Neutral and Cationic Group 4 Complexes Containing Bis(borylamide) Ligands, $[R_2BNCH_2CH_2NBR_2]^{2-}$ (R = 2,4,6-i-$Pr_3C_6H_2$, M = Zr; R = Cyclohexyl, M = Ti, Zr, Hf)

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Reaction of $Li_2(TripBen)(THF)_4$ ($[(2,4,6\text{-i-}Pr_3C_6H_2)_2BNCH_2CH_2NB(2,4,6\text{-i-}Pr_3C_6H_2)_2]^{2-}$ = $(TripBen)^{2-}$) with $ZrCl_4(THF)_2$ in toluene cleanly provides $(TripBen)ZrCl_2$. $(TripBen)ZrCl_2$ can be alkylated with Grignard reagents to yield the dimethyl (**2**), diethyl (**3**), and dibutyl (**4**) derivatives, $(TripBen)ZrR_2$. The structure of $(TripBen)Zr(CD_3)_2$ reveals that π bonding between boron and nitrogen results in one Trip ring on each boron being oriented over the two alkyl groups. The reaction between $(TripBen)ZrMe_2$ and $B(C_6F_5)_3$ in pentane yields colorless crystals of $\{(TripBen)ZrMe\}\{MeB(C_6F_5)_3\}$ (**5a**). The dialkyl complexes **2**−**4** react with $[HNMe_2Ph][B(C_6F_5)_4]$ in toluene to yield free dimethylaniline and species that are identical to **5a** according to NMR spectra. $(CyBen)M(CH_2SiMe_3)_2$ complexes ($[(cyclohexyl)_2BNCH_2CH_2NB(cyclohexyl)_2]^{2-}$ = $(CyBen)^{2-}$) are prepared by the reaction between $Li_2(CyBen)(ether)$ and $M(CH_2SiMe_3)_2Cl_2(ether)_x$ (M = Ti, Zr, or Hf). $(CyBen)MI_2$ complexes are formed upon treating $(CyBen)M(CH_2SiMe_3)_2$ complexes with iodine. A variety of $(CyBen)MR_2$ species can be prepared, including those in which the alkyl contains β protons. The molecular structure of $(CyBen)Zr(CH_2CH_3)_2$ shows it to be a relatively symmetric species in which one cyclohexyl ring on each boron is located directly over the two ethyl ligands. Diisobutyl complexes $(CyBen)M(CH_2CHMe_2)_2$ react with $[Ph_3C][B(C_6F_5)_4]$ in chlorobenzene at −30 °C to give the cations $[(CyBen)M(CH_2CHMe_2)][B(C_6F_5)_4]$, which are believed to be stabilized by coordination of chlorobenzene or toluene. Chlorobenzene solutions of $[(CyBen)M(CH_2CHMe_2)(S)][B(C_6F_5)_4]$ (M = Zr, Hf; S = chlorobenzene) polymerize 225 equiv of 1-hexene quantitatively at −30 °C to give regioregular poly(1-hexene) of high molecular weight ($M_n = (0.4-1.3) \times 10^5$ g/mol) and high polydispersity (5−6).

Introduction

Numerous studies of homogeneous Ziegler−Natta catalysis by group 4 metallocenes have lead to the identification of alkyl cations $[Cp_2MR]^+$ (Cp = cyclopentadienyl-like ligand; M = Ti, Zr, Hf; R = alkyl) as the chain-propagating species.[1−3] An ever growing number of studies concern the design of specific mono(cyclopentadienyl) or bis(cyclopentadienyl) ligand environments that lead to isotactic poly-α-olefins, or syndiotactic poly-α-olefins or even “blocky” variations.[4] The success of this chemistry has elicited questions concerning the development of non-cyclopentadienyl complexes that share some of the properties of metallocenes, in particular, olefin polymerization activity. In this regard, chelating bis(alkoxide)[5−7] and bis(amido)[8−19] complexes have been receiving increased attention.

We recently reported the synthesis of titanium and zirconium complexes containing the di(borylamido) ligand $[Mes_2BNCH_2CH_2NBMes_2]^{2-}$ ($(MesBen)^{2-}$; Mes = mesityl). We had hoped that dialkyl complexes of the type $(MesBen)MR_2$ would mimic $(cyclopentadienyl)_2MR_2$ species in their ability to form cationic species that initiate the polymerization of terminal olefins. The $(MesBen)^{2-}$ ligand is a structurally and electronically

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unusual bidentate diamido ligand, since two mesityl groups should sterically protect two or three coordination sites in a plane roughly perpendicular to the NCCN ligand backbone as a consequence of N−B π bonding.[20] Unfortunately, (MesBen)TiR_2 and especially (MesBen)-ZrR_2 species were found to be relatively unstable. The mode of decomposition consisted of CH activation in the ortho methyl group in the mesityl substituent and loss of 2 equiv of alkane. $B(C_6F_5)_3$ was found to bind to a methyl group in (MesBen)MMe_2 complexes in dichloromethane, but such compounds showed little polymerization activity toward ethylene at 25 °C and 1−2 atm, presumably as a consequence of strong binding of $[B(C_6F_5)_3Me]^-$ to the metal.

In this paper, we report two variations of $[R_2BNCH_2CH_2NBR_2]^{2-}$ ligands and group 4 metal complexes thereof, one in which R = 2,4,6-i-$Pr_3C_6H_2$ ((TripBen)$^{2-}$) and another in which R = cyclohexyl ((CyBen)$^{2-}$). The large *o*-isopropyl substituents in TripBen might be expected to produce a more crowded coordination environment and thereby weaken the binding of an anion such as $[MeB(C_6F_5)_3]^-$ to the metal center. The (CyBen)$^{2-}$ ligand was prepared because it was simple to do so, because we expected its complexes to be highly crystalline, and because cyclohexyl has no CH bonds that should be activated readily. The small size of the cyclohexyl groups also would test the possible benefits of a more *open* coordination sphere. We report here the synthesis and solution behavior of neutral and cationic (TripBen)ZrR_2 complexes and (CyBen)MR_2 complexes (M = Ti, Zr, and Hf) and a brief exploration of their polymerization activity with ethylene and 1-hexene.

Results

The Synthesis of H_2(TripBen) and (TripBen)Zr Complexes. $[Trip_2BNHCH_2CH_2NHBTrip_2]$ (H_2(TripBen)) may be prepared in a manner analogous to that reported for H_2(MesBen), substituting $Trip_2BF$ for Mes_2BF (Mes = 2,4,6-trimethylphenyl; eq 1). Although the

$$H_2NCH_2CH_2NH_2 \xrightarrow[(2)\ 2\ Trip_2BF]{(1)\ 2\ BuLi/THF} Trip_2BNHCH_2CH_2NHBTrip_2 \quad (1)$$

high solubility of H_2(TripBen) in pentane hampers its isolation in good yield, it need not be isolated. Deprotonation of crude H_2(TripBen) with 2 equiv of butyllithium in pentane containing a small amount of THF proceeds cleanly to yield colorless crystals of Li_2(TripBen)-$(THF)_4$. Room temperature ^1H NMR spectra of H_2-(TripBen) and $Li_2(TripBen)(THF)_4$ consist of two sets of sharp isopropyl resonances; other resonances are broad. At ~70 °C, two chemically inequivalent triisopropylphenyl groups may be readily identified and other resonances sharpen to patterns consistent with a freely rotating symmetric molecule. We propose that broad resonances result from hindered aryl group rotation about the $B-C_{ipso}$ bonds as a consequence of a steric interaction between opposing *o*-isopropyl groups, although there are other possibilities for the lithium derivative such as rearrangement of the Li_2N_2 core.

Reaction of $Li_2(TripBen)(THF)_4$ with $ZrCl_4(THF)_2$ in toluene cleanly provides (TripBen)$ZrCl_2$ (**1**), which is isolated in 85−90% yield from pentane as colorless prisms containing 1 equiv of pentane per zirconium (eq 2). All resonances except those of the *p*-$CHMe_2$ groups

$$Li_2(TripBen)(THF)_4 + ZrCl_4(THF)_2 \xrightarrow{toluene} \underset{\mathbf{1}}{(TripBen)ZrCl_2} \quad (2)$$

are broadened in the room temperature ^1H NMR spectrum of **1**. At 75 °C, a readily interpretable ^1H NMR spectrum is obtained in which a single sharp backbone resonance is observed along with six doublets for the isopropyl methyl groups. Six doublet resonances are consistent with slow rotation about the B−N bonds and slow rotation about the $B-C_{aryl}$ bonds on the NMR time scale. We assume that the structure of **1** is analogous to that of the dimethyl derivative (see below and Figure 1) and that at low temperatures some lower symmetry conformation (e.g., a preference for the $Trip_2B$ groups to be oriented as shown in Figure 1) leads to more complex spectra.

Reaction of **1** in ether at −40 °C with the appropriate Grignard reagent cleanly provides the dimethyl (**2**), diethyl (**3**), and dibutyl (**4**) derivatives (eq 3). The

$$(TripBen)ZrCl_2 + 2RMgCl \xrightarrow{ether/-40\ °C} (TripBen)ZrR_2 \quad (3)$$
$$R = Me\ (\mathbf{2}),\ Et\ (\mathbf{3}),\ n\text{-}Bu\ (\mathbf{4})$$

dimethyl complex is isolated in high yield from pentane as colorless crystals that contain 1 equiv of pentane per Zr. However, **3** and **4** crystallize as fine, fibrous needles which are difficult to isolate. They are more easily recovered as off-white powders by exhaustive removal of pentane from pentane solutions in vacuo. With the exception of the distinct *p*-$CHMe_2$ groups, ^1H and ^{13}C NMR spectra of **2**, **3**, and **4** are again broad at room temperature, presumably as a consequence of various hindered rotations, as discussed above for **1**. However, all broad resonances sharpen upon heating a sample to 50−70 °C to give a spectrum consistent with a molecule that contains two planes of symmetry but in which rotation of the Trip group about the B−C bond and rotation of the $B(Trip)_2$ group about the B−N bond are still slow on the NMR time scale, as observed in **1**. Resonances for the coordinated alkyl groups are also broadened and in the case of **3** and **4** are partially obscured by the CH*Me*$_2$ resonances. In order to confirm the identity of the ethyl resonances, (TripBen)$Zr(CD_2CD_3)_2$ was prepared and shown to have broad ^2H NMR resonances for the α and β deuterons in the ethyl groups at δ 0.47 and 0.96 ppm, respectively, at room temperature, which sharpen with increasing temperature. It is important to note that **2**, **3**, and **4** are all much more thermally stable toward formation of alkane via activation of benzylic protons than (MesBen)ZrR_2 complexes,[11] presumably because benzylic protons are relatively inaccessible in the (TripBen)$^{2-}$ ligand. However, (TripBen)ZrR_2 complexes will decompose upon heating, with the rate of decomposition of **4** being qualitatively the fastest.

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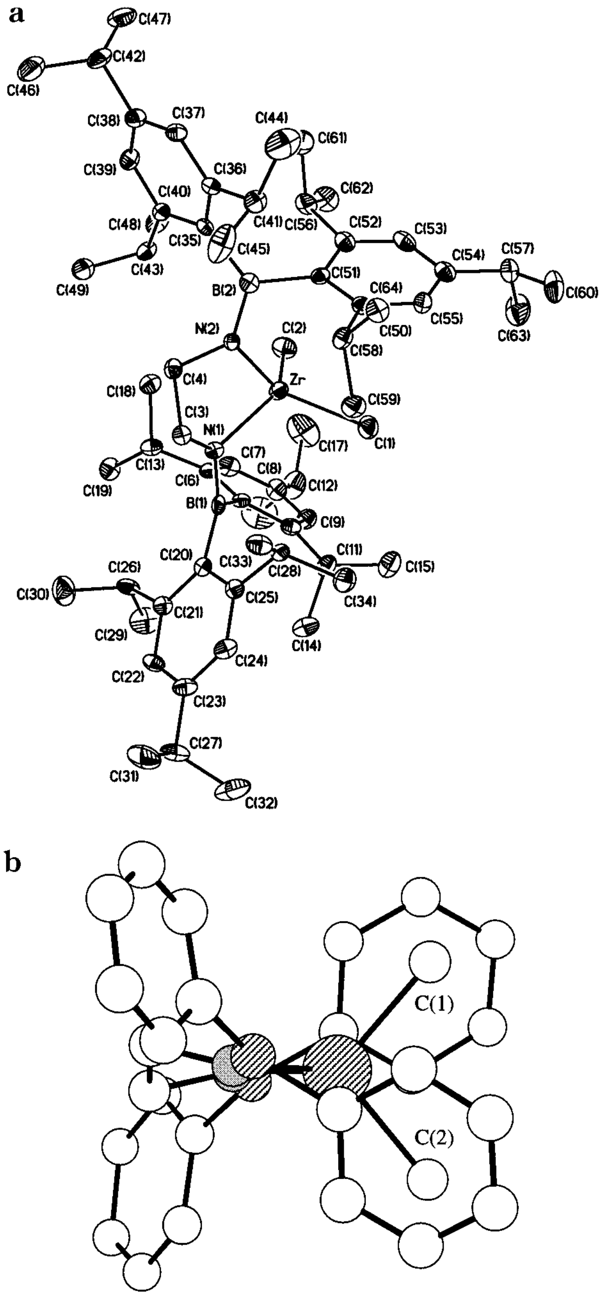

Figure 1. (a) ORTEP drawing of the structure of [TripBen]Zr(CD_3)$_2$. (b) Chem3D top view of the structure of [TripBen]Zr(CD_3)$_2$ with the isopropyl groups removed.

Two views of the structure of (TripBen)Zr(CD_3)$_2$ are shown in Figures 1a and 1b. (See also Tables 1 and 2. The choice of the CD_3 over the CH_3 derivative was circumstantial.) A space-filling view including hydrogen atoms shows that this molecule is impressively crowded. The triisopropylphenyl rings on a given boron are twisted with respect to one another, and the two $Trip_2B$ units are twisted with respect to one another. Therefore, two triisopropylphenyl rings are located approximately above or below a methyl group on the metal. The TripBen ligand symmetrically chelates the zirconium center with a bite angle of 78.4(2)° and Zr−N distances of 2.102(4) and 2.111(4) Å (Table 2). These distances are similar to those found in the doubly metalated species formed upon decomposition of (MesBen)ZrR_2 (2.088(6) and 2.106(6) Å).[11] Borylamide B−N π-interactions are significant, as shown by the B−N distances (1.404(8) and 1.398(8) Å). The Zr−Me distances (2.229(6) and 2.232(6) Å) are essentially identical to the Zr−C distance in (t-Bu_3SiNH)$_3$ZrMe (2.231(7) Å).[21] The short Zr···C(18) and Zr···C(59) separations (3.84 and 3.85 Å) and space-filling views reveal that the sides of the coordination wedge are effectively blocked by the methyl groups of the *o*-isopropyl substituents. Furthermore, the relatively short separations between the isopropyl and metal-bound methyl groups (C(1)···C(59) = 3.37 Å and C(2)···C(18) = 3.36 Å) show that the groups in the coordination wedge strongly feel the presence of the aryl *o*-isopropyl substituents, which may help explain the C(1)−Zr−C(2) angle of only 100.6(2)° compared to a

Table 1. Crystallographic Data, Collection Parameters, and Refinement Parameters for (TripBen)Zr(CD_3)$_2$·pentane and (CyBen)Zr(CH_2CH_3)$_2$ (10a)

	(TripBen)Zr(CD_3)$_2$	(CyBen)Zr(CH_2CH_3)$_2$
empirical formula	$C_{69}H_{114}B_2N_2Zr$	$C_{30}H_{58}B_2N_2Zr$
fw	1084.46	559.62
diffractometer	Siemens SMART/CCD	Siemens SMART/CCD
cryst color, morphology	colorless, plate	colorless, prismatic
cryst dimens, mm	0.30 × 0.22 × 0.12	0.28 × 0.24 × 0.18
cryst syst	triclinic	triclinic
a, Å	11.6475(7)	9.9911(2)
b, Å	16.4594(10)	12.23940(10)
c, Å	18.4034(10)	13.82900(10)
α, deg	101.0020(10)	71.1280(10)
β, deg	100.0960(10)	85.0270(10)
γ, deg	98.1700(10)	77.2990(10)
V, Å^3	3352.9(3)	1560.80(4)
space group	$P\bar{1}$	$P\bar{1}$
Z	2	2
D_{calc}	1.074 g/cm^3	1.191 g/cm^3
F_{000}	1184	604
μ(Mo Kα), mm^{-1}	0.202	0.372
scan type	ω scans	ω scans
temp, K	188(2)	183(2)
total no. unique reflns	7126	4364
no. of variables	643	317
R	0.0654	0.0345
R_w	0.0927	0.0970
GoF	1.093	1.234

Table 2. Selected Bond Distances (Intramolecular Contacts) (Å) and Angles (deg) for (TripBen)Zr(CD_3)$_2$ and (CyBen)Zr(CH_2CH_3)$_2$

	(TripBen)Zr(CD_3)$_2$	(CyBen)Zr(CH_2CH_3)$_2$
	Distances	
Zr−N(1)	2.102(4)	2.067(2)
Zr−N(2)	2.111(4)	2.070(2)
Zr−C(1)	2.232(6)	2.247(3)
Zr−C(2)	2.229(6)	2.253(3)
N(1)−B(1)	1.404(8)	1.392(4)
N(2)−B(2)	1.398(8)	1.398(4)
Zr···C(59)	3.84	
Zr···C(18)	3.85	
C(1)···C(59)	3.37	
C(2)···C(18)	3.36	
	Angles	
N(1)−Zr−N(2)	78.4(2)	78.87(2)
C(1)−Zr−C(2 or 3)	100.6(2)	119.53(12)
N(1)−Zr−C(1)	112.2(2)	115.13(10)
N(2)−Zr−C(1)	127.6(2)	111.12(11)
N(1)−Zr−C(2 or 3)	126.5(2)	110.92(11)
N(2)−Zr−C(2or 3)	113.4(2)	114.43(11)
Zr−C(1)−C(2)		114.8(2)
Zr−C(3)−C(4)		119.7(2)

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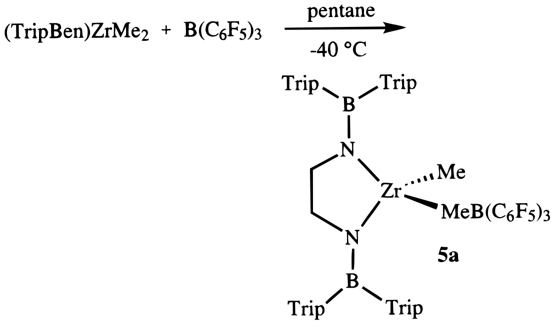
C−Zr−C angle of ~120° in a related CyBen complex (see below). However, a C(1)−Zr−C(2) angle of ~100° is similar to that typically found in a dialkylzirconocene[22] or recently in a diamido complex reported by McConville.[9]

Generation of "Cations". The reaction between **2** and $B(C_6F_5)_3$ in pentane results in formation of an oil that crystallizes upon standing at −40 °C to afford colorless crystals of **5a** in 87% yield (eq 4). In addition to a slightly broadened AA′BB′ pattern ascribed to the ligand backbone in **5a**, 10 or 11 $CHMe_2$ resonances can be detected out of the 12 expected for an unsymmetrically substituted coordination wedge, i.e., no $CHMe_2$ groups within a given $BTrip_2$ unit are equivalent and the two $BTrip_2$ groups are related by a mirror plane. On the basis of several observations of "partial abstraction" of a methyl group by $B(C_6F_5)_3$ in zirconium methyl complexes[23−26] and recently in a zirconium complex that contains a tridentate diamido ether ligand,[16] the $[MeB(C_6F_5)_3]^-$ "ligand" could be occupying one of the two carbon-based coordination positions in the pseudotetrahedral species, as shown in eq 4. Heating an NMR sample of **5a** in toluene leads to a symmetric backbone on the NMR time scale, a fact that would be consistent with either loss of the $B(C_6F_5)_3$ group or the $[MeB(C_6F_5)_3]^-$ ion on the NMR time scale. However, other explanations are possible and are delayed until the discussion of **5b** below.



(4)

The dialkyls **2**−**4** react with $[HNMe_2Ph][B(C_6F_5)_4]$ in toluene to yield species that behave qualitatively like **5a** behaves (eq 5). The dimethylaniline generated in the

$$(\mathrm{TripBen})\mathrm{ZrR}_2 + [\mathrm{HNMe}_2\mathrm{Ph}][\mathrm{B}(\mathrm{C}_6\mathrm{F}_5)_4] \xrightarrow[-\mathrm{RH} \atop -\mathrm{Me_2NPh}]{\text{toluene}/-40\ ^\circ\mathrm{C}} [(\mathrm{TripBen})\mathrm{ZrR}][\mathrm{B}(\mathrm{C}_6\mathrm{F}_5)_4] \quad (5)$$

$$\mathrm{R} = \mathrm{Me}\ (\mathbf{5b}),\ \mathrm{Et}\ (\mathbf{6}),\ \text{n-Bu}\ (\mathbf{7})$$

protonolysis does *not* coordinate to the metal in cations **5b**, **6**, and **7**; the chemical shift of its methyl groups is characteristic of "free" dimethylaniline. We have not been able to isolate **5b**, **6**, or **7** in crystalline form, although concentration of a toluene solution of **5b** to an oil followed by exhaustive washing of this oil with pentane provides a sample of **5b** as a powder. ^1H NMR spectra of this solid are identical to those taken of **5b** prepared in situ, except that resonances corresponding to dimethylaniline are absent. Spectra of **5b** generated in chlorobenzene-d_5 are similar to those generated in toluene-d_8 and similar to NMR spectra of **5a**. In fact, ^1H and ^{13}C NMR spectra of a mixture of **5a** and **5b**, separately prepared in toluene-d_8, show only resonances for a single cationic species between 0 and 60 °C. It seems unlikely that the two anions would behave analogously in terms of binding to the metal to produce an unsymmetric species. Therefore, the asymmetry cannot be ascribed to coordination of the anion to the metal, i.e., the cation in **5a** and **5b** are one in the same. Several explanations that do not involve anion binding are possible, however. (i) The solvent (toluene or chlorobenzene) might coordinate to the metal. (ii) One (reversibly) or two of the methyl groups in an *o*-isopropyl group might be interacting in an agostic manner[27] with the metal center. In the model shown in Figure 1a, C(18) (for example) can virtually take the place of C(2) after a slight rotation about the $B-C_{ipso}$ bond. (iii) The cation may actually be a nonplanar three-coordinate species that inverts its configuration via a planar form and, therefore, yield NMR spectra at higher temperatures that are consistent with a higher symmetry species and a symmetric pattern for the backbone proton and carbon atoms. In the absence of an X-ray structure, we have little hope of distinguishing between these possibilities. Unfortunately, no suitable crystals have been obtained to date.

Attempts to generate cationic species by adding $[Ph_3C][B(C_6F_5)_4]$ to TripBen complexes appeared to fail. No species analogous to those prepared using $B(C_6F_5)_3$ or $[HNMe_2Ph][B(C_6F_5)_4]$ were obtained.

Room temperature ^1H NMR spectra of **6** and **7** in toluene-d_8 exhibit an additional feature not present in the spectra of **5a** and **5b**. Each displays a slightly broadened upfield resonance, which in the case of **6** is a broadened triplet at δ −0.64. In $[(TripBen)Zr(CD_2CD_3)][B(C_6F_5)_4]$, the upfield resonance is absent. We assign the upfield resonance to the β-H atoms of the ethyl ligand. This situation is related to that observed in complexes of the type $[Cp_2M(R)(PMe_3)][BPh_4]$ (R = Et, n-Bu, i-Bu),[28,29] in which the β-H resonance is shifted upfield in each alkyl as a consequence of β-agostic interactions.[27] The dense ^{13}C NMR spectrum of **6** unfortunately prevents unambiguous assignment of the $ZrCH_2CH_3$ resonances and confirmation of β-agostic behavior. The AA′BB′ pattern of the ligand backbone in **5b**, **6**, and **7** coalesces into a broad resonance in the temperature range 60−80 °C; the exact coalescence temperature depends on the nature of the complex. Further sharpening of the backbone resonance is observed with increasing temperature. Unfortunately, additional resonances irreversibly grow in that signal the onset of decomposition, and the origin of the temperature-dependence remains obscure. In addition to temperature dependent processes analogous to those

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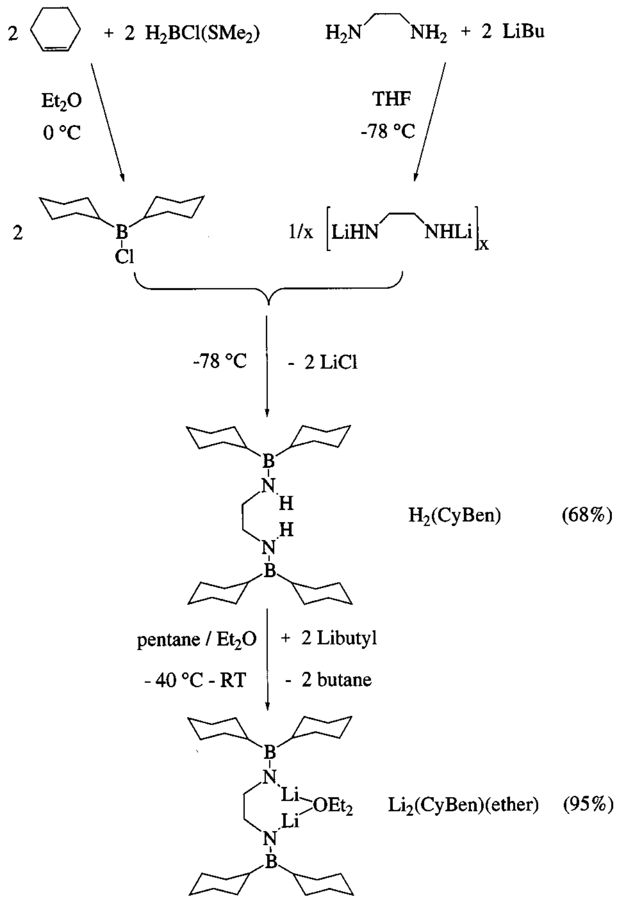
Scheme 1. Synthesis of H_2(CyBen) and Li_2(CyBen)(ether)



proposed in **1**, various possible agostic interactions would also lead to temperature-dependent NMR behavior.

Solutions of **5b**, **6**, and **7** are not active for the polymerization of ethylene. Only traces of polyethylene are recovered from solutions exposed to one atm of ethylene over a period of 15 min to 1 h. We speculate that agostic interactions prevent olefin attack at the metal, a circumstance that is encouraged by the extremely crowded TripBen coordination sphere. This finding led to our increased interest in the more open diamido coordination environment offered by CyBen complexes.

Synthesis of H_2(CyBen) and (CyBen)Zr Complexes. Hydroboration of cyclohexene with commercially available $H_2BCl(SMe_2)$ is a convenient route to an ethereal solution of Cy_2BCl,[30] which may be added to a suspension of $LiNHCH_2CH_2NHLi$ (generated in situ from butyllithium and ethylenediamine) to yield crystalline H_2(CyBen) in ~70% yield (Scheme 1). The lithium salt, Li_2(CyBen)(ether), may be prepared in 95% yield by deprotonating H_2(CyBen) with 2 equiv of butyllithium in pentane containing ~5% ether (Scheme 1). Both syntheses can be carried out readily on a large scale.

Addition of Li_2(CyBen)(ether) to $TiCl_4$ in pentane does not lead to clean formation of (CyBen)$TiCl_2$. Although (CyBen)$TiCl_2$ may be isolated from the reaction mixtures, a significant amount of a byproduct that is believed to be $(CyBen)_2Ti$ severely limits this method as a synthetic route to (CyBen)$TiCl_2$. Reaction of $ZrCl_4$ or $ZrCl_4(THF)_2$ with Li_2(CyBen)(ether) in a variety of solvents in our hands does not cleanly lead to the desired dichloro complexes (CyBen)$ZrCl_2(THF)_x$ ($x = 1$ or 2). These findings contrast with those obtained in the MesBen[11] or TripBen systems and we assume result from a smaller steric demand of the CyBen ligand. Similar results have been reported for other diamido ligand systems.[12]

Preliminary studies showed that Li_2(CyBen)(ether) reacts with $ZrR_2Cl_2(ether)_2$ (R = CH_2Ph, CH_2CMe_3)[31] to provide the corresponding (CyBen)ZrR_2 complexes, but addition of Li_2(CyBen)(ether) to solutions of $M(CH_2SiMe_3)_2Cl_2(ether)_2$[32] prepared in situ proved to be the most convenient synthetic entry into group 4 metal chemistry (eq 6). The zirconium and hafnium derivatives may be isolated in 70−80% yield as colorless crystals from pentane, but the yield of the titanium derivative (**8c**) is only ~50%. The (trimethylsilyl)methyl protecting groups can be cleaved off by adding 2 equivalents of I_2 to afford **9a** and **9b** as colorless crystals in 80−90% yield and **9c** as golden yellow needles in 55% yield (not optimized; eq 7).

$$\begin{gathered}\mathrm{M(CH_2SiMe_3)_2Cl_2(ether)}_x \xrightarrow[\text{ether}]{\mathrm{Li_2(CyBen)(ether)}} \\ \mathrm{M} = \mathrm{Zr}\ (x = 2),\ \mathrm{Hf}\ (x = 2),\ \text{or Ti} \\ \mathrm{(CyBen)M(CH_2SiMe_3)_2} \qquad (6) \\ \mathrm{M} = \mathrm{Ti}\ (\mathbf{8c}),\ \mathrm{Zr}\ (\mathbf{8a}),\ \mathrm{Hf}\ (\mathbf{8b})\end{gathered}$$

$$\begin{gathered}\mathrm{(CyBen)M(CH_2SiMe_3)_2} \xrightarrow[-2\mathrm{Me_3SiCH_2I}]{2\mathrm{I_2/CH_2Cl_2}} \\ \mathrm{(CyBen)MI_2} \qquad (7) \\ \mathrm{M} = \mathrm{Ti}\ (\mathbf{9c}),\ \mathrm{Zr}\ (\mathbf{9a}),\ \mathrm{Hf}\ (\mathbf{9b})\end{gathered}$$

The zirconium and hafnium diiodides are useful precursors to a variety of dialkyl complexes (eq 8). Compounds **12a** and **12b** are oils, but the others can be isolated as colorless crystals in 70−90% yield from pentane at −30 °C. Attempts to prepare methyl derivatives employing MeMgBr or $MgMe_2$ were unsuccessful. For example, although (CyBen)$ZrMe_2$ could be identified in product mixtures by its characteristic ^1H NMR resonances, it could not be isolated from a significant amount of Cy_2BMe (δ 0.68 ppm, BMe). These results suggest that alkylation at boron competes with alkylation at zirconium when methylating agents are employed. In contrast, pale yellow crystalline (CyBen)$TiMe_2$ (**14c**) may be prepared in 90% yield from **9c** and

$$\mathrm{(CyBen)MI_2} + 2\mathrm{RMgX} \rightarrow \mathrm{(CyBen)MR_2} \qquad (8)$$

$$\begin{gathered}\mathrm{M} = \mathrm{Zr}\ (\mathbf{a})\ \text{or Hf}\ (\mathbf{b});\ \mathrm{R} = \text{ethyl}\ (\mathbf{10a,b}),\ \mathrm{CH_2CHMe_2} \\ (\mathbf{11a,b}),\ \mathrm{CH_2CH_2Bu}\ (\mathbf{12a,b}),\ \mathrm{CHBu_2}\ (\mathbf{13a});\ \mathrm{X} = \\ \text{Cl or Br}\end{gathered}$$

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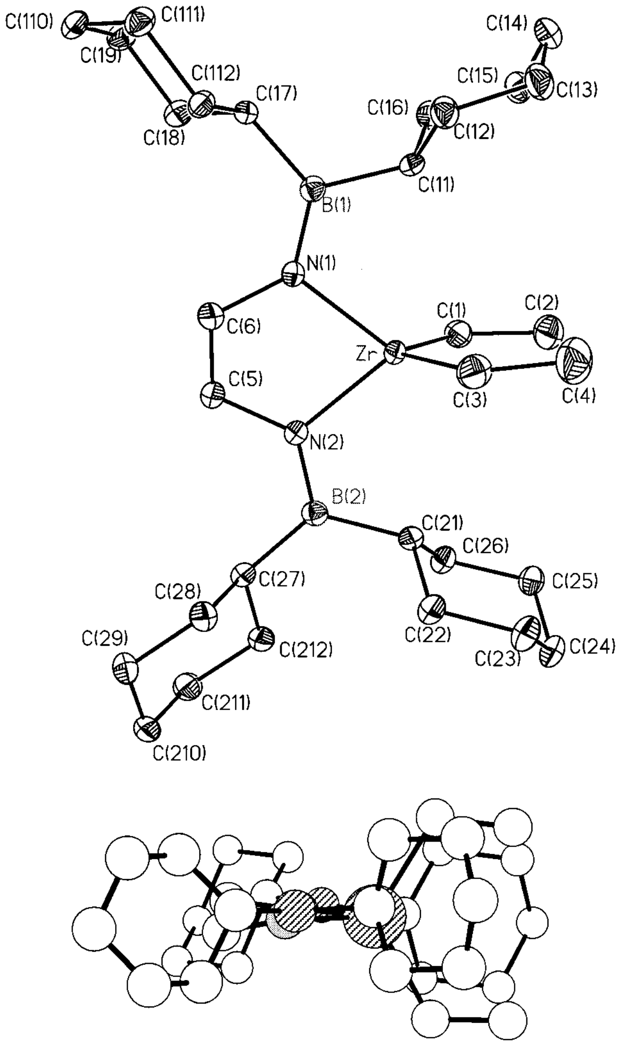


Figure 2. (a) ORTEP drawing of the structure of (CyBen)-$Zr(CH_2CH_3)_2$ (**10a**). (b) Chem3D top view of the structure of (CyBen)$Zr(CH_2CH_3)_2$ (**10a**).

Me_2Mg in dichloromethane (eq 9). Although **9c** reacts

$$(\mathrm{CyBen})\mathrm{TiI_2} + \mathrm{MgR_2} \xrightarrow[-30\ °\mathrm{C}]{\text{dichloromethane}} \begin{array}{c}(\mathrm{CyBen})\mathrm{TiR_2}\\ \mathrm{R} = \mathrm{CH_2CHMe_2}\ (\mathbf{11c})\\ \mathrm{Me}\ (\mathbf{14c})\end{array} \quad (9)$$

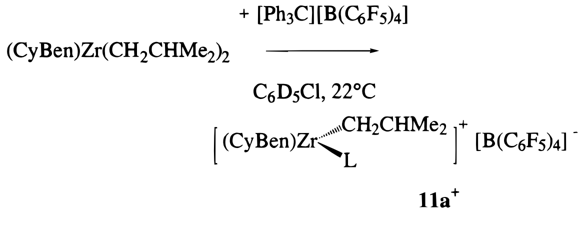
with $Mg(i\text{-}Bu)_2$ to afford (CyBen)$Ti(CH_2CHMe_2)_2$ (**11c**) in 87% yield, addition of $MgEt_2$ to **9c** in dichloromethane at −30 °C leads to an initially light yellow reaction mixture that turns brown at room temperature and from which putative (CyBen)$Ti(CH_2CH_3)_2$ could not be isolated. Solutions of the zirconium and hafnium complexes show no signs of significant decomposition upon standing overnight in benzene-d_6 at room temperature, while **11c** decomposes to give a black suspension under the same conditions.

^1H NMR spectra of the (CyBen)MR_2 complexes show a single sharp resonance for the CyBen ligand backbone methylene protons and resonances for the alkyl group that are consistent with the presence of two mirror planes in a pseudotetrahedral species. The cyclohexyl groups are inequivalent in the Zr and Hf complexes, as judged by the presence of eight cyclohexyl ^{13}C resonances at room temperature, as expected if B−N bond rotation is slow on the NMR time scale. Upon heating samples of **10a** and **11a** in bromobenzene-d_5 to 50−60 °C, the eight cyclohexyl resonances coalesce into four and barriers for B−N bond rotation ($\Delta G^{\ddagger}_{\mathrm{rot}}$) of 16.2(2) and 16.3(2) kcal/mol, respectively, can be calculated. In contrast, each titanium complex exhibits three relatively sharp ^{13}C cyclohexyl resonances (the B−C resonance was generally too broad to be observed at room temperature), indicating more facile rotation of the dicyclohexylboryl units relative to those of the zirconium and hafnium derivatives.

The molecular structure of **10a** is shown in Figure 2, and distances and angles are listed in Table 2. The two planar boryl fragments are linked by the puckered, ethylene bridge and are oriented so that one cyclohexyl ring is located directly over the two ethyl ligands and one ring is located over the ethylene bridge; the dihedral angle between the two BC_2 planes is only 10°, as opposed to 62° in (TripBen)$Zr(CD_3)_2$. The Zr−N distances (2.067(2) and 2.070(2) Å), Zr−C distances (2.247(3) and 2.253(3) Å), and N(1)−Zr−N(2) angle (78.87(2)°) are similar to those in (TripBen)$Zr(CD_3)_2$ (Figure 1). For comparison, in (MesBen)Ti(benzyl)Cl[11] the N(1)−Ti−N(2) angle is slightly larger (89.2(2)°) and the C-Ti-Cl angle (125.5(2)°) is slightly larger than the C−Zr−C angles, perhaps in part because the titanium is interacting with C_{ipso} in the benzyl ligand. The "in,in" conformation of the two ethyl ligands in **10a** is not a consequence of any C_{β}-H interaction with the metal, since the $Zr-C_{\alpha}-C_{\beta}$ angles are 114.8(2)° and 119.7(2)° and the $Zr\cdots C_{\beta}$ distances are 3.20 and 3.28 Å, respectively. The in,in orientation appears to be much less desirable from a steric point of view, so it would appear that some weak attractive interaction between the two cyclohexyl rings and the two ethyl ligands would have to be invoked in order to explain the observed structure.

It should be noted that the cyclohexyl rings do not protect the N_2ZrC face of the pseudotetrahedron to the degree that is found in MesBen[11] or TripBen complexes. However, accessibility of the benzylic CH bonds in the dimesitylboryl complexes leads to loss of alkane and orthometalation, even when the alkyl on the metal (Ti or Zr) contains no β hydrogens (e.g., (trimethylsilyl)-methyl).[11] In the CyBen complexes, there is no readily accessible CH bond that could be activated and cleaved.

Formation of Alkyl Cations. Addition of $[Ph_3C][B(C_6F_5)_4]$[33−35] to **11a** in chlorobenzene-d_5 (L) at −30 °C cleanly produces what we propose to be a cationic complex, $\mathbf{11a^+(L)}$ (eq 10; Figure 3; Table 3), along with 1 equiv of Ph_3CH and variable amounts of isobutylene.



$$(\mathrm{CyBen})\mathrm{Zr}(\mathrm{CH_2CHMe_2})_2 \xrightarrow[\mathrm{C_6D_5Cl,\ 22\,°C}]{+\ [\mathrm{Ph_3C}][\mathrm{B(C_6F_5)_4}]} \left[(\mathrm{CyBen})\mathrm{Zr}\begin{matrix}\mathrm{CH_2CHMe_2}\\ \mathrm{L}\end{matrix}\right]^+ [\mathrm{B(C_6F_5)_4}]^- \quad (10)$$

11a$^+$

We assume that 1 equiv of isobutylene is formed, although the detected amount is always less than 1 equiv. At −30 °C the ^1H NMR spectrum of $\mathbf{11a^+(L)}$ shows sharp, well-resolved AA′BB′ backbone resonances (at 3.46 and 3.79 ppm) consistent with a cation that

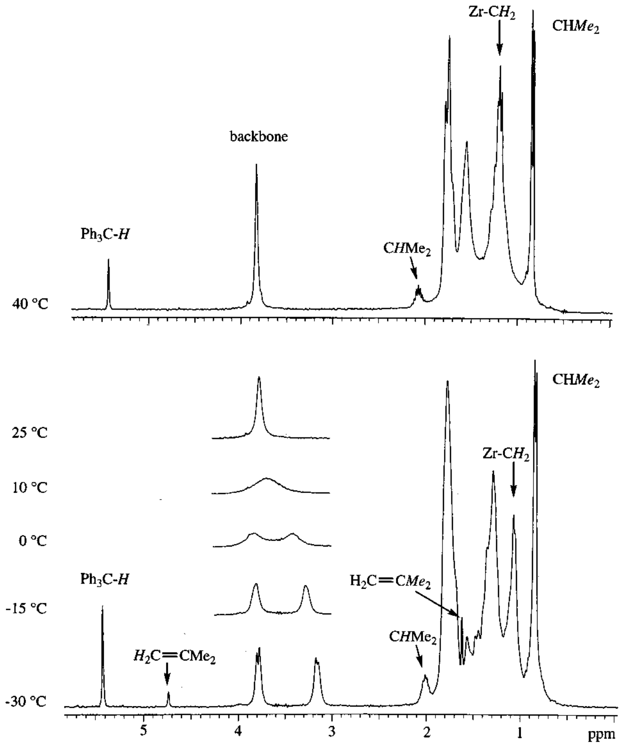


Figure 3. Variable-temperature ^{1}H NMR (300 MHz) spectra of **11a**$^+$ in chlorobenzene-d_5.

contains only one plane of symmetry, as expected if only one alkyl is present in a pseudotetrahedral cationic species. The fourth position in the pseudotetrahedron, we propose, is occupied by a chlorobenzene ligand. At room temperature or above, the spectrum simplifies to one that is consistent with a pseudotetrahedral species that contains two mirror planes analogous to the spectrum of **11a** itself. (Isobutylene is not observed in solution at 40 °C, presumably because it is too volatile.) Except for some variation in the amount of isobutylene in solution, the low-temperature spectrum is regenerated upon cooling the sample. We propose that the "right" and "left" set of backbone methylene protons equilibrate as a consequence of loss of ligand L and formation of a pseudotrigonal planar intermediate. On the basis of coalescence of the AA′ and BB′ backbone resonances at 4 °C (at 300 MHz), we can calculate a value for $\Delta G^{\ddagger}$ of 12.8(3) kcal/mol for the equilibration process. The coalescence temperature did not change over a 6-fold change in concentration of **11a** ((1.3−8.0) × 10^{-2} M). Low-temperature ^{19}F NMR spectra of these chlorobenzene-d_5 solutions are superimposable upon spectra of $[Ph_3C][B(C_6F_5)_4]$ under the same conditions and show no appreciable broadening other than that which may be attributed to increased solvent viscosity at low temperature. On the basis of this result and data in other solvents reported below, the $[B(C_6F_5)_4]^-$ ion does not appear to interact significantly with the metal. The ^{13}C NMR spectrum reveals the isobutyl α carbon atom at 86.24 ppm, close to where it is observed in a ^{13}C-labeled zirconium cation that contains the [(t-Bu-d$_6$-N-o-$C_6H_4)_2O]^{2-}$ ($[NON]^{2-}$) ligand[16,36] and 15−20 ppm downfield of where it appears in the neutral isobutyl complex.

Reaction of $[Ph_3C][B(C_6F_5)_4]$ with **11a** in toluene-d_8 at room temperature yields what we propose is the cationic complex $[(CyBen)Zr(CH_2CHMe_2)(toluene)][B(C_6F_5)_4]$ (**11a$^+$(tol)**) (Table 3) along with 1.0 equiv of Ph_3CH and a variable amount of isobutylene. The ligand backbone methylene resonances are revealed as a sharp, well-resolved AA′BB′ pattern (at 3.27 and 3.78 ppm) analogous to that observed in a sample prepared in chlorobenzene-d_5 at −30 °C, consistent with the presence of a relatively non-labile coordinating ligand (L) next to the alkyl ligand in the coordination wedge. ^{19}F NMR spectra show three sharp resonances for the $[B(C_6F_5)_4]^-$ anion, consistent with its isotropic character on the NMR time scale. The chemical shift of the isobutyl C_β-H resonance in **11a$^+$(tol)** at δ 1.97 ppm is not consistent with any β-agostic C−H interaction.[27,28]

The temperature at which the right and left methylene backbone protons exchange on the NMR time scale in **11a**$^+$ in chlorobenzene-d_5 increases steadily by 10−20 °C upon addition of small amounts of toluene (0.5−2 equiv), i.e., toluene effectively slows the methylene backbone proton equilibration process at a given temperature by binding to the metal more strongly than chlorobenzene binds. The addition of 1−2 equiv of toluene to a 0.01−0.1 M solution of **11a**$^+$ in chlorobenzene-d_5 should not change the bulk properties of the solvent sufficiently to alter the degree of association of the anion with the metal, if the anion were indeed the ligand L. Finally, addition of 1.1 equiv of dimethylaniline to a sample of **11a**$^+$ in chlorobenzene-d_5 leads to formation of a species that contains relatively strongly coordinated dimethylaniline (Me at 2.80 ppm; Table 3), along with a trace of free aniline (Me at 2.67 ppm). Free and coordinated aniline do not exchange rapidly on the NMR time scale. All of these observations are consistent with the binding of some base (solvent or added base) to the metal center in **11a**$^+$, presumably because no agostic interactions in the cyclohexyl ring or the isobutyl ligand are favorable, and the large $[B(C_6F_5)_4]^-$ anion binds much more weakly to the metal than solvent.

The cationic hafnium (**11b**$^+$) and titanium (**11c**$^+$) isobutyl complexes can be generated by analogous methods. In the ^{13}C NMR spectrum of **11b**$^+$ in chlorobenzene-d_5 at −30 °C the HfCH_2CHMe_2 resonance is observed at 85.27 ppm, ~15−20 ppm downfield of where it appears in the neutral isobutyl complex (Table 3). Variable-temperature ^{1}H NMR spectra reveal that the barrier to symmetrization increases in the order Ti < Zr < Hf (Table 3), which is what one would expect on the basis of the strength of the M−Base bond and a rate-limiting loss of base. This same trend is observed qualitatively in terms of the increase in T_c upon adding toluene to **11**$^+$ in chlorobenzene-d_5; titanium is the least sensitive to added toluene, while hafnium is the most sensitive.

The reaction of **10a** and **10b** or **12a** and **12b** with $[Ph_3C][B(C_6F_5)_4]$ in chlorobenzene-d_5 at −30 °C affords the corresponding ethyl and hexyl cations, respectively. The reaction between $(CyBen)ZrEt_2$ and $[Ph_3C][B(C_6F_5)_4]$

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Table 3. ^{1}H NMR Parameters for Alkyl Cations

complex	temp (°C)	solvent (added base)	δ_{Me}(coord)	δ_{Me}(free)	δ (AA′)	δ (BB′)	T_c (°C)	$\Delta G^{\ddagger}_{sym}$ (kcal/mol)	other resonances	
11a$^+$	−30	C_6D_5Cl			3.79	3.46	4	12.8(3)	2.01 (m) 1.07 (d) 0.85 (d) 86.24 (^{13}C)	$CHMe_2$ $ZrCH_2$ $CHMe_2$ $ZrCH_2$
11a$^+$	25	$C_6D_5CD_3$			3.78	3.27			1.97 (m) 0.96 (d) 0.85 (d)	$CHMe_2$ $ZrCH_2$ $CHMe_2$
11a$^+$	25	C_6D_5Cl (1.1 Me_2NPh)	2.80	2.67	3.99	3.48			2.08 (m) 1.08 (d) 0.93 (d) −0.44 (br m)	$CHMe_2$ $ZrCH_2$ $CHMe_2$ BC*H*
11b$^+$	−30	C_6D_5Cl			3.78	3.19	32	14.3(3)	2.14 (m) 0.93 (d) 0.88 (d) 85.27 (^{13}C)	$CHMe_2$ $CHMe_2$ $HfCH_2$ $HfCH_2$
11c$^+$	−30	C_6D_5Cl			4.13	3.65	−13	12.2(3)	2.10 (br) 1.89 (br) 0.77 (br) 112.71 (^{13}C)	$CHMe_2$ $TiCH_2$ $CHMe_2$ $TiCH_2$
10a$^+$	−30	C_6D_5Cl (5 $C_6H_5CH_3$)	2.21	2.17	3.80	3.29	28	14.1(3)	1.39 (t) −0.47 (br)	$ZrCH_2CH_3$ BC*H*
10b$^+$	−30	C_6D_5Cl (5 $C_6H_5CH_3$)	2.26	2.18	3.86	3.35	61	15.8(3)	1.54 (t) 0.45 (br q) −0.24 (br)	$HfCH_2CH_3$ $HfCH_2$ BC*H*
12a$^+$	−30	C_6D_5Cl (5 $C_6H_5CH_3$)	2.26	2.18	3.86	3.33	39	14.7(3)	0.87 (t) −0.29 (br)	CH_2CH_3 BC*H*
12b$^+$	−30	C_6D_5Cl (5 $C_6H_5CH_3$)	2.29	2.17	3.87	3.35	72	16.3 (3)	0.86 (t) 0.58 (br m) −0.21 (br)	CH_2CH_3 $HfCH_2$ BC*H*

produces 0.5 equiv of Ph_3CEt and 0.5 equiv of Ph_3CH plus a variable amount of ethylene in toluene. When (CyBen)$Zr(CD_2CD_3)_2$ was employed, $Ph_3C(CD_2CD_3)$ and Ph_3CD were formed, consistent with competition between a combination of an ethyl radical and trityl radical and abstraction of a deuterium atom by a trityl radical. In the case of **12a** and **12b**, only Ph_3CH is observed, consistent with predominant abstraction of a hydrogen atom from a hexyl radical versus a radical/radical combination. The ethyl and hexyl cations are less stable than the isobutyl cations, however. (We speculate that β-agostic interactions in the alkyl ligands in **10**$^+$ and **12**$^+$ lead to activation of the β hydrogens and migration of one of them to some part of the CyBen ligand, perhaps to the amido nitrogen, which would constitute a "reduction" of the metal, as in any β-hydrogen elimination process.) However, if **10**$^+$ and **12**$^+$ are generated in the presence of 5 equiv of toluene at −30 °C, then ^{1}H NMR spectra can be obtained (Table 3) in which the exchange of free and coordinated toluene is slow on the NMR time scale. Toluene methyl resonances for both bound (δ 2.29−2.21 ppm) and free (δ 2.18 ppm) toluene are observed at −30 °C in each complex. At slightly higher temperatures, only a single resonance is observed for free and coordinated toluene, consistent with rapid exchange of toluene on the NMR time scale. As in the case of cations **10a,b**$^+$, the metal−arene interaction is stronger for **10b**$^+$ and **12b**$^+$ than for **10a**$^+$ and **12a**$^+$. Perhaps in contrast to what might be expected on steric grounds, toluene binds most strongly to the hexyl derivatives than to the ethyl derivatives. That would be consistent with a competition between a β-agostic interaction and solvent binding, since the β-agostic interaction is believed to be most efficient in an ethyl complex.[27,37]

Clean formation of cationic complexes was not observed in all cases. (CyBen)$Zr(CHBu_2)_2$ (**13a**) and (CyBen)$TiMe_2$ (**14c**) did not react cleanly with $[Ph_3C][B(C_6F_5)_4]$ in chlorobenzene, even in the presence of 5 equiv of toluene. Although Ph_3CH and Ph_3CMe could be identified in ^{1}H NMR spectra of reaction mixtures of **13a** and **14c** with $[Ph_3C][B(C_6F_5)_4]$, respectively, no CyBen-based cation could be identified unambiguously in either case. Cationic species also could not be isolated employing $[Me_2PhNH][B(C_6F_5)_4]$ or $B(C_6F_5)_3$ as activators, in spite of the apparent formation of a dimethylaniline adduct of a cation as noted above. The reasons are not known.

Polymerization of 1-Hexene and Ethylene. Polymerization of 1-hexene was explored under conditions where cations **10a**$^+$, **10b**$^+$, or **11a**$^+$ could be generated and observed in the NMR studies discussed above. Addition of 1-hexene to such samples at temperatures between 0 and 25 °C irreproducibly produced little poly(1-hexene) (yields 5−25%) when the monomer/solvent volume ratio was lower than 1/7. GPC analysis of polymers generated at 25 °C with a monomer/cation (1-hexene/**11a**$^+$) ratio of 200−300 showed that the molecular weights ($M_n = 3 \times 10^5$ to 2×10^6 g/mol) and polydispersity indices (2.5−6) of these polymers were much higher than expected. We conclude that although initiator cations can be observed at 25 °C in the absence of 1-hexene, propagating cations must not be stable in the presence of dilute 1-hexene at 25 °C.

Increasing the concentration of 1-hexene to 1.5 mL per 5 mL of chlorobenzene and lowering the temperature to −30 °C led to almost quantitative yields of poly(1-hexene) with **10a**$^+$, **10b**$^+$, and **11a**$^+$ as initiators (Table 4). However, the molecular weight distribution of the poly(1-hexene) in each case was very broad and

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Table 4. Polymerization of 1-Hexene with Activated (CyBen)MR$_2$ Species

(CyBen)MR$_2$	solvent	temp (°C)	yield (%)	$10^4 M_n$ (g/mol)	$10^4 M_w$ (g/mol)	PDI
10a	PhCl[a]	−30	96	3.58	20.7	5.78[b]
10b	PhCl[a]	−30	96	12.7	71.9	5.68[b]
11a	PhCl[a]	−30	97	5.62	30.9	5.49
11a	CH$_2$Cl$_2$[c]	0	45	12.4	16.2	1.31[d]
11a	CH$_2$Cl$_2$	0	58	2.42	3.67	1.53[d]

[a] See Experimental Section for a complete description of the polymerization experiments; 1.50 mL of hexene (225 equiv), 5.0 mL of solvent, 60 min reaction time, quenched with 1 mL of MeOH, M_n(expected) = 1.89×10^4 if PDI = 1.0. [b] A resolved, low molecular weight peak consisting of less than 7% of sample weight was excluded from analysis. [c] Generated in the presence of 1-hexene and quenched after 10 min. [d] Only the low molecular weight peak was used in calculating PDI.

biased toward low molecular weights. The ^{13}C NMR spectra (in chloroform-d_1) of the poly(1-hexene) prepared from **11b**$^+$ and **11a**$^+$ show primarily six resonances (40.24, 34.60, 32.37, 28.71, 23.23, and 14.18 ppm) characteristic of some degree of isotacticity.[5,38−40] ^{1}H NMR spectra of the poly(1-hexene) prepared from **11a**$^+$ as the initiator showed the presence of both disubstituted terminal (δ 4.6, 4.7) and 1,2-disubstituted internal (δ 5.3) olefinic protons,[38] which correspond roughly to one double bond for every 300 monomer repeat units. We think it likely that β-hydride elimination is the origin of the formation of olefins. Intermediates in the polymerization process could not be observed, and we made no effort to further elucidate the details of the decomposition process.

Although [(CyBen)Zr(CH$_2$CHMe$_2$)]$^+$ (**11a**$^+$) could not be observed in dichloromethane-d_2, even in the presence of 15 equiv of toluene, addition of [Ph$_3$C][B(C$_6$F$_5$)$_4$] to **11a** in dichloromethane followed by 1-hexene does lead to rapid heat evolution and formation of poly(1-hexene) in yields between 50% and 75%. In a typical experiment, approximately one-half of the 1-hexene was polymerized after 10 min at room temperature. GPC analysis showed that the molecular weight distribution of this polymer was trimodal, with most of the polymer having a relatively low molecular weight approxmiately corresponding to the number of monomers added. Although M_n for this peak was only somewhat lower than that found for corresponding polymerizations in chlorobenzene (3.65×10^{4} g/mol), it was far more narrow with a PDI of 1.18. The polymerization process was not improved by cooling the reaction to −30 °C or by adding toluene (5−15 equiv) to the reaction medium. ^{1}H and ^{13}C NMR spectra (in chloroform-d_1) of the poly(1-hexene) produced in dichloromethane reveal primarily internal olefinic resonances (5.5−5.0 ppm) in ^{1}H NMR spectra and extremely broad signals in ^{13}C NMR spectra. Poly(1-hexene) prepared in dichloromethane is a viscous oil, in contrast to the rubbery solid produced in chlorobenzene. We conclude that dichloromethane is a poor solvent for the polymerization of 1-hexene, and we have considerable doubt concerning the nature of the catalytically active species.

No polymerization activity toward ethylene was noted for any species containing the TripBen ligand. Polymerization activity was assessed qualitatively for [(CyBen)Zr(CH$_2$CHMe$_2$)][B(C$_6$F$_5$)$_4$]. In both toluene and chlorobenzene ethylene was polymerized immediately but attempts to prepare polymer on a preparative scale did not produce more than 100−150 mg of polyethylene as a consequence of catalyst decomposition. The molecular weight distribution was not determined.

Discussion

The stability of complexes prepared here that contain β protons seems unusual. However, some metallocene dialkyls have been isolated when the alkyl contains a β proton,[29,41] and stable diamido complexes have been known for some time.[42,43] It is beginning to appear that stability of diamido group 4 complexes to β elimination is more often the rule than the exception, at least for Zr and Hf, the least reducible of the group 4 metals.

A variety of group 4 metal cations have now been observed in solution or isolated as base adducts.[35] In some cases the base has been an arene. For example, [CpMMe$_2$(arene)][MeB(C$_6$F$_5$)$_4$] (Cp = Cp*,[44] 1,3-(TMS)$_2$C$_5$H$_3$[45]) complexes are known in which coordinated and free toluene do not exchange rapidly at room temperature. The linked Cp-amide cation, {[(Me$_4$C$_5$)SiMe$_2$(NCMe$_3$)]ZrMe}$^+$, also binds toluene in the coordination site adjacent to the Zr−Me group and only reluctantly undergoes exchange at elevated temperatures in toluene-d_8.[46] Agostic interactions[27] (both α[47] and β[35]) are now believed to be relatively common in neutral or cationic species that contain metals as far to the left as scandium[37] and as far to the right as cobalt.[48] In comparison, however, group 4 transition-metal cations that do not contain at least one cyclopentadienyl ring are rarely observed.[13,14] Perhaps the most interesting are pseudo-four-coordinate zirconium cations that contain the [(t-Bu-d_6-N-o-C$_6$H$_4$)$_2$O]$^{2-}$ ([NON]$^{2-}$) ligand,[16] as they are relatively stable toward β-hydride elimination but they are still active for the polymerization of 1-hexene and can be observed in the form of living polymers during a 1-hexene polymerization reaction.[36] Titanium complexes that contain diamido ligands such as [ArNCH$_2$CH$_2$CH$_2$NAr]$^{2-}$ (Ar = 2,6-i-Pr$_2$C$_6$H$_3$)[17,18] are also initiators for the living polymerization of 1-hexene in the presence of excess 1-hexene. The cationic species in the titanium system is believed to be an unstable pseudo-three-coordinate species, although it has not yet been observed directly by NMR methods. In these diamido catalyst systems, the amido substituents are relatively bulky, thereby reducing the possibility of side reactions involving the amido nitrogen lone pair.

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The key idea at the beginning of this work was to employ B−N π bonding in a dialkyl or diarylboron substituent on amido nitrogens to both orient the bulky boron substituents and to increase the electrophilicity of the metal in a pseudo-three-coordinate cationic relative of a pseudo-three-coordinate metallocene alkyl cation. In light of the success obtained with ordinary diamido ligands noted above, that tactic would now appear to be unnecessary and in fact apparently yields species which decompose too readily compared to reaction with olefins to yield polymers. Metal−nitrogen π bonding may be helpful in stabilizing intermediate cationic species and slowing the rate of β-hydride elimination in the growing polymer chain compared to further reaction of the cation with olefin. Although boryl-substituted amido ligands do not appear to be advantageous for group 4 metal chemistry related to olefin polymerization catalysts, it is conceivable that boryl-substituted chelating diamido ligands of the type described here might be useful in circumstances where a more electron-poor metal is desired than in an analogous chelating diamido complex in which the amido nitrogen contains a carbon-based substituent.

Experimental Section

General Procedures. All experiments were performed under nitrogen in a Vacuum Atmospheres drybox or under argon using standard Schlenk techniques. All solvents were purified by standard techniques, and deuterated NMR solvents were dried and stored over 4 Å molecular sieves before use.

Butyllithium, $H_2BCl(SMe_2)$, and all Grignard reagents were obtained from commercial sources and titrated immediately before use. Ethylenediamine containing 0.6% water was stored over 4 Å molecular sieves before use. $[HNMe_2Ph][B(C_6F_5)_4]$,[49] $[Ph_3C][B(C_6F_5)_4]$, and $B(C_6F_5)_3$[50] were donated by Exxon. $Trip_2BF$ was prepared in an identical fashion to that described for $Xylyl_2BF$.[51] $ZrCl_4(THF)_2$[52] was prepared as described in the literature, as were $M(CH_2SiMe_3)_2Cl_2(ether)_2$ (M = Zr or Hf)[32] derivatives.

^1H, ^{13}C, and ^{19}F spectra were recorded at 300, 75.4, and 282 MHz, respectively. Proton spectra were referenced internally by the residual solvent proton signal relative to tetramethylsilane. Carbon spectra were referenced internally relative to the ^{13}C signal of the NMR solvent relative to tetramethylsilane. Fluorine spectra were referenced externally to neat $CFCl_3$. Elemental analyses were performed on a Perkin-Elmer PE2400 microanalyzer in our laboratories.

Li_2(TripBen)(THF)$_4$. Butyllithium (13.9 mL, 35.3 mmol, 2.53 M in hexane) was added to a solution of ethylenediamine (1.06 g, 17.6 mmol) in THF (150 mL) that had been chilled to −40 °C. A flocculent white precipitate soon formed. The reaction was allowed to warm to room temperature and was stirred for 3 h. The reaction was chilled to −40 °C again and $Trip_2BF$ (15.4 g, 35.28 mmol) was added over a period of 5 min. The flocculent solid was soon consumed to give a clear viscous suspension of LiF. The solution was stirred overnight, concentrated to ∼25 mL in vacuo, and combined with 125 mL of pentane. The mixture was filtered through Celite, and the Celite was washed with pentane (3 × 30 mL) and THF (10 mL). The combined filtrates were then chilled to −40 °C. Butyllithium (13.9 mL, 35.3 mmol, 2.53 M in hexane) was added to the chilled filtrate with stirring, and the mixture was placed in the freezer (∼−35 °C) overnight. Colorless crystals were isolated by filtration the next day and were washed with pentane. Subsequent concentration and cooling of the mother liquor gave a total of 17.4 g (83%) of the product in three crops: ^1H NMR (C_6D_6, 70 °C) δ 7.095 (s, 4, *m*-H), 7.069 (s, 4, *m*-H), 4.042 (br, 4, *o*-C*H*Me$_2$), 3.681 (s, 4, NC*H*$_2$), 3.539 (br m, 4, *o*-C*H*Me$_2$), 3.347 (br m, 16, THF), 2.878 (sept, 2, *p*-C*H*Me$_2$), 2.794 (sept, 2, *p*-C*H*Me$_2$), 1.471 (d, 12, *p*-CH*Me*$_2$), 1.366 (br, 24, *o*-CH*Me*$_2$), 1.293 (d, 12, *p*-CH*Me*$_2$), 1.205 (d, 12, *o*-CH*Me*$_2$), 1.171 (br m, 28, THF and *o*-CH*Me*$_2$); ^{13}C NMR δ 153.70, 151.56 (C_o), 147.21, 126.2 (C_p), 121.46, 120.16 (C_m), 67.95 (THF), 59.91 (N*C*H$_2$), 34.65, 34.57 (*p*-*C*HMe$_2$), 33.15, 32.56 (*o*-*C*HMe$_2$), 27.11 (CH*Me*$_2$), 25.56 (THF), 25.48, 24.51, 24.46, 24.25 (CH*Me*$_2$). Anal. Calcd for $C_{78}H_{128}N_2B_2Li_2O_4$: C, 78.51; H, 10.80; N, 2.35. Found: C, 79.08; H, 11.31; N, 2.46.

(TripBen)ZrCl$_2$ (1). $ZrCl_4(THF)_2$ (0.990 g, 2.62 mmol) was added slowly to a solution of Li_2(TripBen)(THF)$_4$ (3.13 g, 2.62 mmol) in toluene (35 mL) at −40 °C. The solution was allowed to warm to room temperature and was stirred overnight. The volatile components were removed in vacuo, and the residue was triturated with pentane (2 × 5 mL). The residue was subsequently extracted with pentane (50 mL), and the extract was cooled to −40 °C to produce a crop of clear, colorless crystals which were isolated by filtration and gently washed with cold pentane. Further concentration and cooling of the mother liquors provided two additional crops; total 2.27 g (87%). The product contains ∼1 equiv of pentane per zirconium: ^1H NMR (C_6D_6, 75 °C) δ 7.152 (s, 4, *m*-H), 7.132 (s, 4, *m*-H), 4.276 (s, 4, NC*H*$_2$), 3.334 (br m, 8, *o*-C*H*Me$_2$), 2.836 (sept, 2, *p*-C*H*Me$_2$), 2.703 (sept, 2, *p*-C*H*Me$_2$), 1.599 (d, 12, *o*-CH*Me*$_2$), 1.341 (d, 12, *o*-CH*Me*$_2$), 1.245 (d, 12, *p*-CH*Me*$_2$), 1.185 (d, 12, *o*-CH*Me*$_2$), 1.120 (d, 12, *p*-CH*Me*$_2$), 0.910 (br d, 12, *o*-CH*Me*$_2$); ^{13}C NMR δ 157.37 (C_o), 153.52 (C_p), 152.61 (C_o), 149.72 (C_p), 136.82, 134.05 (C_i), 124.26, 121.85 (C_m), 56.95 (N*C*H$_2$), 35.29 (*o*-*C*HMe$_2$), 34.75, 34.54 (*p*-*C*HMe$_2$), 33.19 (*o*-*C*HMe$_2$), 27.37, 26.13 (br), 25.77, 24.16, 24.02, 23.67 (CH*Me*$_2$). Anal. Calcd for $C_{67}H_{108}N_2B_2Cl_2Zr$: C, 71.52; H, 9.66; N, 2.49. Found: C, 71.29; H, 9.90; N, 2.28.

(TripBen)ZrMe$_2$ (2). Methylmagnesium bromide (0.312 mL, 1.02 mmol, 3.26 M in ether) was added to a solution of **1** (0.546 g, 0.485 mmol) in ether (5 mL) at −40 °C; a precipitate formed immediately. The mixture was allowed to stand at −40 °C for 30 min, dioxane was added, and the mixture was filtered through Celite. The volatile components were removed from the filtrate in vacuo, and the residue was extracted with pentane (10 mL). The extract was filtered through Celite, concentrated to ∼1 mL in vacuo, and allowed to stand at −40 °C overnight to yield 0.439 g (83%) of colorless crystals containing 1 equiv of pentane per Zr: ^1H NMR (C_6D_6, 50 °C) δ 7.166 (s, 4, *m*-H), 7.096 (s, 4, *m*-H), 4.106 (s, 4, NC*H*$_2$), 3.422 (m, 8, *o*-C*H*Me$_2$), 2.848 (sept, 2, *p*-C*H*Me$_2$), 2.711 (sept, 2, *p*-C*H*Me$_2$), 1.482 (d, 12, *o*-CH*Me*$_2$), 1.375 (d, 12, *o*-CH*Me*$_2$), 1.259 (d, 12, *p*-CH*Me*$_2$), 1.217 (br d, 12, *o*-CH*Me*$_2$), 1.129 (d, 12, *p*-CH*Me*$_2$), 0.929 (br, 12, *o*-CH*Me*$_2$), 0.012 (br, 6, Zr−C*H*$_3$); ^{13}C NMR (70 °C) δ 156.35 (C_o), 152.42 (C_o), 152.02 (C_p), 149.23 (C_p), 123.17, 121.62 (C_m), 54.72 ($^1J_{CH}$ = 137.9 Hz, N*C*H$_2$), 52.50 ($^1J_{CH}$ = 114.7 Hz, Zr−*C*H$_3$), 34.97 (*o*-*C*HMe$_2$), 34.72, 34.62 (*p*-*C*HMe$_2$), 32.97 (*o*-*C*HMe$_2$), 27.54, 26.05, 25.62, 24.14, 24.10, 23.96 (CH*Me*$_2$). Anal. Calcd for $C_{69}H_{114}N_2B_2Zr$: C, 76.42; H, 10.59; N, 2.58. Found: C, 76.49; H, 10.96; N, 2.50.

(TripBen)Zr(CD$_3$)$_2$ was prepared analogously, employing 2.1 equiv of $LiCD_3{\cdot}LiI$ in ether with the exception that a total of 4 pentane extraction cycles were performed in order to completely remove all lithium halides.

(TripBen)Zr(CH$_2$CH$_3$)$_2$ (3). EtMgCl (0.328 mL, 0.692 mmol, 2.11 M in ether) was added to a solution of **1** (0.371 g, 0.330 mmol) in ether (5 mL) at −40 °C. The reaction mixture was allowed to stand at −40 °C for 30 min, and dioxane (0.060 mL, 0.70 mmol) was added. The mixture was filtered through Celite, and the filtrate was concentrated to dryness. The residue was extracted with pentane (5 mL). The pentane

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extracts were concentrated to dryness, and the residue was again extracted with pentane. After the mixture was filtered once again, the filtrate was concentrated to dryness to afford **3** as a fluffy powder (0.269 g, 78% yield): ^{1}H NMR (C_6D_6, 70 °C) δ 7.147 (s, 4, *m*-H), 7.081 (s, 4, *m*-H), 4.127 (s, 4, NC*H*$_2$), 3.417 (br m, 8, *o*-C*H*Me$_2$), 2.837 (sept, 2, *p*-C*H*Me$_2$), 2.754 (sept, 2, *p*-C*H*Me$_2$), 1.474 (d, 12, *o*-CH*Me*$_2$), 1.371 (d, 12, *o*-CH*Me*$_2$), 1.249 (d, 12, *p*-CH*Me*$_2$), 1.175 (d, 24, *p*-CH*Me*$_2$ and *o*-CH*Me*$_2$), 1.061 (br t, 6, Zr−CH$_2$C*H*$_3$), 0.961 (br, 12, *o*-CH*Me*$_2$), 0.585 (br, 4, Zr−C*H*$_2$CH$_3$); ^{13}C NMR δ 154.71 (C_o), 152.17 (C_p), 150.77 (C_o), 149.01 (C_p), 138.35 (br, C_i), 122.43, 121.60 (C_m), 64.52 (br, Zr−*C*H$_2$CH$_3$), 53.18 (N*C*H$_2$), 34.69 (*p*-*C*HMe$_2$), 34.53, 33.00 (*o*-*C*HMe$_2$), 27.49, 26.22 (br), 25.52, 24.17, 24.11, 23.99 (CH*Me*$_2$), 11.68 (br, Zr−CH$_2$*C*H$_3$). Anal. Calcd for $C_{66}H_{106}N_2B_2Zr$: C, 76.20; H, 10.26; N, 2.69. Found: C, 76.68; H, 10.45; N, 2.63

(TripBen)Zr(CD_2CD_3)$_2$ was prepared analogously from **2** and 2.5 equiv of CD_3CD_2MgI with the exception that a total of four pentane extraction cycles were performed in order to completely remove all magnesium halides: ^{2}H NMR (70 °C) δ 0.938 (Zr−CD$_2$C*D*$_3$), 0.482 (br, Zr−C*D*$_2$CD$_3$).

(TripBen)ZrBu$_2$ (4). BuMgCl (0.105 mL, 0.235 mmol, 2.25 M in ether) was added to a solution of **1** (0.126 g, 0.112 mmol) in ether (5 mL) at −40 °C. The product was obtained as a fluffy powder (0.082g, 65% yield) after an isolation procedure analogous to that described for **3**: ^{1}H NMR (C_6D_6, 50 °C) δ 7.150 (s, 4, *m*-H), 7.085 (s, 4, *m*-H), 4.117 (s, 4, NC*H*$_2$), 3.406 (br m, 8, *o*-C*H*Me$_2$), 2.832 (sept, 2, *p*-C*H*Me$_2$), 2.778 (sept, 2, *p*-C*H*Me$_2$), 1.495 (d, 12, *o*-CH*Me*$_2$), 1.385 (d, 12, *o*-CH*Me*$_2$), 1.245 (d, 12, *p*-CH*Me*$_2$), 1.215 (d, 12, *p*-CH*Me*$_2$), 1.166 (br d, 12, *o*-CH*Me*$_2$), 0.973 (br, 12, *o*-CH*Me*$_2$), 0.817 (br m, 10, Zr−CH$_2$C*H*$_2$CH$_3$ and Zr−CH$_2$CH$_2$C*H*$_3$), 0.654 (br, 4, Zr−C*H*$_2$).

[(TripBen)ZrMe][MeB(C_6F_5)$_3$] (5a). A chilled (−40 °C) solution of B(C_6F_5)$_3$ (0.047 g, 0.092 mmol) in pentane (5 mL) was added dropwise to a solution of **2** (0.100 g, 0.092 mmol) in pentane (5 mL) at −40 °C. During the addition of the triarylborane, the solution became turbid, and after complete addition, a colorless oil separated on the walls of the reaction vial. After the mixture was allowed to stand for 36 h at −40 °C, the oil crystallized to afford 0.128 g (87%) of colorless crystals of **5a**: ^{1}H NMR (C_7D_8) δ 7.184 (s, 6, *m*-H), 7.074 (s, 2, *m*-H), 3.961 (br *AA′*BB′, 2, NC*H*$_2$), 3.489 (br AA′*BB′*, 2, NC*H*$_2$), 2.875 (m, 4, *o*-C*H*Me$_2$), 2.826 (sept, 2, C*H*Me$_2$), 2.726 (br m, 2, C*H*Me$_2$), 2.590 (sept, 2, C*H*Me$_2$), 2.436 (br m, 2, C*H*Me$_2$), 1.413 (d, 6, CH*Me*$_2$), 1.402 (br, 3, B−*Me*), 1.390 (br d, 6, CH*Me*$_2$), 1.254 (d, 18, CH*Me*$_2$), 1.201 (d, 6, CH*Me*$_2$), 1.142 (d, 6, CH*Me*$_2$), 1.109 (d, 6, CH*Me*$_2$), 0.971 (d, 6, CH*Me*$_2$), 0.894 (d, 6, CH*Me*$_2$), 0.755 (d, 6, CH*Me*$_2$), 0.387 (d, 6, CH*Me*$_2$), 0.201 (s, 3, Zr−C*H*$_3$); ^{19}F NMR δ −131.77 (d, $^3J_{FF}$ = 21.2, *o*-C$_6$F$_5$), −164.25 (t, $^3J_{FF}$ = 21.0, *p*-C$_6$F$_5$), −166.67 (m, $^3J_{FF}$ (average) = 22.0, *m*-C$_6$F$_5$). Anal. Calcd for $C_{82}H_{102}N_2B_3F_{15}Zr$: C, 64.61; H, 6.74; N, 1.84. Found: C, 64.50; H, 7.06; N, 1.80

[(TripBen)ZrMe][B(C_6F_5)$_4$] (5b). A solution of **5b** containing free Me$_2$NPh was generated by stirring [HNMe$_2$Ph][B(C_6F_5)$_4$] (0.076 g, 0.095 mmol) with **2** (0.100 g, 0.095 mmol) in toluene-*d*$_8$ (0.5 mL). Gas evolved vigorously. **5b** could be obtained as a powder after exhaustive removal of the toluene in vacuo and washing the precipitate with minimal pentane (3 × 2 mL) to remove the aniline: ^{1}H NMR (C_7D_8) δ 7.188 (s, 2, *m*-H), 7.174 (s, 4, *m*-H), 7.079 (s, 2, *m*-H), 3.976 (br *AA′*BB′, 2, NC*H*$_2$), 3.503 (br AA′*BB′*, 2, NC*H*$_2$), 2.891 (m, 4, *o*-C*H*Me$_2$), 2.818 (sept, 2, C*H*Me$_2$), 2.732 (br m, 2, C*H*Me$_2$), 2.574 (sept, 2, C*H*Me$_2$), 2.452 (br m, 2, C*H*Me$_2$), 1.420 (d, 6, CH*Me*$_2$), 1.381 (br d, 6, CH*Me*$_2$), 1.253 (d, 18, CH*Me*$_2$), 1.200, (d, 6, CH*Me*$_2$), 1.129 (d, 6, CH*Me*$_2$), 1.116 (d, 6, CH*Me*$_2$), 0.971 (d, 6, CH*Me*$_2$), 0.904 (d, 6, CH*Me*$_2$), 0.756 (d, 6, CH*Me*$_2$), 0.399 (d, 6, CH*Me*$_2$), 0.213 (s, 3, Zr−C*H*$_3$); ^{19}F NMR δ −131.80 (br, *o*-C$_6$F$_5$), −163.11 (m, *p*-C$_6$F$_5$), −166.85 (br, *m*-C$_6$F$_5$).

[(TripBen)Zr(CH_2CH_3)][B(C_6F_5)$_4$] (6). A toluene-*d*$_8$ solution (0.5 mL) of **3** was prepared from **1** (0.100 g, 0.092 mmol) and EtMgCl (0.072 mL, 0.193 mmol, 2.67 M in ether). A solution of **6** along with free Me$_2$NPh was generated by adding [HNMe$_2$Ph][B(C_6F_5)$_4$] (0.074 g, 0.092 mmol) with stirring to the toluene-*d*$_8$ solution of freshly prepared **3** at −40 °C: ^{1}H NMR (C_6D_6, 0 °C) δ 7.225 (s, 2, *m*-H), 7.200 (s, 2, *m*-H), 7.155 (s, 2, *m*-H), 7.050 (s, 2, *m*-H), 4.096 (br *AA′*BB′, 2, NC*H*$_2$), 3.745 (br AA′*BB′*, 2, NC*H*$_2$), 2.944 (m, 4, *o*-C*H*Me$_2$), 2.816 (sept, 2, C*H*Me$_2$), 2.700 (br m, 6, C*H*Me$_2$), 1.416 (d, 6, CH*Me*$_2$), 1.327 (d, 6, CH*Me*$_2$), 1.301 (d, 6, CH*Me*$_2$), 1.252 (d, 12, CH*Me*$_2$), 1.205 (d, 6, CH*Me*$_2$), 1.121 (d, 6, CH*Me*$_2$), 1.085 (d, 6, CH*Me*$_2$), 1.048 (d, 6, CH*Me*$_2$), 0.954 (d, 6, CH*Me*$_2$), 0.878 (d, 6, CH*Me*$_2$), 0.368 (d, 6, CH*Me*$_2$), −0.655 (t, $^3J_{HH}$ = 8.0 Hz, 3, Zr−CH$_2$C*H*$_3$). The Zr−C*H*$_2$CH$_3$ resonance is obscured by the *o*-CH*Me*$_2$ resonances.

[(TripBen)Zr($CH_2CH_2CH_2CH_3$)][B(C_6F_5)$_4$] (7). A toluene-*d*$_8$ solution (0.5 mL) of **4** was prepared from **1** (0.100 g, 0.092 mmol) and BuMgCl (0.086 mL, 0.193 mmol, 2.25 M in ether). A solution of **7** plus free Me$_2$NPh was generated by adding [HNMe$_2$Ph][B(C_6F_5)$_4$] (0.074 g, 0.092 mmol) with stirring to the toluene-*d*$_8$ solution of freshly prepared **4** at −40 °C: ^{1}H NMR (C_6D_6) δ 7.272 (s, 2, *m*-H), 7.197 (s, 4, *m*-H), 7.056 (s, 2, *m*-H), 4.096 (br *AA′*BB′, 2, NC*H*$_2$), 3.659 (br AA′*BB′*, 2, NC*H*$_2$), 2.98 (m, 8, *o*-C*H*Me$_2$), 2.819 (sept, 2, C*H*Me$_2$), 2.719 (br m, 2, C*H*Me$_2$), 1.5−0.75 (m, CH*Me*$_2$ and Zr−C*H*$_2$CH$_2$C*H*$_2$CH$_3$), 0.593 (t, $^3J_{HH}$ = 7.0 Hz, Zr−CH$_2$CH$_2$CH$_2$C*H*$_3$), 0.41 (br d, 6, CH*Me*$_2$), −0.11 (br, 2, Zr−CH$_2$C*H*$_2$).

Cy$_2$BNHCH$_2$CH$_2$NHBCy$_2$ (H$_2$(CyBen)). An ethereal solution of Cy$_2$BCl[30] was prepared by addition of H$_2$BCl(SMe$_2$) (25.00 g, 226 mmol) in ether (45 mL) to a stirring solution of cyclohexene (40.9 g, 498 mmol) in ether (150 mL) maintained at 0 °C. The solution became cloudy and was stirred at 0 °C for 1 h. The reaction mixture was then allowed to warm to room temperature and was stirred overnight. A suspension of [LiNHCH$_2$CH$_2$NHLi]$_x$ was prepared by adding butyllithium (95.1 mL, 238 mmol, 2.5 M in hexane) to a stirred solution of ethylenediamine (7.15 g, 118.9 mmol) in THF (375 mL) at −78 °C. After the addition was complete, the reaction mixture was stirred for 30 min at −78 °C, allowed to warm to room temperature, and stirred an additional 90 min. After cooling the suspension of [LiNHCH$_2$CH$_2$NHLi]$_x$ once again to −78 °C, the clear solution of Cy$_2$BCl was added, consuming the white suspension to give a light yellow solution. The solution was then warmed to room temperature and stirred overnight. The volatile components were removed in vacuo, and the residue was extracted with pentane (∼400 mL). The extracts were filtered through Celite and concentrated to ∼100 mL to yield a large amount of crystalline solid. The filtrate was then cooled to −30 °C for 3 h, and the crystalline solid was collected on a large frit, washed with pentane (∼20 mL), and dried in vacuo to give 31.75 g (68%) of colorless crystals: ^{1}H NMR δ (CDCl$_3$) 3.872 (br t, 2, N*H*), 2.993 (pseudo t, 4, NC*H*$_2$), 1.7−0.9 (br resonances, 44, Cy); ^{13}C NMR δ 44.88 (N*C*H$_2$), 29.66 (C_β), 28.95 (B−*C*), 28.72 (C_β), 28.36 (B−*C*), 28.06, 28.00 (C_γ), 27.25, 27.12 (C_δ); ^{11}B NMR δ 46.3; IR (Nujol/KBr) 3396 ν(NH) cm^{-1}. Anal. Calcd for $C_{26}H_{50}N_2B_2$: C, 75.75; H, 12.21; N, 6.80. Found: C, 76.01; H, 12.33; N, 6.83.

Li$_2$(CyBen)(ether). A solution of *tert*-butyllithium (22.0 mL, 36.08 mmol, 1.64 M in hexane) was slowly added over 15 min to a chilled (−30 °C), stirred solution of H$_2$(CyBen) (7.26 g, 17.61 mmol) in pentane (200 mL) with a small amount of ether (10 mL) added. After the addition was complete, the suspension was allowed to stir for 2 h at room temperature. The mixture was concentrated to one-half of its original volume in vacuo and the flask was cooled to −30 °C for 2 h. The white solid was collected by filtration, washed liberally with pentane, and dried in vacuo, to afford 8.30 g (95%) of the product: ^{1}H NMR (C_6D_6 plux 6 drops THF-*d*$_8$) δ 3.589 (br, 4, NC*H*$_2$), 3.252 (q, 4, OC*H*$_2$CH$_3$), 2.0−1.2 (br resonances, 44, Cy), 1.089 (t, 6, OCH$_2$C*H*$_3$); ^{13}C NMR δ 65.86 (O*C*H$_2$CH$_3$), 49.81 (N*C*H$_2$), 33.92 (br, B−*C*), 32.40 (Cy), 31.60 (br, B−*C*), 30.71 (Cy), 49.48 (2 Cy), 28.42 (Cy), 28.30 (Cy), 15.49 (OCH$_2$*C*H$_3$). Elemental analyses (C and H) were consistently low, consistent with gradual loss of ether in the solid state.

(CyBen)Zr(CH_2SiMe_3)$_2$ (8a). $Zr(CH_2SiMe_3)_2Cl_2(ether)_2$ was first prepared in situ as follows: under reduced lighting, a solution of $LiCH_2SiMe_3$ (3.00 g, 31.9 mmol) in ether (95 mL) was added dropwise over a period of 1 h to a vigorously stirred suspension of $ZrCl_4$ (3.71 g, 15.9 mmol) in ether (75 mL) at room temperature. After the reaction was stirred an additional 30 min, the reaction mixture was filtered through Celite and the filter cake was washed with ether (2 × 20 mL) to give a clear, light yellow solution of $Zr(CH_2SiMe_3)_2Cl_2(ether)_2$. This solution was chilled to −30 °C, and solid Li_2(CyBen)(ether) (7.94 g, 15.9 mmol) was added with stirring. The mixture was stirred overnight. The volatile components were removed in vacuo. The residue was first titurated with pentane (25 mL) and then extracted with pentane (350 mL). The extract was filtered through Celite, and the filtrate was concentrated in vacuo to ~25 mL. The mixture was allowed to stand for several hours at −30 °C in order to complete crystallization. The product was collected by filtration, washed with pentane (3 × 5 mL), and dried in vacuo to yield 8.41 g (76%) of colorless crystals: ^{1}H NMR (C_6D_6) δ 3.766 (s, 4, NCH_2), 2.05−1.20 (br m, 44, Cy), 0.590 (s, 4, Zr−CH_2), 0.185 (s, 18, CH_2SiMe_3); ^{13}C NMR δ 55.50, 53.31, 32.78 (B−CH), 30.07 (B−CH), 29.84, 28.62, 28.53, 28.00, 27.60, 26.76 (Cy). Anal. Calcd for $C_{34}H_{70}N_2B_2Si_2Zr$: C, 60.42; H, 10.43; N, 4.15. Found: C, 60.63; H, 10.68; N, 3.96.

(CyBen)Hf(CH_2SiMe_3)$_2$ (8b). $Hf(CH_2SiMe_3)_2Cl_2(OEt_2)_2$ was first prepared in situ as follows: under reduced lighting, a solution of $LiCH_2SiMe_3$ (2.70 g, 28.7 mmol) in ether (90 mL) was added dropwise over 1 h to a vigorously stirring suspension of $HfCl_4$ (4.59 g, 14.3 mmol) in ether (75 mL) at room temperature. The reaction mixture was stirred for an additional 30 min and filtered through Celite. The filter cake was washed with ether (2 × 20 mL) to give a clear, light yellow filtrate. This solution of $Hf(CH_2SiMe_3)_2Cl_2(ether)_2$ was chilled to −30 °C, and solid Li_2(CyBen)·OEt_2 (7.00 g, 14.1 mmol) was added with stirring. The product was isolated as described for **8a**; yield 7.81 g (74%): ^{1}H NMR (C_6D_6) δ 3.786 (s, 4, NCH_2), 2.05−1.20 (br m, 44, Cy), 0.186 (s, 18, CH_2SiMe_3), 0.157 (s, 4, Hf−CH_2); ^{13}C NMR δ 64.42, 49.83, 32.91 (B−CH), 30.20 (B−CH), 29.54, 28.57, 28.08, 27.61, 26.84 (Cy), 3.95 (SiMe_3). Anal. Calcd for $C_{34}H_{70}N_2B_2Si_2Hf$: C, 53.51; H, 9.24; N, 3.67. Found: C, 53.36; H, 9.26; N, 3.53.

(CyBen)Ti(CH_2SiMe_3)$_2$ (8c). $Ti(CH_2SiMe_3)_2Cl_2$[53] was first prepared by the adding a solution of $TiCl_4$ (1.14 g, 6.02 mmol) in dichloromethane (20 mL) to a solution of $Ti(CH_2SiMe_3)_4$ (2.39 g, 6.02 mmol) in dichloromethane (50 mL) at room temperature. An aliquot taken from the bright orange solution indicated that the reaction was 80% complete, as judged by integration of the TiCH_2SiMe_3 resonances in the mixture of the $Ti(CH_2SiMe_3)_{4-x}Cl_x$ ($x = 0-3$) products. After an additional 20% of $TiCl_4$ (0.234 g) was added to the reaction mixture, ^{1}H NMR analysis of a subsequent aliquot indicated the reaction was complete. The volatile components were removed in vacuo, and the deep orange oil was added to chilled (−30 °C) ether (100 mL). Solid Li_2(CyBen)(ether) (5.84 g, 11.7 mmol) was then added in two batches to the stirred ethereal solution of $Ti(CH_2SiMe_3)_2Cl_2$. After the addition was complete, the mixture was stirred for 1 h, a small amount of dichloromethane was added, and the volatile components were removed in vacuo. The residue was extracted with ~350 mL of dichloromethane, and the extract was filtered through Celite. The brown filtrate was concentrated to ~50 mL and was allowed to stand at −30 °C for 1 h to complete crystallization. Thin needles were collected by filtration, which were washed liberally with pentane and dried in vacuo to afford 4.01 g (53%) of dark yellow needles which were used without further purification: ^{1}H NMR (C_6D_6) δ 3.746 (s, 4, NCH_2), 2.05−1.20 (br m, 44, Cy), 1.751 (s, 4, Zr−CH_2), 0.138 (s, 18, CH_2SiMe_3); ^{13}C NMR δ 77.69, 51.02 (NCH$_2$), 28.94, 28.66, 27.61 (Cy), 3.42 (SiMe_3). Anal. Calcd for $C_{34}H_{70}N_2B_2Si_2Ti$: C, 64.56; H, 11.14; N, 4.43. Found: C, 63.83; H, 11.39; N, 4.57.

(CyBen)ZrI_2 (9a). Iodine crystals (3.35 g, 13.20 mmol) were added slowly to a rapidly stirred solution of (CyBen)Zr(CH_2SiMe_3)$_2$ (4.46 g, 6.60 mmol) in dichloromethane (200 mL) at room temperature until the color of the iodine was no longer discharged. (Approximately 0.06 g of iodine remained.) The mixture was stirred for a further 45 min, and the light orange solution was concentrated to ~20 mL in vacuo. The concentrated mixture was allowed to stand at −30 °C overnight. The crystals that formed were collected on a frit and washed with pentane (3 × 10 mL). Two further crops were obtained from the mother liquors combined with the pentane washings to give a total of 4.42 g (88%) of product: ^{1}H NMR (C_6D_6) δ 3.579 (s, 4, NCH_2), 2.35−2.15 (br, 4, Cy), 1.90−1.20 (br m, 40, Cy); ^{13}C NMR δ 56.89 (NCH$_2$), 32.44 (B−CH), 30.28 (Cy), 30.00 (BCH), 28.16, 28.02, 27.35, 27.18, 26.29 (Cy). Anal. Calcd for $C_{26}H_{48}N_2B_2I_2Zr$: C, 41.35; H, 6.40; N, 3.71. Found: C, 41.40; H, 6.81; N, 3.61.

(CyBen)HfI_2 (9b). Iodine crystals (4.92 g, 19.4 mmol) were added slowly to a rapidly stirred solution of (CyBen)Hf(CH_2SiMe_3)$_2$ (7.40 g, 9.70 mmol) in dichloromethane (250 mL) at room temperature until the color of the iodine was no longer discharged upon dissolution. (Approximately 0.20 g of iodine remained.) The product was isolated as described for **9a**; total yield 6.76 g (83%): ^{1}H NMR (C_6D_6) δ 3.579 (s, 4, NCH_2), 2.35−2.15 (br, 4, Cy), 1.90−1.20 (br m, 40, Cy); ^{13}C NMR δ 56.89 (NCH$_2$), 32.44 (B−CH), 30.28 (Cy), 30.00 (BCH), 28.16, 28.02, 27.35, 27.18, 26.29 (Cy). Anal. Calcd for $C_{26}H_{48}N_2B_2I_2Hf$: C, 37.06; H, 5.74; N, 3.33. Found: C, 36.78; H, 5.65; N, 3.28.

(CyBen)TiI_2 (9c). Iodine crystals (3.03 g, 11.95 mmol) were added slowly to a rapidly stirred solution of (CyBen)Ti(CH_2SiMe_3)$_2$ (4.46 g, 6.60 mmol) in dichloromethane (300 mL) at room temperature. At the end of the addition, the color of the solution indicated the presence of excess iodine. The dark solution was filtered through Celite and concentrated to ~25 mL in vacuo. Pentane (~25 mL) was added to assist precipitation of the product. The crude product (contaminated with some I_2) was collected on a frit and washed with pentane (2 × 5 mL). It was recrystallized from a mixture of pentane and dichloromethane (50/50, ~150 mL) to give 2.40 g (56%) of golden orange needles: ^{1}H NMR (C_6D_6) δ 3.579 (s, 4, NCH_2), 2.35−2.15 (br, 4, Cy), 1.90−1.20 (br m, 40, Cy); ^{13}C NMR δ 56.89 (NCH$_2$), 32.44 (BCH), 30.28 (Cy), 30.00 (BCH), 28.16, 28.02, 27.35, 27.18, 26.29 (Cy). Anal. Calcd for $C_{26}H_{48}N_2B_2I_2Ti$: C, 43.86; H, 6.79; N, 3.94. Found: C, 43.72; H, 7.11; N, 3.93.

(CyBen)Zr(CH_2CH_3)$_2$ (10a). A solution of CH_3CH_2MgCl (1.37 mL, 2.78 mmol, 2.03 M in ether) was added to a stirred, chilled (−30 °C) solution of (CyBen)ZrI_2 (1.00 g, 1.32 mmol) in dichloromethane (35 mL). The reaction mixture was allowed to stand at −30 °C for 30 min, and the magnesium salts were precipitated by the adding 1,4-dioxane (0.28 g, 3.2 mmol). The volatile components were removed in vacuo, and the residue was triturated with pentane (10 mL). The powdery residue was extracted with pentane, the extracts were filtered through Celite, and the filtrates were concentrated to dryness in vacuo. The resulting white solid was recrystallized from pentane at −30 °C to afford 0.597 g (81%) of white crystals in two crops: ^{1}H NMR (C_6D_6) δ 3.804 (s, 4, NCH_2), 1.90−1.00 (br m, 44, Cy), 1.538 (t, 6, CH_2CH_3), 0.965 (q, 4, ZrCH_2); ^{13}C NMR δ 53.88 (NCH$_2$), 49.03 (ZrCH$_2$), 32.38, 30.06 (BCH), 29.77, 28.72, 28.59, 28.14, 28.59, 27.64, 26.87 (Cy), 9.95 (Zr−CH_2CH_3). Anal. Calcd for $C_{30}H_{58}N_2B_2Zr$: C, 64.39; H, 10.44; N, 5.01. Found: C, 64.35; H, 10.44; N, 5.07.

(CyBen)Hf(CH_2CH_3)$_2$ (10b). This compound was prepared as described for **10a** from (CyBen)HfI_2 (0.750 g, 0.890 mmol) and CH_3CH_2MgCl (0.886 mL, 1.87 mmol, 2.11 M in ether); yield 0.448 g (78%) of colorless crystals in two crops: ^{1}H NMR

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(53) Beilin, S. I.; Bondarenko, G. N.; Vdovin, V. M.; Dolgoplosk, B. A.; Markevich, I. N.; Nametkin, N. S.; Poletaev, V. A.; Svergun, V. I.; Sergeeva, M. B. *Dokl. Akad. Nauk SSSR* **1974**, *218*, 1347.

(C_6D_6) δ 3.778 (s, 4, NCH_2), 1.95−1.20 (br m, 44, Cy), 1.540 (t, 6, CH_2CH_3), 0.853 (q, 4, Zr−CH_2); ^{13}C NMR δ 61.71 (HfCH_2), 50.66 (NCH_2), 32.49, 30.35 (BCH), 29.52, 28.67, 28.58, 28.18, 27.62, 26.91, 10.07 (Hf-CH_2CH_3). Anal. Calcd for $C_{30}H_{58}N_2B_2$-Hf: C, 55.70; H, 9.03; N, 4.33. Found: C, 55.74; H, 8.90; N, 4.33.

(CyBen)Zr(CH_2CHMe_2)$_2$ (11a). A solution of Me_2CHCH_2-MgCl (1.11 mL, 2.66 mmol, 2.39 M in ether) was added to a stirred, chilled (−30 °C) solution of (CyBen)ZrI_2 (0.980 g, 1.30 mmol) in dichloromethane (35 mL). The reaction mixture was allowed to stand at −30 °C for 45 min, and the magnesium salts were precipitated by the addition of 1,4-dioxane (0.25 g, 2.8 mmol). The volatile components were removed in vacuo, and the residue was triturated with pentane (5 mL). The powdery residue was then extracted with pentane (25 mL), and the extracts were filtered through Celite and concentrated to dryness in vacuo. The resulting white solid was recrystallized from pentane at −30 °C to afford 0.687 g (86%) of white crystals in three crops: ^1H NMR (C_6D_6) δ 3.777 (s, 4, NCH_2), 2.326 (m, 2, $CHMe_2$), 2.05−1.30 (br m, 44, Cy), 1.096 (d, 12, $CHMe_2$), 1.004 (d, 4, Zr−CH_2); ^{13}C NMR δ 76.60 (ZrCH_2), 53.56 (NCH_2), 33.31, 30.07 (B−CH), 29.76, 29.62, 28.85, 28.65, 28.59, 27.93, 27.63, 26.89 (Cy and $CHMe_2$). Anal. Calcd for $C_{34}H_{66}N_2B_2Zr$: C, 66.33; H, 10.79; N, 4.55. Found: C, 66.52; H, 10.85; N, 4.52.

(CyBen)Hf(CH_2CHMe_2)$_2$ (11b). This compound was prepared as described for **11a** from (CyBen)HfI_2 (0.750 g, 0.890 mmol) and Me_2CHCH_2MgCl (0.861 mL, 1.87 mmol, 2.17 M in ether); yield 0.535 g (85%) of white crystals in two crops: ^1H NMR (C_6D_6) δ 3.778 (s, 4, NCH_2), 2.387 (m, 2, $CHMe_2$), 2.1−1.3 (br m, 44, Cy), 1.103 (d, 12, $CHMe_2$), 0.741 (d, 4, HfCH_2); ^{13}C NMR δ 88.34 (HfCH_2), 50.22 (NCH_2), 33.30 (B−CH), 30.34 (BCH), 29.97, 29.64, 29.51, 28.59, 28.00, 27.62, 26.94. Anal. Calcd for $C_{34}H_{66}N_2B_2Hf$: C, 58.09; H, 9.45; N, 3.99. Found: C, 58.22; H, 9.83; N, 3.96.

(CyBen)Ti(CH_2CHMe_2)$_2$ (11c). A solution of diisobutylmagnesium (3.13 mL, 0.938 mmol, 0.30 M in ether) was added with stirring to a chilled (−30 °C) solution of (CyBen)TiI_2 (0.607 g, 0.853 mmol) in dichloromethane (25 mL). The reaction mixture was allowed to stand at −30 °C for 10 min, and the magnesium salts were precipitated by the addition of 1,4-dioxane (0.10 mL, 1.2 mmol). The volatile components were removed in vacuo, and the residue was triturated with pentane (5 mL). The yellow, powdery residue was extracted with pentane (∼25 mL), and the extracts were filtered through Celite and concentrated to dryness in vaacuo. The resulting yellow solid was recrystallized at −30 °C from pentane after filtering to afford 0.424 g (87%) of yellow crystals in three crops: ^1H NMR (C_6D_6) δ 3.802 (s, 4, NCH_2), 2.387 (m, 2, $CHMe_2$), 2.15−1.20 (br m, 44, Cy), 1.750 (d, 4, TiCH_2), 1.007 (d, 12, $CHMe_2$); ^{13}C NMR δ 94.29 (TiCH_2), 52.28 (NCH_2), 32.39, 28.97 (br), 28.65, 27.76, 27.67 (Cy and $CHMe_2$). (The BC resonance was not identified.) Anal. Calcd for $C_{34}H_{66}N_2B_2Ti$: C, 71.35; H, 11.61; N, 4.90. Found: C, 71.34; H, 11.60; N, 4.91.

(CyBen)Zr(CH_2CH_2Bu)$_2$ (12a). A solution of $BuCH_2CH_2$-MgBr (0.506 mL, 1.05 mmol, 2.07 M in ether) was added to a stirred, chilled (−30 °C) solution of (CyBen)ZrI_2 (0.377 g, 0.499 mmol) in dichloromethane (15 mL). The solution was allowed to stand at −30 °C for 45 min before the magnesium salts were precipitated by the addition of 1,4-dioxane (0.10 mL, 1.2 mmol). The volatiles were removed in vacuo, and the oily residue was triturated with pentane (5 mL) and then extracted with pentane (10 mL). The extract was filtered through Celite, and the filtrate was concentrated to dryness. The residue was extracted with pentane, and the filtrate was concentrated to give 0.297 g (98%) of the product as a slightly tan, analytically pure oil: ^1H NMR (C_6D_6) δ 3.825 (s, 4, NCH_2), 1.9−1.2 (br m, 60, Cy and hexyl), 1.063 (m, 4, ZrCH_2), 0.910 (t, 6, CH_3); ^{13}C NMR δ 61.47 (ZrCH_2), 53.77 (NCH_2), 35.75, 32.89 (BCH), 32.12, 30.15 (BCH), 29.85, 28.78, 28.60, 28.17, 27.63, 27.40, 26.91, 23.09, 14.33. Anal. Calcd for $C_{38}H_{74}N_2B_2Zr$: C, 67.94; H, 11.09; N, 4.17. Found: C, 67.90; H, 11.40; N, 3.98.

(CyBen)Hf(CH_2CH_2Bu)$_2$ (12b). This product was prepared in a manner analogous to that described for **12a** from (CyBen)HfI_2 (0.425 g, 0.504 mmol) and $BuCH_2CH_2MgBr$ (0.512 mL, 1.06 mmol, 2.07 M in ether); yield 0.334 g (87%) of the product as a slightly tan, analytically pure oil: ^1H NMR (C_6D_6) δ 3.811 (s, 4, NCH_2), 2.05−1.20 (br m, 60, Cy and hexyl), 1.063 (m, 4, ZrCH_2), 0.912 (t, 6, CH_3), (m, 4, Hf−CH_2); ^{13}C NMR δ 73.57 (HfCH_2), 50.52 (NCH_2), 36.49, 32.91 (BCH), 32.18, 30.36 (BCH), 29.59, 28.69, 28.58, 28.19, 27.61, 27.54, 26.93, 23.11, 14.34. Anal. Calcd for $C_{38}H_{74}N_2B_2Hf$: C, 60.13; H, 9.82; N, 3.69. Found: C, 60.06; H, 9.93; N, 3.42.

(CyBen)Zr($CHBu_2$)$_2$ (13a). $Bu_2CHMgBr$ was prepared in three steps from 5-nonanone: (1) 5-nonanone (10.73 g, 78.79 mmol) was reduced with lithium aluminum hydride (1.50 g, 39.4 mmol) in ether[54] to give 10.81 g (99%) of 5-nonanol after workup with 2 N H_2SO_4, extraction with ether, and removal of all volatiles by rotary evaporation under reduced pressure (water aspirator). (2) The nonanol was degassed and stood over 4 Å molecular sieves for 12 h. 5-Nonanol (5.25 g, 38.00 mmol) was placed in dry, degassed DMF (50 mL), and the solution was chilled to 0 °C under argon. Solid Ph_3PBr_2 (17.58 g, 41.65 mmol)[55] was added to the solution over a period of 45 min, after which time the solution was gently heated to 45 °C for 2 h. Hexane (300 mL) and water (200 mL) were then added, and the organic fraction was collected and washed with water (2 × 200 mL). The hexane layer was dried with $MgSO_4$, filtered, concentrated to ∼5 mL, filtered through activated alumina, and then concentrated in vacuo to a constant weight to yield 4.70 g (61%) of 5-bromononane as an oil. (3) Dry 5-bromononane (2.05 g, 10.17) was added slowly over a period of 2 h to 0.60 g of magnesium powder (activated by heating followed by the addition of an I_2 crystal after the addition of ether) in ether (10 mL). The Grignard solution was filtered, concentrated to <10 mL, transferred to a 10 mL volumetric flask, and diluted to 10.0 mL. Titration with *n*-propanol indicated the yield of Grignard reagent was 45%.

A solution of $Bu_2CHMgBr$ (3.24 mL, 1.46 mmol, 0.45 M in ether) was added to a stirred, chilled (−30 °C) solution of (CyBen)ZrI_2 (0.500 g, 0.662 mmol) in dichloromethane (15 mL). The reaction mixture was allowed to stand at −30 °C for 5 h and the magnesium salts were precipitated by the addition of 1,4-dioxane (0.35 g, 4.0 mmol). The volatiles were removed in vacuo, and the residue was extracted with pentane, filtered through Celite, and concentrated to dryness in vacuo. ^1H NMR analysis of this residue indicated that alkylation was not complete, showing the presence of ∼10% (CyBen)Zr($CHBu_2$)I. This mixture was dissolved in ether (10 mL) and chilled to −30 °C, and an additional 0.35 mL of the $Bu_2CHMgBr$ solution was added. After 5 h, more dioxane (35 μL) was added and the mixture was concentrated to dryness. The residue was extracted with pentane (10 mL), the extracts were filtered through Celite, and the filtrate was concentrated to dryness in vacuo. The residue was recrystallized from pentane at −30 °C to yield 0.354 g (71%) of thin, colorless needles in four crops: ^1H NMR (C_6D_6) δ 3.939 (s, 4, NCH_2), 2.2−1.2 (br m, 68, Cy and Bu), 0.999 (t, 12, CH_2Me), 0.732 (br q, 2, Zr$CHBu_2$); ^{13}C NMR δ 76.23 (Zr−$CHBu_2$), 53.50 (NCH_2), 34.61, 33.67 (BCH), 33.08, 30.94, 30.17 (BCH), 29.56, 28.68, 27.96, 27.69, 27.02, 23.85 (CH_2CH_3), 14.43 (CH_3). Anal. Calcd for $C_{44}H_{86}N_2B_2Zr$: C, 69.91; H, 11.46; N, 3.71. Found: C, 70.15; H, 11.59; N, 3.68.

(CyBen)$TiMe_2$ (14c). A solution of dimethylmagnesium (1.22 mL, 0.973 mmol, 0.80 M in ether) was added to a stirred, chilled (−30 °C) solution of (CyBen)TiI_2 (0.660 g, 0.927 mmol) in dichloromethane (50 mL). The solution immediately turned

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light yellow. The reaction mixture was allowed to stand at −30 °C for 10 min and the Mg salts were precipitated by the addition of 1,4-dioxane (85 μL, 1.0 mmol). The volatile components were removed in vacuo, and the residue was triturated with pentane (5 mL). The yellow, powdery residue was extracted with pentane (50 mL), the extracts were filtered through Celite, and the filtrate was concentrated to dryness. The resulting white solid was recrystallized at −30 °C from pentane after filtering to afford 0.406 g (90%) of pale yellow crystals in three crops: ^{1}H NMR (C_6D_6) δ 3.766 (s, 4, NC*H*$_2$), 2.0−1.2 (br m, 44, Cy), 1.138 (s, 6, Ti*Me*); ^{13}C NMR δ 54.01, 53.47 (Ti*Me* and N*C*H$_2$), 28.73, 28.36, 27.35 (Cy). (The B*C* resonances were not identified.) Anal. Calcd for $C_{28}H_{54}N_2B_2Ti$: C, 68.89; H, 11.14; N, 5.74. Found: C, 68.76; H, 11.36; N, 5.83.

Preparation and NMR Characterization of the Alkyl Cations. A sample of **11** (0.027 mmol) was dissolved in chlorobenzene-d_5, and the solution was chilled to −30 °C. Solid $[Ph_3C][B(C_6F_5)_4]$ (0.025 g, 0.027 mmol) was added to the stirred solution. The light yellow solution was transferred to an NMR tube and was frozen at −78 °C before being inserted into a precooled NMR probe at −30 °C. ^{1}H NMR data are presented in Table 3: ^{19}F NMR (**11a**$^+$, −30 °C) δ −137.97 (br s, 2, *o*-F), −167.83 (t, 1, *p*-F), −171.75 (br s, 2, *m*-F).

1-Hexene Polymerizations. A sample of a dialkyl complex (0.30−0.38 mg) was dissolved in 5.0 mL of chlorobenzene, and the solution was chilled in the freezer (−30 °C) for ~10 min. The solution was briefly removed from the freezer and solid $[Ph_3C][B(C_6F_5)_4]$ (1 equiv) was added with stirring. After all of the $[Ph_3C][B(C_6F_5)_4]$ had dissolved, the solution was returned to the freezer for 2 min prior to the addition of 1-hexene (1.50 mL). The vial was immediately returned to the freezer. In cases where polymerization ensued, the solution became extremely viscous within 5−10 min. After the mixture was allowed to stand at −30 °C for 1 h, it was quenched with 1.0 mL of methanol. The viscous solution was transferred to a preweighed flask, assisted by washing with dichloromethane, and most of the volatile components were removed by rotary evacuation under reduced pressure (water aspirator). The polymer was then dried at 60 mTorr and 110 °C for 8−12 h. The yields reported are not corrected for extra weight due to the metal complex and activator fragments.

X-ray structures of (TripBen)Zr(CD_3)$_2$ and (CyBen)Zr(CH_2CH_3)$_2$. A description of a typical procedure can be found in a recent publication,[56] and the relevant crystallographic data can be found in Table 1. See Supporting Information for more details.

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Supporting Information Available: Tables of final positional parameters, final thermal parameters, and bond lengths and angles for (TripBen)Zr(CD_3)$_2$ and (CyBen)Zr(CH_2CH_3)$_2$ (6 pages). Ordering information is given on any current masthead page.

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