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# Synthesis, Structures, and Ring-Opening Polymerization Reactions of Substituted Cyclopentadienyl Complexes of Zinc

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The reaction of 2 equiv of the new pyrrole-substituted cyclopentadienyl ligand *cyclo*-C<sub>4</sub>H<sub>4</sub>-NSiMe<sub>2</sub>C<sub>5</sub>H<sub>5</sub> (**2a**, Cp<sup>py</sup>H) with Zn[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> gives the bis(cyclopentadienyl)zinc complex Zn(Cp<sup>py</sup>)<sub>2</sub> (**3a**). The reaction of **2a** and the related derivatives *cyclo*-2,5-Me<sub>2</sub>C<sub>4</sub>H<sub>2</sub>NSiMe<sub>2</sub>C<sub>5</sub>H<sub>5</sub> (**2b**, Cp<sup>pyme</sup>H) and 3,5-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>CH<sub>2</sub>CMe<sub>2</sub>C<sub>5</sub>H<sub>5</sub> (**2c**, Cp<sup>mes</sup>H) with dibutylmagnesium gives the corresponding magnesocenes MgCp<sup>R</sup><sub>2</sub> (**3a–c**). Prolonged heating of the appropriate cyclopentadiene with zinc dialkyls in toluene, or alternatively stirring with [XZnN(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> in toluene at 40 °C for 1 h, gives the monocyclopentadienyl zinc alkyl complexes Cp<sup>R</sup>ZnX (**6a**, Cp<sup>R</sup> = Cp<sup>py</sup>, X = Me; **6c**, Cp<sup>R</sup> = Cp<sup>mes</sup>, X = Me; **7a**, Cp<sup>R</sup> = Cp<sup>py</sup>, X = Et; **7c**, Cp<sup>R</sup> = Cp<sup>mes</sup>, X = Et), which provide spectroscopic evidence for a Zn⋯(hetero)arene interaction. Addition of tetramethylethylenediamine (TMEDA) gives Cp<sup>R</sup>ZnX(TMEDA) (**8a**, **b**, X = Me; **9a–c**, X = Et). The crystal structures of **8b** and **9c** show η<sup>2</sup>-bound cyclopentadienyl ligands, with one long and one short Zn–C interaction. The reaction of **7c** with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> in toluene proceeds with alkyl/C<sub>6</sub>F<sub>5</sub> exchange to give Cp<sup>mes</sup>Zn(C<sub>6</sub>F<sub>5</sub>) (**10**). Treatment of **9c** with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> in toluene results in an ionic product, [Cp<sup>mes</sup>Zn(TMEDA)]<sup>+</sup>[EtB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>]<sup>−</sup> (**11**). On the other hand, the reaction of **9a** with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> in toluene or dichloromethane proceeds with β-H abstraction, with concomitant loss of ethene, as well as both ethyl and cyclopentadienyl abstraction. Both **11** and **9a**/B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> mixtures catalyze the polymerization of cyclohexene oxide and ε-caprolactone.

## Introduction

Whereas the reaction of transition metal alkyls with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> is well documented to proceed with alkyl abstraction to give catalytically active metal complexes,<sup>1</sup> main group alkyls tend to react predominantly under alkyl/C<sub>6</sub>F<sub>5</sub> exchange. A prime example is the synthesis of Al(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> from AlMe<sub>3</sub> and B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> in hydrocarbon solvents.<sup>2</sup> Similar exchange reactions are observed between M(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> and MAO (or MMAO) (M = B, Al)<sup>3</sup> and with AlR<sub>3</sub> and [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (R = Me, Et and <sup>t</sup>Bu).<sup>4</sup> Mixtures of AlEt<sub>3</sub> and B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> exhibit modest ethene polymerization activity.<sup>5</sup> In coordinating solvents alkyl exchange is suppressed; for example, aluminum trialkyls and B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> in diethyl ether give solvent-

stabilized ion pairs, [R<sub>2</sub>Al(OEt)<sub>2</sub>]<sub>2</sub><sup>+</sup>[RB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>]<sup>−</sup>, which have been used as activators in high-temperature alkene polymerizations.<sup>6</sup> As we showed recently, zinc dialkyls behave similarly and rapidly undergo ligand exchange with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> in aromatic solvents to give Zn(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(arene), while in ether the ion pairs [RZn(OEt)<sub>2</sub>]<sub>2</sub><sup>+</sup>X<sup>−</sup> (X = RB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> or B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>, R = Me, Et, and <sup>t</sup>Bu) are obtained.<sup>7</sup> Cationic zinc alkyls have previously been prepared by the addition of nitrogen macrocycles or crown ethers to zinc alkyls in the presence of AlR<sub>3</sub> or tetraphenylcyclopentadiene, to give [RZn(crown)]<sup>+</sup>X<sup>−</sup> (X = AlR<sub>4</sub>, C<sub>5</sub>HPh<sub>4</sub>),<sup>8</sup> and by the protolysis of ZnEt<sub>2</sub> with the ammonium salt [Bz<sub>3</sub>TACH]<sup>+</sup>[PF<sub>6</sub>]<sup>−</sup>, which yields [(Bz<sub>3</sub>TAC)ZnEt]<sup>+</sup>[PF<sub>6</sub>]<sup>−</sup> (Bz<sub>3</sub>TAC = 1,3,5-tribenzyl-1,3,5-triazacyclohexane).<sup>9</sup> The triflate complex ZnMe(OTf)[H<sub>2</sub>C<sub>2</sub>(N<sup>t</sup>Bu)<sub>2</sub>] is neutral in the solid state but ionizes in THF or benzene.<sup>10</sup>

The coordination of arenes in Zn(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(arene) and the potential of cationic zinc alkyls as catalysts for ring-

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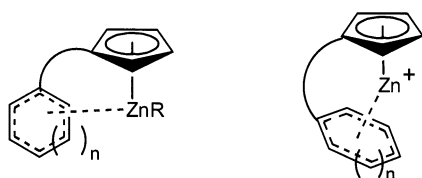
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Scheme 1



opening polymerization reactions of epoxides and lactones prompted us to investigate whether cationic zinc species could be stabilized by means of pendant aryl substituents, to give, for example, *ansa*-arene-Cp structures with electron-rich arenes or heteroarenes, as indicated in Scheme 1. Here we report the synthesis of new zinc complexes with pendant silylpyrrolyl and 3,5-dimethylphenylethyl substituents, their reactions with cation-generating agents, and their reactivity in ring-opening polymerizations of epoxides and lactones.

## Results and Discussion

**Ligand Synthesis.** The addition of lithium pyrrolide salts to a 10-fold excess of  $\text{Me}_2\text{SiCl}_2$  in light petroleum affords 1-(chlorodimethylsilyl)pyrrole (**1a**) and 2,5-dimethyl-1-(chlorodimethyl)silylpyrrole (**1b**), respectively. Subsequent reaction of **1a** and **1b** with  $\text{NaCp}(\text{thf})$  in tetrahydrofuran gave the new *N*-pyrrolyl-substituted cyclopentadienyl compounds *cyclo*- $\text{C}_4\text{H}_4\text{NSiMe}_2\text{C}_5\text{H}_5$  (**2a**,  $\text{Cp}^{\text{py}}\text{H}$ ) and *cyclo*-2,5- $\text{Me}_2\text{C}_4\text{H}_2\text{NSiMe}_2\text{C}_5\text{H}_5$  (**2b**,  $\text{Cp}^{\text{pyme}}\text{H}$ ) as yellow oils, which are conveniently purified by distillation under reduced pressure (Scheme 2). The 3,5-dimethylbenzyl-substituted cyclopentadiene **2c** ( $\text{Cp}^{\text{mes}}\text{H}$ ) was prepared using a modification of a literature method<sup>11</sup> by the addition of 3,5-dimethylbenzyl lithium to dimethylfulvene in tetrahydrofuran as a bright-yellow oil. All three compounds are obtained as a mixture of isomers and can be stored at  $-20^\circ\text{C}$  with no evidence of Diels–Alder dimerization. NMR data of ligands and complexes are given in the Supporting Information.

**Zinc Complexes.** Treatment of **2a** with zinc bis-(bistrimethylsilylamide) in light petroleum at  $40^\circ\text{C}$  gave the zincocene complex  $\text{Cp}^{\text{py}}_2\text{Zn}$  (**3a**) as a white microcrystalline precipitate, which was purified by recrystallization from toluene (Scheme 3). Previously reported zincocenes tend to show “slipped sandwich” structures containing both  $\eta^1$ - and  $\eta^5$ -cyclopentadienyl ligands,<sup>12–15</sup> which undergo rapid haptotropic exchange in solution, as shown by NMR studies. The  $^1\text{H}$  NMR of **3a** at ambient temperature shows both cyclopentadienyl ligands to be equivalent; on cooling to  $-60^\circ\text{C}$  the resonances broaden but could not be fully resolved. The magnesocenes **4a–c** were similarly prepared from **2a–c** and  $\text{MgBu}_2$  in light petroleum as colorless solids which precipitate from the solution during the course of the reaction. All three compounds are very air and moisture

sensitive but can be stored at  $-20^\circ\text{C}$  under nitrogen with no obvious degradation. Recrystallization from light petroleum provides analytically pure samples.

The protolysis of zinc dialkyls is less facile. A reaction between **2a** and  $\text{ZnMe}_2$  in a molar ratio of 1:1 in toluene- $d_8$  in an NMR tube kept at  $90^\circ\text{C}$  showed that after 2 days all the signals associated with **2a** had disappeared and the solution contained  $\text{Cp}^{\text{py}}\text{ZnMe}$  (**6a**), with some unidentified impurities. All attempts to generate the zincocene **3a** by refluxing excess **2a** with  $\text{ZnMe}_2$  in toluene failed.

An alternative route to **6a** involves the reaction of **2a** with  $\text{MeZnN}(\text{SiMe}_3)_2$  (**5**). This has the advantage of proceeding at much lower temperatures, typically  $40^\circ\text{C}$  for 1 h. However, repeated attempts generated **6a** only as an impure oil.  $\text{MeZnN}(\text{SiMe}_3)_2$  was prepared by comproportionating equimolar amounts of  $\text{ZnMe}_2$  and  $\text{Zn}[\text{N}(\text{SiMe}_3)_2]_2$  in light petroleum. Removal of the volatiles after ca. 5 min provides a white solid, which can be sublimed at 0.5 mmHg and  $40^\circ\text{C}$  to give colorless crystals in high yield. The compound forms an amido-bridged dimer in the solid state (Figure 3). Although X-ray crystallography was able to ascertain the overall geometry, the crystals were of poor quality, and the structural parameters will not be discussed further.

Following the same procedure as for **6a**,  $\text{Cp}^{\text{mes}}\text{ZnMe}$  (**6c**) was generated from **2c** and either  $\text{ZnMe}_2$  (toluene- $d_8$ ,  $80^\circ\text{C}$ , 48 h) or  $\text{MeZnN}(\text{SiMe}_3)_2$  (toluene- $d_8$ ,  $40^\circ\text{C}$ , 1 h) and was characterized spectroscopically. Attempts to isolate **6a** and **6c** on a preparative scale led to the formation of impure yellow oils, which were extremely soluble in all solvents; consequently neither compound could be obtained analytically pure. Similarly, the ethyl zinc complexes  $\text{Cp}^{\text{py}}\text{ZnEt}$  (**7a**) and  $\text{Cp}^{\text{mes}}\text{ZnEt}$  (**7c**) were generated in solution and characterized by NMR spectroscopy.

Treatment of light petroleum solutions of **6a** or **7a** with a slight excess of TMEDA generated the adducts  $\text{Cp}^{\text{py}}\text{ZnR}(\text{TMEDA})$  (**8a**,  $\text{R} = \text{Me}$ ; **9a**,  $\text{R} = \text{Et}$ ). Both complexes have only limited solubility in petroleum and precipitated immediately from solution. Recrystallization at  $-20^\circ\text{C}$  from light petroleum with a minimum amount of diethyl ether provided **8a** as a colorless crystalline solid, while **9a** was obtained as yellow crystals. In similar fashion,  $\text{Cp}^{\text{pyme}}\text{ZnR}(\text{TMEDA})$  (**8b**,  $\text{R} = \text{Me}$ ; **9b**,  $\text{R} = \text{Et}$ ) and  $\text{Cp}^{\text{mes}}\text{ZnEt}(\text{TMEDA})$  (**9c**) were obtained as yellow to red crystalline solids after recrystallization from light petroleum/diethyl ether mixtures.

A crystal of **8b** suitable for single-crystal X-ray diffraction was grown from light petroleum/diethyl ether at  $-20^\circ\text{C}$  (Figure 1), while a suitable crystal of **9c** was obtained from light petroleum at room temperature (Figure 2). Selected bond lengths and angles are collected in Table 1. In both structures the zinc atom is in an essentially five-coordinate arrangement. The coordination sphere comprises the two nitrogen atoms of the TMEDA ligand, the alkyl ligand, and two carbons from the cyclopentadienyl rings. In both complexes there is one short and one long Zn–C interaction to the cyclopentadienyl ligands, with Zn–C distances of 2.185(2) and 2.562(2) Å for **8b** and 2.167(2) and 2.558(2) Å for **9c**. The shortest bonds are to the carbon atoms furthest removed from the pendant cyclopentadienyl substituents. These distances are slightly longer than those

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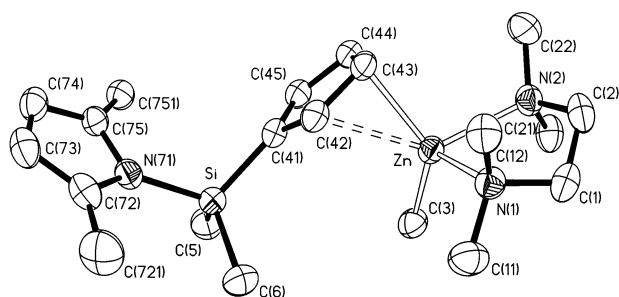
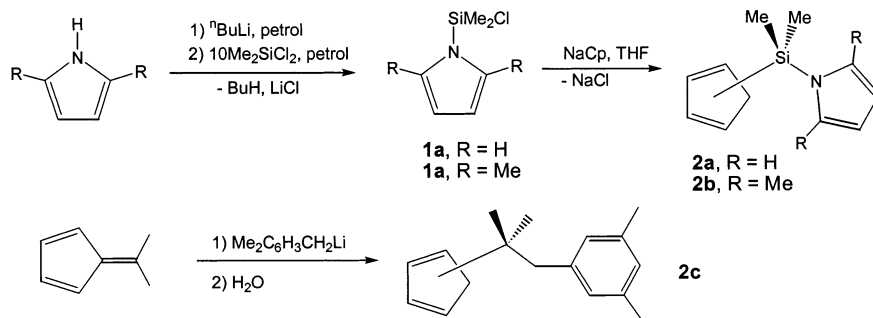
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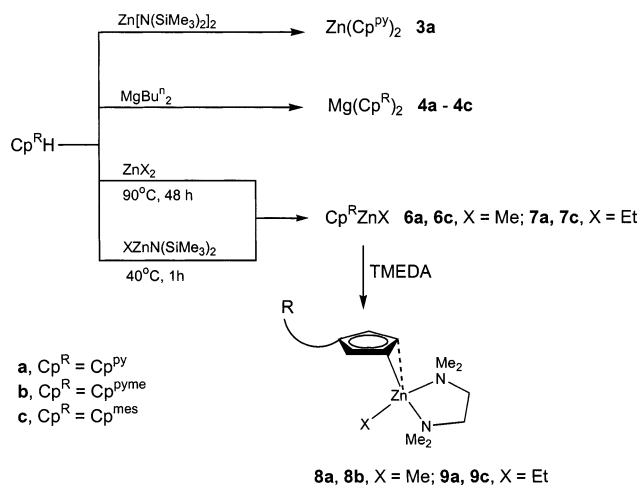
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## Scheme 2

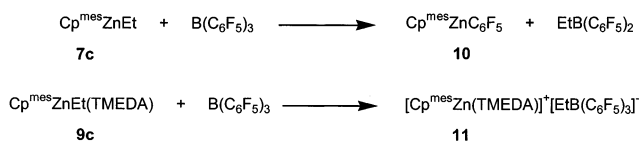


**Figure 1.** Structure of **8b** showing the atomic numbering scheme. Thermal ellipsoids are drawn at the 50% probability level.

## Scheme 3

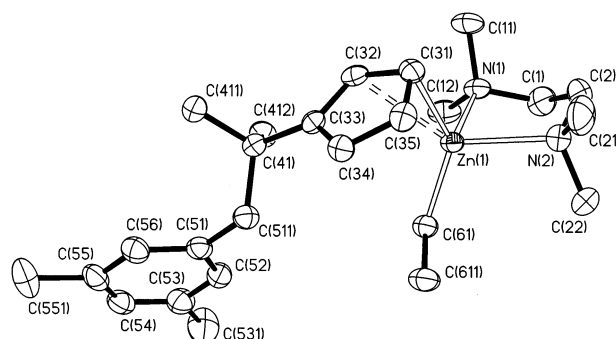


## Scheme 4

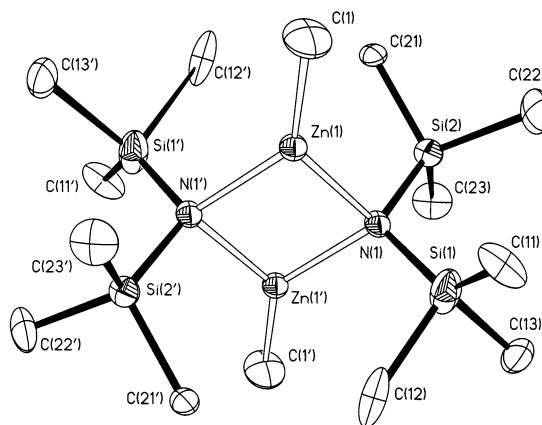


found in polymeric  $[\text{Cp}_2\text{Zn}]_n$  at 2.047 and 2.484 Å.<sup>16</sup> A similar Cp bonding mode is also found in solid  $[\text{MeZn}(\mu\text{-}\eta^2\text{-Cp})]_n$ , while the monomeric molecule in the gas phase prefers  $\eta^5\text{-Cp}$ . Other zinc cyclopentadienyl compounds show  $\eta^1, \eta^5$ -hapticity, e.g.,  $\text{Zn}(\eta^1\text{-Cp})(\eta^5\text{-Cp})$  ( $\text{Cp}' = \text{C}_5\text{H}_4\text{SiMe}_3$ ,  $\text{C}_5\text{Me}_5$ , and  $\text{C}_5\text{Me}_4\text{Ph}$ ).<sup>13,14</sup> For example, the Zn–C distances to the  $\eta^1\text{-C}_5\text{Me}_5$  ligand in  $\text{Zn}(\text{C}_5\text{Me}_5)_2$  are 2.094(3), 2.592(3), 2.509(3), 3.112(3), and 3.066(3) Å, with only the first considered as strongly bonding.

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**Figure 2.** Structure of **9c** showing the atomic numbering scheme. Thermal ellipsoids are drawn at the 50% probability level.



**Figure 3.** Structure of  $\text{MeZnN}(\text{SiMe}_3)_2$  (**5**). Thermal ellipsoids are drawn at the 30% probability level.

The Zn–Me distance in **8b** of 1.985(2) Å is typical of zinc methyl complexes, for example, in  $[\text{MeZnNMe}(\text{CH}_2)_3\text{NMe}_2]_2$  [1.982(7) and 1.976(7) Å],  $[\text{MeZn}\{\text{NMe}(\text{CH}_2)_2\text{NMe}_2\}]_2$  [1.978(4) and 1.991(4) Å], and  $\text{Me}_2\text{Zn}[(\text{CH}_2\text{NMe})_3]_2$  [1.984(5) Å].<sup>17,18</sup> Similarly, the Zn–Et distance in **9c** of 2.001(2) Å compares well with literature values, e.g.,  $[\text{EtZnNMe}(\text{CH}_2)_3\text{NMe}_2]_2$  [2.024(4) and 2.010(3) Å] and  $[\text{EtZnNMe}(\text{CH}_2)_2\text{NMe}_2]_2$  [1.989(3) Å].<sup>17</sup> The cationic zinc ethyl complexes  $[\text{EtZn}(\text{OEt}_2)_3]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ <sup>7</sup> and  $[\text{EtZn}(1,3,5\text{-tribenzyl-1,3,5-triazacyclohexane})]^+[\text{PF}_6]^-$ <sup>9</sup> both show shorter Zn–Et distances (1.964(3) and 1.930(4) Å, respectively). The Zn–N bond distances to the TMEDA ligands of 2.189(2) and 2.231(2) Å in **8b** and 2.2020(14) and 2.245(2) Å in **9c** are

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**Table 1. Selected Interatomic Distances (Å) and Angles (deg) for **8b** and **9c****

(cyclo-2,5-Me-C <sub>4</sub> H <sub>2</sub> NSiMe <sub>2</sub> C <sub>5</sub> H <sub>4</sub> )ZnMe(TMEDA) ( <b>8b</b> )			
Zn(1)–N(1)	2.189(2)	Zn(1)–N(2)	2.231(2)
Zn(1)–C(3)	1.985(2)	Zn(1)–C(42)	2.562(2)
Zn(1)–C(43)	2.185(2)	C(41)–C(42)	1.411(3)
C(42)–C(43)	1.422(3)	C(43)–C(44)	1.420(3)
C(44)–C(45)	1.385(3)	N(71)–C(72)	1.401(2)
C(72)–C(73)	1.361(3)	C(73)–C(74)	1.403(3)
C(74)–C(75)	1.362(3)	C(75)–N(71)	1.407(2)
Si(1)–C(41)	1.837(2)	Si(1)–N(71)	1.800(2)
C(42)–Zn(1)–C(43)	33.67(7)	C(3)–Zn(1)–C(42)	107.28(7)
C(3)–Zn(1)–C(43)	129.86(8)	N(1)–Zn(1)–N(2)	82.57(6)
C(3)–Zn(1)–N(1)	113.63(7)	C(3)–Zn(1)–N(2)	111.59(7)
N(71)–Si(1)–C(41)	110.97(8)		
(3,5-Me <sub>2</sub> C <sub>6</sub> H <sub>3</sub> CH <sub>2</sub> CMe <sub>2</sub> C <sub>5</sub> H <sub>4</sub> )ZnEt(TMEDA) ( <b>9c</b> )			
Zn(1)–N(1)	2.2020(14)	Zn(1)–N(2)	2.245(2)
Zn(1)–C(61)	2.001(2)	Zn(1)–C(31)	2.167(2)
Zn(1)–C(32)	2.558(2)	C(31)–C(35)	1.427(3)
C(31)–C(32)	1.435(3)	C(32)–C(33)	1.392(2)
C(33)–C(34)	1.420(2)	C(33)–C(41)	1.526(2)
C(61)–C(611)	1.536(2)		
C(32)–Zn(1)–C(31)	34.11(6)	C(61)–Zn(1)–C(31)	132.10(7)
C(61)–Zn(1)–C(32)	109.58(7)	N(1)–Zn(1)–N(2)	82.32(6)
C(61)–Zn(1)–N(1)	111.73(6)	C(61)–Zn(1)–N(2)	111.50(7)
Zn(1)–C(61)–C(611)	116.71(13)	C(33)–C(41)–C(511)	108.34(14)

similar to those found in related complexes, for example, ZnMe<sub>2</sub>(TMEDA) [2.278 and 2.260 Å].<sup>18</sup>

It is evident from the crystal structures of **8b** and **9c** that in neither complex is there any interaction between the zinc atom and the pendant aromatic or heteroaromatic ring. This is not surprising since the TMEDA ligand will satisfy any coordination requirements. What is more interesting is the question of interactions in the TMEDA-free complexes. As none of these complexes could be obtained as crystals suitable for X-ray analysis, only NMR evidence is available. However, the addition of TMEDA to **6a** causes a significant low-field shift of the pyrrolyl protons (notably the *ortho*-H, which shift from  $\delta$  6.76 ppm to 7.27 ppm,  $\Delta\delta$  0.51 ppm) and suggests some degree of coordination of the pyrrolyl substituents. In view of the high solubility of these compounds in hydrocarbons, this interaction is more probably intramolecular, to give an *ansa*-sandwich structure, rather than intermolecular as in a coordination polymer. Similar chemical shift changes are seen for **7a** ( $\Delta\delta$  0.48 ppm).

**Cationic Species.** Treatment of toluene-*d*<sub>8</sub> solutions of **6a** with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>, [CPh<sub>3</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>], or [H(OEt)<sub>2</sub>]<sup>+</sup>[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>−</sup> led to the formation of complicated mixtures, which could not be characterized. When the TMEDA adduct **8a** was used, a white solid deposited, which proved to be insoluble, even in dichloromethane. It seems likely that this white solid is a coordination polymer, resulting from intermolecular coordination of the pyrrole to zinc, although bridging TMEDA ligands cannot be ruled out.

An NMR-scale reaction of Cp<sup>mes</sup>ZnEt (**7c**) with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> in toluene-*d*<sub>8</sub> led to the formation of Cp<sup>mes</sup>Zn(C<sub>6</sub>F<sub>5</sub>) (**10**) as the result of ligand exchange, along with EtB(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> and some traces of Et<sub>2</sub>B(C<sub>6</sub>F<sub>5</sub>) and Et<sub>3</sub>B, as shown by comparison to previous spectra.<sup>7</sup> Compound **10** was subsequently prepared in toluene and recrystallized from light petroleum as a white microcrystalline solid. This facile ligand exchange is common for dialkyl zinc species.<sup>7</sup> When the TMEDA adduct **9c** was treated with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> in toluene-*d*<sub>8</sub>, a red oil separated, which was soluble in dichloromethane-*d*<sub>2</sub> and identified as [Cp<sup>mes</sup>Zn-

(TMEDA)]<sup>+</sup>[EtB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>]<sup>−</sup> (**11**), along with some minor impurities. The [EtB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>]<sup>−</sup> anion has NMR characteristics closely similar to that in [EtZn(OEt)<sub>2</sub>]<sup>+</sup>[EtB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>]<sup>−</sup>,<sup>7</sup> with a small chemical shift difference between the *o*-F and *p*-F <sup>19</sup>F NMR resonances ( $\Delta\delta$  2.5 ppm), indicative of a noncoordinating borate.<sup>19</sup> Reactions of **7c** with [H(OEt)<sub>2</sub>]<sup>+</sup>[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>−</sup>, [CPh<sub>3</sub>]<sup>+</sup>[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>−</sup>, or [PhNMe<sub>2</sub>H]<sup>+</sup>[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>−</sup> produced complex mixtures and could not be characterized.

Treatment of a toluene-*d*<sub>8</sub> solution of **9a** with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> afforded a yellow oil, which separated from the toluene. The NMR spectra of this product in CD<sub>2</sub>Cl<sub>2</sub> were complicated, with evidence for the presence of three discrete borate anions, as shown by the <sup>11</sup>B and <sup>19</sup>F NMR. Apart from the [EtB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>]<sup>−</sup> anion, the <sup>11</sup>B spectrum contains two further signals, a broad singlet at  $\delta$  −11.8 and a doublet at  $\delta$  −21.1 (*J*<sub>HB</sub> = 84.8 Hz). The first is thought likely to arise from [Cp<sup>py</sup>B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>]<sup>−</sup>; this is supported by the presence in the <sup>1</sup>H NMR spectrum of signals associated with an  $\eta^1$ -bonded cyclopentadienyl ring. The doublet is assigned to the [HB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>]<sup>−</sup> anion via abstraction of a  $\beta$ -H from the ethyl ligand, with loss of ethene, which was identified in the <sup>1</sup>H NMR spectrum as a sharp singlet at  $\delta$  5.41. The <sup>19</sup>F NMR spectra are in agreement with this assignment and suggest the presence of free anions. In conclusion, the reaction of **9a** with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> is nonselective and proceeds with  $\beta$ -H, ethyl, and cyclopentadienyl abstraction. While the first two processes will result in the same cationic species, the last will not. Why **9a** reacts with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> in this fashion whereas **9c** generates almost exclusively **11** is not clear, although it is noted that an attempt to repeat the formation of **11** on a preparative scale did give evidence of both cyclopentadienyl and  $\beta$ -H abstraction as minor products.

**Polymerization Studies.** Zinc complexes have attracted much interest as single-site catalysts for the ring-opening polymerization of epoxides and lactones.<sup>20,21</sup> Specifically some complexes have been employed as catalysts for the alternating copolymerization of carbon dioxide and epoxides to produce aliphatic polycarbonates.<sup>20b</sup> Darensbourg et al. recently reported zinc halide and acetate complexes with amino-substituted cyclopentadienyl ligands but found only low to modest activity for the polymerization of cyclohexene oxide and propylene oxide and CO<sub>2</sub> copolymerizations.<sup>20e</sup> The use of cationic complexes has the advantage of increasing the Lewis acidity of the metal center and thus providing a greater driving force toward monomer coordination. For this reason it was hoped that the cationic complexes **11** and those arising from the reaction of **9a** with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> would provide active catalysts. The cationic species were generated in toluene solution and then

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Table 2. Polymerization Results Using **11** and **9a/B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>**

initiator (I) ( $\mu$ mol)	monomer (M)	M/I ratio	temp, °C	time, min	conversion %	TON <sup>a</sup>	$M_w^b$	$M_w/M_n^b$
<b>9a/B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub></b> (25) <sup>c</sup>	CHO	2000	0	5	100	24 000	59 700	6.1
<b>11c</b> (25) <sup>c</sup>	CHO	2000	0	5	100	24 000	102 000	1.6
<b>9a/B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub></b> (50) <sup>d</sup>	$\epsilon$ -CL	1000	65	3	1.0	210	30 400	2.0
<b>11c</b> (50) <sup>d</sup>	$\epsilon$ -CL	1000	65	3	8.0	1610	46 100	1.2
<b>9a/B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub></b> (50) <sup>e</sup>	S	1000	25	180	trace			
<b>11c</b> (50) <sup>e</sup>	S	1000	25	180	trace			
<b>9a/B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub></b> (25) <sup>f</sup>	PO	1000	25	2880	0			
<b>11c</b> (25) <sup>f</sup>	PO	1000	25	2880	0			

<sup>a</sup> Turnover numbers in mol monomer (mol Zn)<sup>-1</sup> h<sup>-1</sup>. <sup>b</sup> Determined by GPC relative to polystyrene standards. <sup>c</sup> Polymerization conditions for CHO: 25  $\mu$ mol of initiator (I); [M]/[I] = 2000; toluene 25 mL. <sup>d</sup> Polymerization conditions for  $\epsilon$ -CL: 50  $\mu$ mol of initiator (I); [M]/[I] = 1000; toluene 30 mL. <sup>e</sup> Polymerization conditions for styrene: 50  $\mu$ mol of initiator (I); [M]/[I] = 1000; toluene 10 mL. <sup>f</sup> Polymerization conditions for CHO: 25  $\mu$ mol of initiator (I); [M]/[I] = 1000; toluene 5 mL.

tested with a variety of monomers. The results of these tests are collected in Table 2.

The complexes are inactive for the polymerization of propylene oxide at 25 °C and gave only traces of polystyrene. However, the polymerization of cyclohexene oxide was rapid, and at 0 °C the monomer was quantitatively consumed within 5 min. The polymer produced by **11** was of reasonably high molecular weight ( $\bar{M}_w$  = 102 000), with a narrow polydispersity ( $\bar{M}_w/\bar{M}_n$  = 1.6). It is perhaps significant that the system **9a/B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>** produces poly(cyclohexene oxide) with a lower molecular weight ( $\bar{M}_w$  = 59 700) and a much wider polydispersity ( $\bar{M}_w/\bar{M}_n$  = 6.1), possibly as a consequence of the presence of several cationic species in the solution. Both **11** and **9a/B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>** polymerized  $\epsilon$ -caprolactone at 65 °C to give good quality polymers with narrow polydispersities. The cationic Cp<sup>mes</sup> complex **11** proved to be significantly more reactive than the **9a/B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>** catalyst.

## Conclusion

The starting point of this work was the desire to synthesize zinc *ansa*-sandwich complexes of the type [Zn(Cp-bridge-D)]<sup>+</sup>, where D =  $\pi$ -donor such as an electron-rich arene or heteroarene. Although the solubility characteristics of neutral complexes of this kind precluded crystallization and structural characterization, there is spectroscopic evidence for likely arene–zinc interactions. The facile C<sub>6</sub>F<sub>5</sub> exchange between perfluoroarylborate reagents and zinc alkyls is only suppressed by the presence of donors such as TMEDA. Cationic zinc cyclopentadienyl complexes such as [Cp<sup>mes</sup>Zn(TMEDA)]<sup>+</sup>[EtB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>]<sup>-</sup> are readily accessible in solution. Both [Cp<sup>mes</sup>Zn(TMEDA)]<sup>+</sup>[EtB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>]<sup>-</sup> and Cp<sup>py</sup>ZnEt(TMEDA)/B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> provide active initiators for the polymerization of cyclohexene oxide and  $\epsilon$ -caprolactone to high molecular weight polymers.

## Experimental Section

**General Procedures.** All manipulations were performed under nitrogen using standard Schlenk and glovebox techniques. Solvents were distilled under nitrogen from sodium (toluene), sodium benzophenone (diethyl ether, tetrahydrofuran), and sodium–potassium alloy (light petroleum, bp 40–60 °C). Deuterated solvents were stored over 4 Å molecular sieves and degassed by several freeze–thaw cycles. NMR spectra were recorded on a Bruker Avance DPX300 spectrometer. <sup>1</sup>H NMR spectra are referenced to residual solvent protons, <sup>19</sup>F (282.2 MHz) relative to CFCl<sub>3</sub>, and <sup>11</sup>B (96.2 MHz) relative to BF<sub>3</sub>·OEt<sub>2</sub>. Pyrrole, 2,5-dimethylpyrrole, dichlorodimethylsilane, ZnMe<sub>2</sub> (2.0 M solution in toluene), and ZnEt<sub>2</sub> (1.1 M solution in hexanes) were used as purchased. EtZnN-

(SiMe<sub>3</sub>)<sub>2</sub><sup>22</sup> and Zn[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub><sup>23</sup> were prepared according to literature procedures. TMEDA was dried over CaH<sub>2</sub> and distilled before use.

**1-(Chlorodimethylsilyl)pyrrole (1a).** A solution of pyrrole (20.0 g, 20.7 mL, 298 mmol) in diethyl ether (500 mL) at –78 °C was treated with <sup>n</sup>BuLi (186 mL, 1.6 M in hexanes, 298 mmol) over ca. 20 min. The reaction was allowed to reach room temperature and stirred for a further 2 h. The resulting white precipitate was collected via filtration and pumped in vacuo for 1 h. This solid was slowly added to a rapidly stirred solution of dimethyldichlorosilane (200 mL, 213 g, 1.65 mol) in light petroleum (300 mL). After complete addition the reaction was stirred for a further 10 h. The solids were filtered off and the filtrate was reduced in vacuo to leave **1a** as a colorless oil, contaminated by approximately 10% (C<sub>4</sub>H<sub>4</sub>N)<sub>2</sub>SiMe<sub>2</sub> (**2**), as shown by NMR. **1a** is slightly volatile at 0.5 mmHg. Yield 85%.

**2,5-Dimethyl-1-(chlorodimethylsilyl)pyrrole (1b).** Following the method described for **1a**, **1b** was prepared as a light yellow oil in 78% yield. Neither **1a** nor **1b** was fully purified but were used in situ.

**cyclo-C<sub>4</sub>H<sub>4</sub>NSiMe<sub>2</sub>C<sub>5</sub>H<sub>5</sub> (2a).** A solution of freshly prepared **1a** (10.1 g, 63.2 mmol) in light petroleum (200 mL) was slowly added to a solution of NaCp(THF) (10.1 g, 63.1 mmol) at 0 °C. After stirring for 16 h the reaction was quenched with water (100 mL). The organic layer was separated, dried over magnesium sulfate, and reduced in vacuo to leave crude **2a** as a slightly yellow oil. Distillation at 60–80 °C, 0.5 mmHg, provided pure **2a** as a pale yellow oil. Yield: 8.14 g (68.0%). Anal. Calcd for C<sub>11</sub>H<sub>15</sub>NSi: C, 69.78; H, 7.99; N, 7.40. Found: C, 69.61; H, 7.94; N, 8.00.

**cyclo-2,5-Me<sub>2</sub>C<sub>4</sub>H<sub>2</sub>NSiMe<sub>2</sub>C<sub>5</sub>H<sub>5</sub> (2b).** Following the method described for **2a**, **2b** was prepared as a yellow oil in 87.1% yield. **2b** was purified by distillation at 80–100 °C/0.7 mmHg. Anal. Calcd for C<sub>13</sub>H<sub>19</sub>NSi: C, 71.83; H, 8.81; N, 6.44. Found: C, 71.46; H, 8.45; N, 6.67.

**3,5-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>CH<sub>2</sub>CMe<sub>2</sub>C<sub>5</sub>H<sub>5</sub> (2c).** To a solution of mesitylene (20 g, 166 mmol) in light petroleum (200 mL) at 0 °C was added rapidly <sup>n</sup>BuLi (104 mL, 1.6 M in hexanes, 166 mmol), followed by dry TMEDA (25 mL, 166 mmol). The reaction mixture was stirred overnight to give a bright yellow precipitate, which was filtered off and dissolved in THF (200 mL). The solution was cooled to 0 °C, and dimethylfulvene (17.6 g, 166 mmol) was added rapidly. The reaction mixture was allowed to reach room temperature, stirred for 12 h, quenched with a saturated aqueous solution of ammonium chloride, and extracted with diethyl ether (3 × 100 mL). The organic fractions were dried over magnesium sulfate, filtered, and taken to dryness in vacuo. The residue was distilled under reduced pressure to afford the product as a yellow-orange oil, bp 100 °C/0.1 mmHg. <sup>1</sup>H NMR indicates the presence of two isomers. Yield: 15.0 g (40.0%). Anal. Calcd for C<sub>17</sub>H<sub>22</sub>: C, 90.20; H, 9.80. Found: C, 90.23; H, 9.82.

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**(C<sub>4</sub>H<sub>4</sub>NSiMe<sub>2</sub>C<sub>5</sub>H<sub>4</sub>)<sub>2</sub>Zn (3a).** A solution of Zn[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (2.78 g, 7.20 mmol) in light petroleum (20 mL) was treated with **2a** (2.72 g, 14.4 mmol), heated at 45 °C for 2 h, and then stirred at room temperature for a further 16 h. The resulting white precipitate was filtered off, washed with light petroleum (2 × 20 mL), and pumped to dryness in vacuo. Yield: 2.15 g (67.6%). Anal. Calcd for C<sub>22</sub>H<sub>28</sub>N<sub>2</sub>Si<sub>2</sub>Zn: C, 59.78; H, 6.34; N, 6.39. Found: C, 59.45; H, 6.41; N, 6.25.

**(C<sub>4</sub>H<sub>4</sub>NSiMe<sub>2</sub>C<sub>5</sub>H<sub>4</sub>)<sub>2</sub>Mg (4a).** A solution of **2a** (2.00 g, 10.6 mmol) in light petroleum (40 mL) at 0 °C was treated with MgBu<sub>2</sub> (5.28 mL, 1.0 M solution in heptane, 5.28 mmol). The reaction was stirred at room temperature for 16 h. Concentration to ca. 20 mL and cooling to -20 °C provided **4a** as a white microcrystalline solid, yield 3.05 g (71.8%). Anal. Calcd for C<sub>22</sub>H<sub>28</sub>N<sub>2</sub>Si<sub>2</sub>Mg: C, 65.90; H, 7.04; N, 6.99. Found: C, 65.45; H, 7.03; N, 6.56.

**(2,5-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>CH<sub>2</sub>CMMe<sub>2</sub>C<sub>5</sub>H<sub>4</sub>)<sub>2</sub>Mg (4b).** A solution of **2b** (2.06 g, 9.45 mmol) in light petroleum (100 mL) at 0 °C was treated with MgBu<sub>2</sub> (4.70 mL, 1.0 M solution in heptane, 4.70 mmol). The reaction rapidly became yellow and was stirred at room temperature for 16 h. Concentration to ca. 30 mL and cooling to -20 °C overnight gave **4b** as a white microcrystalline solid, yield 3.11 g (72.0%). Anal. Calcd for C<sub>26</sub>H<sub>36</sub>N<sub>2</sub>Si<sub>2</sub>Mg: C, 68.32; H, 7.94; N, 6.13. Found: C, 68.58; H, 8.04; N, 6.34.

**(3,5-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>CH<sub>2</sub>CMMe<sub>2</sub>C<sub>5</sub>H<sub>4</sub>)<sub>2</sub>Mg (4c).** A solution of Cp<sup>mes</sup>H (1.47 g, 6.49 mmol) in light petroleum (20 mL) at 0 °C was treated with MgBu<sub>2</sub> (3.25 mL, 1.0 M in hexanes). The reaction mixture was stirred vigorously for 7 h followed by concentration of the solvent under reduced pressure. The reaction mixture was cooled to -20 °C to give **4c** a white crystalline solid, yield 0.95 g (31.0%). Anal. Calcd for C<sub>34</sub>H<sub>42</sub>Mg: C, 85.97; H, 8.91. Found: C, 84.98; H, 8.89.

**MeZnN(SiMe<sub>3</sub>)<sub>2</sub> (5).** A solution of ZnMe<sub>2</sub> (4.5 mL, 2 M in toluene, 9.0 mmol) in light petroleum (20 mL) was treated with Zn[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (3.48 g, 3.63 mL, 9.0 mmol). After stirring for 30 min the volatiles were removed in vacuo. The resulting sticky white residue was sublimed at 50 °C/0.7 mmHg to give **5** as colorless crystals, yield 2.41 g (55.6%). Anal. Calcd for C<sub>7</sub>H<sub>21</sub>NSi<sub>2</sub>Zn: C, 34.92; H, 8.79; N, 5.82. Found: C, 34.78; H, 8.43; N, 5.88.

**Generation of (C<sub>4</sub>H<sub>4</sub>NSiMe<sub>2</sub>C<sub>5</sub>H<sub>4</sub>)ZnMe (6a). Method a.** To a solution of ZnMe<sub>2</sub> (0.015 g, 0.157 mmol) in toluene-*d*<sub>8</sub> (0.3 mL) was added a solution of **2a** (0.030 g, 0.158 mmol) also in toluene-*d*<sub>8</sub> (0.3 mL). The reaction was maintained at 90 °C, progress being monitored by <sup>1</sup>H NMR. After 48 h at this temperature the signals for **2a** had disappeared and the solution contained mainly **6a** and CH<sub>4</sub> with some unidentified side products.

**Method b.** To a solution of **5** (0.030 g, 0.125 mmol) in toluene-*d*<sub>8</sub> (0.3 mL) was added a solution of **2a** (0.024 g, 0.127 mmol) also in toluene-*d*<sub>8</sub> (0.3 mL). The reaction was monitored at 40 °C by <sup>1</sup>H NMR spectroscopy. After 1 h the solution contained mainly **6a** and HN(SiMe<sub>3</sub>)<sub>2</sub>.

**Generation of (2,5-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>CH<sub>2</sub>CMMe<sub>2</sub>C<sub>5</sub>H<sub>4</sub>)ZnMe (6c).** To a solution of MeZnN(SiMe<sub>3</sub>)<sub>2</sub> (0.030 g, 0.125 mmol) in C<sub>6</sub>D<sub>6</sub> (0.3 mL) was added a solution of Cp<sup>mes</sup>H (0.028 g, 0.125 mmol) in C<sub>6</sub>D<sub>6</sub> (0.3 mL). The reaction mixture was maintained at a temperature of 50 °C. After 1.5 h the reaction was >90% complete (NMR). Attempts to isolate an analytically pure sample of the product on a preparative scale were frustrated by the oily nature of this compound.

**Generation of (C<sub>4</sub>H<sub>4</sub>NSiMe<sub>2</sub>C<sub>5</sub>H<sub>4</sub>)ZnEt (7a).** Following the procedures described for **6a**, **7a** was similarly generated from **2a** and either ZnEt<sub>2</sub> or EtZnN(SiMe<sub>3</sub>)<sub>2</sub> and characterized spectroscopically in solution.

**Generation of (3,5-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>CH<sub>2</sub>CMMe<sub>2</sub>C<sub>5</sub>H<sub>4</sub>)ZnEt (7c).** To a solution of EtZnN(SiMe<sub>3</sub>)<sub>2</sub> (0.032 g, 0.125 mmol) in C<sub>6</sub>D<sub>6</sub> (0.3 mL) was added Cp<sup>mes</sup>H (0.028 g, 0.125 mmol) in C<sub>6</sub>D<sub>6</sub> (0.3 mL). The reaction mixture was heated to 50 °C and the progress of the reaction monitored by <sup>1</sup>H NMR. After 2 h, NMR indicated a conversion of >90%. Attempts to obtain an analytically pure

sample of the product on a preparative scale were frustrated by the oily nature and high solubility of this compound.

**(C<sub>4</sub>H<sub>4</sub>NSiMe<sub>2</sub>C<sub>5</sub>H<sub>4</sub>)ZnMe(TMEDA) (8a).** A mixture of MeZnN(SiMe<sub>3</sub>)<sub>2</sub> (3.10 g, 12.9 mmol) and **2a** (2.41 g, 12.7 mmol) in light petroleum (90 mL) was stirred at 40 °C for 2 h. After removal of volatiles the oily residue was dissolved in light petroleum (30 mL) and TMEDA (1.60 g, 13.8 mmol) was added, causing the immediate separation of a pale pink oil, which was collected and pumped in vacuo for 2 h, after which time it solidified. The pale pink powder was extracted with light petroleum (40 mL). Concentration and cooling to -20 °C overnight gave **8a** as a colorless crystalline solid, yield 2.45 g (49.3%). Anal. Calcd for C<sub>18</sub>H<sub>33</sub>N<sub>3</sub>SiZn: C, 56.16; H, 8.64; N, 10.92. Found: C, 56.47; H, 8.37; N, 10.27.

**(2,5-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>CH<sub>2</sub>CMMe<sub>2</sub>C<sub>5</sub>H<sub>4</sub>)ZnMe(TMEDA) (8b).** Following the procedure for **8a**, **8b** was prepared from MeZnN(SiMe<sub>3</sub>)<sub>2</sub> (2.05 g, 8.51 mmol), **2b** (1.85 g, 8.51 mmol), and TMEDA (1.05 g, 9.04 mmol) as a pale yellow crystalline solid after recrystallization from light petroleum/diethyl ether at -20 °C, yield 2.52 g (71.7%). Anal. Calcd for C<sub>20</sub>H<sub>37</sub>N<sub>3</sub>SiZn: C, 58.16; H, 9.03; N, 10.17. Found: C, 57.33; H, 8.86; N, 9.85.

**(C<sub>4</sub>H<sub>4</sub>NSiMe<sub>2</sub>C<sub>5</sub>H<sub>4</sub>)ZnEt(TMEDA) (9a).** A mixture of EtZnN(SiMe<sub>3</sub>)<sub>2</sub> (9.86 mL, 1.1 M in toluene, 10.8 mmol) and **2a** (2.00 g, 10.8 mmol) in toluene (80 mL) was heated to reflux for 24 h. Removal of the volatiles gave a dark brown oil, which was dissolved in light petroleum. Addition of TMEDA (1.50 g, 12.9 mmol) caused the immediate formation of a light brown precipitate, which was filtered off, dried in vacuo for 2 h, and recrystallized from light petroleum to give **9a** as a yellow microcrystalline solid, yield 2.39 g (55.5%). Anal. Calcd for C<sub>19</sub>H<sub>35</sub>N<sub>3</sub>SiZn: C, 57.20; H, 8.84; N, 10.53. Found: C, 57.37; H, 8.53; N, 10.18.

**(2,5-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>CH<sub>2</sub>CMMe<sub>2</sub>C<sub>5</sub>H<sub>4</sub>)ZnEt(TMEDA) (9b).** A mixture of EtZnN(SiMe<sub>3</sub>)<sub>2</sub> (2.01 g, 7.89 mmol) and **2b** (1.75 g, 8.05 mmol) in light petroleum (50 mL) was stirred at 40 °C for 2 h. Removal of volatiles left an oil, which was dissolved in light petroleum (40 mL) and treated with TMEDA (1.20 g, 10.3 mmol). A red oil separated from the solvent, which was isolated. Drying in vacuo for 2 h gave a red powder, which was extracted with light petroleum (50 mL). The extract was reduced in vacuo and cooled to -20 °C overnight to give **9b** as orange crystals, yield 2.51 g (74.5%). Anal. Calcd for C<sub>21</sub>H<sub>39</sub>N<sub>3</sub>SiZn: C, 59.07; H, 9.21; N, 9.84. Found: C, 58.52; H, 8.85; N, 9.31.

**(3,5-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>CH<sub>2</sub>CMMe<sub>2</sub>C<sub>5</sub>H<sub>4</sub>)ZnEt(TMEDA) (9c).** A solution of EtZnN(SiMe<sub>3</sub>)<sub>2</sub> (1.85 g, 7.25 mmol) in light petroleum (20 mL) was treated with Cp<sup>mes</sup>H (1.64 g, 7.25 mmol) at 50 °C for 2 h. Removal of the volatiles in vacuo, afforded a yellow oil, which was dissolved in light petroleum and treated with dry TMEDA (1.09 mL, 7.25 mmol). The mixture was stirred for 16 h, during which time a thick white precipitate formed, which was filtered off and washed with light petroleum (10 mL) to give **9c**, yield 2.10 g (68.0%). Anal. Calcd for C<sub>25</sub>H<sub>37</sub>N<sub>2</sub>Zn: C, 68.87; H, 9.71; N, 6.43. Found: C, 68.20; H, 9.66; N, 6.26.

**Reaction of Cp<sup>mes</sup>ZnEt with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> in Toluene-*d*<sub>8</sub>.** An NMR tube was charged with Cp<sup>mes</sup>H (0.022 g, 0.098 mmol) and EtZnN(SiMe<sub>3</sub>)<sub>2</sub> (0.025 g, 0.098 mmol). The reactants were dissolved in toluene-*d*<sub>8</sub> (0.5 mL), and the sealed tube was heated at 60 °C for 3 h, with the progress of the reaction followed by <sup>1</sup>H NMR spectroscopy. Upon completion of the reaction, the volatiles were carefully removed from the NMR tube in vacuo, and a solution of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (0.050 g, 0.098 mmol) in toluene-*d*<sub>8</sub> (0.5 mL) was added. The <sup>11</sup>B NMR spectrum indicated ligand exchange leading to the formation of Cp<sup>mes</sup>-Zn(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> (**10**) and EtB(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> with small amounts of BEt<sub>3</sub> and BEt<sub>2</sub>(C<sub>6</sub>F<sub>5</sub>), which are characterized by comparison with literature spectra.<sup>6</sup>

**(3,5-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>CH<sub>2</sub>CMMe<sub>2</sub>C<sub>5</sub>H<sub>4</sub>)Zn(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> (10).** A solution of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (1.17 g, 2.29 mmol) in toluene (10 mL) was treated with a solution of Cp<sup>mes</sup>ZnEt (2.20 g, 6.88 mmol) in toluene

(10 mL). The mixture was stirred for 1 h, followed by removal of the volatiles in vacuo. The residue was recrystallized from light petroleum, affording an off-white solid, yield 1.35 g (40.7%). Anal. Calcd for  $C_{23}H_{21}F_5Zn$ : C, 60.34; H, 4.62. Found: C, 59.88; H, 4.64.  $^{19}F$  NMR (282.4 MHz, benzene- $d_6$ , 20 °C):  $\delta$  -113.2 (m, 2 F, *o*-F), -153.8 (t, 1 F, *p*-F), -161.2 (m, 2 F, *m*-F).

**Reaction of  $Cp^{mes}ZnEt(TMEDA)$  with  $B(C_6F_5)_3$  in Toluene- $d_8$ .** An NMR tube was charged with  $B(C_6F_5)_3$  (0.030 g, 59  $\mu$ mol) and **9c** (0.025 g, 59  $\mu$ mol). The reactants were dissolved in toluene- $d_8$  (0.5 mL), and the progress of the reaction was monitored by NMR spectroscopy. A red oil was observed to precipitate from the solution and was isolated and dissolved in  $CD_2Cl_2$ . NMR spectroscopy indicated the formation of  $[Cp^{mes}Zn(TMEDA)]^+[EtB(C_6F_5)_3]^-$  (**11**) as the main product.  $^{11}B\{^1H\}$  NMR (96.2 MHz,  $CD_2Cl_2$ , 20 °C):  $\delta$  -9.4  $[EtB(C_6F_5)_3]^-$ .  $^{19}F$  NMR (282.4 MHz,  $CD_2Cl_2$ , 20 °C):  $\delta$  -133.1 (d, 6 F,  $J_{FF}$  = 22.6 Hz, *o*-F), -165.4 (t, 3 F,  $J_{FF}$  = 22.6 Hz, *p*-F), -168.0 (t, 6 F,  $J_{FF}$  = 22.6 Hz, *m*-F).

**Reaction of  $Cp^{py}ZnEt(TMEDA)$  with  $B(C_6F_5)_3$  in Toluene- $d_8$ .** To an NMR tube containing  $B(C_6F_5)_3$  (0.030 g, 59  $\mu$ mol) and **9a** (0.023 g, 59  $\mu$ mol) was added toluene- $d_8$  (0.5 mL). An orange oil precipitated after ca. 5 s, which was isolated and dissolved in  $CD_2Cl_2$ . NMR spectroscopy showed a complicated mixture of products.  $^{11}B$  and  $^{19}F$  NMR showed the presence of three different anions, identified as  $[EtB(C_6F_5)_3]^-$ ,  $[HB(C_6F_5)_3]^-$ , and  $[Cp^{py}B(C_6F_5)_3]^-$ .  $[EtB(C_6F_5)_3]^-$  is characterized by the following parameters:  $^{11}B\{^1H\}$  NMR (96.2 MHz,  $CD_2Cl_2$ , 20 °C):  $\delta$  -9.6.  $^{19}F$  NMR (282.4 MHz,  $CD_2Cl_2$ , 20 °C):  $\delta$  -131.6 (d, 6 F,  $J_{FF}$  = 22.6 Hz, *o*-F), -164.8 (t, 3 F,  $J_{FF}$  = 22.6 Hz, *p*-F), -167.8 (t, 6 F,  $J_{FF}$  = 22.6 Hz, *m*-F).  $[Cp^{py}B(C_6F_5)_3]^-$ :  $^{11}B\{^1H\}$  NMR (96.2 MHz,  $CD_2Cl_2$ , 20 °C):  $\delta$  -11.4.  $^{19}F$  NMR (282.4 MHz,  $CD_2Cl_2$ , 20 °C):  $\delta$  -132.9 (d, 6 F,  $J_{FF}$  = 22.6 Hz, *o*-F), -165.6 (t, 3 F,  $J_{FF}$  = 22.6 Hz, *p*-F), -168.2 (t, 6 F,  $J_{FF}$  = 22.6 Hz, *m*-F).  $[HB(C_6F_5)_3]^-$ :  $^{11}B\{^1H\}$  NMR (96.2 MHz,  $CD_2Cl_2$ , 20 °C): -21.1 (d,  $J_{HB}$  = 84.8 Hz).  $^{19}F$  NMR (282.4 MHz,  $CD_2Cl_2$ , 20 °C):  $\delta$  -134.2 (d, 6 F,  $J_{FF}$  = 22.6 Hz, *o*-F), -164.3 (t, 3 F,  $J_{FF}$  = 22.6 Hz, *p*-F), -167.5 (t, 6 F,  $J_{FF}$  = 22.6 Hz, *m*-F). The  $^1H$  spectrum could not be fully assigned due to the large number of peaks, although there is clear evidence of an  $\eta^1$ -bonded cyclopentadienyl ligand with several multiplets between  $\delta$  6.0 and 7.2 ppm.

**Reaction of  $Cp^{py}ZnEt(TMEDA)$  with  $B(C_6F_5)_3$  in Dichloromethane- $d_2$ .** To an NMR tube containing  $B(C_6F_5)_3$  (0.030 g, 59  $\mu$ mol) and **9a** (0.023 g, 59  $\mu$ mol) was added  $CD_2Cl_2$  (0.5 mL). The reaction was followed by multinuclear NMR spectroscopy. The product distribution was essentially the same as when the reaction was carried out in toluene- $d_8$  (vide supra). Also present in the  $^1H$  NMR was a sharp singlet at  $\delta$  5.41, which is assigned to ethene formed as the result of  $\beta$ -H abstraction.

**General Procedure for Polymerization.** A magnetically stirred 50 mL Schlenk tube was flame-dried in vacuo prior to being charged with the required volume of dry and degassed toluene and monomer. To this was added a solution of the initiator (either **11** or **9a**/ $B(C_6F_5)_3$ ) in a small amount of toluene. For the styrene, cyclohexene oxide, and  $\epsilon$ -caprolactone polymerizations the reaction was terminated by the injection of 2 mL of methanol. The polymer was precipitated with acidified methanol, washed with methanol, and dried in vacuo for 24 h. The propylene oxide tests were monitored by NMR spectroscopy.

**X-ray Crystallography.** From a sample under dried perfluoropolyether, a crystal was mounted on a glass fiber and fixed in the cold nitrogen stream on a Rigaku R-Axis II image plate diffractometer equipped with a rotating anode X-ray source (Mo K $\alpha$  radiation) and graphite monochromator. Data were processed using the DENZO/SCALEPACK programs.<sup>24</sup> The structure was determined by the direct methods routines in the XS program<sup>25</sup> and refined by full-matrix least-squares methods, on  $F^2$ 's, in XL.<sup>24</sup> The non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included in idealized positions, and their  $U_{iso}$  values were set to ride on the  $U_{eq}$  values of the parent carbon atoms, except for H(32) and H(33) for **9c** and H(42) and H(43) for **8b**, which were refined freely. For those methyl groups for which a staggered conformation was not possible to calculate, the group was allowed to rotate about the C-C bond. In the final difference map, the highest peaks (to ca. 0.23 e  $\text{\AA}^{-3}$ ) were close to the zinc atom. In the final difference map, the highest peaks (to ca. 0.32 e  $\text{\AA}^{-3}$ ) were close to the Zn-N(1) bond. Scattering factors for neutral atoms were taken from ref 26. Computer programs were run on a Silicon Graphics Indy at the University of East Anglia.

**Crystal data for **8b**:**  $C_{20}H_{37}N_3SiZn$ , fw 413.0; crystal size 0.5  $\times$  0.3  $\times$  0.3 mm; monoclinic, space group  $P2_1/c$ ,  $a$  = 10.776(1)  $\text{\AA}$ ,  $b$  = 11.755(1)  $\text{\AA}$ ,  $c$  = 18.419(1)  $\text{\AA}$ ;  $\beta$  = 104.40(1)°;  $V$  = 2259(3)  $\text{\AA}^3$ ;  $Z$  = 4,  $D_{calcd}$  = 1.214 g  $\text{cm}^{-3}$ ;  $\mu$  = 1.15 mm $^{-1}$ ; 8034 reflections collected, of which 4131 were unique ( $R_{int}$  = 0.0348) and 3490 with  $I > 2\sigma(I)$  were observed; final  $R_1$  [ $I > 2\sigma(I)$ ] = 0.0272,  $wR_2$  (all data) = 0.0725,  $w = [\sigma^2(F_o^2) + (0.0266P)^2 + 0.606P]^{-1}$  with  $P = (F_o^2 + 2F_c^2)/3$ . Goodness of fit  $S$  = 1.063 for 239 parameters.

**Crystal data for **9c**:**  $C_{25}H_{42}N_2Zn$ , fw 435.98; crystal size 0.5  $\times$  0.6  $\times$  0.9 mm; monoclinic, space group  $P2_1/c$ ,  $a$  = 11.142(2)  $\text{\AA}$ ,  $b$  = 16.157(3)  $\text{\AA}$ ,  $c$  = 14.667(3)  $\text{\AA}$ ;  $\beta$  = 107.52(3)°;  $V$  = 2517(9)  $\text{\AA}^3$ ;  $Z$  = 4,  $D_{calcd}$  = 1.150 g  $\text{cm}^{-3}$ ;  $\mu$  = 0.987 mm $^{-1}$ ; 9002 reflections collected, of which 4607 were unique ( $R_{int}$  = 0.024) and 3739 with  $I > 2\sigma(I)$  were observed; final  $R_1$  [ $I > 2\sigma(I)$ ] = 0.0284,  $wR_2$  (all data) = 0.0743;  $w = [\sigma^2(F_o^2) + (0.0266P)^2 + 0.606P]^{-1}$  with  $P = (F_o^2 + 2F_c^2)/3$ . Goodness of fit  $S$  = 1.029 for 260 parameters.

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**Supporting Information Available:**  $^1H$  and  $^{13}C$  NMR data for new compounds and crystallographic data for compounds **8b** and **9c**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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