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Novel Zinc and Magnesium Alkyl and Amido Cations for Ring-Opening Polymerization Reactions

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The reaction of $[H(OEt_2)_2][B(C_6F_5)_4]$ with $Zn[N(SiMe_3)_2]_2$, $MgBu_2$, and $\{Mg[N(SiMe_3)_2]_2\}_2$ in diethyl ether proceeds in very high yields to give the salts $[(Et_2O)_3ZnN(SiMe_3)_2][B(C_6F_5)_4]$ (**2**), $[(Et_2O)_3Mg^nBu][B(C_6F_5)_4]$ (**3**), and $[(Et_2O)_3MgN(SiMe_3)_2][B(C_6F_5)_4]$ (**4**), respectively. The structures of **2** and **4** were determined by X-ray crystallography; the compounds contain distorted-tetrahedral metal centers and are isostructural. $[(Et_2O)_3ZnCH_2CH_3][B(C_6F_5)_4]$ (**1**) as well as **2**−**4** catalyze the ring-opening polymerization of epoxides and ϵ-caprolactone. Cyclohexene oxide is polymerized extremely rapidly to high molecular weight materials, while the polymerization of propene oxide gives low molecular weight materials via a cationic mechanism. The zinc species are more stable than their magnesium analogues and show higher productivities. ϵ-Caprolactone is polymerized efficiently to high molecular weight polymers.

Introduction

The ring-opening polymerizations of polar monomers such as epoxides and cyclic esters have attracted considerable interest during the past few years.[1] Poly(propene oxide) (PPO) is a key component for the preparation of polyurethanes and is widely used as a bulk commodity material.[2] Aluminum-based complexes have been developed for the living polymerization of propene oxide,[3] whereas cationic aluminum species supported by the salen-type ligands afford high molecular weight poly(propene oxide).[4] Cyclohexene oxide and carbon dioxide are successfully copolymerized by zinc aryloxides,[5] diketiminates,[6] and carboxylates,[7] although these systems proved ineffective for epoxide homopolymerization.[8] The polymerizations of cyclic esters such as ϵ-caprolactone and especially L-lactide for the production of biodegradable polymers have become an important target.[1b] Zinc and to a lesser extent magnesium complexes with sterically hindered ligands have been shown to be the most efficient initiators to date for the controlled ring-opening polymerization of these monomers.[1b,c] Coates and Chisholm independently reported diketiminato and iminophenolato complexes of zinc that are very efficient for the polymerization of lactides;[9] Chisholm also found that tris(pyrazolato) borate complexes of magnesium and especially calcium were highly active.[10] However, these complexes are inactive toward epoxide polymerization.

We showed recently that the reaction of zinc dialkyls with $B(C_6F_5)_3$ in toluene gives $Zn(C_6F_5)_2$(toluene), while in Et_2O the cationic zinc alkyls $[RZn(OEt_2)_3]^+[B(C_6F_5)_4]^-$ are formed (R = Me, Et, ^tBu).[11a] Similarly, zinc cyclopentadienyl complexes stabilized by chelating amines form cationic species that are active for the polymerization of ϵ-caprolactone and cyclohexene oxide.[11b] We also reported the convenient synthesis of three-coordinate zinc cations $[DADZnR]^+[X]^-$ from ZnR_2 and [HDAD][X] (R = Me, Et, $N(SiMe_3)_2$; X = Me-$B(C_6F_5)_3$, $B(C_6F_5)_4$;

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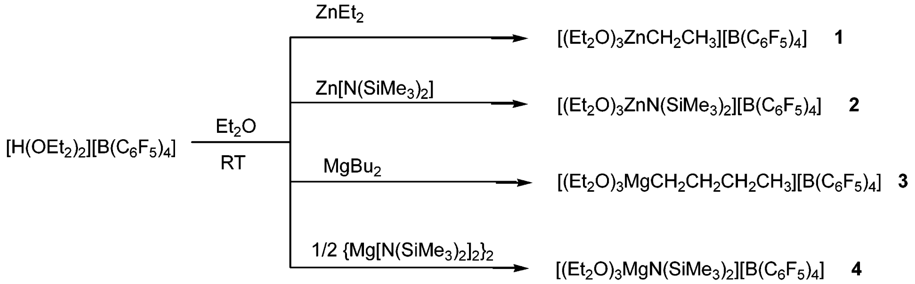
Scheme 1



DAD = (MeC=NC$_6$H$_3$^{i}Pr$_2$-2,6)$_2$) suitable for the ring-opening polymerization of epoxides and ϵ-caprolactone.[12] Previously, cationic zinc alkyls had been synthesized by the addition of nitrogen macrocycles or crown ethers to zinc alkyls in the presence of AlR$_3$ or tetraphenylcyclopentadiene[13] or by the protolysis of ZnEt$_2$ with [Bz$_3$TAC-H]$^+$[PF$_6$]$^-$ (TAC = 1,3,5-tribenzyl-1,3,5-triazacyclohexane).[14]

On the other hand, very little is known about cationic magnesium alkyls or amides. The reaction of MgR$_2$ with the sterically demanding tris(3-R′-pyrazolyl)hydroborato ligands (R′ = Ph, ^{t}Bu) yields [η^3-HB(3-R′pz)$_3$]-MgR,[9b,15] whereas magnesium alkyl cations are obtained by reaction of dialkylmagnesium with the azacrown ether (1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane).[16] Here, we report the syntheses and the structures of novel four-coordinate alkyl and amide zinc and magnesium cations and their behavior in the ring-opening polymerization of cyclohexene oxide, propene oxide, and ϵ-caprolactone.

Results and Discussion

The reaction in diethyl ether of "Jutzi's acid" [H(OEt$_2$)$_2$]-[B(C$_6$F$_5$)$_4$] with a slight excess of [MX$_2$]$_n$ (M = Zn, n = 1, X = N(SiMe$_3$)$_2$; M = Mg, X = Bu, n = 1; X = N(SiMe$_3$)$_2$, n = 2) affords the corresponding salts [(Et$_2$O)$_3$ZnN(SiMe$_3$)$_2$][B(C$_6$F$_5$)$_4$] (**2**), [(Et$_2$O)$_3$MgCH$_2$CH$_2$CH$_2$CH$_3$][B(C$_6$F$_5$)$_4$] (**3**), and [(Et$_2$O)$_3$MgN(SiMe$_3$)$_2$][B(C$_6$F$_5$)$_4$] (**4**), where three molecules of diethyl ether are coordinated to the cationic metal center and where the counteranion is the poorly coordinating pentafluorophenyl borate anion. Following the procedure we reported for the synthesis of [(Et$_2$O)$_3$ZnCH$_2$CH$_3$][B(C$_6$F$_5$)$_4$] (**1**),[11] compounds **2**−**4** were prepared in very good yields when the reactions were carried out for 1 to 2 h in diethyl ether at room temperature (Scheme 1). In the case of the Mg species, the yields of isolated products were typically well above 90%, and the reactions were complete within 1 h. Analytically pure products **2**−**4** were isolated as white crystalline materials from a diethyl ether/light petroleum mixture (5:1) at −26 °C. All compounds are extremely air and moisture sensitive. They are highly soluble in diethyl ether, THF, and dichloromethane, but only moderately in toluene and insoluble in light petroleum.

The new complexes were characterized by NMR spectroscopy (^{1}H, {^{1}H}^{13}C, ^{19}F, and ^{11}B) and elemental analyses. In all cases, the ^{11}B NMR of the borate anion displays a single sharp peak at δ −13.6. Elemental analyses showed good agreement with the theoretical values. The synthesis of **3** from MgBu^{s}Bu^n gave exclusively the n-butyl complex, either by selective protonation of s-Bu or via isomerization of the s-Bu groups.

Attempts to prepare aryloxy derivatives of compounds **1** and **2** either by direct reaction of Jutzi's acid with {Zn-(OAr)$_2$}$_2$ (Ar = 2,6-bis-Bu^t-4-methylphenyl) or via addition of an excess of ArOH to **2** proved unsuccessful. In both cases, off-white sticky solids were obtained, and neither washing with petrol nor attempts to recrystallize in diethyl ether allowed the recovery of a clean product.

Whereas single crystals of **2** suitable for X-ray diffraction crystallography were readily grown from diethyl ether/light petroleum at −26 °C, the isolation of crystals of the magnesium derivatives **3** and **4** was complicated by the extreme sensitivity and relative instability of these compounds. The smallest crystals decomposed almost immediately when removed from the Schlenk tube under nitrogen, whereas the bigger ones degraded in the diffractometer during the course of the acquisition of the crystallographic data. Suitable crystals of **4** were eventually obtained by recrystallization from an 8:1 mixture of diethyl ether and light petroleum after several weeks at −26 °C, whereas suitable crystals of **3** could not be isolated. The difference in stability between Zn compounds **1** and **2** and their Mg analogues **3** and **4** was further evidenced by the fact that the latter decomposed in the inert atmosphere of the glovebox over a period of a few months, while the former remained unchanged under identical conditions.

The single-crystal X-ray structures of the salts **2** and **4** were determined (Figures 1 and 2). Selected bond lengths and angles are collected in Table 1. They both contain two anions and two cations per asymmetric unit. The structure of the cation in **4** (**4**$^+$) confirms the presence of three molecules of diethyl ether coordinated to the metal center and exhibits a distorted tetrahedral arrangement, with N−Mg−O angles ranging from 107.93(12)° to 127.46(12)°. The Mg−N bond length in **4**$^+$ of 1.986(3) Å compares well with the literature values for [(Et$_2$O)Mg(Cl){N(SiMe$_3$)$_2$}]$_2$ [1.970(3) Å] and Mg-[N(SiMePh$_2$)$_2$]$_2$ [1.963(6) and 1.969(6) Å],[17] [{(Me$_3$-Si)$_2$NMg[μ-OC(Me)-^{t}BuCH$_2$C(^{t}Bu)=O]}$_2$] [1.9920(19) Å],[18]

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Table 1. Selected Interatomic Distances (Å) and Angles (deg) for 2$^+$ and 4$^+$

$[(Et_2O)_3ZnN(SiMe_3)_2]^+$ (**2**$^+$)		$[(Et_2O)_3MgN(SiMe_3)_2]^+$ (**4**$^+$)	
Zn(1)−N(4)	1.907(3)	Mg(1)−N(4)	1.986(3)
Zn(1)−O(1)	2.092(2)	Mg(1)−O(3)	2.045(2)
Zn(1)−O(2)	2.050(3)	Mg(1)−O(1)	2.056(3)
Zn(1)−O(3)	2.056(3)	Mg(1)−O(2)	2.060(3)
N(4)−Si(1)	1.735(3)	N(4)−Si(2)	1.720(3)
N(4)−Si(2)	1.728(3)	N(4)−Si(1)	1.724(3)
N(4)−Zn(1)−O(2)	113.86(11)	N(4)−Mg(1)−O(3)	127.46(12)
N(4)−Zn(1)−O(3)	133.52(11)	N(4)−Mg(1)−O(1)	108.24(12)
N(4)−Zn(1)−O(1)	110.73(11)	N(4)−Mg(1)−O(2)	107.93(12)
O(2)−Zn(1)−O(1)	112.23(11)	O(3)−Mg(1)−O(2)	95.25(11)
O(3)−Zn(1)−O(1)	91.56(10)	O(1)−Mg(1)−O(2)	125.99(12)
O(2)−Zn(1)−O(3)	92.39(11)	O(3)−Mg(1)−O(1)	93.24(10)
Si(2)−N(4)−Zn(1)	116.7(2)	Si(1)−N(4)−Mg(1)	121.67(14)
Si(1)−N(4)−Zn(1)	118.0(2)	Si(2)−N(4)−Mg(1)	114.0(2)

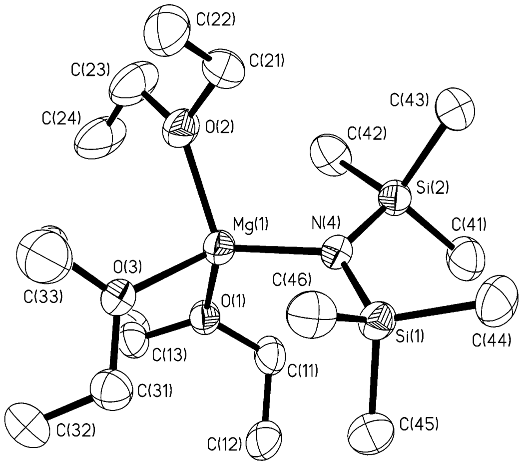

Figure 1. X-ray structure of the cation $(Et_2O)_3MgN(SiMe_3)_2^+$ (**4**$^+$) showing the atomic numbering scheme. Thermal ellipsoids are drawn at the 50% probability level.

or $[(Me_3Si)_2NMg(\mu\text{-Br})(OEt_2)]_2$ [1.962(4) Å] and $[(Me_3Si)_2NMg(\mu\text{-OEt})(THF)]_2$ [2.006(3) Å].[19] The corresponding Zn−N distance in the cation **2**$^+$ of 1.907(3) Å is comparable to those in the neutral β-diketiminato complex (BDI)ZnN(SiMe$_3$) [1.896(2) Å][6b] or $[\{CH(Ph_2PNC_6H_2Me_3\text{-}2,4,6)_2\}ZnN(SiMe_3)_2]$ [1.907(4) Å],[20] but longer than in $Zn[N(SiMePh_2)_2]_2$ [1.849(5) and 1.850(3) Å].[21]

Compounds **2** and **4** are isostructural, and the only noticeable difference resides in the metal−nitrogen bond length. Although the ionic radius of Mg^{2+} is smaller than that of Zn^{2+} (0.71 and 0.74 Å, respectively[22]), the magnesium compound shows the longer M−N bond length, indicative of weaker bonding.

The crystal packing diagrams of **2** and **4** indicate the presence of some close C−H···F contacts, as illustrated in Figure 2 for the structure of **2**. Interactions can be seen between some of the fluorine atoms in *ortho* and *meta* positions of the pentafluorophenyl substituents of the counteranion and some of the hydrogen atoms of coordinated diethyl ether. Distances range from 2.463 to 2.550 Å, i.e., close to the sum of the van der Waals radii. The presence of such H···F contacts leads to the formation of infinite chains in the crystal packing.[23] Whereas in many cases salts with $B(C_6F_5)_4^-$ as anion are extremely difficult to crystallize or remain oils, it may be that these interactions assist in the facile crystallization of compounds such as **2** and **4**.

Polymerization Studies. Complexes **1**−**4** were tested for the ring-opening polymerization of various polar monomers. In principle, polymerization can be envisaged to occur by two mechanisms: either the transfer of the nucleophilic alkyl or amide ligand to the monomer, with formation of a metal alkoxide-propagating species (Scheme 2, path A), or ring opening and propagation via a cationic (activated chain end, ACE) mechanism (path B).

Compounds **1**−**4** polymerize cyclohexene oxide (CHO) under very mild conditions (Table 2). At room temperature, the polymerization of CHO with **1** was extremely rapid and highly exothermic. Even diluted in 5 volumes of toluene, the polymerization of CHO (CHO:Zn = 5000:1) at an initial temperature of 0 °C was complete within 30 s (entry 1), with a productivity of 5.9×10^7 g polymer $(mol{\cdot}Zn)^{-1}{\cdot}h^{-1}$. This corresponded to a 20-fold increase in activity compared with that reported for $[ZnMe(DAD)]^+[B(C_6F_5)_4]^-$ under similar conditions, most likely due to the facile displacement of diethyl ether ligands by the epoxide.[12] There was a considerable reaction exotherm, with the temperature of the solution rising quickly to >60 °C. However, this could be controlled by lowering the temperature or by dilution in a large volume of toluene. When the polymerizations were carried out at very low temperatures (Table 2, entries 2, 3), the percentages of conversion and productivities achieved were much lower, but the molecular weights of the polymers increased significantly and at −78 °C reached $M_w = 380\,000$ g·mol^{-1} (entry 3). On the other hand, no increase of temperature was observed when the polymerization of 5.1 mL of CHO was performed in 200 mL of toluene on an ice-bath (Table 2, entries 4, 5).

The percentage of conversion of 5000 equiv of CHO varied considerably from one complex to another. Whereas **1** achieved 64% within 30 min (6.2×10^5 g polymer $(mol{\cdot}Zn)^{-1}{\cdot}h^{-1}$, entry 5), **2**, **3**, and **4** under the same conditions converted only 27%, 13%, and 4%, respectively (entries 6, 7, and 9). Complete conversion was reached with **1** after 2 h. However, the productivities decreased consistently with time, indicative of slow deactivation processes. The polymers possessed high molecular weights, which ranged from ca. 80 000 to >100 000 g mol^{-1} for all complexes, whereas the polydispersities were usually around 3.0. The poly(CHO) was a very tough, nonstretchable material and soluble in THF at room temperature.

From these results, the trend in activity is **1** > **2** > **3** > **4**; that is, the zinc species were far more active than their magnesium analogues. The order of activity was rather surprising since Mg is the more electropositive metal and the Mg^{2+} compounds were expected to be the stronger Lewis acids. The first and second ionization enthalpies of Mg are 737 and 1450 kJ mol^{-1}, respec-

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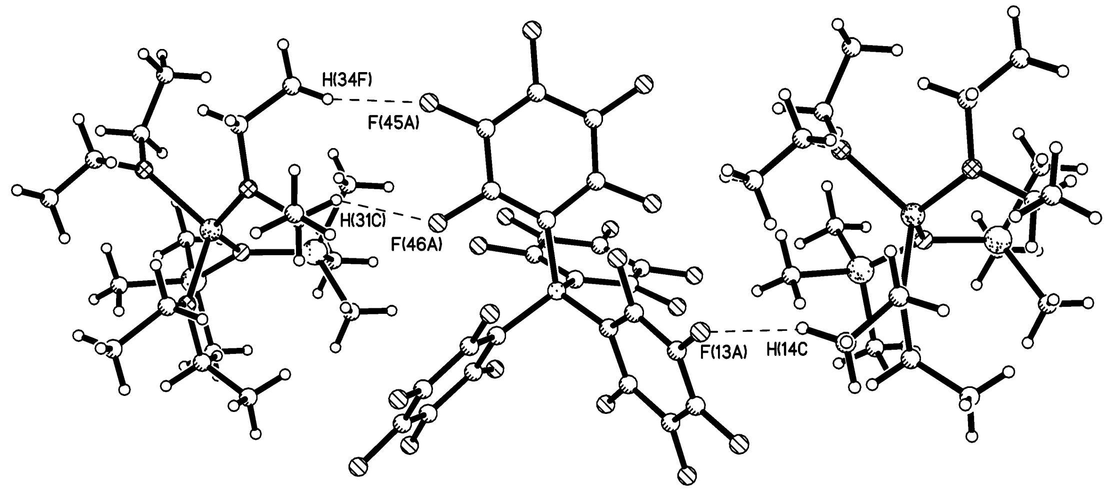


Figure 2. Crystal packing and anion−cation close contacts in **2**.

Scheme 2

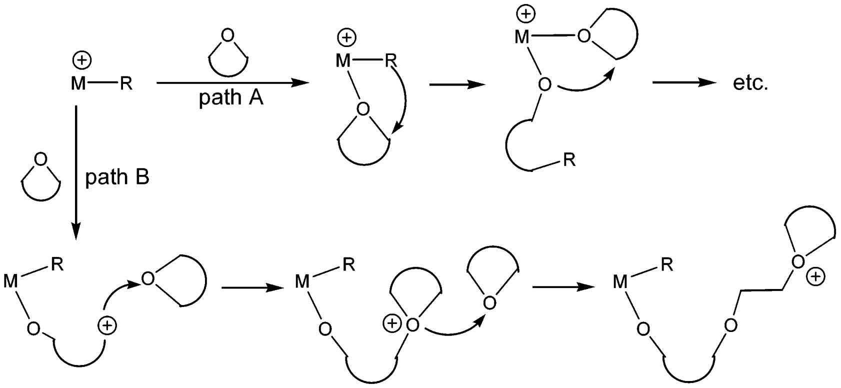


Table 2. Cyclohexene Oxide Polymerizations

entry	initiator[a]	toluene [mL]	temp [°C]	time [min]	yield [g]	conv[b]	prod[c]	$M_w \times 10^{-3}$	M_w/M_n
1	**1**	25	0	0.5	4.9	100	58,800	88	3.1
2	**1**	25	−35	10	1.5	31	900	190	2.2
3	**1**	25	−78	120	1.9	39	95	380	3.8
4	**1**	200	0	15	2.2	46	880	76	3.2
5	**1**	200	0	30	3.1	64	620	80	3.0
6	**2**	200	0	30	1.3	27	260	104	2.0
7	**3**	200	0	30	0.6	13	120	85	2.6
8	**3**	200	0	45	0.9	20	123	82	2.1
9	**4**	200	0	30	0.2	4	40		

[a] 10 μmol of initiator, CHO 5.1 mL; CHO:initiator ratio 5000:1. [b] Percentage conversion of the monomer (weight monomer/weight of polymer recovered × 100). [c] kg polymer (mol metal)$^{-1}$·h^{-1}.

tively, while those of Zn are noticeably higher, 906 and 1734 kJ mol^{-1}. The magnesium derivatives were therefore expected to bind the monomer more easily than their zinc counterparts, which should result in an enhanced polymerization ability, as has already been reported for lactide polymerizations.[9a,b,10a,b] It appears therefore that while the ligand environments around the metal centers are essentially identical, the relative instability of the Mg complexes **2** and **4** is responsible for the inferior activity.

Due to its comparatively weaker ring strain, propene oxide (PO) is significantly more difficult to polymerize than CHO. In each case, 30 μmol of complexes **1**−**4** were reacted at room temperature with 20 000 equiv of neat PO (Table 3). Polymerization times were usually kept below 24 h. Aliquots were taken directly from the reaction mixture and immediately quenched with methanol. The yields in Table 3 are related to the total amount of monomer used for the polymerization. A high excess of monomer was necessary to ensure that the solution did not become too viscous since no other solvent was used.

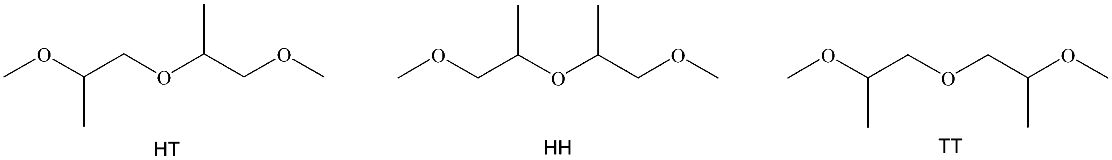
As described earlier for the polymerization of CHO, the results here changed noticeably for each initiator. Again, the highest conversions were obtained with Zn complexes, with 58% conversion for **1** in 24 h (2.8 × 10^4 g PPO (mol·Zn)$^{-1}$·h^{-1}, entry 11), while **2**, **3**, and **4** converted, respectively, only 11%, 9%, and <1% over the same period of time (entries 13, 14, and 16). The same trend as previously noted could be observed for the polymerization of PO: **1** ≫ **2** > **3** ≫ **4**. As expected, the productivities were low in comparison with those found for CHO, but were better than those reported in the literature for the polymerization of PO with aluminum complexes.[3f,g] The molecular weights of the polymers were low, typically $M_w \approx (1-3) \times 10^3$ g mol^{-1}, and were

Table 3. Propene Oxide Polymerizations[a]

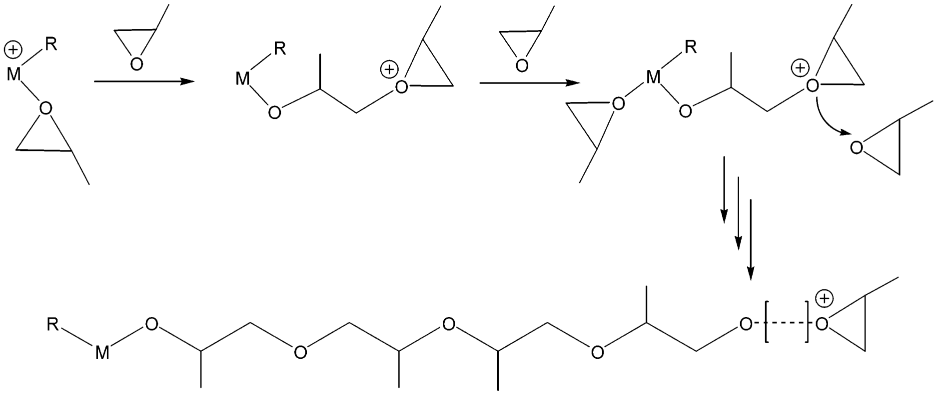
entry	initiator[b]	feed ratio[c]	time [h]	yield [g]	conv[d]	prod[e]	M_w	M_w/M_n
10	**1**	20 000:1	3	1.7	5	19.4	1 000	1.8
11	**1**	20 000:1	24	20.2	58	28.0	1 600	2.9
12	**2**	20 000:1	5	1.0	3	7.0	oligomer	
13	**2**	20 000:1	24	3.8	11	5.3	oligomer	
14	**3**	20 000:1	24	3.1	9	4.4	1 200	1.8
15	**3**	20 000:1	120	0.47	28	2.7	2 900	3.6
16	**4**	20 000:1	24	traces	<1			

[a] Performed in neat monomer at room temperature. [b] 30 μmol of initiator. [c] Initial PO/initiator ratio. [d] Percentage conversion of the monomer (weight monomer/weight of polymer recovered × 100). [e] kg polymer·(molmetal)$^{-1}$·h^{-1}.

Scheme 3



Scheme 4



comparable to those achieved with aluminum initiators. However, **2** led to the formation of oligomers only, and the molecular weights never exceeded 1000 g mol^{-1}, even after 24 h (entries 12, 13). **3** gave the polymers with highest molecular weights, which reached almost 3000 g mol^{-1} (entry 15). Even though with **1**, **2**, and **3** the conversion increased linearly with time during the first 24 h of the reaction, clearly such a linear relationship between molecular weights and reaction time or percentage of conversion could not be established.

As stated above, the polymerization of cyclic monomers can be thought to occur via different mechanisms. Whereas most Zn and Mg initiators for the controlled ROP of epoxides proceed via a coordination mechanism, where binding to an electrophilic metal center renders the monomer more susceptible to intra- or intermolecular attack by a nucleophilic moiety,[24] in the case of cationic metal complexes a simple acidic mechanism had to be considered. The coordination mechanism is characterized by high regioregularity, where the polymer chain consists mainly of head-to-tail (H−T) diad sequences (Scheme 3). By contrast, acidic polymerization gives little regioselectivity, and the resulting polymers usually exhibit high contents of head-to-head (H−H) and tail-to-tail (T−T) defects.[25]

Microstructure analyses of PPO samples produced with **1**−**4** indicated that the polymers had a random distribution of primary and secondary hydroxyl end groups. On the basis of the signals in the area of the CH_2 groups, the polymers consisted of about equal proportions of H−T diads and H−H, T−T defect diads; that is, the distribution was random. GPC characterization of PPO samples indicated the presence of a significant amount of oligomeric species together with the low molecular weight polymers. This was further confirmed by GC−MS analysis, which allowed the qualitative and quantitative determination of low molecular weight byproducts. The analysis showed that some of the samples contained up to 6.5% of volatile organic compounds that are typically formed in the acid-catalyzed polymerization of PO.

This, together with the NMR characterization of the polymer microstructure, indicated that the epoxide polymerizations initiated by cationic Zn and Mg alkyls and amides follow a cationic (ACE) mechanism (Scheme 4). Following the reaction of **1** with 1−10 equiv of PO by ^1H NMR in CD_2Cl_2 or toluene-d_8 indicated very fast PO/Et_2O exchange followed by the formation of oligomers after ca. 15 min.

Complexes **1** and **2** were also tested for the polymerization of ϵ-caprolactone (CL) and L-lactide (Table 4).

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Table 4. Polymerization of ϵ-Caprolactone with Complexes 1 and 2

entry	init (μmol)	feed ratio[a]	toluene [mL]	temp [°C]	time [h]	yield [g]	conv[b]	prod[c]	M_w	M_w/M_n
17	**1** (15)	1000	50	22	120	1.6	93.5	53.3		
18	**2** (30)	6000		50	20	3.0	14.5	300	55 000	2.3

[a] Initial monomer/initiator ratio. [b] Percentage conversion of the monomer (weight monomer/weight of polymer recovered × 100). [c] kg polymer (mol metal)$^{-1}\cdot$h^{-1}.

Whereas there was no reaction between L-lactide and **2**, complex **1** initiates very rapid polymerization of CL at room temperature (entry 17) and gives almost complete conversion of 1000 equiv of CL in 2 h, with a productivity of more than 5.3×10^4 g PCL (mol Zn)$^{-1}\cdot$h^{-1}. **1** is therefore considerably more active at room temperature than the diazadiene complex [ZnMe(DAD)][B(C_6F_5)$_4$]$^-$ (ca. 1.5×10^4 g PCL (mol Zn)$^{-1}\cdot$h^{-1}) was at 60 °C.[12] The bulk polymerization of CL performed at 50 °C with complex **2** was extremely efficient (entry 18). High molecular weight polymer ($M_w = 55\,000$, $M_w/M_n = 2.3$) was obtained with an excellent productivity of 3×10^5 g PCL (mol Zn)$^{-1}\cdot$h^{-1}. Due to the high molecular weight, end-group analysis was not possible.

Conclusion

Four-coordinate cationic zinc and magnesium amides and alkyls stabilized by diethyl ether are readily accessible from magnesium or zinc alkyls and amides and [H(OEt_2)$_2$][B(C_6F_5)$_4$] in almost quantitative yields, to our knowledge the first structurally characterized examples of such simple group 2 and 12 metal amido cations. In the solid state the zinc and magnesium $-$N(SiMe$_3$)$_2$ compounds are isostructural. In contrast to neutral zinc aryl oxides, these cationic species are highly active in the polymerization of epoxides. Cyclohexene oxide is rapidly polymerized to high molecular weight polymers, whereas the polymerization of propene oxide proceeds more slowly to give low molecular weight materials. There is strong evidence that in these cases the Lewis acidic metal centers act as initiators for an acidic polymerization mechanism. Nevertheless, there was a marked dependence of the polymerization activity on the nature of the catalyst, with zinc compounds being significantly more active than magnesium analogues. ϵ-Caprolactone is also polymerized very efficiently by the zinc cations, and high molecular weight polyesters were obtained.

Experimental Section

General Procedures. All manipulations were performed under nitrogen, using standard Schlenk techniques. Solvents were predried over sodium wire (toluene, light petroleum, THF, diethyl ether) or calcium hydride (dichloromethane) and distilled under nitrogen from sodium (toluene), sodium–potassium alloy (light petroleum, bp 40–60 °C), sodium-benzophenone (THF, diethyl ether), or calcium hydride (dichloromethane). Deuterated solvents were stored over activated 4 Å molecular sieves and degassed by several freeze–thaw cycles. ZnEt$_2$ (1.1 M solution in toluene) and MgBu$_2$ (1.0 solution in heptane) were used as purchased (Aldrich). Compounds [H(OEt_2)$_2$][B(C_6F_5)$_4$],[25] [(Et_2O)$_3$ZnCH$_2$CH$_3$] [B(C_6F_5)$_4$] (**1**),[11] zinc bis[bis(trimethylsilyl)amide],[27] and magnesium bis[bis(trimethylsilyl)amide][28] were prepared according to literature methods. Propene oxide, cyclohexene oxide, and ϵ-caprolactone were dried for a minimum of 24 h over fresh calcium hydride, then distilled under vacuum and stored over activated 4 Å molecular sieves. NMR spectra were recorded using a Bruker Avance DPX-300 spectrometer. ^{1}H NMR spectra (300.1 MHz) were referenced to the residual solvent proton of the deuterated solvent used. ^{13}C NMR spectra (75.5 MHz) were referenced internally to the D-coupled ^{13}C resonances of the NMR solvent. Gel permeation chromatography (GPC) measurements were performed on a Polymer Laboratories PL-GPC-220 instrument equipped with a PLgel 5 Å Mixed-C column, a refractive index detector, and a PD2040 light-scattering detector. The GPC column was eluted with THF at 40 °C at 1 mL/min and was calibrated using eight monodisperse polystyrene standards in the range 580–483 000 Da.

[(Et_2O)$_3$ZnN(SiMe$_3$)$_2$][B(C_6F_5)$_4$] (2). A solution of [H(OEt_2)$_2$]-[B(C_6F_5)$_4$] (0.97 g, 1.17 mmol) in diethyl ether (150 mL) was added dropwise over 45 min at room temperature to a solution of Zn[N(SiMe$_3$)$_2$]$_2$ (0.710 mL, 1.75 mmol) in diethyl ether (20 mL). The resulting colorless solution was stirred at room temperature for 1 h and was then concentrated under vacuum to 50 mL. Light petroleum (10 mL) was added. Recrystallization at -26 °C afforded **2** as colorless crystals, yield 0.95 g (72.0%). Anal. Calcd for $C_{42}H_{48}BF_{20}NO_3Si_2Zn$: C 44.75; H 4.29; N 1.24. Found: C 44.08; H 3.98; N 1.30. ^{1}H NMR (300 MHz, CD$_2$Cl$_2$, 25 °C): δ 3.95 (q, 12 H, $J_{HH} = 7.1$ Hz, CH$_3$CH_2O), 1.43 (t, 18 H, $J_{HH} = 7.1$ Hz, CH_3CH$_2$O), 0.16 (s, 18 H, SiMe$_3$). ^{13}C {^{1}H} NMR (75.5 MHz, CD$_2$Cl$_2$, 25 °C): δ 69.5 (CH$_3$$CH_2$O), 15.2 ($CH_3CH_2$O), 5.2 (SiMe$_3$). ^{19}F NMR (CD$_2Cl_2$, 282.4 MHz, 25 °C): δ -133.6 (br, 8 F, *o*-F), -164.1 (t, 4 F, $J_{FF} = 19.8$ Hz, *p*-F), -167.9 (t, 8 F, $J_{FF} = 19.8$ Hz, *m*-F). ^{11}B NMR (96.3 MHz, CD$_2$Cl$_2$, 25 °C): δ -13.6.

[(Et_2O)$_3$MgBu^n][B(C_6F_5)$_4$] (3). [H(OEt_2)$_2$][B(C_6F_5)$_4$] (0.65 g, 0.78 mmol) and MgBu^{s}Bu^n (1.0 mL, 1.2 M, 1.2 mmol) were reacted as described for **2**. Volatiles were removed under vacuum to leave a white sticky solid, which was washed with 3 × 20 mL of light petroleum to afford a white powder. Attempt to recrystallize from a diethyl ether/light petroleum mixture at -26 °C led to a white crystalline powder, yield 0.76 g (99.1%). Anal. Calcd for $C_{40}H_{39}BF_{20}MgO_3$: C 48.88; H 4.00. Found: C 48.13; H 3.35. ^{1}H NMR (300 MHz, CD$_2$Cl$_2$, 25 °C): δ 3.96 (q, 12 H, $J_{HH} = 7.1$ Hz, CH$_3$CH_2O), 1.40 (t, 18 H, $J_{HH} = 7.1$ Hz, CH_3CH$_2$O), 1.28 (m, 2 H, MgCH$_2$CH_2CH$_2$CH$_3$), 1.20 (m, 2 H, MgCH$_2$CH$_2$CH_2CH$_3$), 0.89 (t, 3 H, $J_{HH} = 7.1$ Hz, MgCH$_2$CH$_2$CH$_2$CH_3), -0.44 (m, 2 H, MgCH_2CH$_2$CH$_2$CH$_3$). ^{13}C {^{1}H} NMR (75.5 MHz, CD$_2$Cl$_2$, 25 °C): δ 67.1 (CH$_3$$CH_2$O), 31.8 (MgCH$_2$$CH_2CH_2CH_3$), 25.2 (MgCH$_2CH_2$$CH_2CH_3$), 14.1 ($CH_3CH_2$O), 13.9 (MgCH$_2CH_2CH_2$$CH_3$), 6.1 (Mg$CH_2CH_2CH_2CH_3$). ^{19}F NMR (CD$_2Cl_2$, 282.4 MHz, 25 °C): δ -133.5 (br, 8 F, *o*-F), -164.2 (t, 4 F, $J_{FF} = 19.8$ Hz, *p*-F), -168.0 (t, 8 F, $J_{FF} = 19.8$ Hz, *m*-F). ^{11}B NMR (96.3 MHz, CD$_2$Cl$_2$, 25 °C): δ -13.6.

[(Et_2O)$_3$MgN(SiMe$_3$)$_2$][B(C_6F_5)$_4$] (4). A procedure identical to that of **2** was followed to react [H(OEt_2)$_2$][B(C_6F_5)$_4$] (1.56 g, 1.88 mmol) with {Mg[N(SiMe$_3$)$_2$]$_2$}$_2$ (0.708 g, 1.02 mmol). Recrystallization from diethyl ether/light petroleum afforded colorless crystals, yield 1.90 g (93.0%). Single crystals suitable for X-ray diffraction crystallography were obtained from diethyl ether/light petroleum (8:1) after several weeks at -26 °C. Anal. Calcd for $C_{42}H_{48}BF_{20}NO_3Si_2Mg$: C 46.45; H 4.45; N 1.29. Found: C 45.94; H 4.09; N 1.28. ^{1}H NMR (300 MHz, CD$_2$-

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Cl_2, 25 °C): δ 4.03 (q, 12 H, $J_{HH} = 7.0$ Hz, CH_3CH_2O), 1.42 (t, 18 H, $J_{HH} = 7.0$ Hz, CH_3CH_2O), 0.08 (s, 18 H, $SiMe_3$). $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_2Cl_2, 25 °C): δ 66.7 (CH_3CH_2O), 13.8 (CH_3-CH_2O), 5.6 ($SiMe_3$). ^{19}F NMR (CD_2Cl_2, 282.4 MHz, 25 °C): δ -133.5 (br, 8 F, *o*-F), -164.1 (t, 4 F, $J_{FF} = 19.8$ Hz, *p*-F), -168.0 (t, 8 F, $J_{FF} = 19.8$ Hz, *m*-F). ^{11}B NMR (96.3 MHz, CD_2Cl_2, 25 °C): δ -13.6.

X-ray Crystallography. Crystals coated with dry Nujol were mounted on a glass fiber under a cold nitrogen steam. Data were collected on a Rigaku R-Axis IIc image plate diffractometer equipped with a rotating-anode X-ray source (Mo Kα radiation, $\lambda = 0.71073$ Å) and graphite monochromator. Data were processed using the DENZO/SCALE-PACK programs.[29] The structures were determined by direct methods in the SHELXS program[30] and refined by full-matrix least-squares methods, on F^2 values, in SHELXL.[31] 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. Scattering factors for neutral atoms were taken from ref 32.

Crystal Data for 2: $C_{18}H_{48}ZnNO_3Si_2{\cdot}BC_{24}F_{20}$, fw 1127.17; crystal size 0.4 × 0.4 × 0.3 mm; triclinic, space group $P\bar{1}$; $a = 16.039(3)$ Å, $b = 17.607(4)$ Å, $c = 18.853(4)$ Å; $\alpha = 105.45(3)°$, $\beta = 104.25(3)°$, $\gamma = 92.57(3)°$; $V = 4939\ (2)$ Å^3; $Z = 4$; $D_{calc} = 1.516$ g/cm^3; $\mu = 0.660$ mm^{-1}; $F(000) = 2296$; $-1.82° \le \theta \le 25.44°$; $-19 \le h \le 17$, $-21 \le k \le 21$, $-22 \le l \le 22$; 28 338 reflections collected, of which 16 976 were independent ($R_{int} = 0.0661$) and 11 331 with $I > 2\sigma(I)$ were observed; final R_1 [$I > 2\sigma(I)$] $= 0.0497$, wR_2 (all data) $= 0.1336$, $w = [\sigma^2(F_o^2) + (0.0614P)^2]^{-1}$ with $P = (F_o^2 + 2F_c^2)/3$; no. of data/restraints/parameters 16 976/0/1261; goodness of fit, $F^2 = 1.018$. In the final difference map, the highest peaks (to ca. 0.84 e A^{-3}) were close to Zn(2).

Crystal Data for 4: $C_{18}H_{48}MgNO_3Si_2{\cdot}BC_{24}F_{20}$, fw 1086.11; crystal size 0.45 × 0.45 × 0.10 mm; triclinic, space group $P\bar{1}$; $a = 15.985(3)$ Å, $b = 17.603(4)$ Å, $c = 18.918(4)$ Å; $\alpha = 105.32(3)°$, $\beta = 104.00(3)°$, $\gamma = 92.66(3)°$; $V = 4947(2)$ Å^3; $Z = 4$; $D_{calc} = 1.458$ g/cm^3; $\mu = 0.198$ mm^{-1}; $F(000) = 2224$; $1.16° \le \theta \le 23.50°$; $-19 \le h \le 19$, $-21 \le k \le 21$, $-21 \le l \le 21$; 22 489 reflections collected, of which 13 476 were independent ($R_{int} = 0.0922$) and 8612 with $I > 2\sigma$(I) were observed; final R_1 [$I > 2\sigma(I)$] $= 0.082$, wR_2 (all data) $= 0.1336$, $w = [\sigma^2(F_o^2) + (0.0533P)^2]^{-1}$ with $P = (F_o^2 + 2F_c^2)/3$; no. of data/restraints/parameters 13 476/0/1261; goodness of fit, $F^2 = 0.941$. In the final difference map, the highest peaks (to ca. 0.34 e A^{-3}) were close to C(23) and C(24).

Polymerization Procedures. Polymerizations of cyclohexene oxide (CHO) were carried out on a Schlenk line in a flame-dried round-bottom flask equipped with a magnetic stirrer. In a typical procedure, the initiator was dissolved in the appropriate amount of toluene, and temperature equilibration was ensured by stirring the solution for 15 min on an ice-bath. CHO, kept at 0 °C, was then injected, and polymerization times were measured from that point. Polymerizations were terminated by addition of a solution of hydrochloric acid (10% vol.) in methanol, and the polymers were precipitated in methanol. After filtration, the polymers were washed with methanol and then dried in vacuo to constant weight. When it was necessary to take samples from the reaction, the reaction mixture was stirred for the measured amount of time, and an aliquot was removed with a gastight syringe, poured in acidified methanol, and then treated as described above.

Polymerizations of neat propene oxide (PO) at room temperature were performed in a flame-dried Schlenk tube on a Schlenk line. The flask was charged in the glovebox with the required amount of initiator and attached to the vacuum line. The appropriate amount of PO was added via syringe. Vigorous stirring ensured the initiator was immediately dissolved. Polymerizations were stopped by injecting a solution of hydrochloric acid (10 vol. %) in methanol. Volatiles were removed in vacuo, and the polymers were dried in an oven at 60 °C to constant weight. When necessary, aliquots were taken from the reaction mixture and injected in a vial containing acidified methanol. The vial was evacuated, and the remaining polymer was dried in the oven to determine the conversion.

Polymerizations of ϵ-caprolactone (CL) were carried out using the same procedure. The initiator was dissolved in the desired amount of toluene, and after temperature equilibration CL was added via syringe and the polymerization time measured from that point. Polymerizations were stopped by addition of a solution of acetic acid in methanol. The polymers were precipitated in methanol, filtered, dissolved in THF, reprecipitated in methanol, and dried in vacuo to constant weight.

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Supporting Information Available: Full listings of crystallographic details for compounds **2** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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