Bulky Bis(alkylamidinate) Complexes of Group 4. Syntheses and Characterization of $M(CyNC(R')NCy)_2Cl_2$ and $Zr(CyNC(Me)NCy)_2Me_2$ (R'= Me, M = Ti, Zr, Hf; R' = ^{t}Bu, M = Zr)

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Synthesis of a series of bis(alkylamidinate) group 4 compounds of the general formula $M(CyNC(CH_3)NCy)_2Cl_2$ (M = Ti (**1**), Zr (**2**), Hf (**3**); Cy = cyclohexyl), $Zr(CyNC(CMe_3)NCy)_2Cl_2$ (**4**), and $Zr(CyNC(CH_3)NCy)_2(CH_3)_2$ (**5**) are reported. In the presence of methylaluminoxane (MAO) as a cocatalyst, compounds **1**−**5** are active ethylene polymerization catalysts.

Introduction

The quest for alternatives to cyclopentadienyl-based ligands in early transition metal chemistry has recently generated a great deal of effort on preparing complexes with N-centered donor ligands.[1−10] Within this realm, a variety of amidinato complexes of the group 4 metals have been reported.[11−24] However, they have been, by and large, limited to the use of *N*,*N′*-bis(trimethylsilyl)-benzamidinate-based ligands, $[Me_3SiNC(C_6H_4R)NSiMe_3]$. Steric analysis of this ligand system places it intermediate between the Cp and Cp* ligands.[25−27] However, substantial differences have been noted between the electronic features of these two systems.[26] Most notably, bis(trimethylsilyl)benzamidinate anions are four-electron donors that are expected to have polarized M−N bonds. These effects are anticipated to lead to more electrophilic metal centers.

Our initial attraction to the amidinate ligand system was motivated by the possibility of exploring the effects of making rational modifications to both the steric bulk and electronic properties of these ligands through changes to the organic substituents on the nitrogen and the bridging carbon positions. We wish to report a portion of our systematic study of complexes of these ligands with early transition metals. These efforts compliment our work with these ligands and the main group elements.[28−32] Included in this report are the syntheses and characterization of a novel family of bis-

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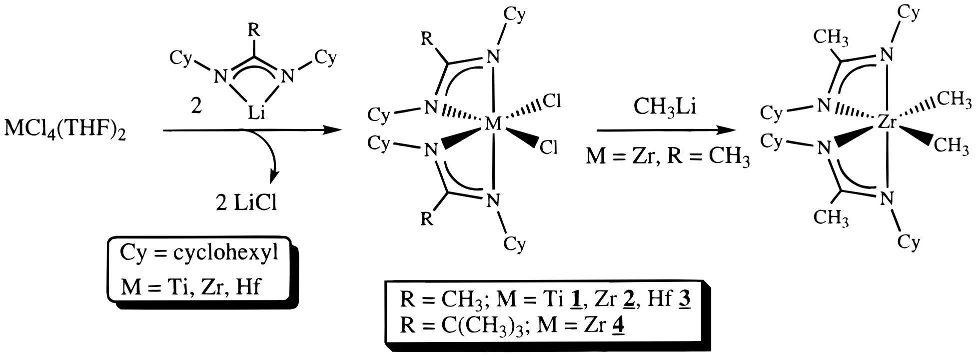
Scheme 1



(alkylamidinate) group 4 compounds of the general formula $M(CyNC(CH^3)NCy)_2Cl_2$ (M = Ti (**1**), Zr (**2**), Hf (**3**); Cy = cyclohexyl), a ${}^tBu$-substituted analog $Zr(CyNC({}^tBu)NCy)_2Cl_2$ (**4**), and a dimethyl complex $Zr(CyNC(CH_3)NCy)_2(CH_3)_2$ (**5**). Furthermore, in the presence of methylaluminoxane (MAO) as a cocatalyst, compounds **1**−**5** are capable of polymerizing ethylene.

Results and Discussion

Reaction of MeLi with 1,3-dicylohexylcarbodiimide proceeded smoothly in ether at room temperature to yield Li[CyNC(Me)NCy]. Subsequent addition of 0.5 equiv of $MCl_4(THF)_2$ (M = Ti, Zr, Hf) followed by recrystallization resulted in the isolation of a series of bis(alkylamidinate) complexes $M(CyNC(Me)NCy)_2Cl_2$ (**1**−**3**) (Scheme 1) with isolated yields in the 60% range. Spectroscopic characterization and microanalysis confirmed the formulas of these materials. Specifically, all three compounds exhibited similar ^1H and ^{13}C NMR spectra with the most notable features being the appearance of single resonances for the cyclohexyl α-H, α-C, and the CH_3 group on the methyne bridge. Spectroscopic equivalence of the Cy groups in **1**−**3** is further supported by the ^{13}C NMR spectroscopy. However, on the basis of the NMR observations for **4** and the molecular structure of **2** (*vide infra*), we provide the C_2-symmetric structures for these complexes shown in Scheme 1. Furthermore, **1**−**3** gave similar NMR spectra to those previously observed for the analogous Sn complexes $Sn(CyNC(Me)NCy)_2Cl_2$.[31]

We have found that other alkylamidinate ligands are also accessible through a similar reaction scheme. Thus, reaction of ${}^tBuLi$ with 1,3-dicyclohexylcarbodiimide in ether followed by addition of $ZrCl_4(THF)_2$ in a 2:1 ratio yielded the corresponding bis(amidinato)dichloro complex $[CyN(CMe_3)NCy]_2ZrCl_2$ (**4**) (Scheme 1). On the basis of the ^1H NMR, complex **4** appeared to exhibit equivalent Cy groups, as indicated by a single resonance for the cyclohexyl proton a to N at 3.85 ppm. However, the greater dispersion provided by ^{13}C NMR spectra indicated otherwise. At room temperature, a single broad resonance was observed at 56.3 ppm, which was assigned to the α-C of the cyclohexyl groups. This resonance sharpened upon warming the sample and split into two signals upon cooling to 263 K. These observations are consistent with inequivalent cyclohexyl groups that are part of a fluxional molecule.

Table 1. Crystallographic Data for 2 and 5

	2	**5**
formula	$C_{28}H_{50}N_4C_{l2}Zr$	$C_{30}H_{58}N_4Zr$
fw	604.86	566.02
cryst color and habit	colorless block	colorless block
cryst size, mm	0.2 × 0.2 × 0.2	0.3 × 0.3 × 0.3
space group	$P2_1/n$	$P2_1/n$
a, Å	13.034(3)	10.491(3)
b, Å	13.693(2)	14.380(5)
c, Å	18.036(4)	21.516(7)
β, deg	106.49(5)	92.43(2)
V, Å^3	3086(5)	3243(2)
Z, Å^3	4	4
ρ(calcd), g cm^{-3}	1.193	1.159
μ, cm^{-1}	4.68	3.61
diffractometer	Rigaku AFC6S	Siemens SMART CCD
λ, Å	1.540 56 (Cu Kα)	0.710 73 (Mo Kα)
T, K	120	297
no. of reflns collected	3354	12 967
no. of indep reflns	3177	4226
no. of obs reflns	3067 ($I > 2.5\sigma I$)	4186 ($I > 2\sigma I$)
R(F), %	7.8	5.84
R(w*F*) or [$R_w(F)^2$], %	11.4	[15.58]
data/parameter	10.02	13.25

The dimethyl derivative of **2** was easily prepared from the metathesis reaction with MeLi. Isolated yields of crystalline $Zr(CyNC(Me)NCy)_2Me_2$ (**5**) from this procedure were in the range of 50%. New signals in the ^1H and ^{13}C NMR spectra at 0.88 and 42.74 ppm, respectively, are consistent with the formulation of this species and comparable to those observed for bis(trimethylsilyl)benzamidinates.[12,21]

X-ray Crystallographic Analyses of 2 and 5. Single-crystal X-ray diffraction analyses of **2** and **5** were undertaken in order to establish the coordination geometry of the metal center and the connectivity of the ligand for these compounds (Table 1).

Structural analysis revealed the molecular geometry for **2** shown in Figure 1. The metal center is in a distorted pseudo-octahedral environment consisting of the four nitrogen atoms of the two amidinate anions with *cis*-chloride ligands completing the coordination sphere. Tables 2 and 3 present a summary of selected bond distances and angles for **2**. The bonding parameters within the two amidinate ligands are not dramatically different, and the two nitrogens and bridging carbon atoms for each of the individual amidinate ligands lie in a plane which includes the Zr atom, resulting in a solid-state molecular geometry with approximately C_2 symmetry. The termini of the amidi-

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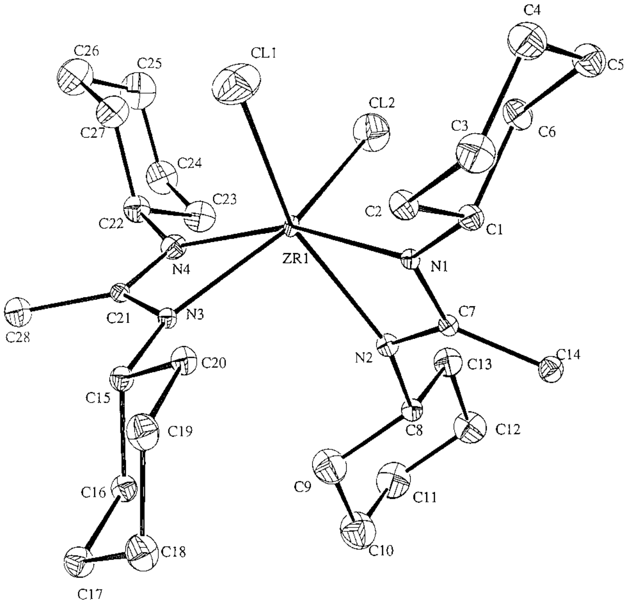

Figure 1. Molecular structure and atom-numbering scheme for Zr[CyNC(Me)NCy]$_2$Cl$_2$ (**2**) (Cy = cyclohexyl). Hydrogen atoms have been omitted for clarity.

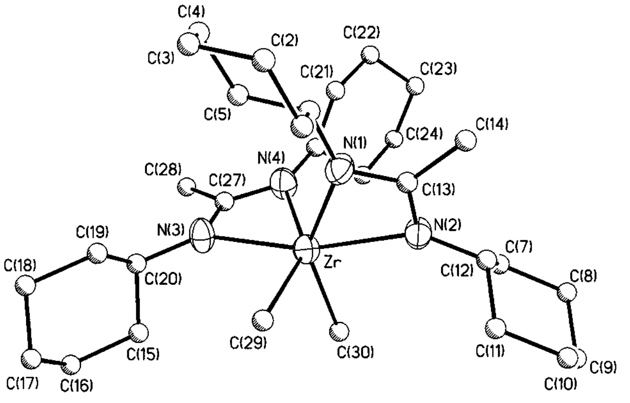

Figure 2. Molecular structure and atom-numbering scheme for Zr[CyNC(Me)NCy]$_2$(CH$_3$)$_2$ (**5**) (Cy = cyclohexyl). Carbon atoms were refined anisotropically but are depicted as spheres due to high thermal activity. Hydrogen atoms have been omitted for clarity.

Table 2. Selected Atomic Bond Distances (Å) for Compound 2

Zr−Cl1	2.426(3)	N2−C7	1.355(12)
Zr−Cl2	2.436(3)	N2−C8	1.466(12)
Zr−N1	2.228(70	N3−C15	1.470(12)
Zr−N2	2.186(8)	N3−C21	1.317(12)
Zr−N3	2.192(7)	N4−C21	1.326(12)
Zr−N4	2.234(8)	N4−C22	1.466(13)
N1−C1	1.470(12)	C7−C14	1.501(13)
N1−C7	1.325(12)	C21−C8	1.495(13)

Table 3. Selected Atomic Bond Angles (deg) for Compound 2

Cl1−Zr−Cl2	93.11(11)	C1−N1−C7	121.2(8)
Cl1−Zr−N1	90.57(20)	Zr−N2−C7	93.6(5)
Cl1−Zr−N2	105.90(21)	Zr−N2−C8	143.0(6)
Cl1−Zr−N3	94.68(21)	C7−N2−C8	121.7(8)
Cl1−Zr−N4	101.92(22)	Zr−N3−C15	141.1(6)
N1−Zr−N2	60.3(3)	Zr−N3−C21	94.9(6)
N1−Zr−N3	104.8(3)	Zr−N4−C21	122.7(8)
N1−Zr−N4	160.0(3)	Zr−N4−C2	92.7(6)
N2−Zr−N3	94.0(3)	C21−N4−C22	141.6(6)
N2−Zr−N4	106.4(3)	C21−N4−C22	121.7(8)
N3−Zr−N4	59.2(3)	N3−C21−N4	111.6(8)
Zr−N1−C1	143.2(6)	N1−C7−N2	111.8(8)
Zr−N1−C7	92.6(5)		

Table 4. Selected Atomic Bond Distances (Å) for Compound 5

Zr−N1	2.225(4)	C27−C28	1.523(7)
Zr−N4	2.231(4)	N1−C13	1.327(6)
Zr−C30	2.244(6)	N1−C6	1.463(7)
Zr−C29	2.245(6)	N2−C13	1.314(6)
Zr−N2	2.291(4)	N2−C12	1.473(6)
Zr−N3	2.284(4)	N3−C27	1.327(6)
N1−C1	1.470(12)	N3−C20	1.460(7)
N1−C7	1.325(12)	N4−C27	1.313(7)
C13−C14	1.509(8)	N4−C26	1.467(7)

Table 5. Selected Atomic Bond Angles (deg) for Compound 5

C30−Zr−C29	92.4(3)	C6−N1−Zr	139.5(3)
N1−Zr−N4	96.0(2)	C13−N2−C12	121.4(4)
N1−Zr−N2	58.2(2)	C13−N2−Zr	93.4(3)
N1−Zr−N3	113.1(2)	C12−N2−Zr	144.7(3)
N4−Zr−N2	107.3(2)	C27−N3−C20	122.3(4)
N4−Zr−N3	58.2(2)	C27−N3−Zr	92.2(3)
N2−Zr−N3	163.8(2)	C20−N3−Zr	142.4(4)
N1−Zr−C29	94.1(2)	C27−N4−C26	123.6(5)
N4−Zr−C29	145.9(2)	C27−N4−Zr	95.0(3)
C29−Zr−N2	105.7(2)	C26−N4−Zr	139.6(4)
C29−Zr−N3	87.9(2)	N2−C13−N1	112.4(4)
C13−N1−C6	124.5(4)	N4−C27−N3	112.7(5)
C13−N1−Zr	96.0(3)		

nate ligand can be divided roughly into two types, the *cis*-NCy groups (N2, N3) with a N2−Zr−N3 angle of 94.0(3)° and *trans*-NCy groups (N1, N4) with a N1−Zr−N4 angle of 160.0(3)°. The two *cis*-ZrN bond lengths are slightly longer (2.186(8), 2.192(7) Å) than the *trans*-ZrN values (2.228(7), 2.234(8) Å), and all four bond lengths are only slightly shorter (approx 0.02 Å) than for the benzamidinate complex [Me$_3$SiNC(C$_6$H$_5$)NSiMe$_3$]$_2$ZrCl$_2$.[12,19,21] A further comparison of the structures of **2**, [Me$_3$SiNC(C$_6$H$_5$)NSiMe$_3$]$_2$ZrCl$_2$, and Cp$_2$ZrCl$_2$[33] is made in Figure 3. Both the Cl−Zr−Cl angles and Zr−Cl bond lengths indicate that the bis(dicylohexylacetamidinate) ligand set in **2** appears to be a good imitation of the bis(Cp) ligand set. The longer Zr−Cl bonds for **2** compared to the bis(benzamidinate) complex perhaps reflect to a lesser degree the ionic bonding for **2**.

Complex **5** crystallized in the monoclinic space group $P2_1/n$ with the molecular geometry shown in Figure 2. Monomeric **5** displays a distorted pseudo-octahedral Zr(IV) center similar to that of **2** with methyl groups replacing the chloride ligands. Again, the Zr atom lies on an approximate 2-fold axis that bisects the C29−Zr−C30 angle, resulting in an approximately C_2-symmetric solid-state molecular geometry. Tables 4 and 5 present a summary of selected bond distances and angles for **5**.

As with **2**, the termini of the two planar amidinate ligands in **5** can be divided into two types, the *cis*-NCy groups (N1, N4) and *trans*-NCy groups (N2, N3), and the Zr−N bond lengths are slightly longer than the reported values for the bis(trimethylsilyl)benzamidinate analog. In addition, the *cis*-ZrN bond lengths (2.225(4), 2.231(4) Å) are slightly longer than the *trans*-ZrN distances (2.291(4), 2.284(4) Å). This feature is likely due to the relative steric congestion experienced by the two groups. Comparison of the structures of **5**, [Me$_3$SiNC(C$_6$H$_5$)NSiMe$_3$]$_2$ZrMe$_2$,[12,21] and Cp$_2$ZrMe$_2$[34] (Figure 3) shows a similar trend as that for the dichlorides.

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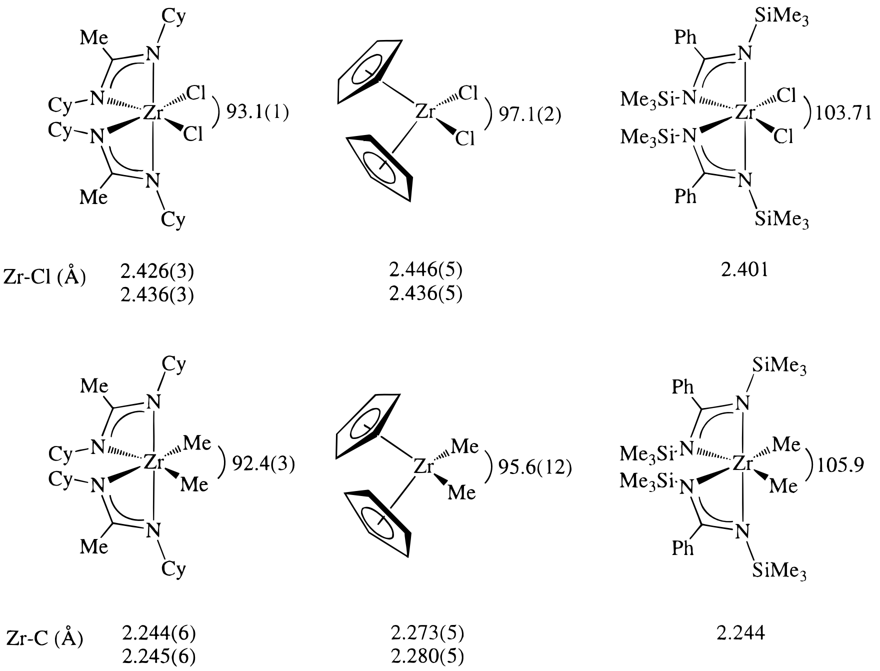
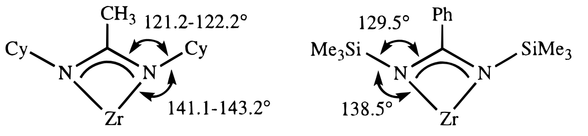


Figure 3. Comparison of the structures of Zr[CyNC(Me)NCy]$_2$Cl$_2$ (**2**), [Me$_3$SiNC(C$_6$H$_5$)NSiMe$_3$]$_2$ZrCl$_2$,[12,19,21] and Cp$_2$ZrCl$_2$[33] and the structures of Zr(CyNC(Me)NCy)$_2$Me$_2$ (**5**), [Me$_3$SiNC(C$_6$H$_5$)NSiMe$_3$]$_2$ZrMe$_2$,[12,21] and Cp$_2$ZrMe$_2$.[34] The values for the benzamidiante complexes are averages for the values reported it the literature.

Scheme 2



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However, in this case the Zr−Me bond lengths of the two amidinate complexes are identical and both are slightly shorter (approximately 0.03Å) than those of Cp$_2$ZrMe$_2$.

A comparison of the angles around the N atoms of **2** and [Me$_3$SiNC(C$_6$H$_5$)NSiMe$_3$]$_2$ZrCl$_2$ is provided in Scheme 2. In particular, the increase in the C$_{\text{bridge}}$−N−R (R = Cy, SiMe$_3$) angle and concomitant decrease in the Zr−N−R angle for the benzamidinate relative to our alkylamidinate is presumably due principally to steric interactions of the SiMe$_3$ and Ph substituents versus the corresponding Me and Cy groups.

Ethylene Polymerization Studies. Olefin polymerization catalysts were generated from bis(alkylamidinate) complexes (**1**−**5**) using MAO as a cocatalyst. The results of this study are summarized in Table 6. The most effective catalysts in this series are the Zr species **1** and **4**. Entries 2, 3, and 4 indicated a slight improvement in M_w with a decreasing ratio of Al:Zr. This result is similar to what has been noted for [Me$_3$SiNC(C$_6$H$_5$)NSiMe$_3$]$_2$ZrCl$_2$.[19] The activity of zirconium complex **2** was also superior among the series of dichloro complexes (**1**−**3**), exhibiting an activity of about twice that of the Ti derivative (e.g., 16 × 10^{3}g (mol of Zr)$^{-1}$ (atm of ethylene)$^{-1}$ h^{-1} for **2** and 7 × 10^3 g (mol of Ti)$^{-1}$ (atm of ethylene)$^{-1}$ h^{-1} for **1**). This is the same trend as that for both metallocene and bis(benzamidinate) compounds, and while the activities are comparable to the bis(benzamidinate) systems, they are substantially lower than those of the metallocene systems.[19,35−38]

Table 6. Reaction Conditions and Molecular Weight for Polyethylene Using Compounds 1−5 as Catalysts

entry	compound	catalyst (mmol)	Al:M mol ratio	M_w	M_n	M_w/M_n
1	**1**	0.0303	361:1	503 900	12 700	40
2	**2**	0.00827	1322:1	695 100	14 300	49
3	**2**	0.0347	346:1	790 100	9 060	87
4	**2**	0.0413	106:1	754 600	20 100	38
5	**3**	0.0318	385:1	754 900	49 300	15.3
6	**4**	0.00871	1254:1	865 200	42 900	20
7	**5**	0.00353	1238:1	448 700	14 400	31

In all cases, fairly high molecular weights of polyethylene (PE) were obtained but with a very broad weight distribution (M_w/M_n). Our alkylamidinate complexes gave comparable M_w values to the reported benzamidinate systems.[17,19] Unfortunately, there are no published values for the weight distribution for comparison with these systems. In contrast, a typical metallocene system gives 10^6 g (mol of M)$^{-1}$ (atm of ethylene)$^{-1}$ h^{-1} with ratios of Al/M of 10^2−10^4 and M_w/M_n values of about 2.[35−38]

Mixed cyclopentadienyl-amidinato Ti, Zr, and Hf systems have been prepared and the activity of the Ti and Zr compounds toward PE formation using MAO as a cocatalyst have been investigated.[15,16,39] These materials had activities that were similar to the benzamidinate and our alkylamidinate analogs but yielded low molecular weight PE.

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A comparison of the two alkylamidinates in this report and the effect of replacing the chlorides on Zr with methyl groups is provided by entries 2, 6, and 7 of Table 6. These results suggest that **4**, which has a ^{t}Bu substituent on the amidinate ligand, may be superior to **2** in terms of the M_w of the resultant PE. They also indicate that the dichloro complex is a better catalyst precursor than the corresponding dialkyl compound.

In summary, amidinate ligands have proven to be useful in the preparation of a family of six-coordinate group 4 complexes. A combination of X-ray crystallographic and spectroscopic studies confirm the C_2-symmetric structures of these compounds and indicate the fluxional nature of these species in solution. With MAO as a cocatalyst, complexes **1**−**5** polymerize ethylene to yield relatively high M_w PE but very broad polydispersities. Further experiments are underway to investigate the effects of ligand and olefin variation, cocatalyst, and ethylene pressure on this process. In addition to these studies, our continuing investigations are oriented at further revealing the steric and electronic features that influence the reactivity of transition metal amidinate compounds.

Experimental Section

General Considerations. All manipulations were carried out in either a nitrogen-filled drybox or under nitrogen using standard Schlenk-line techniques. Solvents were distilled under nitrogen from Na/K alloy. Deuterated benzene was distilled from potassium. MeLi (1.4 M in diethyl ether), ^{t}BuLi (1.7 M in hexane), and 1,3-dicyclohexylcarbodiimide were purchased from Aldrich and used without further purification. Ethylene (CP grade) was purchased from Air Products and used as received. Methylaluminoxane (6.7 wt % Al solution in toluene, $d = 0.88$g/mL) was purchased from Akzo Nobel and used as received. $TiCl_4(THF)_2$, $ZrCl_4(THF)_2$, and $HfCl_4(THF)_2$ were prepared by literature procedures. Thermal analyses were performed with a Polymer Laboratories STA1500HF. All measurements were carried out with an alumina sample pan. Molecular weight determinations of the polymers was performed on a Waters 150C GPC with Shodex AT 10^3, 10^4, 10^5, and 10^6 Å columns at 140 °C with 1,2,4-trichlorobenzene as the mobile phase. ^{1}H NMR spectra were run on a Gemini 200 MHz spectrometer with deuterated benzene as the solvent and internal standard. All elemental analyses were run on a Perkin-Elmer PE CHN 4000 elemental analysis system.

Preparation of $Ti[C_6H_{11}NC(Me)NC_6H_{11}]_2Cl_2$ (1), $Zr[C_6H_{11}NC(Me)NC_6H_{11}]_2Cl_2$ (2), and $Hf[C_6H_{11}NC(Me)NC_6H_{12}]_2Cl_2$ (3). A 100 mL Schlenk flask was charged with 1,3-dicyclohexylcarbodiimide (0.87g, 4.2 mmol), diethyl ether (30 mL), and a stir bar. To this solution was added MeLi (3 mL, 4.2 mmol, 1.4 M in diethyl ether) dropwise via syringe at room temperature. The solution was stirred for 30 min and then added dropwise via pipette to a yellow slurry of $TiCl_4(THF)_2$ (0.70 g, 2.1 mmol) in diethyl ether (10 mL). An immediate color change to deep red-purple was observed. The resulting solution was then stirred overnight and filtered to remove LiCl. Evaporation of the solvent yielded 0.66 g (1.2 mmol, 56%) of a very dark red-purple solid. Recrystallization from hexane−diethyl ether at −30 °C afforded an analytically pure dark purple microcrystalline solid.

Spectroscopic data for **1**: ^{1}H NMR (C_6D_6, ppm) 3.35−3.15 (br, C_6H_{11}, 4H), 2.40−1.10 (m, C_6H_{11}, 40H), 1.49 (s, CH_3, 6H); ^{13}C NMR (C_6D_6, ppm) 175.6 (s, NC(Me)N), 60.3, 33.9, 26.3, 25.9, (4s, C_6H_{11}), 10.3 (s, CH_3). Anal. Calcd for $C_{28}H_{50}N_4Cl_2Ti$: C, 59.89; H, 8.97; N, 9.98. Found: C, 58.94; H, 9.09; N, 9.81.

Following a procedure similar to the synthesis of **1,** analytically pure yellow-green crystals of **2** were isolated from ether at −30 °C (64%) and colorless crystals of **3** were isolated from hexane/diethyl ether at −30 °C (68%).

Spectroscopic data for **2**: ^{1}H NMR (C_6D_6, ppm) 3.06 (br, C_6H_{11}, 4H), 2.15−1.15 (m, C_6H_{11}, 40H), 1.51 (s, CH_3, 6H). ^{13}C NMR (C_6D_6, ppm) 178.1 (s, NC(Me)N), 57.4, 35.0, 26.2, 25.8 (4s, C_6H_{11}), 10.7 (s, CH_3); IR (KBr pellet, cm^{-1}) 1655 (s, C−N stretch). Anal. Calcd for $C_{28}H_{50}N_4Cl_2Zr$ (**2**): C, 55.60; H, 8.33; N, 9.26. Found: C, 55.54; H, 8.62; N, 9.10.

Spectroscopic data for **3**: ^{1}H NMR (C_6D_6, ppm) 3.30−3.10 (br, C_6H_{11}, 4H), 2.15−1.10 (m, C_6H_{11}, 40H), 1.52 (s, CH_3, 6H); ^{13}C NMR (C_6D_6, ppm) 177.6 (s, NC(Me)N), 57.1, 35.0, 26.2, 25.8 (4s, C_6H_{11}), 11.0 (s, CH_3). Anal. Calcd for $C_{28}H_{50}N_4Cl_2Hf$ (**3**): C48.59; H 7.28; N 8.09. Found: C48.41; H 7.26; N 8.10.

Preparation of $Zr[C_6H_{11}NC(CMe_3)NC_6H_{11}]_2Cl_2$ (4). Following a procedure similar to the synthesis of **1,** ^{t}BuLi (3.1 mL, 5.3 mmol) and 1,3-dicyclohexylcarbodiimide (l.09 g, 5.3 mmol) were combined in diethyl ether (30 mL). This solution was then added to a slurry of $ZrCl_4(THF)_2$ (1.0 g, 2.7 mmol) in diethyl ether (l0 mL). The resulting solution was initially bright orange in color, but after stirring overnight, it became yellow. Filtration, evaporation of the solvent, and recrystallization from toluene at −30 °C yielded l.06 g (58%) of yellow microcrystalline **4**.

Spectroscopic data: ^{1}H NMR (C_6D_6, ppm) 3.85 (br, C_6H_{11}, 4H), 2.50−1.10 (m, C_6H_{11}, 40H), 1.23 (s, CMe_3, 18H); ^{13}C NMR (C_7D_8, ppm) 263 K 185.01(s), 57.97, 55.34 (2br s) 40.97 (s), 36.24, 35.24, 33.72 (3 br), 30.30 (s), 26.85 (br), 26.00 (br); 300 K 185.06 (s) 56.30 (br) 40.92 (s) 35.12 (br), 30.32 (s), 26.53 (s), 25.89 (s); 343 K 185.13 (s), 57.08 (s), 40.93 (s), 34.93 (s), 30.58 (s), 26.51 (s), 25.79 (s). Anal. Calcd for $C_{34}H_{62}N_4Cl_2Zr$: C, 59.27; H, 9.07; N, 8.13. Found: C, 59.29; H, 9.24: N, 7.98.

Preparation of $Zr[C_6H_{11}NC(Me)NC_6H_{11}]_2Me_2$ (5). A 50 mL Schlenk flask was charged with **2** (0.17 g, 0.28 mmol), diethyl ether (15 mL), and a stir bar. The solution was cooled to −78 °C, and MeLi (0.40 mL, 0.56 mmol) was added dropwise via syringe. After the mixture was warmed to room temperature, the solvent was removed in vacuo and the residue was extracted with 20 mL of hexane and filtered. Concentration to approximately 10 mL and cooling to −30 °C gave clear, colorless crystals (0.08 g, 0.14 mmol, 50%).

Spectroscopic data: ^{1}H NMR (C_6D_6, ppm) 3.20−3.05 (br, C_6H_{11}, 4H), 2.00−1.10 (m, C_6H_{11}, 40H), 1.66 (s, NC(CH_3)N, 6H), 0.88 (s, Zr-CH_3, 6H); ^{13}C NMR (C_6D_6, ppm) 177.35 (s, NC-(Me)N) 57.08, 35.45, 26.32, 26.18 (4s, C_6H_{11}), 42.74 (s, Zr−CH_3), 10.70 (s, NC(CH_3)N). Anal. Calcd for $C_{30}H_{56}N_4Zr$: C, 63.89; H, 10.01; N, 9.93. Found: C, 63.69; H, 9.93; N, 9.88.

Ethylene Polymerization Experiments. In a glovebox, a Schlenk flask equipped with a teflon stopcock was charged with a weighed quantity of the bis(alkylamidinate) metal complex, measured amounts of MAO and toluene, and a stir bar. The flask was sealed, removed from the glovebox, and attached to a high-vacuum line. Gaseous ethylene was admitted to the vessel with rapid stirring, and the pressure was maintained at 1 atm by means of a bubbler. After a measured time interval (2 h), the reaction was quenched by addition of acidified methanol. The polymeric product was collected by filtration, washed and sonicated in 6 M HCl for 1 hr, filtered and washed sequentially with methanol and hexane, then dried overnight under vacuum.

Crystallographic Study of 5. A suitable crystal of **5** was mounted, under an inert atmosphere, in a thin-walled, glass capillary. Systematic absences and the unit-cell parameters are uniquely consistent for the reported space group. No absorption correction was required ($\mu = 3.6$ cm $^{-1}$). The structure was solved by direct methods and refined by full-matrix least-squares procedures based on $|F|^2$. All non-hydrogen atoms were refined with anisotropic displacement coefficients. Hydrogen atoms were treated as idealized contributions. All computations used the SHELXTL (5.03) program library (G. Sheldrick, Siemens XRD, Madison, WI).

Crystallographic Study of 2. Data were collected on a Rigaku AFC6S diffractometer with graphite-monochromated Cu Kα radiation at −153 °C using the $\omega-2\theta$ scan technique to a maximum 2θ value of 50° for crystals mounted on glass fibers. Cell constants and orientation matrices were obtained from the least-squares refinement of 24 carefully centered high-angle reflections. Absorption corrections (ψ scan) were made. The minimum and maximum transmission factors were 0.238 668 and 0.372 842. The structure was solved by direct methods. The non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were located in the difference Fourier maps and refined isotropically in the case of a favorable observation/parameter ratio. The final cycle of full-matrix least-squares refinement was based on the number of observed reflections with $[I > 2.5\sigma(I)]$. All calculations were performed using the NRCVAX package.

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Supporting Information Available: Text providing a description of the structural solutions, tables of atomic positions, thermal parameters, crystallographic data, and bond distances and angles, ORTEP drawings for compound **2** and **5**, and GPC traces for the polymers reported in Table 6 (27 pages). Ordering information is given on any current masthead page.

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