred upon addition of the $Zr(NMe_2)_4$. The reaction was stirred for 15 min, then allowed to stand at RT for 24 h. The reaction solution was concentrated until a precipitate formed. The precipitate was collected by filtration and washed with pentane, yielding 1.440 g (76%) of **3a** as an off-white crystalline solid. ^{1}H NMR (500 MHz, C_6D_6): δ 7.07 (app d, 3H), 7.00 (app t, 3H), 6.94 (s, 1H), 6.90 (s, 1H), 6.85 (app t, 2H), 6.54 (d, 1H), 6.44 (t, 1H), 6.20 (d, 1H), 4.30 (t, 1H), 3.70 (td, 1H), 3.62 (app d, 1H), 3.02 (dd, 1H), 2.48 (s, 9H), 2.38 (s, 3H), 2.37 (s, 3H), 2.34 (s, 3H), 2.24 (s, 9H), 2.17 (s, 3H). Anal. Calcd for $C_{36}H_{47}N_5Zr$: C, 67.45; H, 7.39; N, 10.93. Found: C, 67.32; H, 7.28; N, 11.06.

[1]ZrCl$_2$ (3b). TMSCl (0.22 mL, 1.73 mmol) was added dropwise to a cold (−25 °C) solution of 0.552 g (0.861 mmol) of **3a** in 10 mL of toluene. The reaction was allowed to stir at RT for 24 h. All volatiles were removed in vacuo, leaving 0.400 g (75%) of **3b** as a white powder. ^{1}H NMR (500 MHz, C_6D_6): δ 7.28 (d, 2H), 7.05 (app t, 3H), 6.92 (t, 1H), 6.89 (s, 1H), 6.85 (s, 1H), 6.81 (t, 1H), 6.66 (s, 1H), 6.48 (t/d, 2H), 6.05 (d, 1H), 3.90 (td, 1H), 3.62 (td, 1H), 3.47 (dd, 1H), 3.37 (dd, 1H), 2.57 (s, 3H), 2.48 (s, 3H), 2.45 (s, 3H), 2.19 (s, 3H), 2.04 (s, 3H), 2.02 (s, 3H). Anal. Calcd for $C_{32}H_{35}Cl_2N_3Zr$: C, 61.62; H, 5.66; Cl, 11.37; N, 6.74. Found: C, 61.54; H, 5.73; Cl, 11.43; N, 6.79.

[1]ZrMe$_2$ (3c). A solution of 0.29 mL (0.87 mmol) of MeMgBr (3.0 M in Et_2O) was added dropwise to a cold (−25 °C) suspension of 0.256 g (0.410 mmol) of **3b** in 10 mL of diethyl ether. The reaction was allowed to warm to RT and stir for 1 h, during which time the contents of the reaction went into solution and a small amount of precipitate formed. 1,4-Dioxane (0.1 mL, 1.17 mmol) was added to the reaction to precipitate the magnesium salts. The reaction was filtered through Celite, and the volatiles were removed in vacuo to give 0.225 g (90%) of **3c** as a white powder. Crystals suitable for X-ray diffraction were grown from a concentrated ether/pentane solution. ^{1}H NMR (500 MHz, C_6D_6): δ 7.25 (d, 2H), 7.05 (s, 1H), 7.04 (s, 1H), 7.01 (t, 2H), 6.91 (s, 1H), 6.87 (m, 2H), 6.80 (s, 1H), 6.67 (d, 1H), 6.46 (t, 1H), 6.15 (d, 1H), 3.78 (td, 1H), 3.53 (dd, 1H), 3.36 (m, 2H), 2.61 (s, 3H), 2.42 (s, 3H), 2.37 (s, 3H), 2.25 (s, 3H), 2.11 (s, 3H), 1.77 (s, 3H), 0.41 (s, 3H), 0.40 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6): δ 153.48, 145.74, 143.86, 143.31, 141.79, 136.81, 136.48, 136.08, 135.76, 135.54, 135.11, 131.06, 130.74, 130.55, 130.26, 130.10, 129.82, 126.98, 125.23, 120.98, 117.71, 113.72, 57.54, 54.72, 49.23, 43.94, 21.49, 21.33, 19.75, 19.53, 18.65, 17.84. Anal. Calcd for $C_{34}H_{41}N_3Zr$: C, 70.05; H, 7.09; N, 7.21. Found: C, 69.87; H, 6.96; N, 7.12.

[1]Hf(NMe$_2$)$_2$ (4a). Compound **4a** was prepared in fashion that was strictly analogous to the synthesis of **3a** starting from 2.67 g (5.75 mmol) of H$_2$**1** and 2.044 g (5.76 mmol) of $Hf(NMe_2)_4$. Compound **4a** was isolated as 3.714 g (89%) of white cubes. ^{1}H NMR (500 MHz, C_6D_6): δ 7.03 (m, 5H), 6.95 (s, 1H), 6.92 (s, 1H), 6.85 (m, 3H), 6.51 (d, 1H), 6.42 (t, 1H), 6.20 (d, 1H), 4.29 (td, 1H), 3.64 (m, 2H), 3.12 (dd, 1H), 2.50 (s, 9H), 2.42 (s, 3H), 2.38 (s, 3H), 2.36 (s, 3H), 2.29 (s, 6H), 2.25 (s, 3H), 2.19 (s, 3H). Anal. Calcd for $C_{36}H_{47}N_5Hf$: C, 59.37; H, 6.50; N, 9.62. Found: C, 59.46; H, 6.38; N, 9.55.

[1]HfCl$_2$ (4b). Compound **4b** was prepared in fashion similar to the synthesis of **3b** by treating **4a** (3.710 g, 5.095 mmol) with 2 equiv of TMSCl. The reaction required additional heating at 45 °C for 3.5 days to go to completion (84% isolated yield). ^{1}H NMR (500 MHz, C_6D_6): δ 7.25 (d, 2H), 7.03 (app t, 3H), 6.91 (app t, 2H), 6.87 (s, 1H), 6.81 (t, 1H), 6.68 (s, 1H), 6.45 (t, 1H), 6.40 (d, 1H), 6.07 (d, 1H), 4.08 (m, 1H), 3.57 (m, 1H), 3.42 (dd, 1H), 2.56 (s, 3H), 2.50 (s, 3H), 2.48 (s, 3H), 2.20 (s, 3H), 2.13 (s, 3H), 2.06 (s, 3H). Anal. Calcd for $C_{32}H_{35}Cl_2N_3Hf$: C, 54.05; H, 4.96; Cl, 9.97; N, 5.91. Found: C, 54.11; H, 5.06; Cl, 9.93; N, 5.88.

[1]HfMe$_2$ (4c). Compound **4c** was prepared in a fashion analogous to the synthesis of **3c** from **4b** (0.8135 g, 1.144 mmol) and 2 equiv of MeMgBr. The crude product was formed in 90% yield and could be recrystallized from toluene/ether. ^{1}H NMR (500 MHz, C_6D_6): δ 7.23 (d, 2H), 7.02 (m. 4H), 6.91 (s, 1H), 6.87 (app t, 2H), 6.81 (s, 1H), 6.61 (d, 1H), 6.45 (t, 1H), 6.15 (d, 1H), 3.96 (td, 1H), 3.45 (m, 2H), 3.35 (m, 1H), 2.59 (s, 3H), 2.42 (s, 3H), 2.39 (s, 3H), 2.24 (s, 3H), 2.12 (s, 3H), 1.91 (s, 3H), 0.22 (s, 3H), 0.11 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6): δ 154.16, 145.80, 144.43, 143.43, 141.76, 136.75, 136.51, 136.21, 135.86, 135.47, 134.80, 131.03, 130.74, 130.57, 130.11, 129.93, 129.90, 126.69, 125.45, 121.41, 117.96, 114.53, 58.83, 58.19, 56.61, 55.36, 21.48, 21.32, 19.50, 19.47, 18.69, 17.89. Anal. Calcd for $C_{34}H_{41}N_3Hf$: C, 60.93; H, 6.17; N, 6.27. Found: C, 61.08; H, 6.12; N, 6.23.

[2]Zr(NMe$_2$)$_2$ (5a). To a cold (−25 °C) solution of 2.50 g (6.13 mmol) of H$_2$**2** in 50 mL of pentane was added dropwise a cold solution of 1.653 g (6.179 mmol) of $Zr(NMe_2)_4$ in 20 mL of pentane. The amber solution was allowed to warm to room temperature and stir for 15 h. The solution was then concentrated to ∼10 mL and set aside at −25 °C for several hours, during which time white crystals formed. The mother liquor was concentrated further and chilled to −25 °C, yielding a second crop of crystals. The crystals were collected by filtration, washed with cold pentane, and dried in vacuo, giving 2.245 g (63%) of **5a**. The crude residue also could be dissolved in toluene and used directly in the proceeding step without isolation of crystalline **5a**. ^{1}H NMR (500 MHz, C_6D_6): δ 7.15 (t, 1H), 7.10 (d, 1H), 7.04 (m, 4H), 6.97 (s, 1H), 6.83 (m, 1H), 6.79 (s, 1H), 6.73 (d, 1H), 6.58 (t, 1H), 4.03 (td, 1H), 3.39 (td, 1H), 3.20 (dd, 1H), 2.74 (dd, 1H), 2.71 (s, 6H), 2.61 (br s, 6H), 2.50 (s, 3H), 2.18 (s, 3H), 1.74 (s, 3H), 1.48 (s, 3H).

[2]ZrCl$_2$ (5b). To a cold (−25 °C) solution of 2.245 g (3.84 mmol) of **5a** in toluene was added 0.97 mL (7.6 mmol) of TMSCl. The reaction was allowed to stir at room temperature for 3 days. All volatiles were removed in vacuo, and the residue was treated with pentane, giving 1.927 g (88%) of **5b** as a pale yellow crystalline powder. ^{1}H NMR (500 MHz, C_6D_6): δ 7.04 (m, 5H), 6.92 (d, 1H), 6.88 (s, 1H), 6.87 (t, 1H), 6.73 (s, 1H), 6.66 (t, 1H), 6.60 (d, 1H), 4.35 (td, 1H), 3.30 (td, 1H), 3.06 (dd, 1H), 2.67 (dd, 1H), 2.62 (s, 3H), 2.11 (s, 3H), 1.78 (s, 3H), 1.41 (s, 3H). Anal. Calcd for $C_{27}H_{27}D_6Cl_2N_3Zr$: C, 57.12; H, 6.92; Cl, 12.49; N, 7.40. Found: C, 57.22; H, 7.08; Cl, 12.37; N, 7.34.

[2]ZrMe$_2$ (5c). Compound **5b** (1.010 g, 1.779 mmol) was suspended in 45 mL of diethyl ether and cooled to −25 °C. A 1.10 mL (3.60 mmol) quantity of chilled MeMgBr was added and the mixture allowed to stir at room temperature for 20 min. The ether was removed in vacuo, and the residue was extracted into 70 mL of pentane and filtered through Celite. The pentane was removed in vacuo, leaving 0.778 g (83% yield) of **5c** as an off-white crystalline powder. Crystals suitable for X-ray diffraction were grown from a concentrated pentane solution at −25 °C. ^{1}H NMR (500 MHz, C_6D_6): δ 7.13 (t, 1H), 7.02 (m, 4H), 6.89 (d, 2H), 6.82 (m, 2H), 6.77 (s, 1H), 6.66 (t, 1H), 3.83 (td, 1H), 3.53 (td, 1H), 3.19 (dd, 1H), 2.88 (dd, 1H), 2.73 (s, 3H), 2.15 (s, 3H), 1.81 (s, 3H), 1.42 (s, 3H), 0.58 (s, 3H), 0.29 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6): δ 149.60, 148.42, 148.07, 135.16, 134.96, 134.29, 132.11, 130.35, 130.02, 129.19, 125.22, 123.27, 121.86, 120.02, 118.44, 55.67, 55.52, 54.48, 45.57, 42.90, 31.01, 21.36, 19.60, 18.13. Anal. Calcd for $C_{29}H_{33}D_6N_3Zr$: C, 66.11; H, 8.61; N, 7.97. Found: C, 66.15; H, 8.48; N, 8.06.

[2]Hf(NMe$_2$)$_2$ (6a). To a cold (−25 °C) solution of 1.51 g (3.70 mmol) of **2** in 15 mL of toluene was added 1.317 g (3.712 mmol) of $Hf(NMe_2)_4$ in 15 mL of toluene. The resulting amber solution was heated at 70 °C for 20 h. The toluene was removed in vacuo, the resulting residue was dissolved in ∼5 mL of pentane, and the solution was set aside at −25 °C for several hours. During this time, white crystalline blocks formed in the

solution. The crystals were collected by filtration and dried in vacuo, giving 1.629 g (65%) of **6a**. ^{1}H NMR (500 MHz, C_6D_6): δ 7.14 (m, 2H), 7.04 (m, 4H), 6.99 (s, 1H), 6.84 (m, 1H), 6.80 (s, 1H), 6.70 (d, 1H), 6.58 (t, 1H), 3.99 (td, 1H), 3.38 (td, 1H), 3.18 (dd, 1H), 2.89 (dd, 1H), 2.75 (s, 6H), 2.66 (br s, 6H), 2.52 (s, 3H), 2.19 (s, 3H), 1.74 (s, 3H), 1.49 (s, 3H). Anal. Calcd for $C_{31}H_{39}D_6N_5Hf$: C, 55.39; H, 7.65; N, 10.42. Found: C, 55.46; H, 7.61; N, 10.47.

[2]HfCl$_2$ (6b). Compound **6b** was prepared in an analogous fashion to **5b** starting from 0.512 g (0.762 mmol) of **6a** and 0.21 mL (1.7 mmol) of TMSCl. The reaction required heating at 100 °C for 2.5 days to go to completion. The toluene was removed in vacuo and the residue treated with pentane to give 0.324 g (65%) of **6b** as a white crystalline powder that could be recrystallized from ether. ^{1}H NMR (500 MHz, C_6D_6): δ 7.09 (t, 1H), 7.00 (m, 4H), 6.97 (d, 1H), 6.91 (s, 1H), 6.86 (m, 1H), 6.76 (s, 1H), 6.63 (t, 1H), 6.54 (d, 1H), 4.31 (td, 1H), 3.31 (td, 1H), 3.06 (dd, 1H), 2.83 (dd, 1H), 2.62 (s, 3H), 2.13 (s, 3H), 1.82 (s, 3H), 1.44 (s, 3H). Anal. Calcd for $C_{27}H_{27}D_6Cl_2N_3Hf$: C, 49.51; H, 6.00; Cl, 10.83; N, 6.42. Found: C, 49.62; H, 5.91; Cl, 10.87; N, 6.49.

[2]HfMe$_2$ (6c). Compound **6c** was prepared in an analogous fashion to **5c** starting from 0.210 g (0.320 mmol) of **6b** and 0.20 mL (0.65 mmol) of MeMgBr. After stirring the reaction at room temperature for 30 min, the ether was removed in vacuo, the resulting residue was extracted into ~10 mL of toluene, and the toluene solution was filtered through Celite. The toluene was removed in vacuo from the filtrate, and the residue was dissolved in 1−2 mL of pentane. The pentane solution was set aside at −25 °C for several days, during which time off-white crystals formed in solution. The material was isolated and dried in vacuo, giving 0.173 g (88%) of **6c**. ^{1}H NMR (500 MHz, C_6D_6): δ 7.14 (t, 1H), 7.00 (m, 4H), 6.90 (app d, 2H), 6.83 (t, 1H), 6.77 (s, 1H), 6.74 (d, 1H), 6.65 (t, 1H), 3.96 (td, 1H), 3.44 (td, 1H), 3.14 (dd, 1H), 3.00 (dd, 1H), 2.69 (s, 3H), 2.16 (s, 3H), 1.81 (s, 3H), 1.45 (s, 3H), 0.33 (s, 3H), 0.10 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6): δ 149.45, 148.65, 148.43, 135.28, 135.25, 134.17, 132.24, 130.20, 130.08, 129.18, 128.98, 124.88, 123.62, 121.50, 120.48, 118.60, 56.39, 55.32, 54.44, 54.22, 53.90, 30.93, 30.4 (m, CD_3), 21.34, 19.48, 17.96. Anal. Calcd for $C_{29}H_{33}D_6N_3Hf$: C, 56.71; H, 7.38; N, 6.84. Found: C, 56.85; H, 7.32; N, 6.87.

Compound **6c** also was prepared using $^{13}CH_3MgI$ in ether. ^{13}C{^{1}H} NMR (125 MHz, C_6D_5Br): δ 58.93 ppm (J_{CH} = 111 Hz, J_{CC} = 2.9 Hz), 57.17 ppm (J_{CH} = 112 Hz, J_{CC} = 2.9 Hz).

Observation of Cationic Initiators by ^{1}H NMR. Equivalent amounts of the dimethyl precatalyst (**3c**, **4c**, **5c**, or **6c**) and trityl tetrakis(pentafluorophenyl)borate were weighed out and dissolved in an equal amount of bromobenzene-d_5 (in the case of dimers **5e** and **6e**, half an equivalent of $[Ph_3C][B(C_6F_5)_4]$ was used). The two solutions were chilled to −25 °C in the glovebox freezer. The solutions were then mixed, producing an orange-yellow solution, which was immediately transferred to a J-Young tube and frozen in liquid nitrogen. The tube was transported to the NMR spectrometer, warmed until the solvent melted, and placed in the precooled spectrometer. The spectrum was then recorded, giving the following spectra.

{**[1]ZrMe**}{**B(C$_6$F$_5$)$_4$**} **(3d):** (500 MHz, −10 °C) δ 7.26 (m, 2H), 7.20 (t, 1H), 7.16−6.99 (solvent, *Ph*$_3$CMe, and Lig), 6.95 (t, 1H), 6.90 (s, 1H), 6.88 (s, 1H), 6.80 (d, 1H), 6.66 (t, 1H), 6.62 (br s, 1H), 6.52 (br s, 1H), 5.76 (d, 1H), 4.04 (dd, 1H), 3.78 (m, 1H), 3.69 (m, 1H), 3.62 (m, 1H), 2.23 (s, 3H), 2.10 (s, 3H), 2.04 (Ph$_3$C*Me*, 3H), 2.01 (s, 3H), 2.00 (s, 3H), 1.92 (br s, 3H), 1.40 (br s, 3H), −0.05 (s, 3H).

{**[1]HfMe**}{**B(C$_6$F$_5$)$_4$**} **(4d):** (500 MHz, 0 °C) δ 7.27 (m, 4H), 7.21 (t, 1H), 7.17−7.02 (*Ph*$_3$CMe and Lig), 7.01 (br s, 1H), 6.97 (t, 1H), 6.90 (br s, 1H), 6.65 (m, 3H), 5.81 (d, 1H), 4.03 (m, 2H), 3.91 (m, 1H), 3.74 (m, 1H), 2.25 (s, 3H), 2.12 (s, 3H), 2.08 (app d, Ph$_3$C*Me* and Lig, 6H), 2.02 (br s, 3H), 1.57 (br s, 3H), −0.14 (s, 3H).

{**[2]ZrMe**}{**B(C$_6$F$_5$)$_4$**} **(5d):** (500 MHz, −10 °C) δ 7.28 (m, 2H), 7.24 (d, 1H), 7.22−7.03, (solvent, *Ph*$_3$CMe and Lig), 6.95 (d, 1H), 6.66 (d, 1H), 3.86 (dd, 1H), 3.62 (td, 1H), 3.50 (td, 1H), 2.76 (dd, 1H), 2.2 (v br s, 3H), 2.08 (s, 3H), 2.02 (Ph$_3$C*Me*, 3H), 1.3 (v br s, 3H), 0.90 (s, 3H), 0.60 (s, 3H).

{**([2]Zr)$_2$$\mu$-Me$_3$**}{**B(C$_6F_5$)$_4$**} **(5e):** (500 MHz, 0 °C) δ 7.27 (m, 4H), 7.16−6.90 (solvent, *Ph*$_3$CMe and Lig), 6.89 (s, 2H), 6.80 (d, 2H), 6.67 (d, 4H), 6.53 (s, 2H), 3.83 (m, 2H), 3.35 (dd, 2H), 3.24 (td, 2H), 2.76 (dd, 2H), 2.50 (s, 6H), 2.09 (s, 6H), 2.02 (Ph$_3$C*Me*, 3H), 1.11 (s, 6H), 0.90 (s, 3H), 0.27 (s, 6H), 0.01 (s, 3H).

{**[2]Hf)Me**}{**B(C$_6$F$_5$)$_4$**} **(6d):** (500 MHz, 0 °C) δ 7.36 (t, 1H), 7.28 (m, 2H), 7.16−6.94, (solvent, *Ph*$_3$CMe and Lig), 6.75 (d, 2H), 6.59 (br s, 2H), 3.99 (td, 1H), 3.68 (dd, 1H), 3.15 (td, 1H), 2.96 (dd, 1H), 2.18 (v br s, 3H), 2.08 (s, 3H), 2.02 (Ph$_3$C*Me*, 3H), 1.16 (v br s, 3H), 0.93 (s, 3H), 0.68 (s, 3H).

A ^{13}C-labeled version of **6d** also was prepared from ^{13}C-labeled **6e**. ^{13}C{^{1}H} NMR (125 MHz, C_6D_5Br): δ 66.27 (J_{CH} =113.4 Hz).

{**([2]Hf)$_2$$\mu$-Me$_3$**}{**B(C$_6F_5$)$_4$**} **(6e):** (500 MHz, 0 °C) δ 7.30 (m, 4H), 7.16−6.92 (solvent, *Ph*$_3$CMe and Lig), 6.91 (s, 2H), 6.84 (d, 2H), 6.70 (d, 4H), 6.52 (s, 2H), 3.89 (td, 2H), 3.38 (dd, 2H), 3.14 (td, 2H), 2.85 (dd, 2H), 2.47 (s, 6H), 2.09 (s, 6H), 2.02 (Ph$_3$C*Me*, 3H), 1.13 (s, 6H), 0.86 (s, 6H), 0.13 (s, 3H), 0.06 (s, 6H).

A ^{13}C-labeled version of **6e** also was prepared from ^{13}C-labeled **6c**. ^{13}C{^{1}H} NMR (125 MHz, C_6D_5Br): δ 64.78 (two methyl groups, J_{CH} =113.6 Hz), 50.20 ppm (bridging methyl group, J_{CH} = 132.6 Hz).

General Procedure for Polymerization Experiments. In a general experiment, equivalent amounts of the dimethyl precatalyst (**3c**, **4c**, or **5c**) and trityl tetrakis(pentafluorophenyl)borate were weighed out and dissolved in an equal amount of bromobenzene. The solutions were cooled to −25 °C, as was the 1-hexene. The cold bromobenzene solutions were mixed thoroughly and transferred to a sealable reaction vessel equipped with a stir bar. The 1-hexene was immediately added in one bulk sum, and the contents were either allowed to react at −25 °C or warmed to 0 °C. Reaction times were 20 min for **3d** and **4d** and 6 h for **5d**. The reaction was quenched with MeOH/HCl (95/5 v/v). The volatiles were removed in vacuo, and the polymer was extracted into pentane. The pentane solution was passed through a plug of silica gel, and pentane was removed in vacuo at 60 °C over a period of several hours, leaving a colorless gel, which was identified as atactic poly-[1-hexene] by ^{13}C NMR.[37]

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Supporting Information Available: Experimental details, labeled thermal ellipsoid drawings, crystal data and structure refinement, atomic coordinates, bond lengths and angles, and anisotropic displacement parameters for **3c**, **5c**, and **1d**. This material is available free of charge via the Internet at http://pubs.acs.org.

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