Bulky Chelating Diamide Complexes of Zirconium: Synthesis, Structure, and Reactivity of d^0 Alkyl Derivatives

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The reaction of 2 equiv of LiNHAr (Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$) with 1,3-dibromopropane yields the diamine ArHN(CH$_2$)$_3$NHAr ((BAIP)H$_2$, **1**). The reaction of (BAIP)H$_2$ with Zr(NMe$_2$)$_4$ yields the complex (BAIP)Zr(NMe$_2$)$_2$ (**2**) and 2 equiv of NHMe$_2$. Compound **2** reacts with 2 equiv of [Me$_2$NH$_2$]Cl to yield (BAIP)ZrCl$_2$(NHMe$_2$)$_2$ (**3**) and in the presence of excess pyridine affords the complex (BAIP)ZrCl$_2$py$_2$ (**4**). The base-free dichloride complex (BAIP)ZrCl$_2$ (**5**) can be prepared from **2** and excess ClSiMe$_3$. The alkylation of **4** or **5** with 2 equiv of MeMgBr, 2 equiv of PhCH$_2$MgCl, and 1 equiv of NaCp(DME) yields the alkyl derivatives (BAIP)ZrR$_2$ (**6a**, R = Me; **6b**, R = CH$_2$Ph) and (BAIP)Zr(η^5-C$_5$H$_5$)Cl (**8**), respectively. The reaction of 2 equiv of PhMe$_2$CCH$_2$MgCl with complex **4** yields the η^2-pyridyl complex (BAIP)Zr(η^2-N,C−NC$_5$H$_4$)(CH$_2$CMe$_2$Ph) (**7**). An X-ray study of **7** revealed a capped tetrahedron geometry with the pyridyl nitrogen occupying the capping position. Complex **7** is likely formed via proton abstraction from coordinated pyridine. The catalyst system **6a**/MAO polymerizes 1-hexene to a mixture of high polymer and oligomers. Activation with {Ph$_3$C}[B(C$_6$F$_5$)$_4$] yields only oligomers (n = 2−7). Rapid β-hydride elimination precludes polymer formation in these systems.

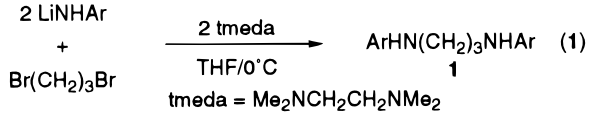
Introduction

The design and synthesis of well-defined olefin polymerization catalysts has developed rapidly in the last fifteen years with the group 4 metallocene class of compounds receiving considerable attention.[1−3] Detailed studies in this area have been concerned with the way in which the stereoregularity, catalytic activity, and comonomer incorporation can be altered with changes to the Cp ligand(s). For example, although the putative complex Cp$_2$ZrR$^+$ will polymerize ethylene with high activity, the homopolymerization of 1-alkenes is relatively slow. In contrast, linked Cp−amide derivatives such as [(η^5-C$_5$Me$_4$)SiMe$_2$(NCMe$_3$)]TiR$^+$ readily incorporate α-olefins.[4,5] Given the success associated with Cp−amide derivatives, there is growing interest in the use of chelating diamide[6−12] ligands in olefin polymerization catalysis.

We recently reported that the chelating diamide complex [ArN(CH$_2$)$_3$NAr]TiMe$_2$ (Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$) serves as a precursor for the highly active[13] and living[14] polymerization of α-olefins. In contrast, the analogous zirconium compounds (e.g., [ArN(CH$_2$)$_3$NAr]ZrX$_2$, X = Me,[15] Cl) show little or no activity for the polymerization of α-olefins under the same conditions. Strong binding of the cocatalyst to the electrophilic, low-coordinate zirconium metal center may preclude formation of a cationic alkyl complex, as has been observed for other chelating diamides of Ti and Zr.[8] We report here the synthesis, structure, and reactivity of chelating diamide complexes of zirconium, including a new, high-yield route to base-free diamide dichloride materials. Some of this work has appeared in a preliminary form.[15]

Results

The reaction of 2 equiv of LiNHAr (generated from H$_2$NAr and BuLi at −78 °C, Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$) with 1,3-dibromopropane affords the diamine (BAIP)H$_2$ (**1**) as a viscous yellow oil in about 47% yield (eq 1). The



diamine is formed in a 1:1 ratio with the elimination

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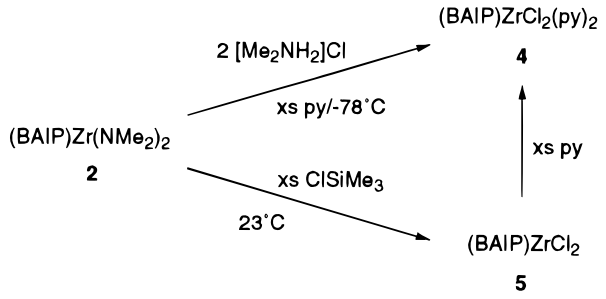
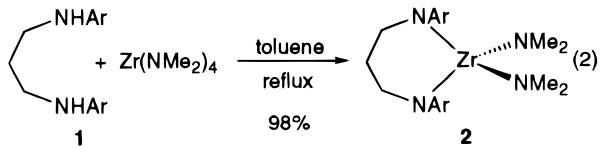
Scheme 1



product $ArHNCH_2CH{=}CH_2$ (**A**, identified by ^1H NMR spectroscopy). The facile formation of **A** necessitates the use of tetramethylethylenediamine (tmeda) (reactions performed without tmeda contain about 80% **A**). The diamine is easily separated from **A** via formation of the ether- and water-insoluble salt $[ArH_2N(CH_2)_3NH_2Ar]^{2+}$-$\{2Cl^-\}$.

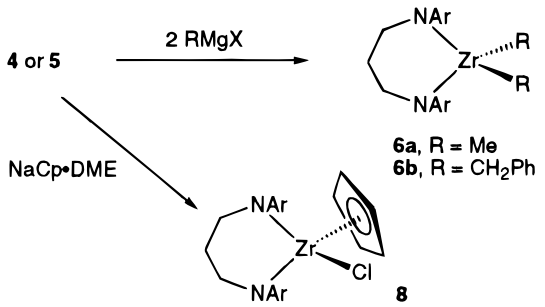
The aminolysis reaction between $(BAIP)H_2$ and $Zr(NMe_2)_4$[16] provides 2 equiv of $HNMe_2$ and the mixed amide complex $(BAIP)Zr(NMe_2)_2$ (**2**) in excellent yield (eq 2). A characteristic second-order pattern is observed



for the methylene protons (NCH_2) of the coordinated BAIP ligand in the proton NMR spectrum of complex **2**. Additionally, the isopropyl methyl groups of the arene are diastereotopic, which we interpret as a consequence of restricted rotation about the $N-C_{ipso}$ bond. The steric bulk of the ligand precludes formation of the bis(ligand) complex $(BAIP)_2Zr$.

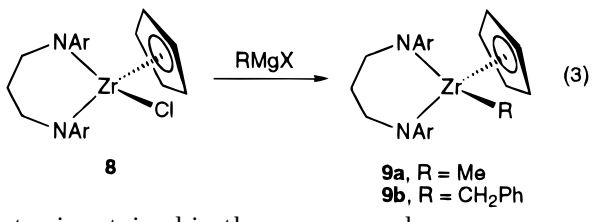
Chloride derivatives were sought as precursors to alkyl derivatives. Our initial[15] attempts to prepare a dichloride complex met with mixed success. Compound **2** reacts with 2 equiv of $[Me_2NH_2]Cl$ to afford the octahedral dimethylamine adduct, $(BAIP)ZrCl_2(NHMe_2)_2$ (**3**) in nearly quantitative yield. The BAIP ligand appears to be stable to protonolysis in contrast to what we have observed for pyridine diamide derivatives of zirconium-bearing ancillary dimethylamido ligands.[17] However, the dimethylamine protons in **3** are attacked by alkylating reagents; for example, the reaction of **3** and 2 equiv of MeMgBr affords the mixed amide alkyl complex $(BAIP)ZrMe(NMe_2)$ (identified by NMR spectroscopy).[18] Reaction of complex **2** with 2 equiv of $[Me_2NH_2]Cl$ in the presence of excess pyridine affords a single bis(pyridine) geometrical isomer $(BAIP)ZrCl_2(py)_2$ (**4**) in 77% yield (Scheme 1). The proton and carbon NMR spectra of **4** are consistent with a species with C_{2v} symmetry; however, it is not possible to distinguish whether the chloride or pyridine ligands are trans to the BAIP ligand. Although **4** is useful for the preparation of a number of bis(alkyl) derivatives, large alkyl groups (i.e., CH_2SiMe_3, CH_2CMe_2Ph) give rise to products derived from proton abstraction from the coordinated pyridine (*vide infra*). We have previously reported[17] that $ClSiMe_3$ reacts selectively with the dimethylamido ligands in $[2,6\text{-}(ArNCH_2)_2NC_5H_3]Zr(NMe_2)_2$. Similarly, the BAIP ligand in **2** is inert to excess $ClSiMe_3$, affording the base-free dichloride (**5**) in excellent yield (Scheme 1). **5** is highly electrophilic, irreversibly coordinating bases such as THF, pyridine, and PMe_3.

Scheme 2



Alkyl derivatives can be prepared from **4** or **5,** depending on the bulk of the alkyl group. For example, the bis(alkyl) complexes $(BAIP)ZrR_2$ (**6a**, R = Me; **6b**, R = CH_2Ph) and the monocyclopentadienyl derivative $(BAIP)Zr(\eta^5\text{-}C_5H_5)Cl$ (**8**) are obtained cleanly from the bis(pyridine) or the base-free dichlorides (Scheme 2). Unlike all other complexes we have prepared bearing the BAIP ligand, the proton NMR spectrum of **6a** is temperature dependent; in particular, the isopropyl methyl groups appear as a broad featureless peak at 25 °C. The low-temperature-limiting spectrum (−20 °C) shows two doublets for the isopropyl methyl groups. The high-temperature limiting spectrum (60 °C) shows only one doublet for the isopropyl methyls, suggesting that the aryl groups pass through a molecular plane of symmetry, in other words, free rotation about the $N-C_{ipso}$ bond ($\Delta G_{rot}^{\ddagger} = 13.3(5)$ kcal mol^{-1}). As previously noted,[15] the proton NMR spectrum of the bis(benzyl) complex **6b** displays a high-field resonance for the ortho protons of the benzyl groups; however, we have been unable to observe η^n-coordination of these benzyl groups at low temperature (to −80 °C). In addition, the carbon NMR spectrum of **6b** shows a $Zr-CH_2Ph$ resonance at 64.2 ppm with $^1J_{CH} = 124$ Hz, which is normal for η^1-coordinated benzyl groups.

The ^1H and $^{13}C\{^1H\}$ NMR spectra of $(BAIP)Zr(\eta^5\text{-}C_5H_5)Cl$ are consistent with a pseudotetrahedral geometry and C_s symmetry about zirconium. This gives rise to two isopropyl methine ($CHMe_2$) resonances and four isopropyl methyl resonances, which is consistent with restricted rotation about the $N-C_{ipso}$ bond. Monoalkyl complexes of the type $(BAIP)Zr(\eta^5\text{-}C_5H_5)R$ (**9a**, R = Me; **9b**, R = CH_2Ph) are obtained cleanly from **8** and the appropriate Grignard reagent (eq 3). The local C_s symmetry is retained in these compounds.



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Scheme 3

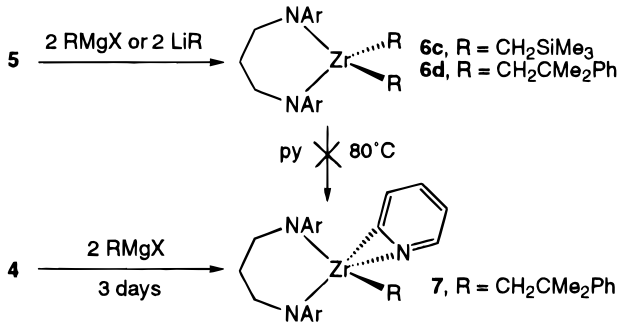


Table 1. Summary of Crystallographic Data, Collection Parameters, and Refinement Parameters for Compound 7[a]

empirical formula	$C_{45}H_{57}N_3Zr$
fw	695.13
temperature (°C)	25
wavelength (Å)	0.71073 (Mo Kα)
cryst syst	triclinic
space group	$P\bar{1}$
a (Å)	10.146(2)
b (Å)	12.336(2)
c (Å)	16.723(2)
α (deg)	81.00(2)
β (deg)	76.99(2)
γ (deg)	76.24(2)
volume (Å^3)	1953.6(6)
Z	2
ρ(calc) (g/mol)	1.182
F_{000}	740
no. of reflns collected	6209
no. of indep reflns	5405
no. of obs with $F_o \geq 4\sigma(F_o)$	2999
no. of variable params	289
*R*1	0.0951
wR2	0.2287
goodness of fit (GOF)	1.014

[a] $R1 = \sum(||F_o| - |F_c||)/\sum|F_o|$; $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$; $GOF = [\sum w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ (where *n* is the number of reflections and *p* is the number of parameters refined).

The bis(alkyl) complexes (BAIP)ZrR_2 (**6c**, R = CH_2SiMe_3; **6d**, R = CH_2CMe_2Ph) are obtained as oils in high yield from **5** and 2 equiv of the suitable alkylating reagent (Scheme 3). Compounds **6c,d** are exceedingly soluble in pentane and failed to crystallize at −30 °C. In contrast to the alkylation chemistry of the base-free dichloride, the reaction of the bis(pyridine) complex **4** with 2 equiv of $PhMe_2CCH_2MgCl$ in THF did not give the anticipated bis(neophyl) complex, but rather the η^2-pyridyl compound (BAIP)Zr(η^2-N,C−NC_5H_4)(CH_2CMe_2Ph) (**7**). Resonances attributable to an η^2-pyridyl moiety were also observed in the crude ^{1}H NMR spectrum of **4** and 2 equiv of $LiCH_2SiMe_3$, but this compound proved difficult to isolate from other byproducts. The solid state structure of **7** was determined by X-ray crystallography (Table 1). The molecular structure of **7** can be found in Figure 1 and relevant bond distances and angles in Table 2. Overall the structure is best described as a face-capped tetrahedron with the pyridyl nitrogen occupying the capping position. The Zr1−N3−C30 ring is structurally similar to the Zr−N−C ring in the cationic complex [$Cp_2Zr(\eta^2$-picolyl)(PMe_3)](BPh_4).[19] Each amide donor in **7** is sp^2-hybridized as evidenced by the sum of the angles about each nitrogen (N1 = 360.0° and N2 = 359.8°). The solid state C_1 symmetry of **7** coupled with its spectroscopically observed C_s symmetry in solution suggests that rapid rotation about the Zr1−C30 bond is occurring on the NMR time scale. The C_s symmetry of **7** is maintained down to −80 °C.

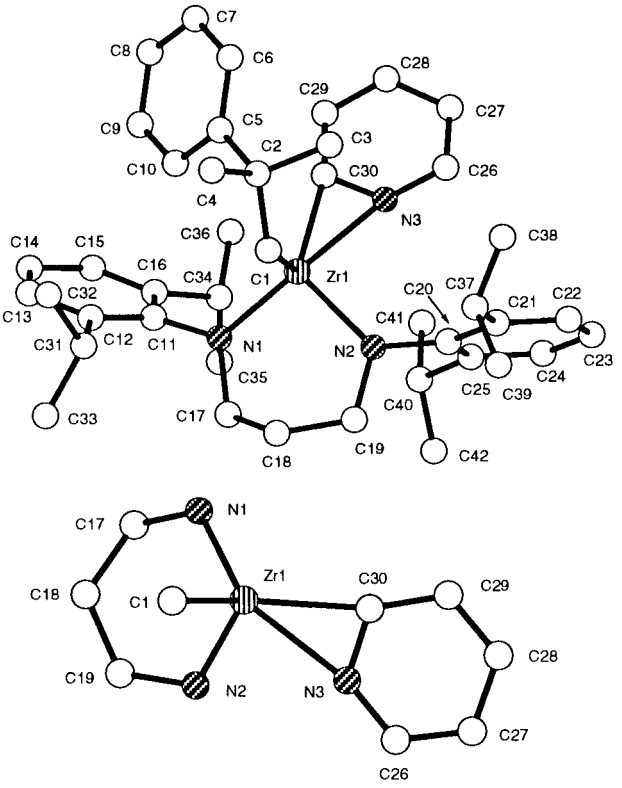


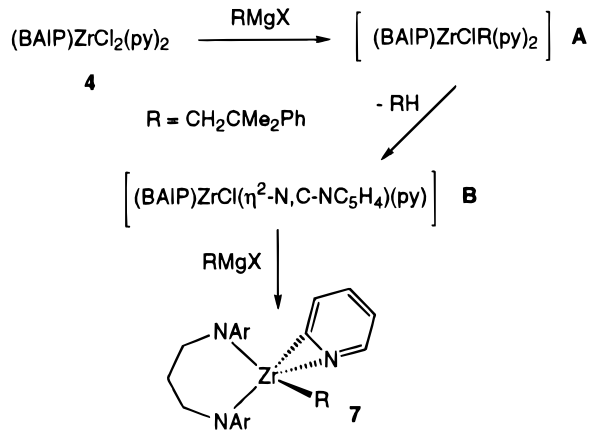
Figure 1. (top) Chem 3D representation of **7**. (bottom) Chem 3D representation of the core of **7**.

Table 2. Selected Bond Distances (Å) and Angles (deg) for Compound 7

	Bond Distances		
Zr1−C1	2.268(12)	Zr1−C30	2.219(12)
Zr1−N1	2.050(9)	Zr1−N2	2.031(9)
Zr1−N3	2.260(10)	C30−N3	1.31(2)
	Bond Angles		
N1−Zr1−N2	95.4(4)	C1−Zr1−C30	113.2(4)
N1−Zr1−C1	103.9(4)	N2−Zr1−C1	104.0(4)
N3−Zr3−C3	126.4(3)	N3−Zr1−C30	34.0(4)

We have studied[15] the mechanism of formation of **7**. A deuterium labeling experiment showed that the pyridine ortho proton is abstracted by either a coordinated neophyl group (most likely) or by the neophyl Grignard reagent. It seemed reasonable that heating a solution of **6d** in neat pyridine would lead to formation of complex **7** and 1 equiv of $^tBuC_6H_5$ (Scheme 3). Surprisingly, no reaction occurs even after several days at 80 °C, suggesting that (1) precoordination of pyridine is required during the formation of **7** and (2) that it is unlikely that the reaction proceeds via a bis(neophyl) intermediate. On the basis of these results and the labeling experiment, we propose that a transient monoalkyl derivative (BAIP)ZrCl(CH_2CMe_2Ph)(py)$_2$ (**A**) loses $^tBuC_6H_5$ slowly to yield the pyridine-stabilized pyridyl complex (BAIP)ZrCl(η^2-N,C-NC_5H_4)(py) (**B**) (Scheme 4). Alkylation of intermediate **B** and loss of pyridine affords complex **7** (free pyridine is observed in the crude reaction mixture by ^{1}H NMR spectroscopy). Attempts to prepare the mononeophyl complex (BAIP)-ZrCl(CH_2CMe_2Ph)(py)$_n$ (n = 1 or 2) from **4** and 1 equiv of $ClMgCH_2CMe_2Ph$ have been unsuccessful, leading to intractable material. We have isolated the bis(alkyl) monopyridine complexes (BAIP)ZrR_2(py) (R = Me, CH_2-

Scheme 4



Ph), prepared from **6a,b** and excess pyridine;[18] however, these species do not eliminate alkane at 80 °C. In fact, the pyridine adducts are stable for days at this temperature. This suggests that **A** is likely six-coordinate and that the elimination of $^{t}BuC_6H_5$ is a result of the steric congestion in this complex.

Given our interest in the polymerization chemistry of group 4 diamide complexes,[13,14] we undertook a study of the 1-hexene polymerization chemistry of (BAIP)-$ZrMe_2$ with the cocatalysts methylaluminoxane (MAO), $B(C_6F_5)_3$,[20] and $\{Ph_3C\}[B(C_6F_5)_4]$.[21] When activated with MAO (500 equiv), **6a** yields both high polymer (M_w = 26 000, M_n = 15 100; polydispersity 1.72) and oligomers (n = 2−7, confirmed by GC−MS). Activities up to 150 g of poly(1-hexene)/mmol of catalyst·h were obtained in neat 1-hexene at 68 °C. For comparison, the titanium analogue (BAIP)$TiMe_2$ yields only high polymer (M_w = 81 500, M_n = 47 000; polydispersity 1.73) with an activity of 350 000 g of poly(1-hexene)/mmol of catalyst·h under the same reaction conditions.[13] Based on chain end analysis,[22] the putative cationic alkyl $[(BAIP)ZrP]^+$ (P = polymer) inserts 1-hexene in a 1,2 fashion followed by β-hydride elimination. The titanium complex (BAIP)$TiMe_2$ also inserts 1-hexene in a primary fashion; however, these systems do not engage in β-hydride elimination.[23] It would appear that at least two active species are generated with MAO since both oligomers and high polymer are formed.

We have previously reported that the catalysts system (BAIP)$TiMe_2$/$B(C_6F_5)_3$ effects the living polymerization of α-olefins at room temperature.[14] In contrast, **6a**/$B(C_6F_5)_3$ is completely inactive for the polymerization of 1-hexene at 23 °C. The following spectroscopic data suggest that several species are formed. The $^{11}B\{^1H\}$ NMR spectrum of equimolar amounts of **6a** and $B(C_6F_5)_3$ shows three boron-containing species; one that is three-coordinate (free $B(C_6F_5)_3$), and two that are four-coordinate. In addition, the $^{19}F\{^1H\}$ NMR spectrum shows a total of nine resonances, which is in agreement with the boron NMR data. The ^1H NMR spectrum of **6a**/$B(C_6F_5)_3$ shows at least three different species which we are unable to assign. Attempts to isolate these species have been unsuccessful.

Borate-stabilized cations of zirconium can be generated with more reactive methide abstraction reagents; for example, equimolar amounts of **6a** and $\{Ph_3C\}[B(C_6F_5)_4]$ oligomerize (n = 2−7, confirmed by GC−MS) neat 1-hexene at 23 °C with an activity of 130 g of oligo(1-hexene)/mmol of catalyst·h. The MAO-activated systems are slightly more active that the trityl borate-activated systems, as has been observed in the analogous titanium systems.[23] In contrast to the MAO-activated system above, we see no evidence of high polymer formation in the trityl borate-activated complexes. For comparison, the catalyst system (BAIP)-$TiMe_2$/$\{Ph_3C\}[B(C_6F_5)_4]$ is an active (104,000 g of poly(1-hexene)/mmol of catalyst·h) living polymerization catalyst at 68 °C (M_w = 239 100, M_n = 177 500; polydispersity 1.35).[23] The zirconium MAO- and trityl borate-activated systems above are dramatically effected by the presence of toluene;[13] for example, **6a**/MAO and **6a**/$\{Ph_3C\}[B(C_6F_5)_4]$ are inactive in a 10% toluene in 1-hexene mixture, likely a result of competitive binding of the arene to the electrophilic metal center.

Conclusions

In summary, a high-yield route to chelating diamide complexes of zirconium has been demonstrated. The base-free dichloride (BAIP)$ZrCl_2$ serves as a starting point for the synthesis of a variety of bis(alkyl) derivatives, while the pyridine-stabilized dichloride complex (BAIP)$ZrCl_2(py)_2$ affords pyridyl complexes when the alkylating reagent is bulky. Moderately active olefin polymerization and oligomerization catalyst systems are obtained when (BAIP)$ZrMe_2$ is activated with MAO and $\{Ph_3C\}[B(C_6F_5)_4]$, respectively. Although the lack of polymerization activity in the borane system (BAIP)-$ZrMe_2$/$B(C_6F_5)_3$ may reflect a strong binding of the cocatalyst to the electrophilic metal center, spectroscopic data suggest that at least three different species are formed when these reagents are mixed, resulting in an ill-defined system.

Experimental Details

General Details. All experiments were performed under an atmosphere of dry dinitrogen using standard Schlenk techniques or in an Innovative Technology Inc. drybox. Solvents were distilled from sodium/benzophenone ketyl (dimethoxyethane, THF, hexanes, diethyl ether, benzene) or molten sodium (toluene) under argon and stored over activated 4 Å molecular sieves. $ZrCl_4$ and 1,3-dibromopropane (Aldrich Chemicals) were used as received. *N,N,N′N′*-tetramethylethylenediamine (tmeda), 2,6-diisopropylaniline, and chlorotrimethylsilane were distilled prior to use. $Zr(NMe_2)_4$ was synthesized following Bradley's method.[16] Proton (300 MHz) and carbon (75.46 MHz) NMR spectra were recorded in C_6D_6 at approximately 22 °C on Varian Gemini-300 and Varian XL-300 spectrometers. The proton chemical shifts were referenced to internal C_6D_5H (δ = 7.15 ppm) and the carbon resonances to C_6D_6 (δ = 128.0 ppm). Mass spectra were performed on a Finnigan MAT Model 8230 spectrometer coupled to a Varian 3400 gas chromatograph. GPC analyses (in THF) versus polystyrene standards were performed using a Waters GPC equipped with Waters Styragel columns (HR 1, HR 3, HR 4). Elemental analyses were performed by Oneida Research Services Inc., Whitesboro, NY, and by Mr. Peter Borda at the University of British Columbia. Ar = 2,6-$^{i}Pr_2C_6H_3$.

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ArHN(CH$_2$)$_3$NHAr ((BAIP)H$_2$, 1). *n*-BuLi (2.50 M, 79.2 mL, 198 mmol) was added dropwise to a stirring THF (150 mL) solution of 2,6-diisopropylaniline (35.12 g, 198.1 mmol) at −78 °C. The solution was warmed to 22 °C, where it was kept for 30 min. The solution was cooled to 0 °C and tmeda (23.0 g, 198 mmol) was added dropwise followed by 1,3-dibromopropane (20.0 g, 99.1 mmol) dropwise. The solution was warmed to 22 °C and stirred overnight. The solution was poured into H_2O (100 mL) and extracted with CH_2Cl_2 (3 × 100 mL). The organic layer was dried over anhydrous Na_2SO_4 and the CH_2Cl_2 removed in *vacuo*. The resulting yellow oil was dissolved in diethyl ether (30 mL), and concentrated HCl (20 mL) was added. The resulting salt ([ArH$_2$N(CH$_2$)$_3$NH$_2$Ar]Cl$_2$) was removed by filtration, washed with diethyl ether (20 mL), and dissolved in dichloromethane. This solution was poured into aqueous saturated $NaHCO_3$ (100 mL). The organic layer was separated and dried over anhydrous Na_2SO_4. Removal of the solvent yielded **1** as a viscous oil (18.2 g, 46.1 mmol; 47%). ^{1}H NMR δ 7.10 (m, 6H, Ar), 3.36 (sept, 4H, C*H*Me$_2$), 3.01 (t, 4H, NC*H*$_2$), 2.97 (s, 2H, N*H*), 1.77 (pent, 2H, NCH$_2$C*H*$_2$), 1.22 (d, 24H, CH*Me*$_2$). ^{13}C{^{1}H} NMR δ 144.0, 143.7, 123.9, 124.4, 50.8, 32.7, 28.1, 24.5. MS (EI) *m*/*z* 394.3342 (M$^+$). Calcd for $C_{27}H_{42}N_2$: 394.3348.

(BAIP)Zr(NMe$_2$)$_2$ (2). Compound **1** (2.95 g, 7.48 mmol) and Zr(NMe$_2$)$_4$ (2.00 g, 7.48 mmol) were dissolved in toluene, sealed in a heavy-walled glass pressure vessel, and heated to 110 °C for 3 h. The solvent was removed in *vacuo* and the resulting solid extracted with pentane (3 × 100 mL) and filtered through Celite. The volume of the filtrate was reduced to 50 mL and cooled to −30 °C for 12 h. A white crystalline solid was isolated by filtration and dried under vacuum (4.21 g, 7.34 mmol, 98%). ^{1}H NMR δ 7.20 (m, 6H, Ar), 3.78 (sept, 4H, C*H*Me$_2$), 3.55 (m, 4H, NC*H*$_2$), 2.64 (s, 12H, N*Me*$_2$), 2.44 (m, 2H, NCH$_2$C*H*$_2$), 1.34 (d, 12H, CH*Me*$_2$), 1.32 (d, 12H, CH*Me*$_2$). ^{13}C{^{1}H} NMR δ 146.4, 145.8, 125.2, 124.1, 59.1, 41.8, 32.3, 28.3, 26.2, 25.0. Anal. Calcd for $C_{31}H_{52}N_4Zr$: C, 65.09; H, 9.16; N, 9.79. Found: C, 64.75; H, 9.19; N, 9.65.

(BAIP)ZrCl$_2$(NHMe$_2$)$_2$ (3). Compound **2** (1.92 g, 3.37 mmol) was dissolved in CH_2Cl_2 (25 mL) and cooled to −78 °C. [Me$_2$NH$_2$]Cl (0.550 g, 6.74 mmol) was added slowly as a solid. The resulting solution was allowed to warm to room temperature and stirred overnight. The solvent was removed in *vacuo* and the resulting yellow solid dissolved in toluene and filtered through Celite. The solution volume was reduced until a slurry formed. Hexane (60 mL) was added, and the solution was filtered to yield a yellow crystalline solid (2.16 g, 3.35 mmol, 99%). ^{1}H NMR δ 7.13 (m, 6H, Ar), 3.97 (sept, 4H, C*H*Me$_2$), 3.67 (m, 4H, NC*H*$_2$), 2.58 (m, 2H, NCH$_2$C*H*$_2$), 2.17 (s, 2H, N*H*), 1.86 (s, 12H, N*Me*$_2$), 1.45 (d, 12H, CH*Me*$_2$), 1.29 (d, 12H, CH*Me*$_2$). This compound loses NHMe$_2$ upon isolation.

(BAIP)ZrCl$_2$(py)$_2$ (4). Compound **2** (4.80 g, 8.39 mmol) was dissolved in a mixture of CH_2Cl_2 (50 mL) and pyridine (2 mL) and cooled to −78 °C. [Me$_2$NH$_2$]Cl (1.37 g, 16.8 mmol) was added slowly as a solid. The resulting solution was allowed to warm to room temperature and stirred overnight. The solvent was removed in *vacuo* and the resulting yellow solid dissolved in toluene and filtered through Celite. The solution volume was reduced until a slurry formed. Hexanes (60 mL) was added, and the solution was filtered to yield a yellow crystalline solid (4.60 g, 6.45 mmol, 77%). ^{1}H NMR δ 8.86 (dd, 4H, py), 7.11 (m, 6H, Ar), 6.52 (tt, 2H, py), 6.27 (tt, 4H, py), 4.29 (sept, 4H, C*H*Me$_2$), 4.05 (m, 4H, NC*H*$_2$), 2.43 (m, 2H, NCH$_2$C*H*$_2$), 1.30 (d, 12H, CH*Me*$_2$), 1.15 (d, 12H, CH*Me*$_2$). ^{13}C{^{1}H} NMR δ 151.7, 145.8, 137.6, 128.5, 125.7, 124.0, 123.2, 61.3, 33.0, 28.2, 27.8, 23.3. Carbon analyses for this compound were low (three attempts). Anal. Calcd for $C_{37}H_{48}Cl_2N_4Zr$: C, 62.33; H, 7.07; N, 7.86. Found: C, 60.65; H, 7.22; N, 7.35.

(BAIP)ZrCl$_2$ (5). Compound **2** (0.50 g, 0.87 mmol) was dissolved in hexanes. Excess chlorotrimethylsilane (1.0 g, 9.26 mmol) was added dropwise at room temperature and the solution stirred overnight. After 12 h, **5** precipitated from the solution and was collected by filtration and washed with cold hexanes. Analytically pure **5**·$^1/_2$ *n*-C$_5$H$_{12}$ was obtained as a yellow microcrystalline powder (0.43 g, 0.78 mmol, 90%) from the recrystallization of **5** at −30 °C from a mixture of toluene/pentane. ^{1}H NMR δ 7.07 (m, 6H, Ar), 3.59 (sept, 4H, C*H*Me$_2$), 3.51 (t, 4H, NC*H*$_2$), 2.39 (m, 2H, NCH$_2$C*H*$_2$), 1.35 (d, 12H, CH*Me*$_2$), 1.23 (d, 12H, CH*Me*$_2$). ^{13}C{^{1}H} NMR δ 146.9, 145.6, 129.8, 126.9, 62.1, 31.9, 30.9, 28.4, 27.4. Anal. Calcd for $C_{27}H_{40}Cl_2N_2Zr$·C_5H_{12}: C, 59.97; H, 7.85; N, 4.74. Found: C, 59.84; H, 7.69; N, 4.21 (the pentane of crystallization was confirmed by ^{1}H NMR spectroscopy).

(BAIP)ZrMe$_2$ (6a). MeMgBr (2.4 M, 1.17 mL, 2.8 mmol) was added dropwise to a stirring suspension of **4** (1.00 g, 1.40 mmol) in Et$_2$O (50 mL) at −20 °C. The solution was warmed to 23 °C and stirred overnight. Dimethoxyethane (2 mL) was added and the solvent removed in *vacuo*. The resulting solid was extracted with toluene and filtered through Celite. The toluene was removed in *vacuo*, and the product recrystallized from pentane at −30 °C (0.42 g, 0.82 mmol, 58%). ^{1}H NMR δ 7.17 (m, 6H, Ar), 3.75 (sept, 4H, C*H*Me$_2$), 3.47 (m, 2H, NC*H*$_2$), 2.25 (m, 2H, NCH$_2$C*H*$_2$), 1.36 (m, 12H, CH*Me*$_2$), 1.34 (m, 12H, CH*Me*$_2$), 0.42 (s, 6H, Zr*Me*$_2$). ^{13}C{^{1}H} NMR δ 145.6, 143.2, 126.8, 124.5, 59.4, 39.9 (Zr*Me*), 29.9, 28.6, 25.8. Anal. Calcd for $C_{29}H_{46}N_2Zr$: C, 67.78; H, 9.02; N, 5.45. Found: C, 68.04; H, 9.27; N, 5.40.

(BAIP)Zr(CH$_2$Ph)$_2$ (6b). PhCH$_2$MgCl (1.40 M, 2.00 mL, 2.80 mmol) was added dropwise to a stirring suspension of **4** (1.00 g, 1.40 mmol) in Et$_2$O (50 mL) at −20 °C. The solution was warmed to room temperature and stirred overnight. The solvent was removed in *vacuo* and the solid extracted with toluene and filtered through Celite. The solution was concentrated and cooled to −30 °C to yield yellow crystalline **6b** (0.40 g, 0.60 mmol, 43%). ^{1}H NMR δ 7.19 (m, 6H, Ar), 7.01 (tt, 4H, Ph), 6.82 (tt, 2H, Ph), 6.65 (dd, 4H, Ph), 3.78 (sept, 4H, C*H*Me$_2$), 3.49 (m, 2H, NC*H*$_2$), 2.31 (m, 2H, NCH$_2$C*H*$_2$), 1.95 (s, 2H, C*H*$_2$Ph), 1.32 (d, 12H, CH*Me*$_2$), 1.27 (d, 12H, CH*Me*$_2$). ^{13}C{^{1}H} NMR δ 145.9, 145.1, 145.0, 130.1, 126.6, 126.5, 124.7, 122.7, 64.2 (*C*H$_2$Ph, $^1J_{CH}$ = 124 Hz), 58.8, 29.1, 28.4, 26.6, 25.1. Anal. Calcd for $C_{41}H_{54}N_2Zr$: C, 73.93; H, 8.17; N, 4.21. Found: C, 73.54; H, 8.33; N, 4.27.

(BAIP)Zr(CH$_2$SiMe$_3$)$_2$ (6c). Compound **5** (1.00 g, 1.40 mmol) was suspended in Et$_2$O (50 mL). LiCH$_2$SiMe$_3$ (0.264 g, 2.80 mmol) was then added as a solid. The solution was allowed to warm to room temperature and stirred overnight. The solvent was removed in *vacuo* and the resulting solid dissolved in hexanes and filtered through Celite. The hexanes was removed in *vacuo* yielding **6c** as a light yellow oil (0.860 g, 1.30 mmol, 93%). ^{1}H NMR δ 7.19 (m, 6H, Ar), 3.85 (sept, 4H, C*H*Me$_2$), 3.50 (m, 4H, NC*H*$_2$), 2.43 (m, 2H, NCH$_2$C*H*$_2$), 1.44 (d, 6H, CH*Me*$_2$), 1.35 (d, 6H, CH*Me*$_2$), 0.51 (s, 2H, C*H*$_2$SiMe$_3$), 0.08 (s, 9H, Si*Me*$_3$). ^{13}C{^{1}H} NMR δ 145.0, 144.7, 126.6, 124.7, 58.9, 58.2, 29.1, 28.2, 26.3, 25.6, 2.7.

(BAIP)Zr(CH$_2$CMe$_2$Ph)$_2$ (6d). Compound **5** (1.00 g, 1.40 mmol) was suspended in THF (50 mL) and cooled to −20 °C. (PhMe$_2$CCH$_2$)$_2$Mg (0.190 M, 14.7 mL, 2.80 mmol, prepared from PhMe$_2$CCH$_2$MgCl and 1,4-dioxane) was added dropwise. The solution was allowed to warm to room temperature and stirred overnight. The solvent was removed in *vacuo* and the resulting solid dissolved in hexanes and filtered through Celite. The hexanes was removed in *vacuo* yielding **6d** as a yellow oil (0.90 g, 1.2 mmol, 86%). ^{1}H NMR δ 7.22 (m, 10H, Ar), 7.05 (m, 6H, Ar), 3.89 (sept, 4H, C*H*Me$_2$), 3.47 (m, 4H, NC*H*$_2$), 2.18 (m, 2H, NCH$_2$C*H*$_2$), 1.42 (d, 6H, CH*Me*$_2$), 1.31 (d, 6H, CH*Me*$_2$), 1.31 (s, 6H, C*Me*$_2$Ph), 1.18 (s, 2H, C*H*$_2$CMe$_2$Ph). ^{13}C{^{1}H} NMR δ 153.7, 146.5, 145.0, 128.5, 126.4, 125.3, 125.3, 124.8, 87.6, 58.5, 42.0, 33.9, 28.2, 26.9, 25.1.

(BAIP)Zr(η^2-N,C-NC$_5$H$_4$)(CH$_2$CMe$_2$Ph) (7). PhMe$_2$CCH$_2$MgCl (0.89 M, 3.15 mL, 2.80 mmol) was added dropwise to a stirring THF (50 mL) suspension of **4** (1.00 g, 1.40 mmol) at −20 °C. The solution was allowed to warm to room temperature and stirred overnight. The solvent was removed in *vacuo* and the resulting solid extracted with pentane and filtered through Celite. The solution was concentrated and cooled to

−30 °C to yield colorless crystalline **7** (0.40 g, 0.58 mmol, 43%). ^{1}H NMR δ 7.33−7.10 (m, 10H, Ar, Ph, py), 6.88 (m, 1H, Ph), 6.78 (tt, 1H, py), 6.72 (m, 2H, Ph), 6.35 (ddd, 1H, py), 4.26 (sept, 2H, C*H*Me$_2$), 3.82 (m, 2H, NC*H*$_2$), 3.58 (m, 2H, NC*H*$_2$), 3.26 (sept, 2H, C*H*Me$_2$), 2.76 (m, 1H, NCH$_2$C*H*$_2$), 2.64 (m, 1H, NCH$_2$C*H*$_2$), 1.70 (s, 2H, C*H*$_2$CMe$_2$Ph), 1.59 (d, 6H, CH*Me*$_2$), 1.47 (d, 6H, CH*Me*$_2$), 1.18 (d, 6H, CH*Me*$_2$), 1.17 (s, 6H, C*Me*$_2$-Ph), 0.64 (d, 6H, CH*Me*$_2$). ^{13}C{^{1}H} NMR δ 153.9, 149.7, 145.5, 144.6, 144.5, 134.8, 129.3, 128.1, 125.3, 125.1, 125.1, 124.7, 124.0, 123.8, 68.0, 59.6, 41.0, 35.5, 31.7, 28.3, 28.1, 27.0, 26.6, 25.2, 24.1. Anal. Calcd for $C_{42}H_{57}N_3Zr$: C, 72.57; H, 8.26; N, 6.04. Found: C, 72.85; H, 8.61; N, 5.95.

(BAIP)Zr(η^5-C$_5$H$_5$)Cl (8). NaCp(DME) (0.250 g, 1.40 mmol) was added as a solid to a stirring toluene (50 mL) solution of **4** (1.00 g, 1.40 mmol). The solution was stirred overnight at room temperature and then filtered through Celite. The volume of toluene was reduced to 10 mL and hexane (50 mL) added. Cooling to −30 °C afforded white crystals of **5c** (0.770 g, 1.32 mmol, 94%). ^{1}H NMR δ 7.12 (m, 6H, Ar), 5.93 (s, 5H, C$_5$*H*$_5$), 3.91 (m, 1H, NCH$_2$C*H*$_2$), 3.61 (sept, 2H, C*H*Me$_2$), 3.60 (sept, 2H, C*H*Me$_2$), 3.60 (m, 2H, NC*H*$_2$), 3.35 (m, 2H, NC*H*$_2$), 2.01 (m, 1H, NCH$_2$C*H*$_2$), 1.40 (d, 6H, CH*Me*$_2$), 1.32 (d, 6H, CH*Me*$_2$), 1.27 (d, 6H, CH*Me*$_2$), 1.23 (d, 6H, CH*Me*$_2$). ^{13}C{^{1}H} NMR δ 151.1, 145.1, 142.3, 125.9, 124.6, 124.2, 114.7, 57.9, 28.0, 27.9, 27.2, 25.9, 25.6, 25.1, 25.0. Anal. Calcd for $C_{32}H_{45}ClN_2Zr$: C, 65.77; H, 7.76; N, 4.79. Found: C, 66.24; H, 7.86; N, 4.72.

(BAIP)Zr(η^5-C$_5$H$_5$)Me (9a). Compound **8** (1.00 g, 1.40 mmol) was suspended in Et$_2$O (50 mL) at 23 °C. MeMgCl (3.0 M, 0.47 mL, 1.40 mmol) was added all at once. The solution was stirred overnight at room temperature and the solvent removed *in vacuo*. The resulting oil was taken up in hexane (50 mL) and filtered. Compound **9a** formed as white crystals (0.637 g, 1.12 mmol, 80%) upon cooling to −30 °C. ^{1}H NMR δ 7.11 (m, 6H, Ar), 5.79 (s, 5H, C$_5$*H*$_5$), 3.67 (sept, 2H, C*H*Me$_2$), 3.54 (m, 2H, NC*H*$_2$), 3.47 (sept, 2H, C*H*Me$_2$), 3.46 (m, 1H, NCH$_2$C*H*$_2$), 3.29 (m, 2H, NC*H*$_2$), 2.07 (m, 1H, NCH$_2$C*H*$_2$), 1.42 (d, 6H, CH*Me*$_2$), 1.31 (d, 6H, CH*Me*$_2$), 1.23 (d, 6H, CH*Me*$_2$), 1.20 (d, 6H, CH*Me*$_2$), 0.36 (s, 3H, Zr*Me*). ^{13}C{^{1}H} NMR δ 151.0, 144.7, 142.9, 128.3, 125.4, 124.2, 112.8, 58.1, 28.0, 27.6, 27.3, 27.2, 25.4, 25.0, 20.8, 19.9.

(BAIP)Zr(η^5-C$_5$H$_5$)(CH$_2$Ph) (9b). Compound **8** (1.0 g, 1.4 mmol) was suspended in Et$_2$O (50 mL). PhCH$_2$MgCl (.69M, 2.03 mL, 1.4 mmol) was then added all at once. The solution was stirred overnight at room temperature and the solvent removed *in vacuo*. The resulting oil was dissolved in hexane (50 mL), filtered through Celite, reduced in volume, and cooled to −30 °C. Compound **9b** formed as white crystals (0.677 g, 1.05 mmol, 75%). ^{1}H NMR δ 7.29 (m, 2H, Ph), 7.13 (m, 1H, Ph), 7.13 (m, 6H, Ar), 7.01 (m, 2H, Ph), 5.77 (s, 5H, C$_5$*H*$_5$), 3.55 (sept, 2H, C*H*Me$_2$), 3.51 (sept, 2H, C*H*Me$_2$), 3.51 (m, 2H, NC*H*$_2$), 3.38 (m, 1H, NCH$_2$C*H*$_2$), 3.28 (m, 2H, NC*H*$_2$), 2.48 (s, 2H, ZrC*H*$_2$Ph), 2.07 (m, 1H, NCH$_2$C*H*$_2$), 1.40 (d, 6H, CH*Me*$_2$), 1.29 (d, 6H, CH*Me*$_2$), 1.28 (d, 6H, CH*Me*$_2$), 1.25 (d, 6H, CH*Me*$_2$). ^{13}C{^{1}H} NMR δ 153.0, 151.6, 144.5, 142.6, 128.6, 125.9, 125.6, 124.4, 124.4, 120.8, 113.8, 69.6, 57.4, 51.1, 28.0, 27.7, 27.1, 25.9, 25.4, 24.8.

Polymerization Details. Compound **6a** (5.0 mg, 9.7 μmol) was mixed with 500 equiv of MAO or 1 equiv of {Ph$_3$C}-[B(C$_6$F$_5$)$_4$] in pentane (1 mL) and added to 5.0 g of 1-hexene at 23 or 68 °C. The polymerizations were quenched after 30 (23 °C) or 10 min (68 °C) by the addition of a 1 N solution of HCl (2 mL). The polymer/oligomer was extracted with hexanes and dried under vacuum overnight. The samples were dissolved in THF for GPC analysis.

X-ray Crystallographic Analysis. A suitable crystal of **7** was grown from a saturated pentane solution at −30 °C. Crystal data may be found in Table 1. Data were collected on a Siemens P4 diffractometer with the XSCANS software package.[24] The cell constants were obtained by centering 20 reflections ($21.0 \le 2\theta \le 24.6°$). The Laue symmetry $\bar{1}$ was determined by merging symmetry-equivalent positions. The data were collected in the θ range 2.0−23° ($-1 \le h \le 11$, $-13 \le k \le 13$, $-17 \le l \le 18$) in $\theta-2\theta$ scan mode at variable scan speeds (2−20 deg/min). Background measurements were made at the ends of the scan range. Four standard reflections monitored at the end of every 297 reflections collected showed no decay of the crystal. The data processing, solution, and refinement were done using SHELXTL-PC[25] and SHELXL-93[26] programs. An empirical absorption correction was applied to the data using the routine XEMP on the ψ scans data (μ = 0.312 mm^{-1}). Anisotropic thermal parameters were refined for all non-hydrogen atoms except for two phenyl ring carbon atoms. No attempt was made to locate the hydrogen atoms. All the bonds and angles in the isopropyl groups were restrained to be equal using the option SADI. In the final difference Fourier synthesis the electron density fluctuates in the range +1.03 to −0.635 e Å^{-3}.

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Supporting Information Available: Tables of data collection and experimental details, final atomic coordinates, final thermal parameters, bond distances and angles, calculated hydrogen positions, selected torsional angles, and least-squares planes and a full ORTEP diagram of **7** (10 pages). Ordering information is given on any current masthead page.

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