Zirconium Complexes That Contain a Diamido O-Donor Ligand with a Restricted Geometry

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Addition of LiNH(2,6-$Me_2C_6H_3$) (LiNHAr′) to *cis*-2,5-bis((tosyloxy)methyl)tetrahydrofuran gave *cis*-2,5-(Ar′$NHCH_2)_2(C_4H_6O)$ (H_2[**1**]). The reaction between $Zr(NMe_2)_4$ and H_2[**1**] yielded [**1**]$Zr(NMe_2)_2$, from which [**1**]$ZrCl_2$ and [**1**]$ZrMe_2$ were prepared readily. An unsymmetric relative of H_2[**1**], *cis*-2,5-(Ar′$NHCH_2$)(Ar$NHCH_2)(C_4H_6O)$ (H_2[**2**]; Ar = 2,6-*i*-$Pr_2C_6H_3$), was also prepared via the imine of 5-(hydroxymethyl)furaldehyde. Cations of the type {[**1**]ZrMe-$(PhNMe_2)$}$[B(C_6F_5)_4]$ and {[**2**]ZrMe$(PhNMe_2)$}$[B(C_6F_5)_4]$, prepared in the reaction between the dimethyl species and $[PhNHMe_2][B(C_6F_5)_4]$, could be observed and were stable toward exchange of free and coordinated dimethylaniline on the NMR time scale, while cations prepared in the reaction between the dimethyl species and $[Ph_3C][B(C_6F_5)_4]$ did not have interpretable NMR spectra and appeared to be relatively unstable. Nevertheless, poly(1-hexene) that had a molecular weight approximately equal to the amount employed (up to 500 equiv) could be prepared by employing the latter at 0 °C in chlorobenzene.

Introduction

We recently reported the synthesis of zirconium dialkyl complexes that contain a variety of diamido/O-donor ligands such as $[(RN\text{-}o\text{-}C_6H_4)_2O]^{2-}$ (R = *t*-Bu,[1,2] *i*-Pr,[3] cyclohexyl[3]), $[(t\text{-}Bu\text{-}d_6\text{-}N\text{-}o\text{-}C_6H_4)_2S]^{2-}$,[4] [(Aryl-$NCH_2CH_2)_2O]^{2-}$,[5] $[(ArylNCH_2CH_2)_2S]^{2-}$,[5] [(ArylNSi-$Me_2CH_2)_2PPh]^{2-}$,[6] and $[(ArylNCH_2CH_2)_2NR]^{2-}$ (R = H, Me).[7] Zirconium dimethyl complexes activated with $[PhNMe_2H][B(C_6F_5)_4]$ or $[Ph_3C][B(C_6F_5)_4]$ behave as catalysts for the living polymerization of 1-hexene (at 0 °C) in the case of $[(t\text{-}Bu\text{-}d_6\text{-}N\text{-}o\text{-}C_6H_4)_2O]ZrMe_2$, but activated $[(i\text{-}PrN\text{-}o\text{-}C_6H_4)_2O]ZrMe_2$ only oligomerized 1-hexene, while activated $[(t\text{-}Bu\text{-}d_6\text{-}N\text{-}o\text{-}C_6H_4)_2S]ZrMe_2$ showed little sustained activity toward oligomerization or polymerization of 1-hexene. We have postulated that an important feature of the successful living polymerization using activated $[(t\text{-}Bu\text{-}d_6\text{-}N\text{-}o\text{-}C_6H_4)_2O]ZrMe_2$ is the stabilization of crowded tetrahedral cationic intermediates in which the olefin inserts into the metal−carbon bond virtually exclusively in a 1,2-manner to give intermediates in which β-elimination is slow.[2] β-Elimination is inherently slower in diamido complexes, but the crowded pseudotetrahedral coordination geometry also restricts the β-proton's accessibility by the metal. To encourage the formation of tetrahedral cationic zirconium alkyls, we have begun to explore diamido/O-donor ligands in which the donor cannot invert configuration when bound to zirconium, namely N[7] or P.[6] We report here an alternative method of encouraging the formation of tetrahedral cationic zirconium alkyls, by tying the two "arms" that contain the amido donors together, i.e., by building a *cis*-2,5-bis(amidomethyl)-tetrahydrofuran ligand. One additional interesting feature of *cis*-2,5-bis(amidomethyl)tetrahydrofuran ligands, a consequence of the preparative method that employs 5-(hydroxymethyl)furaldehyde as a starting material, is the possibility of preparing unsymmetrically substituted versions, which would form racemic chiral metal complexes with no meso form. In this paper we report the synthesis and characterization of zirconium dimethyl complexes that contain such ligands, along with the results for the polymerization of 1-hexene. These results are compared with those obtained for catalysts that contain the related $[(ArylNCH_2CH_2)_2O]^{2-}$ ligand.

Results and Discussion

Synthesis of Ligands. The starting material of choice for the synthesis of *cis*-2,5-bis(amidomethyl)-tetrahydrofuran ligands is 5-(hydroxymethyl)furaldehyde. The most convenient route that we have found so far to 5-(hydroxymethyl)furaldehyde is the reaction between D-fructose and pyridinium hydrochloride in the solid state at 130 °C.[8] 5-(Hydroxymethyl)furaldehyde is readily extracted from the crude reaction mixture with ethyl acetate and can be isolated in a reproducible yield of ∼50% on a multigram scale. Typically D-fructose (98

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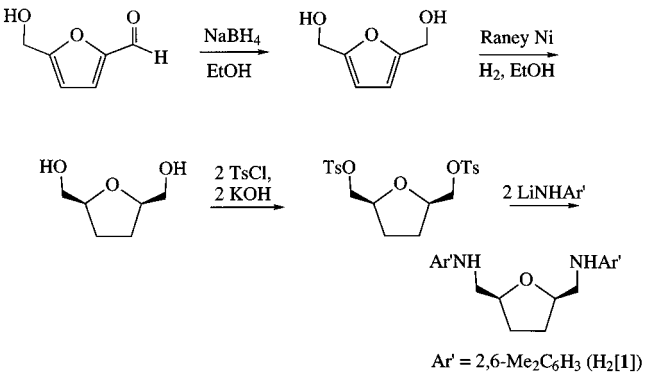
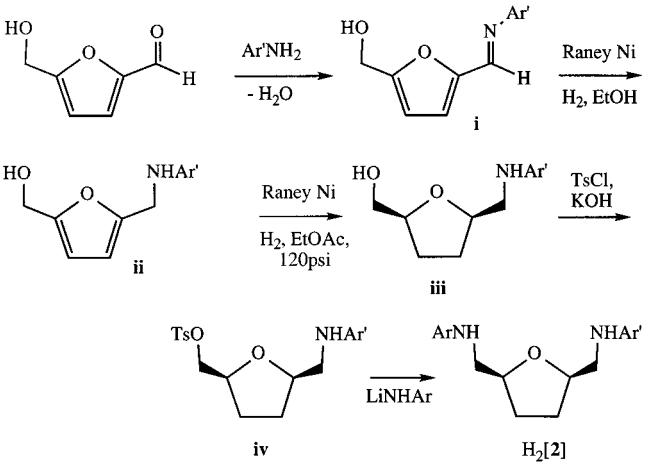
Scheme 1



Scheme 2



g) and pyridinium hydrochloride (63 g) gave ~36 g of 5-(hydroxymethyl)furaldehyde that was sufficiently pure to be reduced directly to 2,5-bis(hydroxymethyl)furan with sodium borohydride.[9] Subsequent hydrogenation yielded *cis*-2,5-bis(hydroxymethyl)tetrahydrofuran[10] (Scheme 1). The ditosylate was prepared straightforwardly and treated with LiNH(2,6-$Me_2C_6H_3$) to yield diamine H_2[**1**] (Scheme 1). Compound H_2[**1**] is a relative of H_2[(Ar′$NHCH_2CH_2)_2O$], in which the two "arms" are not connected.[5]

An unsymmetrically substituted analogue of H_2[**1**] can be prepared as shown in Scheme 2. The reaction of 5-(hydroxymethyl)furaldehyde with 2,6-dimethylaniline in benzene using a Dean−Stark trap afforded the imine (**i**, Scheme 2) as an orange oil in ~95% yield, according to ^{1}H NMR spectroscopy of the crude product. Since the imine decomposes slowly even when stored under dinitrogen in the dark, it was immediately hydrogenated with Raney nickel in ethanol (P = 40 psi, T = 25 °C) to afford amine **ii** in 58% isolated yield. The actual yield of the reaction is ~95%, according to the ^{1}H NMR spectra of the reaction mixture. No further hydrogenation of the ring in **ii** is observed in ethanol at 40 psi and 25 °C, and hydrogenation of **i** to **ii** has not been successful in ethyl acetate.

We found that **ii** could be hydrogenated to **iii**, although the reaction is sensitive to conditions. Using Raney nickel in ethyl acetate the optimum conditions were found to be a pressure of 120 psi and a relatively high catalyst loading (9.3 g per 6.5 g of substrate in 140 mL of ethyl acetate). Under these conditions a 97% yield of **iii** was realized. If relatively high substrate to catalyst ratios are employed in ethanol as a solvent, then reduction is inhibited. (Crude **ii** could not be reduced directly with Raney Ni in ethyl acetate, perhaps as a consequence of inhibition by residual ethanol.) If the ratio of substrate to catalyst is too low, then hydrogenolysis of the carbon−nitrogen bond becomes a significant side reaction. (Use of 10% palladium on carbon as the catalyst led to primarily hydrogenolysis.) Unfortunately, we have not found conditions yet that would allow hydrogenation of **i** directly to **iii** in ethyl acetate. Reduction of crude **i** directly to **iii** in high yield would facilitate construction of an unsymmetrically substituted ligand to a significant degree.

Tosylation of **iii** to yield **iv** was straightforward, as was treatment of **iv** with the lithium salt of 2,6-isopropylaniline to give the unsymmetrically substituted diamine H_2[**2**].

Proton and carbon NMR spectra of H_2[**1**] and H_2[**2**] are those expected for molecules in which the aryl rings are rotating rapidly on the NMR time scale about the N−C_{ipso} bond and which have (in the case of H_2[**1**]) or do not have (in the case of H_2[**2**]) a plane of symmetry.

Synthesis of Zirconium Complexes. Reactions between $Zr(NMe_4)_4$ and H_2[**1**] or H_2[**2**] in pentane at room temperature produced [**1**]$Zr(NMe_2)_2$ and [**2**]$Zr(NMe_2)_2$ in virtually quantitative yield. Whereas [**1**]$Zr(NMe_2)_2$ could be recrystallized readily, [**2**]$Zr(NMe_2)_2$ was very soluble in common solvents and was not purified further. The [**1/2**]$Zr(NMe_2)_2$ complexes react with an excess of Me_3SiCl in toluene at room temperature to form relatively insoluble [**1/2**]$ZrCl_2$ complexes. (The [**1/2**]$^{2-}$ notation refers to either [**1**]$^{2-}$ or [**2**]$^{2-}$.) Alkylation of [**1/2**]$ZrCl_2$ by MeMgBr afforded the corresponding dimethyl complexes, [**1/2**]$ZrMe_2$ (eqs 1−3).

$$H_2[\mathbf{1/2}] + Zr(NMe_2)_4 \rightarrow [\mathbf{1/2}]Zr(NMe_2)_2 + 2Me_2NH \quad (1)$$

$$[\mathbf{1/2}]Zr(NMe_2)_2 + 2Me_3SiCl \rightarrow [\mathbf{1/2}]ZrCl_2 + 2Me_3SiNMe_2 \quad (2)$$

$$[\mathbf{1/2}]ZrCl_2 + 2MeMgBr \rightarrow [\mathbf{1/2}]ZrMe_2 + 2MgBrCl \quad (3)$$

$$ZrCl_4 + H_2[\mathbf{1}] \rightarrow \text{"}ZrCl_4\{H_2[\mathbf{1}]\}\text{"} \xrightarrow{4MeMgBr} [\mathbf{1}]ZrMe_2 \quad (4)$$

It is interesting to note that [**1**]$ZrMe_2$ also can be prepared using a "direct" route that involves the addition of H_2[**1**] with $ZrCl_4$ in diethyl ether followed by 4 equiv of MeMgBr. (This synthesis is analogous to that employed to prepare [(MesitylN$CH_2CH_2)_2$NH]$ZrMe_2$[7] and [(*i*-PrN-*o*-$C_6H_4)_2$O]$ZrMe_2$.[3]) The initial complex is believed to be an adduct, i.e., $ZrCl_4\{H_2$[**1**]$\}$, which is then doubly dehydrohalogenated and dialkylated. Although the yield of the product on a small scale in ether is only ~50%, we expect that conditions can be devised that will produce it on a larger scale, since the syntheses of [(MesitylN$CH_2CH_2)_2$NH]$ZrMe_2$ and [(*i*-PrN-*o*-$C_6H_4)_2$O]-$ZrMe_2$ by analogous procedures in toluene proceed in

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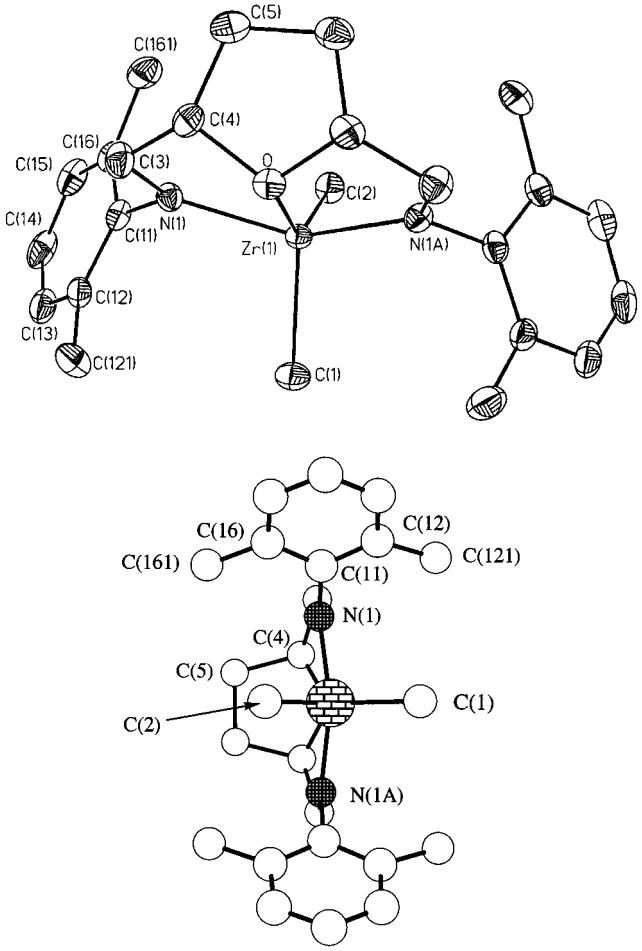

Figure 1. (a, top) ORTEP drawing of the structure of [**1**]-$ZrMe_2$. (b, bottom) Chem3D drawing of the structure of [**1**]-$ZrMe_2$.

high yield. Such "direct" procedures may become useful, "one-pot" syntheses for a variety of diamido/O-donor complexes.

Proton NMR spectra of [**1**]$Zr(NMe_2)_2$ and [**1**]$ZrMe_2$ at 22 °C show two different NMe_2 and ZrMe resonances, respectively, and a single broad resonance for the two *o*-methyl groups of the 2,6-$Me_2C_6H_3$ substituent. Sharp *o*-methyl resonances can be observed below 0 °C. At higher temperatures the *o*-methyl resonances coalesce to give a single resonance, but two NMe_2 and ZrMe resonances remain, as one would expect in view of the presence of the furan ring. (In [(*t*-BuN-*o*-$C_6H_4)_2O$]-$ZrMe_2$[1,2] and [(ArylN$CH_2CH_2)_2O$]$ZrMe_2$[5] separate ZrMe resonances cannot be resolved at low temperatures, while in [(*t*-Bu-d_6-N-*o*-$C_6H_4)_2S$]$ZrMe_2$[4] and [(ArylN-$CH_2CH_2)_2S$][2−5] the significantly higher barrier to inversion at sulfur allows separate ZrMe resonances to be observed at low temperatures.) The ^1H NMR spectrum of [**2**]$ZrMe_2$ displays two separate, relatively broad resonances belonging to two *o*-methyl Ar′ groups and four sharp doublets and two septets corresponding to two isopropyl groups in the Ar ring. These data are consistent with rotation of the Ar′ group around the N−C_{ipso} bond at a rate of the order of the NMR time scale near room temperature, slower rotation of the Ar′ group in a more sterically demanding environment in [**2**]$ZrMe_2$, and relatively slow rotation on the NMR time scale of the more sterically demanding Ar ligand in [**2**]$ZrMe_2$. Varying degrees of restricted rotation of 2,6-disubstituted aryl groups in diamido ligands is common in four- or five-coordinate group 4 dialkyl complexes.[4,11−17]

Table 1. Crystallographic Data, Collection Parameters, and Refinement Parameters for [1]$ZrMe_2$[a]

empirical formula	$C_{24}H_{34}N_2OZr$
fw	457.75
cryst dimens (mm)	0.22 × 0.22 × 0.10
cryst syst	orthorhombic
a (Å)	14.5727(10)
b (Å)	21.858(2)
c (Å)	7.1900(5)
α (deg)	90
β (deg)	90
γ (deg)	90
V (Å^3), *Z*	2290.3(3), 4
space group	*Pnma*
D_{calcd} (Mg/m^3)	1.328
μ (mm^{-1})	0.496
F_{000}	960
no. of rflns collected	8679
no. of indep rflns	1690
no. of data/restraints/params	16878/0/134
final *R* indices ($I > 2\sigma(I)$)	R1 = 0.0361, wR2 = 0.1014
R indices (all data)	R1 = 0.0486, wR2 = 0.1242
GOF on F^2	1.080

[a] Data were collected on a Siemens SMART/CCD diffractometer with λ(Mo Kα) = 0.710 73 Å using ω scans at 183(2) K and solved using a full-matrix least-squares refinement on F^2. No absorption correction was applied.

An X-ray study of [**1**]$ZrMe_2$ revealed it to have a structure in which the two amido nitrogens occupy positions approximately trans to one another (parts a and b of Figure 1, Tables 1 and 2). It is informative and important to compare the structure of [**1**]$ZrMe_2$ with the "*mer*" structure observed for [(Ar′N$CH_2CH_2)_2O$]$ZrMe_2$ (Table 2).[5] The O/Zr/C(1)/C(2) plane is a plane of symmetry in each. Bond lengths and angles in the two molecules are similar, with four notable differences. The first is that the C(4)−O−C(4A) bond angle in [**1**]$ZrMe_2$ is necessarily restricted as a consequence of the C_4O ring and, therefore, is significantly less (104.4(4)°) than it is in [(Ar′N$CH_2CH_2)_2O$]$ZrMe_2$ (113.7(4)°). The second is that the C(1)−Zr−O (118.7(2)°) and C(2)−Zr−O (139.7-(2)°) bond angles are significantly different, although the average is close to the analogous and approximately equal C−Zr−C angles in [(Ar′N$CH_2CH_2)_2O$]$ZrMe_2$. Finally, the external angle between the N−Zr−O planes is 180° in [(Ar′N$CH_2CH_2)_2O$]$ZrMe_2$, but only 167° in [**1**]-$ZrMe_2$. All of these data suggest that [**1**]$ZrMe_2$ is significantly distorted toward a square-pyramidal structure. In an approximate trigonal-bipyramidal structure in which the two amido nitrogens occupy equatorial positions and the two methyl groups are in axial and equatorial positions (the "*fac*" structure), the external angle between the N−Zr−O planes has been observed

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Table 2. Selected Bond Lengths (Å) and Angles (deg) in [1]$ZrMe_2$ and [(Ar′$NCH_2CH_2)_2O$]$ZrMe_2$

[**1**]$ZrMe_2$		[(Ar′$NCH_2CH_2)_2O$]$ZrMe_2$	
Zr−N1	2.083(3)	Zr−N1	2.084(3)
Zr−C1	2.259(5)	Zr−C1	2.255(6)
Zr−C2	2.246(6)	Zr−C2	2.253(6)
Zr−O	2.326(3)	Zr−O	2.336(3)
N1−Zr−N1A	137.9(2)	N1−Zr−N2	139.1(2)
N1−Zr−C1	105.09(9)	N1−Zr−C1	102.9(1)
N1−Zr−C2	100.95(9)	N1−Zr−C2	103.1(1)
N1−Zr−O	70.01(8)	N1−Zr−O	69.54(9)
C1−Zr−C2	101.6(2)	C1−Zr−C2	100.0(2)
C1−Zr−O	118.7(2)	C1−Zr−O	129.7(2)
C2−Zr−O	139.7(2)	C2−Zr−O	130.2(2)
C4−O−C4A	104.4(4)	C3−O−C4	113.7(4)
Zr−O−C4	115.4(2)	Zr−O−C4	114.9(2)
Zr−N1−C11	118.8(2)	Zr−N1−C	120.2(2)
N1−Zr−O/ N1A-Zr−O[a]	167	N1−Zr−O/ N2−Zr−O[a]	180

[a] The external angles between the planes, ideally 120° in a *fac* structure and 180° in a *mer* structure; obtained from a Chem 3D model.

to be 120−125°,[3] while in approximately square-pyramidal [(Ar$NCH_2CH_2)_2O$]$HfEt_2$ (Ar = 2,6-*i*-$Pr_2C_6H_3$)[5] the external angle between the N−Zr−O planes is 160°. According to the N1−Zr−O/N2−Zr−O angle of 167°, [**1**]-$ZrMe_2$ is only a few degrees away from a square pyramid with C(1) in the axial position. Therefore, it seems clear that restraining the two "arms" in the ligand with the C_4O ring leads to a significant distortion away from the ideal *mer* structure of a five-coordinate dialkyl species. We believe that a *fac* dialkyl structure is a good indicator that a weakly coordinating anion (e.g., [$B(C_6F_5)_4$]$^-$) will be readily displaced by an incoming olefin in a monoalkyl pseudotetrahedral cation/anion pair. On this basis we can conclude that the presence of the C_4O ring is likely to lead to a more significant distortion of the cation toward a pseudotetrahedral geometry than is the case in complexes that contain [(2,6-$R_2C_6H_3NCH_2$-$CH_2)_2O$]$^{2-}$ ligand systems.[5]

Generation of Cations. Addition of 1 equiv of [$PhNMe_2H$][$B(C_6F_5)_4$] in C_6D_5Br to [**1**]$ZrMe_2$ leads to protonolysis of one of the methyl groups and formation of a cationic complex that contains 1 equiv of dimethylaniline (eq 5). The reaction is relatively clean, according to proton NMR spectra at room temperature. The ^{1}H NMR spectrum of "{[**1**]ZrMe(NMe_2Ph)}[$B(C_6F_5)_4$]" shows a resonance corresponding to the Zr−Me group at 0.03 ppm and a resonance corresponding to the two equivalent methyl groups of bound dimethylaniline at 2.52 ppm. Two sharp singlets at 2.59 and 2.63 ppm are observed for the *o*-methyl groups in the Ar′ groups as a consequence of now slow rotation on the NMR time scale around the C_{ipso} bond in the more crowded coordination environment created by the possibly shorter metal−ligand bonds in the five-coordinate cation and by the bulk of the bound dimethylaniline. Proton NMR spectra of a mixture of {[**1**]ZrMe(NMe_2Ph)}[$B(C_6F_5)_4$] and 1 equiv of $PhNMe_2$, in which resonances for free and coordinated dimethylaniline are observed, are essentially unchanged at 80 °C, which suggests that exchange of coordinated and free dimethylaniline is slow on the NMR time scale at that temperature. {[**1**]ZrMe(NMe_2-Ph)}[$B(C_6F_5)_4$] appeared to be stable in C_6D_5Br for at least 4 h at room temperature, according to its ^{1}H NMR spectrum, but appeared to decompose slowly over the course of several days.

$$[\mathbf{1}]ZrMe_2 + [PhNMe_2H][B(C_6F_5)_4] \rightarrow \{[\mathbf{1/2}]ZrMe(NMe_2Ph)\}[B(C_6F_5)_4] + CH_4 \quad (5)$$

Table 3. Polymerization of 1-Hexene by [1]$ZrMe_2$ Activated with [Ph_3C][$B(C_6F_5)_4$] at 0 °C in Chlorobenzene

run no.	amt of 1-hexene, equiv	M_n(calcd)	M_n(found)	M_w/M_n
1	200	16 800	33 000	1.1
2	200	16 800	35 000	1.1
3	400	33 600	36 000	1.5
4	400	33 600	42 000	1.2
5	600	50 500	46 000	1.2
6	600	50 500	39 000	1.4

The ^{1}H NMR spectrum of {[**2**]ZrMe(NMe_2Ph)}[$B(C_6F_5)_4$] in C_6H_5Br exhibited two sharp resonances for the *o*-methyl groups in the 2,6-$Me_2C_6H_3$ substituents and four doublets and two septets for the isopropyl groups in the 2,6-*i*-$Pr_2C_6H_3$ substituents, consistent with the relatively slow rotation of each about the N−C_{ipso} bond. The presence of two methyl resonances for the bound dimethylaniline confirms the asymmetry of the metal center, although where specifically the dimethylaniline is bound to the metal cannot be determined. Whereas relatively sharp resonances are observed for the aromatic protons of $PhNMe_2$ in {[**1**]ZrMe(NMe_2Ph)}-[$B(C_6F_5)_4$], broader resonances are observed for the aromatic protons of $PhNMe_2$ in {[**2**]ZrMe(NMe_2Ph)}-[$B(C_6F_5)_4$], perhaps as a consequence of a more restricted rotation of the phenyl ring in bound dimethylaniline in the more crowded environment created by the 2,6-i-$Pr_2C_6H_3$ substituent in the [**2**]$^{2-}$ ligand system.

The use of [Ph_3C][$B(C_6F_5)_4$] as an activator led to apparently less stable cationic species. The $^{13}C\{^1H\}$ NMR spectrum of a freshly prepared solution of [**1**]Zr-($^{13}CH_3)_2$ and [Ph_3C][$B(C_6F_5)_4$] (1 equiv) in C_6D_5Br at room temperature showed a resonance characteristic of $PhC^{13}CH_3$, but no distinct resonance for a cationic $Zr^{13}CH_3$ species. A precipitate also was observed ∼15 min after the two reactants were mixed. Further studies will be required in order to elucidate the nature of the species that are generated under these conditions. Apparently they are relatively stable in chlorobenzene at 0 °C, according to preliminary polymerization studies described below.

1-Hexene Polymerization Studies. Preliminary NMR experiments revealed that 30 equiv of 1-hexene were completely consumed to form poly(1-hexene) within minutes by a freshly made solution of {[**2**]ZrMe(NMe_2-Ph)}[$B(C_6F_5)_4$] at 0 °C. However, resonances belonging to the starting cation were also observed, suggesting that only part of the catalyst is active, or that $k_p \gg k_i$.

To eliminate the complication involving dissociation of base, preparative-scale polymerizations were performed employing [**1**]$ZrMe_2$ activated with [Ph_3C]-[$B(C_6F_5)_4$] in chlorobenzene at 0 °C (Table 3). Analyses of polymers that had been purified by extraction into hot hexane and filtration through silica gel are reproducible, although the reproducibility of the analyses decreases with increasing amount of monomer. The molecular weights of the polymers seem to reach a

maximum of ~45 000. The relatively well-behaved polymerization activity of [**1**]$ZrMe_2$ activated with $[Ph_3C][B(C_6F_5)_4]$ for the polymerization of 1-hexene is somewhat surprising in view of the failure to observe a well-defined methyl resonance for the presumed {[**1**]ZrMe}$[B(C_6F_5)_4]$ initiator. More extensive experiments will needed in order to resolve this discrepancy and to explore further the polymerization activity of activated dialkyl complexes that contain the $[\mathbf{1}]^{2-}$ ligand.

Finally, polymerization of propylene in chlorobenzene at 0 °C using [**2**]$ZrMe_2$ activated with $[PhNHMe_2][B(C_6F_5)_4]$ gave atactic polypropylene according to $^{13}C\{^1H\}$ NMR spectroscopy.[18] Note that it has not been proven that the olefin approaches the N/N/C face of the four-coordinate cation, where the asymmetry is likely to be felt most strongly. Therefore, these results may indicate either that enantiomorphic site control at the N/N/C face in inefficient or that the olefin actually approaches one of the two C/N/O faces of the four-coordinate cation where enantiomorphic site control presumably would be less successful.

It is interesting to compare these results with those obtained with the analogous "unlinked" analogue $[(Ar'NCH_2CH_2)_2O]ZrMe_2$,[5] where the molecular weight of a polymer made from 200 equiv of 1-hexene is less than half that obtained employing [**1**]$ZrMe_2$ under analogous conditions (M_w(calcd) = 16 800, M_n(found) = 11 700, PDI = 1.6). Although more experiments are needed in order to elaborate upon these results, it appears that restricting the conformation of the diamido/O-donor ligand and therefore the geometry of intermediate cationic alkyl complexes is beneficial, at least in terms of molecular weight of the resulting poly(1-hexene). The tetrahydrofuran ring also simply creates more steric hindrance near the metal, which would encourage 1,2-insertion to give more reactive intermediates that are more stable toward β-hydride elimination than the "mistakes" that are the result of a 2,1-insertion.[18] It is interesting to note, although the effect cannot yet be adequately explained, that in $\{[(2,6\text{-}R_2C_6H_3NCH_2CH_2)_2O]MMe\}^+$ (M = Zr, Hf) catalyst systems,[5] the length of the poly(1-hexene) decreases from the molecular weight expected for a purely living system as the R group increases in size (Me to Et to *i*-Pr). Therefore, future studies will be aimed at exploring variations of the aryl groups in complexes analogous to [**1**]$ZrMe_2$ and [**2**]$ZrMe_2$.

Conclusions

A route to symmetric and asymmetric diamido/O-donor ligands has been developed that employs D-fructose as the starting material, and zirconium dialkyl complexes incorporating these new ligands have been prepared. Reaction of the dimethyl complexes in C_6D_5Br with $[PhNHMe_2][B(C_6F_5)_4]$ leads to cationic complexes that are stable for hours at room temperature. Cationic complexes using $[Ph_3C][B(C_6F_5)_4]$ as the activator have not been observed, although a limited study has shown that cations prepared in this manner are active for the polymerization of 1-hexene in a relatively well-controlled manner. The results reported here suggest that further exploration of diamido/O-donor ligands in which the geometry is restricted, or ligands that yield inherently unsymmetric complexes when coordinated to the metal, is warranted.

Experimental Section

All experiments were performed under a nitrogen atmosphere in a Vacuum Atmospheres drybox or by standard Schlenk techniques, unless otherwise specified. D-Fructose was purchased from Aldrich and used as received. Pyridinium hydrochloride was synthesized by bubbling dry HCl through dry pyridine. Raney nickel and $ZrCl_4$ were purchased from Strem Chemicals. 2,6-Dimethylaniline, 2,6-diisopropylaniline, and pyridine were distilled over CaH_2 and stored over molecular sieves (4 Å). *cis*-2,5-Bis((tosyloxy)methyl)tetrahydrofuran[10] and $Zr(NMe_2)_4$[19] were prepared according to the literature. Reagent grade benzene and ethyl acetate were used as received. Tetrahydrofuran and diethyl ether were sparged with nitrogen and passed through two columns of activated alumina. Toluene was distilled from sodium/benzophenone under nitrogen. Pentane was sparged with nitrogen, then passed through one column of activated alumina, and then through another of activated Q5. Chlorobenzene (Aldrich HPLC grade, 99.9%) and 1-hexene were distilled from CaH_2 under nitrogen. All solvents were stored in the drybox over 4 Å molecular sieves.

NMR data were recorded at 500, 300, or 250 MHz (^1H) and 125, 75, or 63 MHz (^{13}C). Chemical shifts are listed in parts per million downfield from tetramethylsilane unless specified otherwise. Coupling constants are listed in hertz. Spectra were obtained at 25 °C in C_6D_6 unless otherwise noted. NMR solvents were sparged with nitrogen and stored over 4 Å molecular sieves. Elemental analyses were performed by H. Kolbe, Mikroanalytisches Laboratorium (Mühlheim an der Ruhr, Germany). X-ray data were collected on a Siemens SMART/CCD diffractometer.

Gel permeation chromatography (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 CH_2Cl_2 was continuously dried and distilled from CaH_2. Solvent 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 to a Knauer differential refractometer was employed for molecular weight determination. Solutions of samples dissolved in CH_2Cl_2 were filtered through a Millex-SR 0.5 μm filter. All GPC data were analyzed using Astrette 1.2 (Wyatt Technology). Values of d*n*/d*c* were obtained under the assumption that all of the sample eluted from the column and were averaged for various runs. The low value of d*n*/d*c* for poly(1-hexene) in dichloromethane limited the accuracy of the data obtained via light scattering.

5-(Hydroxymethyl)furaldehyde. In a slight modification of the published procedure,[8] D-fructose (98 g, 0.54 mol) and pyridinium hydrochloride (63 g, 0.54 mol) were mixed in the solid state in a 2 L flask under N_2 and the mixture was heated to 130−135 °C for 1 h. The mixture was cooled, ethyl acetate (400 mL) was added, and the resulting mixture was stirred for 1 h. The organic phase was decanted and the extraction procedure repeated five times. The organic extracts were combined, dried with $MgSO_4$, and filtered. The solvent was removed from the filtrate under reduced pressure (10 mmHg) at 40 °C. The residue was dissolved in ether, and the solution

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(19) Diamond, J. M.; Jordan, R. F.; Petersen, J. L. *Organometallics* **1996**, *15*, 4030.

was decanted from an oily dark red impurity. The ether was removed under reduced pressure, and the residue was dried under high vacuum to give an orange solid; yield 36.1 g (53%). The proton NMR spectrum is identical with that reported in the literature.[10] The unpurified compound is suitable for subsequent reactions.

2,5-Bis(hydroxymethyl)furan.[9] 5-(Hydroxymethyl)furaldehyde (12.6 g, 0.1 mol) was dissolved in 600 mL of absolute ethanol, and 4 g of sodium borohydride (excess) was added. The solution was stirred for 16 h at 25 °C, and concentrated hydrochloric acid was added to make the mixture acidic. The mixture was immediately neutralized with solid sodium bicarbonate and dried with $MgSO_4$. The mixture was filtered, and the volume of the filtrate was reduced in vacuo to give 11.75 g of crude product (92%). Recrystallization from warm acetone yielded 8.7 g of pure product (68%). The proton NMR spectrum was identical with that reported in the literature.[9]

***cis*-2,5-Bis(hydroxymethyl)tetrahydrofuran.**[10] A mixture of 2,5-bis(hydroxymethyl)furan (5.00 g, 0.039 mol), absolute ethanol (50 mL), and Raney Ni (1 g, fine, 50/50 w/w aqueous solution) was heated to 100 °C under a dihydrogen atmosphere (800 psi) for 24 h. The catalyst was filtered off, and all solvent was removed in vacuo to give the product as a pale yellow oil (4.13 g, 80%) that was suitable for subsequent reactions. It can be distilled at 80−95 °C (0.3−0.4 mmHg) (lit. bp 80−90 °C (0.1 mmHg)).

***cis*-2,5-Bis((tosyloxy)methyl)tetrahydrofuran.**[9] The tosylation of *cis*-2,5-bis(hydroxymethyl)tetrahydrofuran was not carried out in pyridine as described in the literature. Instead, a slurry of pulverized KOH pellets (5.7 g, 0.1 mol) in THF (20 mL) was added to a solution of *cis*-2,5-bis(hydroxymethyl)-tetrahydrofuran (3.36 g, 0.025 mol) in THF (25 mL). The mixture was stirred vigorously at room temperature for 2 h, and a solution of tosyl chloride (9.69 g, 0.05 mol) in THF (25 mL) was added dropwise over a period of ∼1 h. The reaction mixture was stirred for an additional 24 h at room temperature and filtered through a glass frit. The orange filtrate was dried with $MgSO_4$ and the solvent was removed in vacuo to a obtain the off-white product (5.73 g, 53%), which can be used without further purification. It also can be recrystallized from a mixture of acetone and ether: ^{1}H NMR ($CDCl_3$): δ 1.72 (m, 2, CH (thf)), 1.96 (m, 2, CH (thf)), 2.46 (s, 6, CH_3), 3. 93 (m, 4, CH_2OH), 4.10 (m, 2, OC*H*CH_2OH), 7.36 (d, 4, H aryl), 7.79 (d, 4, H aryl).

H_2[1]. Solid *cis*-2,5-bis((tosyloxy)methyl)tetrahydrofuran (4.0 g, 9.1 mmol) was added to a chilled (−30 °C) solution of LiNH(2,6-$Me_2C_6H_3$) (2.31 g, 18.2 mmol) in THF (50 mL). The reaction was stirred at room temperature for 40 h, and all volatile components were then removed in vacuo. The residue was extracted with toluene (3 × 50 mL), and the extract was dried in vacuo to afford an off-white residue; crude yield 2.8 g (91%). The product was recrystallized at −30 °C from pentane; yield 2.5 g (81%). ^{1}H NMR ($CDCl_3$): δ 1.72 (m, 2, CH_2 (thf)), 2.00 (m, 2, CH_2 (thf)), 2.33 (s, 6, $Me_2C_6H_3N$), 3.00 (dd, ^2J = 12.4, ^3J = 7.7, 2, CH_2N), 3.20 (dd, ^2J = 12.4, ^3J = 3.3, 2, CH_2N), 3.5 (br s, 2, NH), 4.11 (m, 2, CH (thf)), 6.84 (t, ^3J = 7, H (aryl)), 7.01 (d, ^3J = 7, 4, H (aryl)). Anal. Calcd for $C_{22}H_{30}N_2O$: C, 78.06; H, 8.93; N, 8.28. Found: C, 78.30; H, 8.87; N, 8.20.

***N*-(5-(Hydroxymethyl)furfuryl)-2,6-dimethylaniline.** 5-(Hydroxymethyl)furaldehyde (30.0 g, 0.238 mol) and 2,6-dimethylaniline (29.1 g, 0.240 mol) were refluxed in benzene (300 mL) in a Dean−Stark trap apparatus. The reaction was monitored by ^{1}H NMR spectroscopy. After 4.5 h the solution was concentrated to ∼80 mL by collecting the benzene in the Dean−Stark trap. The rest of the solvent was removed in vacuo at 40 °C. The resulting dark red oil was dissolved immediately in absolute ethanol (300 mL) to avoid decomposition and the solution transferred to a pressure bottle. Raney nickel (16 g, 50% w/w in water) was washed with absolute ethanol (5 × 20 mL) and added to the solution. The autoclave was pressurized to 40 psi of H_2 and the stirring resumed. After 24 h the autoclave was vented, the solution was filtered, and the ethanol was removed under reduced pressure (10 mmHg) at 40 °C. The residue was dried under high vacuum to give a red-orange solid which was finely pulverized, placed on a frit, and washed with cold methanol (3 × 10 mL) to give an off-white hygroscopic solid which was dried under vacuum; yield 32.0 g (58%). ^{1}H NMR ($CDCl_3$): δ 2.27 (s, 6, $Me_2C_6H_3N$), 3.37 (br s, 2, NH, OH), 4.12 (s, 2, CH_2N), 4.58 (s, 2, CH_2N), 6.06 (d, ^3J = 3, 1, CH (thf)), 6.20 (d, ^3J = 3, 1, CH (thf)), 6.85 (t, ^3J = 7, 1, H (aryl)), 7.00 (d, ^3J = 7, 2, H (aryl)). ^{13}C{^{1}H} NMR (acetone-d_6): δ 18.5 (CH_3), 45.5, 57.3 (CH_2), 108.0, 108.3 (CH), 122.7, 129.3, 130.8, 146.4 (C (aryl)), 154.5, 155.6 (C (thf)). Anal. Calcd for $C_{14}H_{17}NO_2$: C, 72.70; H, 7.41; N, 6.06. Found: C, 72.76; H, 7.50; N, 6.04.

***cis*-*N*-(5-(Hydroxymethyl)tetrahydrofurfuryl)-2,6-dimethylaniline.** *N*-(5-(Hydroxymethyl)furfuryl)-2,6-dimethylaniline (6.50 g, 28.1 mmol) was dissolved in 140 mL of absolute ethyl acetate, and the solution was transferred to a 300 mL Parr autoclave. Raney nickel (9 g, 50% w/w in water) that had been washed with absolute ethanol (5 × 20 mL) and ethyl acetate (3 × 20 mL) was added to the solution, the autoclave was pressurized to 120 psi of H_2, and stirring was resumed. After 42 h the system was vented, the solution was filtered, and the solvent was removed under reduced pressure to give the product as a pale yellow oil quantitatively. The product can be purified by distillation (bp 155 °C (0.18 mmHg)). ^{1}H NMR ($CDCl_3$): δ 1.79 (m, 2, CH_2 (thf)), 1.99 (m, 2, CH_2 (thf)), 2.33 (s, 6, $Me_2C_6H_3N$), 3.00 (dd, ^2J = 12.6, ^3J = 7.1, 1, CH_2N), 3.17 (dd, ^2J = 12.6, ^3J = 3.7, 1, CH_2N), 3.19 (br s, 2, NH, OH), 3.55 (dd, ^2J = 11.6, ^3J = 5.4, 1, CH_2N), 3.76 (dd, ^2J = 11.6, ^3J = 3.5, 1, CH_2N), 4.11 (m, 2, CH (thf)), 6.85 (t, ^3J = 7, 1, H (aryl)), 7.01 (d, ^3J = 7, 2, H (aryl)). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 18.3 (CH_3), 27.2, 28.9 (CH_2 (thf)), 52.8 (CH_2N), 65.3 (CH_2OH), 79.0, 79.9 (CH (thf)), 122.0, 128.7, 129.5, 145.6 (C (aryl)). Anal. Calcd for $C_{14}H_{21}NO_2$: C, 71.46; H, 8.99; N, 5.95. Found: C, 71.48; H, 8.89; N, 6.04.

***cis*-*N*-(5-((Tosyloxy)methyl)tetrahydrofurfuryl)-2,6-dimethylaniline.** *cis*-*N*-(5-(Hydroxymethyl)tetrahydrofurfuryl)-2,6-dimethylaniline (4.30 g, 18.3 mmol) was dissolved in THF (80 mL), and pulverized KOH (1.7 g, 30 mmol) was added. The slurry was vigorously stirred for 10 min and cooled to 0 °C, and tosyl chloride (3.48 g, 18.3 mmol) was added as a solid. The slurry was stirred overnight and filtered, and the filtrate was dried with $MgSO_4$. The volatile components were removed under reduced pressure to give a brown oil that was ∼95% pure by ^{1}H NMR spectroscopy; crude yield 6.86 g (96%). ^{1}H NMR ($CDCl_3$): δ 1.76 (m, 2, CH_2 (thf)), 2.00 (m, 2, CH_2 (thf)), 2.27 (s, 6, $Me_2C_6H_3N$), 2.45 (s, 3, MeC_6H_4S), 2.88 (dd, ^2J = 12.6, ^3J = 7.4, 1, CH_2N), 3.11 (dd, ^2J = 12.6, ^3J = 3.5, 1, CH_2N), 3.38 (br s, 1, NH), 4.06 (m, 1, CH (thf)), 4.07 (m, 2, CH_2OTs), 4.14 (m, 1, CH (thf)), 6.83 (t, ^3J = 7, 1, $Me_2C_6H_3N$), 7.00 (d, ^3J = 7, 2, $Me_2C_6H_3N$), 7.33 (d, ^3J = 8.0, 2, MeC_6H_4S), 7.81 (d, ^3J = 8.0, 2, MeC_6H_4S). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 18.3 ($Me_2C_6H_4N$), 21.5 (MeC_6H_4S), 27.8, 28.3 (CH_2 (thf)), 52.5 (CH_2N), 71.4, 76.3, 79.4, 121.8, 127.8, 128.7, 129.6, 129.8, 133.0, 145.7, 144.8 (C (aryl)).

H_2[2]. Crude cis-*N*-(5-((tosyloxy)methyl)tetrahydrofurfuryl)-2,6-dimethylaniline (6.86 g, 17.6 mmol) was dissolved in THF (100 mL), and solid LiNH(2,6-*i*-$Pr_2C_6H_3$) (3.21 g, 17.6 mmol) was added at room temperature while the mixture was stirred. The reaction mixture was stirred at room temperature for 24 h, and all volatile components were then removed in vacuo. The residue was extracted with pentane (3 × 80 mL) and the pentane removed in vacuo to give an orange oil. The oil was heated at 130 °C under high vacuum (0.060 mmHg) to remove most of the unreacted NH_2(2,6-*i*-$Pr_2C_6H_3$). The final product is ∼95% pure according to ^{1}H NMR spectroscopy and can be used for subsequent reactions; yield 4.86 g (70%). ^{1}H NMR ($CDCl_3$): δ 1.25 (d, ^3J = 6.9, 6, Me_2CH), 1.26 (d, ^3J = 6.9, 6, Me_2CH), 1.75 (m, 2, CH_2 (thf)), 2.02 (m, 2, CH_2 (thf)), 2.35 (s,

6, $Me_2C_6H_3N$), 2.95 (dd, ^2J = 12.3, ^3J = 7.2, 1, CH_2N), 3.02 (dd, ^2J = 12.3, $^3J_{HH}$ = 7.5, 1, CH_2N), 3.07 (dd, ^2J = 12.3, ^3J = 3.3, 1, CH_2N), 3.23 (dd, ^2J = 12.3, $^3J_{HH}$ = 3.3, 1, CH_2N), 3.35 (sept, J = 6.9, 2, Me_2CH), 3.38 (br s, 1, NH), 4.11 (m, 1, CH (thf)), 4.20 (m, 1, CH (thf)), 6.85 (t, ^3J = 7, 1, $Me_2C_6H_3N$), 7.02 (d, ^3J = 7, 2, $Me_2C_6H_3N$), 7.09 (m, 3, $(Me_2CH)_2C_6H_3N$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 18.4 ($Me_2C_6H_4N$), 24.2, 24.3 ($(Me_2CH)_2$), 27.5, 28.85 (CH_2 (thf)), 28.87 (Me_2CH), 53.1, 56.2 (CH_2N), 78.9, 79.0 (CH (thf)), 121.8, 123.5, 123.7, 128.8, 129.4, 142.5, 143.0, 145.9 (C (aryl)).

[2]ZrCl$_2$. H$_2$[**2**] (1.89 g, 4.79 mmol) was dissolved in pentane (40 mL) and Zr(NMe$_2$)$_4$ (1.28 g, 4.79 mmol) was added as a solid at room temperature. The resulting solution was stirred overnight and filtered to remove a small amount of precipitate. The volatile components were then removed under reduced pressure to give [**2**]Zr(NMe$_2$)$_2$ as a sticky solid: ^1H NMR (C_6D_6) δ 1.32 (d, ^3J = 7, 3, Me_2CH), 1.34 (d, ^3J = 7, 3, Me_2CH), 1.36 (d, ^3J = 7, 3, Me_2CH), 1.39 (d, ^3J = 7, 3, Me_2CH), 1.2−1.6 (m, 4, CH_2 (thf)), 2.16 (s, 6, Me_2NZr), 2.42 (s, 3, $Me_2C_6H_3N$), 2.53 (s, 3, $Me_2C_6H_3N$), 3.18 (s, 6, Me_2NZr), 3.27 (dd, ^2J = 12, ^3J = 5, 1, CH_2N), 3.38 (dd, ^2J = 12, ^3J = 6.5, 1, CH_2N), 3.45 (d, ^2J = 5.5, 2, CH_2N), 3.78 (sept, ^3J = 7, 1, Me_2CH), 3.89 (sep, ^3J = 7, 1, Me_2CH), 4.22 (m, 1, CH (thf)), 4.34 (m, 1, CH (thf)), 6.94−7.22 (m, 6, H (aryl)).

The crude [**2**]Zr(NMe$_2$)$_2$ was dissolved in toluene (25 mL), Me_3SiCl (2.3 g, 21 mmol) was added, and the reaction mixture was stirred vigorously for 20 h. The pale orange solid was isolated on a frit, washed with toluene (3 × 5 mL) and pentane (2 × 10 mL), and dried in vacuo; yield 2.26 g (85%). Although the product is pure enough for subsequent reactions, it can be recrystallized from CH_2Cl_2/pentane in 72% yield. ^1H NMR (C_6D_6): δ 1.24 (m, 4, CH_2 (thf))), 1.25 (d, ^3J = 6.9, 3, Me_2CH), 1.31 (d, ^3J = 6.9, 3, Me_2CH), 1.52 (d, ^3J = 6.8, 3, Me_2CH), 1.60 (d, ^3J = 6.8, 3, Me_2CH), 2.50 (s, 3, $Me_2C_6H_3N$), 2.52 (dd, ^2J = 12.6, ^3J = 11, 1, CH_2N), 2.57 (s, 3, $Me_2C_6H_3N$), 2.92 (dd, ^2J = 12.6, ^3J = 6, 1, CH_2N), 3.62 (sept, ^3J = 6.8, 1, Me_2CH), 3.79 (dd, ^2J = 12.3, $^3J_{HH}$ = 9.9, 1, CH_2N), 3.93 (dd, ^2J = 12.3, ^3J = 9.6, 1, CH_2N), 4.00 (sept, ^3J = 11, 1, Me_2CH), 4.45 (m, 1, CH (thf)), 4.55 (m, 1, CH (thf)), 6.94−7.08 (m, 6, H (aryl)). Anal. Calcd for $C_{26}H_{36}N_2OCl_2Zr$: C, 56.30; H, 6.54; N, 5.05. Found: C, 56.08; H, 6.48; N, 4.97.

[2]ZrMe$_2$. [**2**]ZrCl$_2$ (0.288 g, 0.52 mmol) was suspended in ethyl ether (10 mL), and the suspension was cooled to −30 °C. A 3.0 M solution of MgMeBr in ethyl ether (0.35 mL, 1.05 mmol) was added dropwise while the mixture was stirred and the suspension was warmed to room temperature. After 1 h dioxane (100 μL, 1.17 mmol) was added and the suspension was stirred for 20 min. The volatile components were removed in vacuo, the residue was extracted with toluene, and the extract was filtered through Celite. The filtrate was concentrated to ∼0.5 mL in vacuo, and pentane was added to afford [**2**]ZrMe$_2$ as a white solid; yield 0.187 g (70%). ^1H NMR (C_6D_6): δ 0.08 (s, 3, ZrMe), 0.46 (s, 3, ZrMe), 1.19 (d, ^3J = 7, 3, Me_2CH), 1.27 (d, ^3J = 7, 3, Me_2CH), 1.36 (d, ^3J = 7, 3, Me_2CH), 1.43 (d, ^3J = 7, 3, Me_2CH), 1.62 (m, 2, CH_2 (thf))), 1.71 (m, 2, CH_2 (thf)), 2.44 (br s, 3, $Me_2C_6H_3N$), 2.52 (s, 3, $Me_2C_6H_3N$), 3.14 (dd, ^2J = 12, $^3J_{HH}$ = 4, 1, CH_2N), 3.30 (dd, ^2J = 12, ^3J = 4, 1, CH_2N), 3.56 (dd, ^2J = 12, ^3J = 6, 1, CH_2N), 3.78 (sept, ^3J = 7, 1, Me_2CH), 3.79 (dd, ^2J = 12, ^3J = 6, 1, CH_2N), 3.92 (m, 2, CH (thf)), 4.01 (sept, ^3J = 7, 1, Me_2CH), 6.97 (t, ^3J = 7.5, 1, $Me_2C_6H_3N$), 7.10 (d, ^3J = 7.5, 2, $Me_2C_6H_3N$), 7.16 (m, 3, $(Me_2CH)_2C_6H_3N$). Anal. Calcd for $C_{28}H_{42}N_2OZr$: C, 65.45; H, 8.24; N, 5.45. Found: C, 65.56; H, 8.19; N, 5.53.

[1]Zr(NMe$_2$)$_2$. A solution of Zr(NMe$_2$)$_4$ (1.975 g, 7.38 mmol) in pentane (10 mL) was added to a solution of H$_2$[**1**] (2.50 g, 7.38 mmol) in pentane (40 mL) at room temperature. The solution was stirred overnight and filtered to remove a small amount of precipitate. The filtrate was concentrated in vacuo to give a white solid that was recrystallized from pentane at −30 °C to give analytically pure product; yield 3.53 g (93%). ^1H NMR (C_6D_6): δ 1.53 (m, 2, CH_2 (thf)), 1.69 (m, 2, CH_2 (thf)), 2.17 (s, 6, Me_2NZr), 2.42 (br s, 12, $Me_2C_6H_3N$), 3.13 (s, 6, Me_2NZr), 3.25 (dd, ^2J = 12, ^3J = 6, 2, CH_2N), 3.32 (dd, ^2J = 12, $^3J_{HH}$ = 6, 2, CH_2N), 4.24 (m, 2, CH (thf)), 6.88 (t, ^3J = 7, 2, H (aryl)), 7.08 (d, ^3J = 7, 4, H (aryl)). Anal. Calcd for $C_{26}H_{40}N_4OZr$: C, 60.54; H, 7.82; N, 10.86. Found: C, 60.37; H, 7.74; N, 10.65.

[1]ZrCl$_2$. Neat Me_3SiCl (2.2 g, 20 mmol) was added to a solution of [**1**]Zr(NMe$_2$)$_2$ (3.43 g, 6.65 mmol) in 35 mL of toluene at room temperature. The solution was stirred overnight, and the solvent was removed in vacuo to give a white solid; yield 3.31 g (100%). ^1H NMR (C_6D_6): δ 1.17 (m, 2, CH_2 (thf)), 1.28 (m, 2, CH_2 (thf)), 2.46 (s, 6, $Me_2C_6H_3N$), 2.56 (s, 6, $Me_2C_6H_3N$), 2.57 (dd, ^2J = 12.3, ^3J = 5.9, 2, CH_2N), 3.73 (dd, ^2J = 12.3, ^3J = 9.7, 2, CH_2N), 4.40 (m, 2, CH (ring)), 7.00 (m, 6, H (aryl)). Anal. Calcd for $C_{22}H_{28}N_2OCl_2Zr$: C, 53.00; H, 5.66; N, 5.62; Cl, 14.22. Found: C, 52.82; H, 5.77; N, 5.80; Cl, 14.31.

[1]ZrMe$_2$. Method a. A solution of MeMgBr (3.0 M in ethyl ether, 0.67 mL, 2.0 mmol) was added to a suspension of [**1**]-ZrCl$_2$ (0.500 g, 1.00 mmol) in ethyl ether (20 mL) at −30 °C. The mixture was stirred for 1 h at room temperature, and dioxane (0.684 mL, 8.03 mmol) was added. After 20 min of additional stirring, the volatile components were removed in vacuo and the residue was extracted with toluene. The extract was filtered through Celite, and all volatile components were then removed from the filtrate to give a white-orange residue. The residue was recrystallized from toluene/pentane at −30 °C; yield 0.4 g (87%). Crystals suitable for X-ray crystallography were obtained by crystallization from ether at −30 °C. [**1**]Zr^{13}Me$_2$ was synthesized similarly using ^{13}MeMgI (0.95 M in diethyl ether).

Method b. ZrCl$_4$ (0.688 g, 2.95 mmol) was added to a solution of H$_2$[**1**] (1.00 g, 2.95 mmol) in diethyl ether (20 mL) at −30 °C as a solid. The suspension was warmed to room temperature while the reaction mixture was stirred over a period of 4 h. During this time the initial solid dissolved and a new white precipitate appeared. The suspension was cooled again to −30 °C, and a solution of MeMgBr (3.0 M in ethyl ether, 4.0 mL, 12 mmol) was added. The suspension was stirred for 30 min, and dioxane (1.2 mL, 14 mmol) was added to give a white precipitate. The suspension was stirred for an additional 30 min period and filtered through Celite. The orange filtrate was concentrated to 20 mL and cooled to −30 °C. The resulting white solid was isolated by filtration, washed with ethyl ether (2 mL) and pentane (2 × 2 mL), and dried in vacuo; yield 0.555 g. Concentration of the filtrate and cooling to −30 °C yielded a second crop (0.120 g); overall yield 0.675 g (50%). ^1H NMR (toluene-d_8): δ 0.11 (s, 3, ZrMe), 0.26 (s, 3, ZrMe), 1.49 (m, 2, CH_2 (thf)), 1.80 (m, 2, CH_2 (thf)), 2.42 (br s, 6, $Me_2C_6H_3N$), 2.48 (br s, 6, $Me_2C_6H_3N$), 3.01 (dd, ^2J = 12.3, ^3J = 5.9, 2, CH_2N), 3.82 (dd, ^2J = 12.3, ^3J = 5.9, 2, CH_2N), 3.87 (m, 2, CH (thf)), 6.96 (t, ^3J = 7, 2, H (aryl)), 7.08 (d, ^3J = 7, 4, H (aryl)). $^3C\{^1H\}$ NMR (C_6D_6): δ 42.3, 44.4 (Zr^{13}Me$_2$). Anal. Calcd for $C_{24}H_{34}N_2OZr$: C, 62.97; H, 7.49; N, 6.12. Found: C, 62.90; H, 7.38; N, 6.07.

Generation of {[1]ZrMe(PhNMe$_2$)}[B(C$_6$F$_5$)$_4$]. A chilled (−30 °C) solution of [**1**]ZrMe$_2$ (0.011 g, 0.024 mmol) in C_6D_5Br (0.6 mL) was added to a chilled (−30 °C) suspension of [PhNHMe$_2$][B(C$_6$F$_5$)$_4$] (0.019 mg, 0.024 mmol) in C_6D_5Br (0.2 mL). The reaction mixture was stirred for 30 min while being warmed to room temperature, and the resulting solution was transferred to a NMR tube. ^1H NMR (250 MHz, C_6D_5Br): δ 0.03 (s, 3, ZrMe), 1.65 (m, 2, CH_2 (thf)), 1.87 (m, 2, CH_2 (thf)), 2.08 (s, 3, $Me_2C_6H_3N$), 2.09 (s, 3, $Me_2C_6H_3N$), 2.44 (dd, $^2J_{HH}$ = 12.5, $^3J_{HH}$ = 5, 2, CH_2N), 2.52 (s, 6, PhNMe_2), 3.68 (dd, $^2J_{HH}$ = 12.5, $^3J_{HH}$ = 11, 2, CH_2N), 4.66 (m, 2, CH (thf)), 5.62 (d, $^3J_{HH}$ = 8.5, 2, PhNMe$_2$), 5.86 (br, 3, PhNMe$_2$), 6.94−7.03 (m, H (aryl)).

Generation of {[2]ZrMe(PhNMe$_2$}[B(C$_6$F$_5$)$_4$]. A chilled (−30 °C) solution of [**2**]ZrMe$_2$ (0.030 g, 0.058 mmol) in C_6D_5Br (0.6 mL) was added to a chilled (−30 °C) suspension of [PhNHMe$_2$][B(C$_6$F$_5$)$_4$] (0.046 g, 0.058 mmol) in C_6D_5Br (0.2

mL). The reaction mixture was stirred and warmed to room temperature over a period of 30 min, and the resulting solution was transferred to a NMR tube. ^{1}H NMR (500 MHz, C_6D_5Br): δ 0.03 (s, 3, ZrMe), 0.97 (d, ^3J = 6.5, 3, *Me*$_2$CH), 1.14 (d, ^3J = 6.5, 3, *Me*$_2$CH), 1.22 (d, ^3J = 7, 3, *Me*$_2$CH), 1.34 (d, ^3J = 7, 3, *Me*$_2$CH), 1.70 (m, 2, CH_2 (thf)), 1.91 (m, 2, CH_2 (thf)), 2.07 (s, 3, *Me*$_2$C$_6$H$_3$N), 2.19 (s, 3, *Me*$_2$C$_6$H$_3$N), 2.47 (dd, ^2J = 13, ^3J = 5, 1, CH_2N), 2.59 (br, 3, PhN*Me*$_2$), 2.63 (br, 3, PhN*Me*$_2$), 3.83 (dd, ^2J = 13, ^3J = 5, 1, CH_2N), 3.08 (sept, ^3J = 6.5, 1, Me$_2$C*H*), 3.33 (sept, ^3J = 7, 1, Me$_2$C*H*), 3.72 (dd, ^2J = 12.5, ^3J = 11, 1, CH_2N), 4.07 (dd, ^2J = 12.5, ^3J = 11, 1, CH_2N), 4.77 (m, 1, CH (thf)), 4.88 (m, 1, CH (thf)), 5.73 (br, 4, *Ph*NMe$_2$), 6.11 (br, 1, *Ph*NMe$_2$), 6.91−7.21 (m, H (aryl)).

Polymerization of 1-Hexene using Activated [1]ZrMe$_2$. Stock solutions of [**2**]ZrMe$_2$ (8.4 mM in chlorobenzene) and [Ph$_3$C][B(C$_6$F$_5$)$_4$] (8.0 mM in chlorobenzene) were employed. The molarity of these two stock solutions was arbitrarily controlled in a ratio of 1.1:1 with the limiting reagent being [Ph$_3$C][B(C$_6$F$_5$)$_4$]. A 100 mL one-necked round-bottom flask was charged with a magnetic stir bar and a stock solution of [Ph$_3$C][B(C$_6$F$_5$)$_4$] (2.0 mL, 16.8 μmol) and capped with a rubber septum. The solution was kept in an isothermal bath at 0 °C. A stock solution of [**1**]ZrMe$_2$ (2.0 mL, 16.0 μmol) was then added, and the yellow solution was stirred for 10 min. 1-Hexene (0.40 mL, 200 equiv; 0.80 mL, 400 equiv; 1.20 mL, 600 equiv) was then syringed into this solution. After 1 h the polymerization reaction was quenched with HCl (1.0 M diethyl ether, 2 mL). Most of the volatile components were removed under reduced presure (10 Torr/80 °C). During this time the residue turned green. The green residue was dried under high vacuum (60 mTorr/100 °C). The product weight did not change after 20 h. The resulting polymer was extracted into hot hexane (4 × 30 mL), and the solution was filtered through silica. The hexane was removed under reduced pressure, and the polymers were dried under high vacuum (60 mTorr, 100 °C). Yields were in the 91−96% range.

Polymerization of Propylene using Activated [2]-ZrMe$_2$. A 100 mL one-necked round-bottom flask was charged with a magnetic stir bar and 20 mL of chlorobenzene. The flask was cooled to 0 °C, and the solvent was saturated with propylene. A 10 mL solution of {[**2**]ZrMe(PhNMe$_2$}[B(C$_6$F$_5$)$_4$] (29.2 μmol) prepared as described above was injected into the flask. The solution was stirred for 10 min, and the reaction was quenched with HCl (1.0 M in diethyl ether, 2 mL). The solution was poured into a large volume of MeOH and the polymer collected by filtration. The polymer was dried under high vacuum (60 mTorr/100 °C).

X-ray Study of [1]ZrMe$_2$. A Siemens SMART/CCD area detection system with Mo Kα radiation (λ = 0.710 73 Å) was employed. Cell determination, data collection, and structure solution and refinement was performed with the SMART SAINT and SHELXTL 5.0 software packages. All non-hydrogen atoms were refined anisotropically; all hydrogen atoms were placed in calculated positions. Further details can be found in Table 1.

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Supporting Information Available: A fully labeled ORTEP drawing and tables of atomic coordinates, bond lengths and angles, and anisotropic displacement parameters for [**1**]-ZrMe$_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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