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Neutral and Cationic Tetracoordinated Aluminum Complexes Featuring Tridentate Nitrogen Donors: Synthesis, Structure, and Catalytic Activity for the Ring-Opening Polymerization of Propylene Oxide and (D,L)-Lactide

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The dilithium salts of *N*,*N′*,*N″*-tris(trimethylsilyl)diethylenetriamine (**1**), *N*-methyl-*N′*,*N″*-bis(trimethylsilyl)diethylenetriamine (**2**), and *N*-methyl-*N′*,*N″*-bis(diisopropyl)diethylenetriamine (**3**) reacted in THF, at −40 °C, with $AlCl_3$ affording monomeric aluminum chloride derivatives **4** (55% yield), **5** (76% yield), and **6** (71% yield), respectively. Addition of 1 equiv of $AlMe_3$ to the amine **2** gave rise to the five-coordinate dimethylaluminum derivative **9** (67% yield); heating a toluene solution of **9** overnight at 80 °C induces a loss of methane giving rise to the four-coordinate methylaluminum compound **10** (50% yield). The amine **2** also reacted at low temperature with $LiAlH_4$ affording derivative **11** (38% yield). Compounds **4**−**6** reacted subsequently in toluene with 1 equiv of HCl and 1 equiv of $AlCl_3$ to afford the first chiral tetracoordinated aluminum cations **12** (94% yield), **13** (93% yield), and **14** (90% yield), respectively. Single-crystal X-ray diffraction studies of derivatives **4**, **5**, **8**, **10**, **11**, **12**, and **15** have been carried out. They revealed that the tridentate nitrogen donors enforce an approximately trigonal-monopyramidal coordination geometry for neutral and cationic four-coordinate aluminum complexes. All cationic aluminum derivatives **12**−**14** and the neutral aluminum chloride **4** brought about the oligomerization of propylene oxide (PO). Low molecular weight polymers having narrow molecular weight distributions were obtained. The ^{13}C NMR spectra of these polymers indicate that they consist exclusively of head-to-tail linkages and that these macromolecules are rich in meso diad and isotactic triad sequences. Due to the presence of a free axial site, a new mechanism for PO polymerization is proposed. Methyl- and hydridoaluminum derivatives **10** and **11**, as well as aluminum alkoxide, prepared in situ by reacting derivative **13** with PO, initiated the polymerization of (D,L)-lactide in benzene at 80 °C. High molecular weight polymers of broad molecular weight distributions were obtained in good yields.

Introduction

Nowadays, nitrogen ligands play an important role in organometallic chemistry and homogeneous catalysis.[1] They are often used as a part of a chelating system for stabilizing low-valent species or achieving unusual geometries.[1b,2] In this field, triamidoamine ligands $[(RNCH_2CH_2)_3N]^{3-}$, featuring bulky Me_3Si substituents, have found widespread application[2a−f] for stabilizing Lewis acids such as four-coordinate aluminum **A**[2a] or vanadium **B**[2d] centers (Scheme 1). The very unusual trigonal-monopyramidal (TMP) geometry is enforced by the tetradentate nature of the ligand, with the presence of sterically demanding Me_3Si substituents protecting the free apical coordination site. Of particular interest is the use of nitrogen donors to prepare coordinatively unsaturated group 13 complexes, which are powerful

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(1) See, for examples: (a) Togni, A.; Venanzi, L. M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 497. (b) Verkade, J. G. *Acc. Chem. Res.* **1993**, *26*, 483. (c) Hey-Hawkins, E. *Chem. Rev.* **1994**, *94*, 1661. (d) Kold, H. C.; van Nieuwenhze, M. S.; Sharpless, K. B. *Chem. Rev.* **1994**, *94*, 2483. (e) Gruter, G.-J. M.; van Klink, G. P. M.; Akkerman, O. S.; Bickelhaupt, F. *Chem. Rev.* **1995**, *95*, 2405. (e) Abu-Surrah, A. S.; Rieger, B. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2475. (g) Plenio, H. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 348. (h) Herrmann, W. A.; Cornils, B. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1048.

(2) (a) Pinkas, J.; Wang, T.; Jacobson, R. A.; Verkade, J. G. *Inorg. Chem.* **1994**, *33*, 4202. (b) Pinkas, J.; Gaul, B.; Verkade, J. G. *J. Am. Chem. Soc.* **1993**, *115*, 3825. (c) Cummins, C. C.; Schrock, R. R.; Davis, W. M. *Inorg. Chem.* **1994**, *33*, 1448. (d) Cummins, C. C.; Lee, J.; Schrock, R. R.; Davis, W. M. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1501. (e) Zanetti, N. C.; Schrock, R. R.; Davis, W. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *107*, 2184. (f) Power, P. P. *Angew. Chem., Int. Ed. Engl.* **1993**, *35*, 850. (f) Mealli, C.; Ghilardi, C. A.; Orlandini, A. *Coord. Chem. Rev.* **1992**, *120*, 361. (g) Ray, M.; Yap, G. P. A.; Rheingold, A. L.; Borovik, A. S. *J. Chem. Soc., Chem. Commun.* **1995**, 1777. (h) Ray, M.; Golombek, A.; Hendrich, M. P.; Young, V. G., Jr.; Borovik, A. S. *J. Am. Chem. Soc.* **1997**, *118*, 66084. (i) Hammes, B. S.; Ramos-Maldonado, D.; Yap, G. P. A.; Liable-Sands, L.; Rheingold, A. L.; Young, V. G., Jr.; Borovik, A. S. *Inorg. Chem.* **1997**, *36*, 3210. (j) Gruter, G. J. M.; van Klink, G. P. M.; Akkerman, O. S.; Bickelhaupt, F. *Chem. Rev.* 1995, *95*, 2405. (k) Schrock, R. R. *Acc. Chem. Res.* **1997**, *30*, 9.

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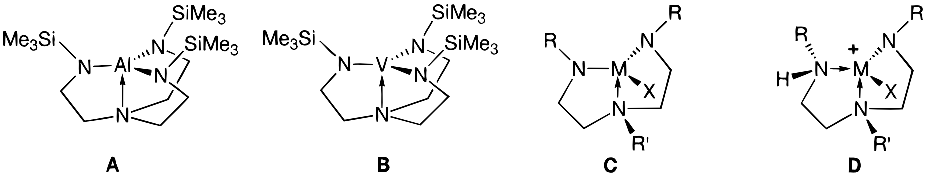
Scheme 1



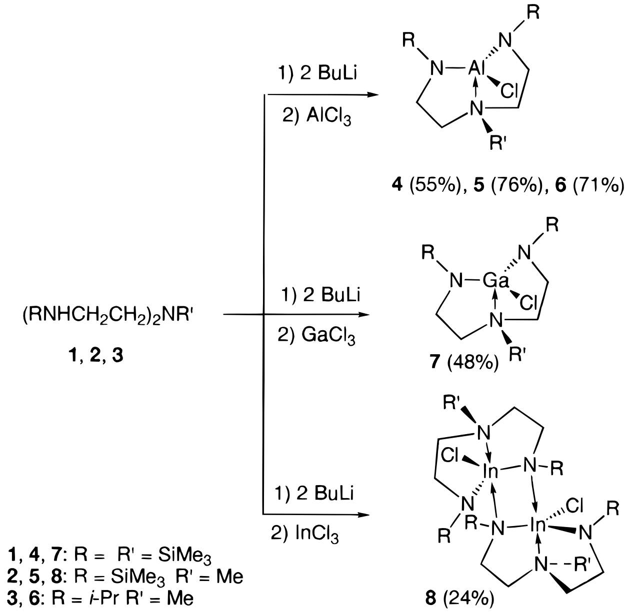
catalysts for the Diels−Alder reaction,[3] the Mukaiyama aldol reaction,[4] and the living polymerization of heterocycles.[5] Recent reports have shown that cationic complexes, which should possess enhanced Lewis acidity in comparison with their neutral analogues, constitute a very promising type of catalysts.[3c,6]

Following our work devoted to the Lewis-acid-promoted ring-opening reactions of heterocycles,[7] we became interested in the synthesis of tetracoordinated group 13 derivatives as potential initiators for the polymerization of heterocycles. Since the polymerization is considered to be initiated by the insertion of the monomer into a group 13 element−X bond (X = Cl, H, alkyl...),[5e,f] our strategy was based on the synthesis of Lewis acids **C** (Scheme 1) featuring diamidoamine ligands $[(RNCH_2CH_2)_2NR']$.[8] Here, we report the synthesis of a variety of derivatives of type **C** (M = Al, Ga, In; X = Cl, Me, H).[9] The tridentate nitrogen ligands are not only "spectator ligands", a chemical modification in the coordination sphere of the metal, leading to the first chiral tetracoordinated aluminum cations **D**, is also reported. Last, the catalytic activity of neutral and cationic aluminum and gallium complexes in the ring-opening polymerization of propylene oxide and (D, L)-lactide is presented.

Synthesis and Structure

The dilithium salts of amines **1**−**3** reacted in THF, at −40 °C, with $AlCl_3$ affording aluminum chloride derivatives **4** (55% yield), **5** (76% yield), and **6** (71% yield), respectively, which were isolated after sublimation under vacuum (Scheme 2). The ^{13}C NMR spectra for complexes **4**−**6** show the presence of only two types of CH_2 groups, which is consistent with monomeric structures. In the case of **4**, the coordination of the amino nitrogen to the aluminum center, leading to a symmetrical bicyclic structure, is strongly supported by the observation of four different ^1H NMR resonances for the four backbone protons of the two equivalent CH_2-CH_2 moieties. In the case of both derivatives **5** and **6**, the coordination of the amino nitrogen atom is indicated by a shielding of the signal of the NCH_3 compared to that of the free ligand ($\Delta\delta$ **5**, 0.23; $\Delta\delta$ **6**, 0.18). The ^{27}Al NMR chemical shift of these derivatives (**4**, +125; **5**, +121; **6**, +112) confirms that the central aluminum atoms are tetracoordinated.[10] Single-crystal X-ray diffraction studies performed on derivatives **4**[9a] and **5** definitively proved the proposed structures (Figure 1, Tables 1 and 2).

Scheme 2



Derivatives **4** and **5** crystallize as a pair of enantiomers due to an envelope conformation of the two five-membered rings (the "flap" carbon atoms are bonded to the four-coordinate nitrogen atom N(3)). The comparison of the structural parameters for compounds **A**,[2a] a trigonal-monopyramidal complex featuring a tris(trimethylsilyl)triamidoamine ligand, **4**, and **5** is of interest. The coordination geometry of the aluminum center in **4** and **5** approaches the TMP geometry observed for **A**: The aluminum atom is only slightly displaced from the

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[3] (a) *Selectivities in Lewis Acid Promoted Reactions*; Schinzer, D., Ed.; Kluwer Academic Publishers: Dordrecht, 1989. (b) Kagan, H. B.; Riant, O. *Chem. Rev.* **1992**, *92*, 1007. (c) Hayashi, Y.; Rohde, J. J.; Corey, E. J. *J. Am. Chem. Soc.* **1996**, *118*, 5502. (d) Pindur, U.; Lutz, G.; Otto, C. *Chem. Rev.* **1993**, *93*, 741. (e) Deloux, L.; Srebnik, M. *Chem. Rev.* **1993**, *93*, 763.

[4] (a) Kiyooba, S.; Kaneko, Y.; Kume, K. *Tetrahedron Lett.* **1992**, *33*, 4927. (b) Parmee, E. R.; Tempkin, O.; Masamune, S.; Abiko, A. *J. Am. Chem. Soc.* **1991**, *113*, 9365. (c) Parmee, E. R.; Hong, Y.; Tempkin, O.; Masamune, S. *Tetrahedron Lett.* **1992**, *33*, 1729.

[5] (a) Inoue, S. *Acc. Chem. Res.* **1996**, *29*, 39. (b) Asano, S.; Aida, T.; Inoue, S. *J. Chem. Soc., Chem. Commun.* **1985**, 1148. (c) Sugimoto, H.; Kawamura, C.; Kuroki, M.; Aida, T.; Inoue, S. *Macromolecules* **1994**, *27*, 2013. (d) Kuroki, M.; Watanabe, T.; Aida, T.; Inoue, S. *J. Am. Chem. Soc.* **1991**, *113*, 5903. (e) Aida, T.; Mizuta, R.; Yoshida, Y.; Inoue, S. *J. Makromol. Chem.* **1981**, *182*, 1073. (f) Aida, T.; Inoue, S. *Macromolecules* **1981**, *14*, 1166. (g) Trofimoff, L.; Aida, T.; Inoue, S. *Chem. Lett.* **1987**, 991.

[6] (a) Atwood, D. A.; Jegier, J. A.; Rutherford, D. *J. Am. Chem. Soc.* **1995**, *117*, 6779. (b) Atwood, D. A.; Jegier, J. A.; Rutherford, D. *Inorg. Chem.* **1996**, *35*, 63.

[7] (a) Bon, E.; Réau, R.; Bertrand, G.; Bigg, D. C. H. *Tetrahedron Lett.* **1996**, *37*, 1217. (b) Bon, E.; Bigg, D. C. H.; Bertrand, G. *J. Org. Chem.* **1994**, *59*, 1904. (c) Bon, E.; Bigg, D. C. H.; Bertrand, G. *J. Org. Chem.* **1994**, *59*, 4035. (d) Bon, E.; Bigg, D. C. H.; Bertrand, G. *Synlett* **1992**, 747.

[8] (a) Cloke, F. G. N.; Hitchcock, P. B.; Love, J. B. *J. Chem. Soc., Dalton Trans.* **1995**, 25. (b) Clark, H. C. S. C.; Cloke, F. G. N.; Hitchcock, P. B.; Love, J. B.; Wainwright, A. P. *J. Organomet. Chem.* **1995**, *501*, 333. (c) Horton, A. D.; de With, J.; van der Linden, A. J.; van de Weg, H. *Organometallics* **1996**, *15*, 2672.

[9] (a) For preliminary accounts, see: Emig, N.; Réau, R.; Krautscheid, H.; Fenske, D.; Bertrand, G. *J. Am. Chem. Soc.* **1996**, *118*, 5822. (b) Bertrand, G.; Cazaux, J. B.; Emig, N.; Réau, R. Eur. Pat. Appl. 96400938.5, 1996.

[10] (a) Benn, R.; Janssen, E.; Lehmkuhl, H.; Rufinska, A. *J. Organomet. Chem.* **1987**, *333*, 155. (b) Müller, J.; Englert, U. *Chem. Ber.* **1995**, *128*, 493. (c) Hinton, J. F.; Briggs, R. W. *NMR and the Periodic Table*; Academic Press: New York, 1978; Chapter 9.

Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) for Tetracoordinated Aluminum Derivatives A (X = $N(SiMe_3)CH_2CH_2$), 4 (X = Cl),[9a] 5 (X = Cl), 10 (X = CH_3), and 11 (X = H), 12 (X = Cl)[9a]

	A^{2b}	4	5	10	11	12
Al(1)−N(1)	1.812(6)	1.811(1)	1.816(4)	1.836(2)	1.835(2)	1.947(3)
Al(1)−N(1a)			1.816(4)	1.836(2)	1.835(2)	
Al(1)−N(2)	1.805(5)	1.803(1)				1.782(3)
Al(1)−N(3)	1.983(6)	1.998(1)	1.993(2)	2.019(2)	2.014(3)	1.963(3)
Al(1)−X	1.810(6)[a]	2.144(1)	2.152(1)	1.962(3)	1.47(3)	2.103(4)
N(1)−Si(1)	1.697(6)	1.713(1)	1.718(4)	1.709(2)	1.714(2)	1.830(3)
N(1a)−Si(1a)			1.718(4)	1.709(2)	1.714(2)	
N(2)−Si(2)	1.684(5)	1.710(1)				1.720(4)
N(3)−Si(3)		1.815(1)				1.849(3)
N(3)−C(3)			1.459(4)	1.471(5)	1.450(5)	
N(1)−Al−N(2)	119.6(3)	124.4(1)				114.9(1)
N(1)−Al−N(1a)			126.5(1)	122.3(1)	125.4(1)	
N(1)−Al−N(3)	92.3(3)	92.8(1)	91.6(1)	89.7(6)	89.8(1)	91.8(1)
N(1)−Al−X	119.9(3)[a]	113.1(1)	113.8(1)	116.1(1)	114.4(3)	109.4(1)
N(2)−Al−N(3)	92.3(3)	92.8(1)				−95.0(1)
N(1a)−Al−N(3)			91.6(1)	89.7(6)	89.8(1)	
N(2)−Al−X	120.2(3)[a]	113.1(1				123.0(1)
N(1a)−Al−X			113.8(1)	116.1(1)	114.4(3)	
N(3)−Al−X	91.8(3)[a]	116.5(1)	112.7(1)	114.5(1)	116.1(14)	117.8(1)
Al−N(1)−Si(1)	134.4(3)	133.1(1)	132.4(1)	131.4(1)	127.7(1)	123.2(5)
Al−N(1a)−Si(1a)			132.4(1)	131.4(1)	127.7(1)	
Al−N(2)−Si(2)	135.1(4)	133.3(1)				134.0(2)
Al−N(3)−Si(3)		122.5(1)				119.1(3)
Al−N(3)−C(3)			118.4(2)	117.7(2)	118.0(3)	

[a] X represents a $NSiMe_3$ moiety.

Table 2. Crystallographic Data for Compounds 5, 8, 10, 11, and 15

	5	8	10	11	15
chem formula	$C_{11}H_{29}N_3AlClSi_2$	$C_{22}H_{58}N_6Cl_2Si_4In_2$	$C_{12}H_{32}N_3AlSi_2$	$C_{11}H_{30}N_3AlSi_2$	$C_{11}H_{26}N_3AlCl_2$
fw	321.98	819.64	301.63	287.60	298.23
cryst syst	monoclinic	monoclinic	monoclinic	orthorhombic	monoclinic
space group	$P2_1/m$	$P2_1/n$	$P2_1/m$	$Pnma$	$P2_1/c$
a, Å	6.526(1)	8.049(1)	6.475(10)	28.870(1)	11.010(1)
b, Å	18.664(4)	13.317(1)	18.359(4)	19.893(1)	13.860(2)
c, Å	7.744(1)	16.411(1)	7.870(2)	6.226(1)	11.450(1)
β, deg	96.81(3)	95.67(1)	95.58(3)	90	114.20(1)
V, Å^3	936.6(3)	1750.5(3)	931.1(3)	3575.7(8)	1593.7(3)
$F(000)$	348	840	334	1264	640
Z	2	2	2	8	4
D_{calc}, g cm^{-3}	1.142	1.555	1.079	1.068	1.243
T, K	230	200	160	190	190
μ (Mo Kα), mm^{-1}	0.370	1.630	0.229	0.236	0.448
2θ range, deg	4−56	6−52	6−48	5−50	5−48
no. of data collected	5035	6315	6226	14629	6024
no. of unique data	2320	2907	1503	3251	2327
R(int)	0.016	0.046	0.036	0.075	0.125
no. of params varied	103	170	147	191	164
Goof	1.093	1.026	1.060	0.933	0.924
R1	0.034	0.042	0.040	0.040	0.046
wR2	0.100	0.103	0.093	0.118	0.106
$(\Delta/\rho)_{max}$, $(\Delta/\rho)_{min}$, eÅ^{-3}	0.323 −0.415	1.202 −0.678	0.385 −0.344	0.295 −0.275	0.412 −0.321

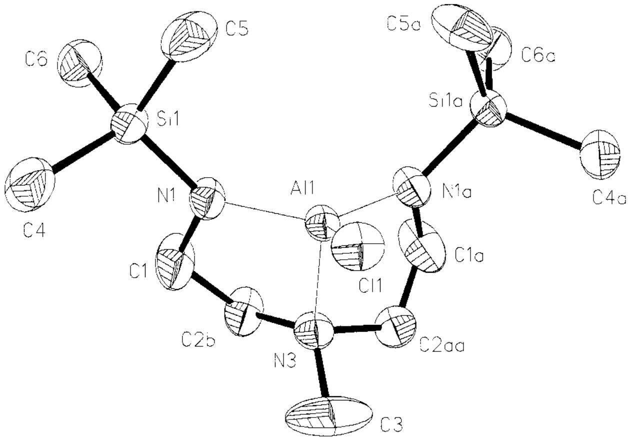


Figure 1. Molecular structure of **5** in the solid state. Hydrogen atoms have been omitted for clarity.

trigonal plane Cl(1)N(1)N(1a) in the direction of the apically coordinated donor (**A**, 0.07 Å; **4**, 0.34 Å; **5**, 0.30 Å). The angles of the basal triangular face, defined by the two equatorial nitrogens and the chlorine atoms, deviate by less than 7° from the ideal value of 120°, and the value of the N(1)−Al(1)−N(3) and N(1a)−Al(1)−N(3) (**4**, 92.8°(1); **5**, 91.6°(1)) angles are close to 90°. The equatorial nitrogen−aluminum bond lengths are similar (1.803−1.816 Å) and significantly shorter than the dative axial N(3)−Al bonds (1.993−1.998 Å); note that replacing an electron-withdrawing trimethylsilyl substituent by a methyl group on the axial nitrogen atom (**4** versus **5**) does not affect the bicyclic structure. All of the equatorial nitrogen atoms are planar (mean sum of angles for **A** = 359.5(5)°, **4** = 357.2(7)°, **5** = 354.1(4)°), and the N(equatorial)−Si bonds (1.684−1.718 Å) are considerably shorter than the N(axial)−Si bond of

Table 3. Bond Lengths (Å) and Bond Angles (deg) for Derivative 8

In(1)−N(1)	2.280(5)	In(1)−N(1a)	2.280(5)
In(1)−N(2)	2.095(5)	N(1)−Si(1)	1.781(5)
In(1)−N(3)	2.390(4)	N(2)−Si(2)	1.727(5)
In(1)−Cl(1)	2.406(4)	N(3)−C(3)	1.459(8)
N(1)−In(1)−N(2)	148.9(2)	N(2)−In(1)−N(1a)	103.9(2)
N(1)−In(1)−N(3)	77.1(2)	N(2)−In(1)−Cl(1)	104.3(3)
N(1)−In(1)−N(1a)	84.8(2)	N(3)−In(1)−N(1a)	138.3(4)
N(1)−In(1)−Cl(1)	100.9(1)	N(3)−In(1)−Cl(1)	111.6(1)
N(2)−In(1)−N(3)	76.9(2)		

compound **4** (1.815 Å). It is thus very likely that, as demonstrated for **A**,[2a] the equatorial nitrogen lone pairs are engaged in π-bonding with the adjacent silicon center rather than with the aluminum atom. The Al−Cl distances (**4**, 2.144(1) Å; **5**, 2.152(1) Å) are typical for tetracoordinated aluminum chloride complexes.[11e]

The stability of the aluminum derivatives **4**−**6** toward dimerization prompted us to extend our study to the higher group 13 homologues, gallium and indium. Addition of 1 equiv of GaCl$_3$ to the dilithium salt of **1** in THF, at −40 °C, gave rise to complex **7**, which was isolated in 48% yield after sublimation under vacuum (Scheme 2). The similarity of the ^{1}H and ^{13}C NMR spectra for **4** and **7** demonstrated the monomeric nature of the gallium compound. Interestingly, all the CH$_2$ hydrogen atoms of the bicyclic ligand in **4** and **7** appeared as doublets of doublets of doublets, and the J_{HH} coupling constants compare well (**4** 12.3, 7.6, and 5.3 Hz; **7** 12.2, 7.4, and 5.2 Hz). Considering that the covalent radii of aluminum and gallium are very similar and that the gallium−nitrogen bonds are only slightly longer than the aluminum−nitrogen bonds,[2b,12] the monomeric nature of **7** is not surprising. Reaction of InCl$_3$, in refluxing THF, with the dilithium salt of **2** afforded derivative **8** in a moderate yield (Scheme 2). In contrast to the aluminum and gallium complexes **4**−**7**, the indium derivative **8** is almost insoluble in all common solvents and the NMR spectra much more complex. These results are not consistent with a monomeric structure. Indeed, an X-ray diffraction study (Table 3, Figure 2) revealed that the indium chloride derivative **8** possesses a dimeric structure.

Derivative **8** contains a central rectangular (In−N)$_2$ four-membered ring which is centered on the crystallographically imposed inversion center of the molecule. The indium atoms are displaced by approximately 0.6 Å above the plane defined by the four nitrogen atoms and therefore feature a very distorted square-pyramidal geometry. The In(1)−N(1) (2.280(5) Å) and In(1)−N(3) (2.390(4) Å) distances are slightly longer than the sum of the covalent radii (2.19 Å)[13a] but significantly shorter than the sum of the van der Waals radii (3.45 Å);[13b] long indium−nitrogen distances (2.40−2.50 Å) are also found in other intramolecularly stabilized pentacoordinated indium chloride complexes.[2j,14]

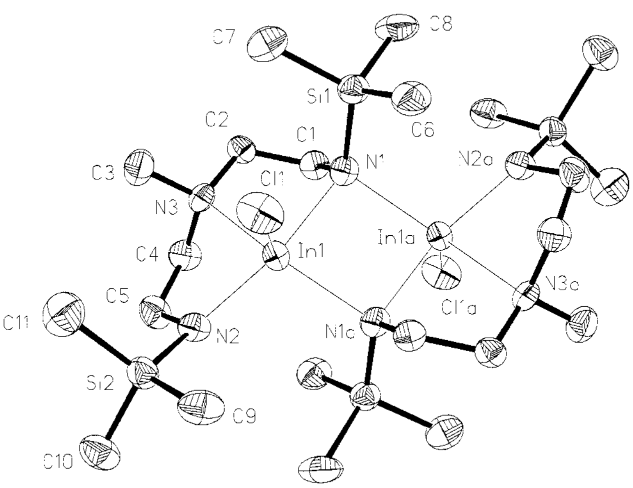
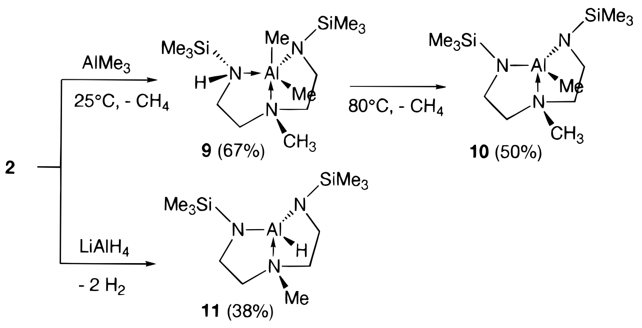


Figure 2. Molecular structure of **8** in the solid state. Hydrogen atoms have been omitted for clarity.

Scheme 3



Inoue has shown the dramatic influence of the nature of the metal−X bond on the catalytic activity of (porphinato)aluminum derivatives for the polymerization of heterocycles.[5a] As a representative example, the (tetraphenylporphinato)aluminum chloride is inert toward lactide while (tetraphenylporphinato)aluminum alkoxides bring about the polymerization of this monomer.[5g] Therefore, after varying the metal M, we chose to “tune” the X substituent of **C**. Reactions of secondary amines with AlMe$_3$ and LiAlH$_4$ offer straightforward routes to methyl-[15] and hydridoaluminum[11c,16] complexes, respectively. In a similar way, addition of 1 equiv of AlMe$_3$ to the tris(amino) ligand **2** gave rise to the five-coordinate dimethylaluminum derivative **9**, which was isolated after crystallization in 67% yield (Scheme 3). The identity of **9** is based on its ^{13}C NMR spectrum, which exhibits two AlMe (−7.52, −7.18) and two NSiMe$_3$

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(11) (a) Atwood, D.; Jegier, J. *J. Chem. Soc., Chem. Commun.* **1996**, 1507. (b) Atwood, D.; Jegier, J. *Inorg. Chem.* **1997**, *36*, 1507. (c) Gardiner, M. G.; Lawrence, S. M.; Raston, C. L. *Inorg. Chem.* **1996**, *35*, 1349. (d) Andrews, P. C.; Raston, C. L.; Skelton, B. W. *J. Chem. Soc., Chem. Commun.* **1997**, 1183. (e) Gardiner, M. G.; Koutsantonis, G. A.; Lawrence, S. M.; Lee, F. C.; Raston, C. L. *Chem. Ber.* **1996**, *129*, 545. (f) Atwood, D.; Jegier, J. *Inorg. Chem.* **1996**, *35*, 4278.

(12) (a) Waggoner, K. M.; Ruhlandt-Senge, K.; Wehmschulte, R. J.; He, X.; Olmstead, M. M.; Power, P. P. *Inorg. Chem.* **1993**, *32*, 2557. (b) Huheey, J. E. *Inorganic Chemistry*, 3rd ed.; Harper and Row: New York, 1983.

(13) (a) Khan, M.; Steevensz, R. C.; Tuck, D. G.; Noltes, J. G.; Corfield, P. W. R. *Inorg. Chem.* **1980**, *19*, 3407. (b) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

(14) (a) Kümmel, C.; Meller, A.; Noltemeyer, M. *Z. Naturforsch.* **1996**, 209. (b) Gruter, G. J. M.; van Klink, G. P. M.; Akkermann, O.; Bickelhaupt, F. *Chem. Rev.* **1995**, *95*, 2405. (c) Leman, J. T.; Roman, H. A.; Barron, A. R. *Organometallics* **1993**, *12*, 2986.

(15) See, for examples: (a) Waezsada, S. D.; Liu, F. Q. L.; Murphy, E. F.; Roesky, H. W.; Teichert, M.; Uson, I.; Schmidt, H. G.; Albers, T.; Parisini, E.; Noltemeyer, M. *Organometallics* **1997**, *16*, 1260. (b) Power, P. P.; Waggoner, K. M.; Hope, H. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1699. (c) Waggoner, K. M.; Power, P. P. *J. Am. Chem. Soc.* **1991**, *113*, 3385.

(16) See, for examples: (a) Klein, C.; Noth, H.; Tacke, M.; Thomann, M. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 886. (b) Stalke, D.; Heine, A. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 854. (c) Montero, M. L.; Wessel, H.; Roesky, H. W.; Teichert, M.; Uson, I. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 629.

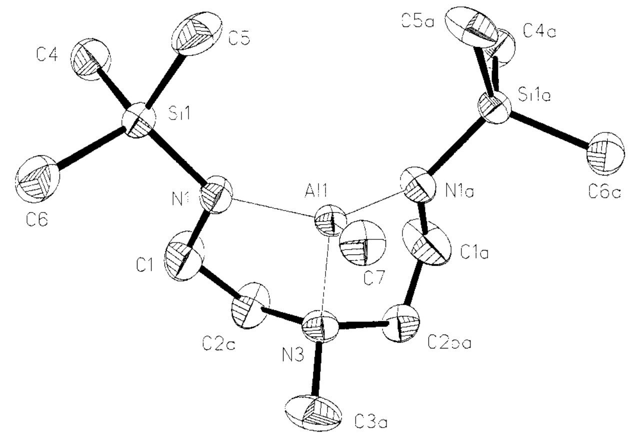


Figure 3. Molecular structure of **10** in the solid state. Hydrogen atoms have been omitted for clarity.

(0.30, 0.92) resonances and four singlets for the inequivalent CH_2 groups (37.81, 41.75, 61.92, 62.10). Note that as observed for other pentacoordinated dimethylaluminum complexes,[11a,b] the ^1H NMR spectra shows only one resonance (−0.32, 6 H) for the two AlMe groups. Heating a toluene solution of **9** overnight at 80 °C induces a 1,2-elimination of methane, giving rise to the four-coordinate methylaluminum compound **10**, which was isolated by sublimation under vacuum in 50% yield. The ^1H and ^{13}C NMR spectra for **10** are very simple and compare well with those of the related monomeric aluminum chloride complex **5**.

The ligand **2** also reacted at low temperature with $LiAlH_4$ affording derivative **11**, which was isolated in 38% yield after sublimation, as an extremely moisture-sensitive solid (Scheme 3). As observed for compound **10**, the protons of each of the CH_2 groups are diastereotopic and the signal of the CH_3N group (1.88 ppm) is deshielded compared to the free ligand, strongly suggesting a bicyclic structure. As expected for a monomeric structure, only four singlets are observed in the $^{13}C\{^1H\}$ NMR spectra (δ 1.53 (CH_3Si), 41.81 (CH_3N), 42.08 (CH_2), 59.45 (CH_2)). The resonance for the hydride appeared as a broad singlet (3.45), and the presence of an Al−H stretching vibration (1811 cm^{-1}) is observed in the IR spectrum.[11] The ^{27}Al NMR chemical shift (+133 ($\nu_{1/2} = 500$ Hz)) is consistent with a four-coordinate aluminum center and comparable to that of the related derivatives **5** and **10**.

The definitive proof for the proposed structures **10** and **11** was given by single-crystal X-ray diffraction studies (Figures 3 and 4, Table 1); the hydrogen of the AlH moiety of **11** was located and refined.

Both derivatives **10** and **11** are monomeric species, and the coordination geometry around the aluminum atom approaches a TMP geometry (Table 1). The Al−C (1.962(3) Å) and Al−H (1.47(3) Å) distances are typical for tetracoordinated aluminum complexes.[11] It is of interest to compare the geometric data of derivatives **5**, **10**, and **11**, which feature the same tridentate ligand and different X substituents (Scheme 1, **C** X = Cl, Me, H). It is striking to note that along this series, all the bonds lengths and bond angles of the ligand remain almost constant. For example, the values of the Al−N(equatorial) and Al−N(axial) distances are 1.85 ± 0.03 and 2.01 ± 0.07 Å, respectively, and the N(axial)−Al−N(equatorial) bond angles are 90.4 ± 2.4°. Note that the N−Si bond lengths are also in the same range (1.71 ± 0.02 Å).

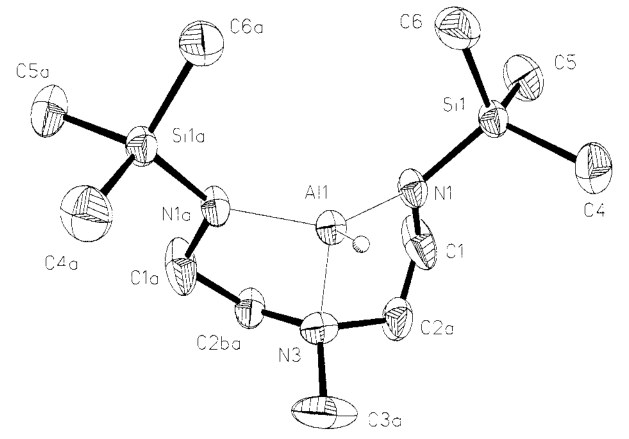
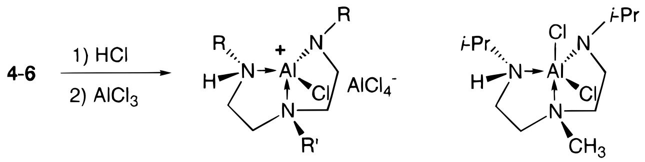


Figure 4. Molecular structure of **11** in the solid state. Hydrogen atoms except H1 have been omitted for clarity.

Scheme 4



12 (94%),**13** (93%), **14** (90%) **15**

4,**12**: R = R' = $SiMe_3$
5,**13**: R = $SiMe_3$ R' = Me
6,**14**: R = *i*-Pr R' = Me

Compared to the neutral species, the chemistry of cationic low-coordinated aluminum derivatives remains relatively unexplored,[11] although they possess a high potential in organic and catalytic transformations.[17] Therefore, we studied the conversion of neutral aluminum complexes **C** into cationic derivatives **D**, which would be the first chiral examples of a tetracoordinated aluminum cation. These complexes, even when not enantiomerically pure, should be of significant importance in controlling the tacticity of polymers such as poly(propylene oxide) (PPO).[18] Due to the coordination of the amino nitrogen to the aluminum center, a chemioselective quaternization of one of the amido nitrogen atoms[19] of complexes **4**−**6** was achieved by addition of an anhydrous ether solution of HCl. Subsequent addition of $AlCl_3$ cleanly afforded the four-coordinate cationic derivatives **12** (94% yield), **13** (93% yield), and **14** (90% yield) as highly air- and moisture-sensitive solids (Scheme 4).

The good solubility of compounds **12**−**14** in toluene suggested that these derivatives were monomeric species. As observed for $Me_2AlCl{-}HN(alkyl)_2$ complexes,[11a] the IR absorptions of the secondary N−H moieties were manifested as broad peaks (**13**, 3207 cm^{-1}; **14**, 3192

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[17] Dohmeier, C.; Schnöckel, H.; Robl, C.; Schneider, U.; Ahlrichs, R. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1655.

[18] (a) Ewen, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 6355. (b) Brintzinger, H. H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143. (c) Coates, G. W.; Waymouth, R. M. *Science* **1995**, *267*, 217.

[19] Quaternization of an equatorial nitrogen in azasilatranes has been reported, see: Woming, J.; Verkade, J. G. *J. Am. Chem. Soc.* **1991**, *113*, 944.

Table 4. Bond Lengths (Å) and Bond Angles (deg) for Derivative 15

Al(1)−N(1)	1.819(3)	Al(1)−Cl(2)	2.258(4)
Al(1)−N(2)	2.040(3)	N(1)−Al−N(2)	115.3(4)
Al(1)−N(3)	2.130(3)	N(1)−Al−N(3)	83.0(3)
Al(1)−Cl(1)	2.206(4)		
N(1)−Al−Cl(1)	110.1(2)	N(2)−Al−Cl(2)	89.6(3)
N(1)−Al−Cl(2)	121.9(1)	N(3)−Al−Cl(2)	171.6(9)
N(2)−Al−N(3)	81.9(2)	N(3)−Al−Cl(1)	91.1(9)
N(2)−Al−Cl(1)	121.0(3)		

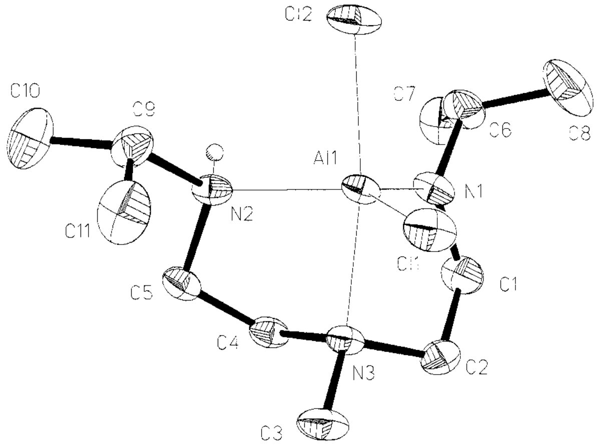

Figure 5. Molecular structure of **15** in the solid state. Hydrogen atoms except H2 have been omitted for clarity.

cm^{-1}). Typical sharp ^{27}Al NMR signals were observed for $AlCl_4^-$ (+107 ($\nu_{1/2}$ = 60 Hz)) along with broader signals (**13** +110 ($\nu_{1/2}$ = 300 Hz); **14** +120 ($\nu_{1/2}$ = 320 Hz)), consistent with four-coordinate complexes.[10] Due to the presence of several diastereomers, ^{1}H and ^{13}C NMR spectra are not of valuable interest to this discussion. All attempts to separate the diastereomers by fractional crystallization at low temperature failed due to decomposition of the salts. Nevertheless, colorless crystals of **12** were obtained from a saturated benzene solution, and the structure of one of the diastereomers was clearly established by a single-crystal X-ray diffraction study (Table 1).[9a] Complex **12** is monomeric and exhibits no significant interaction with the counteranion. The hydrogen atom of the NH moiety was located and refined. The molecular structures of **4** and **12** offer the opportunity to compare structural parameters in related neutral and cationic tetracoordinated aluminum compounds (Table 1). As with **4**, the cation **12** features a central aluminum atom which adopts an almost TMP coordination environment. The aluminum atom is only slightly displaced from the trigonal plane Cl(1)N(1)N(3) in the direction of the apically coordinated donor (**4**, 0.34 Å; **12**, 0.40 Å), and the endocyclic N−Al−N angles are close to 90°. As expected, the protonation induces an important lengthening of the Al(1)−N(1) and N(1)−Si(1) bond distances (Δd = 0.137 and 0.117 Å) and a shortening of the Al(1)−Cl(1), Al(1)−N(2), and Al(1)−N(3) bond lengths (Δd = 0.041, 0.022, and 0.035 Å, respectively).

Note that during the course of the reaction of HCl with **6**, very few crystals of **15** suitable for a single-crystal X-ray diffraction study (Table 4, Figure 5) were isolated. Compound **15** is a five-coordinate aluminum dichloride complex resulting from the quaternization of an amido nitrogen atom and coordination of the chlorine atom. This is clearly the direct precursor of **14**.

Table 5. Bulk Polymerization of PO[a]

catalyst	*T* (°C)	yield (%)	activity (g mmol^{-1} h^{-1})	M_n	M_w/M_n
4	30	10		318	1.14
5	30	1		141	1.11
11	30	1		696	1.02
12	30	35		1416	1.18
13	30	8		632	1.25
14	30	2			
12	80	58		2158	1.24

[a] Reaction conditions: mol of PO/mol of catalysts = 16/1; 2 days.

The coordination geometry of the aluminum center in **15** approaches a trigonal-bipyramidal geometry. The pyramidal axis deviates only slightly from linearity (N(3)−Al(1)−Cl(2) = 171.6°(9)), with the sum of the three angles being 358.2°. As expected, the equatorial Al−Cl bond (2.206(4) Å) is shorter than the axial one (2.258(4) Å) and the Al(1)−N(2) distance (2.040(3) Å) longer than the Al(1)−N(1) distance (1.819(3) Å). The distance between the aluminum and the axial nitrogen atom N(3) (2.130(3) Å) is considerably longer than those observed for low-coordinate complexes **4** (1.998(1) Å) and **5** (1.993(2) Å) and close to classical values for dative Al−N bond distances.[20]

Catalytic Activity for Ring-Opening Polymerizations

Polypropylene oxide (PPO) has found an application as a precursor for the synthesis of thermotropic liquid crystal polymers[21a] or semipermeable membranes,[21b] whereas polylactides (PLA) are biocompatible polymers used as materials for controlled drug delivery devices and other medicinal applications such as surgical sutures.[22] In addition, these hydrodegradable materials are good candidates to replace nonbioresorbable polymers since they possess good mechanical properties[22e] and are made using lactic acid derived from natural renewable sources (e.g., corn). Therefore, we investigated the catalytic properties of complexes **4**−**7** and **10**−**14** for the ring-opening polymerization of propylene oxide (PO) and (D,L)-lactide.

Among the neutral derivatives possessing a chloride (**4**−**7**), methyl (**10**), or hydrido ligand (**11**), only the aluminum chloride **4** featuring three $SiMe_3$ substituents appeared to be an initiator for the bulk polymerization of PO at room temperature (Table 5). According to GPC analyses, based on poly(ethylene glycol) standards, oligomers (M_n = 318) of a narrow molecular weight distribution (M_w/M_n = 1.14) were obtained in moderate yield. It is interesting to note that complex **5** is almost inactive, although its solid-state structure and NMR data are very similar to that of **4**. This is an indication of the subtle importance of the Lewis-acid character on the catalytic activity.

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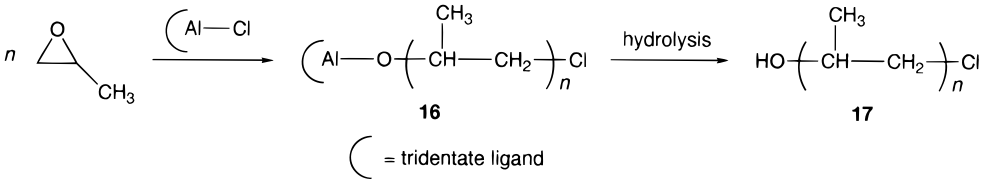
(20) Haaland, A. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 992.

(21) *Recent Advances in Liquid Crystalline Polymers*; Chapoy, L. L., Ed.; Elsevier Applied Science: London, 1985.

(22) (a) Langer, R. *Acc. Chem. Res.* **1993**, *26*, 537. (b) Shindler, A.; Jeffcoat, R.; Kimmel, G. L.; Pitt, C. G.; Wall, M. E.; Zweidinger, R. In *Contempory Topics in Polymer Science*; Pearce, E. M., Schaefgen, J. R., Eds.; Plenum Press: New York, 1977. (c) Pennings, J. P.; Dijkstra, H.; Pennings, A. *Polymer* **1993**, *34*, 942. (d) Vert, M.; Christel, P.; Chabot, F.; Leray, J. In *Macromolecular Biomaterials*; Hastings, G. W., Ducheyne, P., Eds; CRC Press: Bocca Raton, FL, 1984. (e) Vert, M.; Schwarch, G.; Coudane, J. *J. Macromol. Sci.*—*Pure Appl. Chem.* **1995**, *A32*, 787.

Scheme 5



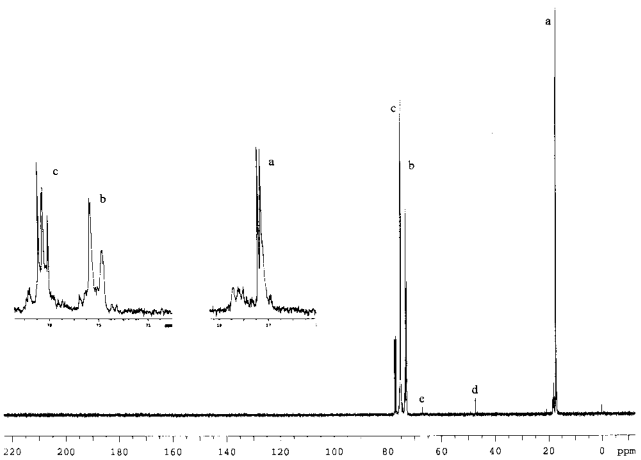


Figure 6. ^{13}C NMR spectrum of poly(propylene oxide) obtained with **12** ($M_n = 1418$, $M_w/M_n = 1.18$).

All cationic derivatives initiated the polymerization of PO, but again the fully silylated derivative **12** showed the highest catalytic activity (Table 5). With this initiator, after 2 days at room temperature, a conversion of 35% was achieved. GPC analyses revealed that the product is a low molecular weight polymer ($M_n = 1416$) having a narrow molecular weight distribution ($M_w/M_n = 1.18$). When the reaction temperature was raised to 80 °C, a polymer of higher molecular weight ($M_n = 2158$) was obtained in 58% yield, the molecular weight distribution ($M_w/M_n = 1.24$) remaining almost constant. The ^{13}C NMR spectra of the macromolecules **17** (Scheme 5) obtained with **10** as the catalyst are very similar to those observed for PPO prepared with aluminum porphyrin systems (which are actually the best systems in terms of chain end control of stereochemistry).[5c] Signals at 17−17.5 (a), 72.8−73.3 (b), and 75.0−75.8 ppm (c) correspond to methyl, methylene, and methine carbons, respectively (Figure 6). The two singlets at 47.5 (d) and 67.7 (e) are due to the terminal CH_2Cl and HOCH groups, respectively (Figure 6).[5c,23] The hydroxyl group was formed by the hydrolysis of the aluminum alkoxide bond of derivative **16**. The simplicity of the methyl signals (a) indicates that the polymers consist exclusively of head-to-tail linkages.[5c] The intensity ratios of the racemic “r” (72.9) and meso “m” (73.3) diads on the one hand and of the syndiotactic “S” (75.0), heterotactic “H” (75.2), and isotactic “I” (75.3) triads on the other hand indicate that these macromolecules are rich in meso diad (60%) and isotactic triad (50%) sequences (Figure 6). The catalytic activity of **10** toward PO polymerization at 80 °C is similar to that obtained with Schiff's-base−$AlEt_2Cl$ initiator systems[24] but considerably lower than that observed with porphynato−aluminum chloride complexes.[5a] In all cases, there is a difference between the observed and the expected M_n's of the polymer, which indicates that initiation and propagation steps do not involve every molecule of the starting aluminum chloride complexes.

The mechanism for the aluminum chloride complexes of porphyrin and Schiff-base-catalyzed PO polymerization has been studied. It proceeds via an aluminum alkoxide of type **16** as the propagating species,[5a,c,f,6b,23a] which is first formed via the nucleophilic attack of the dissociated counteranion Cl^- on a PO molecule coordinated to a cationic aluminum center.[6b] The growth of the polyether chain then involves insertion of PO into the Al−O bond through a four-center intermediate. A different mechanism may be envisaged with the tetracoordinate aluminum initiators since, in contrast to aluminum chloride complexes of porphyrin and Schiff base, they possess a free coordination site. We propose that the growing aluminum alkoxide species **F** is formed via coordination of a PO molecule on the catalyst leading to **E**, followed by a inner-sphere migratory-insertion step which induces the ring opening of the oxirane (Scheme 6). Complex **F** possessing a free coordination site can coordinate a second molecule of PO affording **G**. Chain growth proceeds via further successive migratory-insertion and coordination sequences. The fact that macromolecules **17** feature terminal CH_2Cl and CHOH groups, identified by ^{13}C NMR spectroscopy, is the fingerprint for intermediates of type **F**−**H**. Furthermore, intermediates of type **E** and **G** are strongly supported by ^{1}H and ^{13}C NMR data which show that the cation **12** readily coordinates oxygen-containing substrates such as ether or THF. Indeed, when 1 equiv of diethyl ether was added to a toluene-d_8 solution of **12**, a deshielding and a shielding, respectively, of the CH_3 [$\Delta\delta$ ^{1}H, 0.2 ppm; ^{13}C, 1.0 ppm] and CH_2 [$\Delta\delta$ ^{1}H, 0.1 ppm; ^{13}C, 2.5 ppm] signals of the OCH_2CH_3 fragment were observed (with respect to the position for free ether). As expected, THF totally displaces ether. Again, compared to free THF, a deshielding and a shielding of the $OCH_2\mathit{CH}_2$ [$\Delta\delta$ ^{1}H, 0.1 ppm; ^{13}C, 0.2 ppm] and OCH_2 [$\Delta\delta$ ^{1}H, 0.5 ppm; ^{13}C, 1.5 ppm] signals was observed. In both cases, when a slight excess of the ether was added, an equilibrium was established with the signals corresponding to the coordinated solvent molecule moving significantly toward those of free ether. These results clearly show that **12** can coordinate oxygen-donor ligands, even though this coordination is relatively weak.

Methyl- and hydridoaluminum derivatives **10** and **11** initiated the polymerization reaction of (D,L)-lactide in benzene at 80 °C (Table 6). As estimated from GPC, similar polymers are obtained with both complexes (**10** $M_n = 14475$, $M_w/M_n = 1.79$; **11** $M_n = 13453$, $M_w/M_n =$

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[23] (a) Jun, C. L.; Leborgne, A.; Spassky, N. *J. Polym. Sci.: Polym. Symp.* **1986**, *74*, 31. (b) Sugimoto, H.; Inoue, S. *Macromolecules* **1990**, *23*, 2869. (c) Sugimoto, H.; Kawamura, C.; Kuroki, M.; Aida, T.; Inoue, S. *Macromolecules* **1994**, *27*, 2013.

[24] Vincens, V.; Le Borgne, A.; Spassky, N. *Makromol. Chem. Rapid. Commun.* **1989**, *10*, 623.

Scheme 6

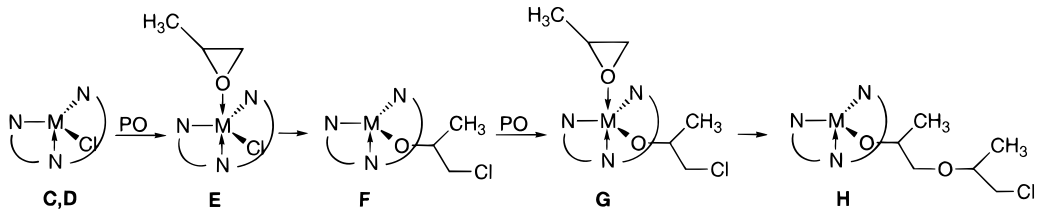

Table 6. Polymerization of (D,L)-Lactide[a]

catalyst	reaction time (days)	[(D,L)-lactide]/[catalyst]	yield (%)	M_n	M_w/M_n
10	5	50	37	14 475	1.79
11	5	50	68	13 453	1.61
11	7	50	76	16 930	1.72
13/PO	5	50	46	1476	1.23
13/PO	25	500	85	18 504	1.39

[a] Reaction conditions: benzene (30 mL), 80 °C.

1.61), hydride complex **11** being about twice as active as the methylaluminum derivative **10**. Polymers possessing higher molecular weights could be obtained by increasing the reaction time, without modification of the molecular weight distribution. Carrying out the reaction at 100 °C, using **10** as initiator, led to higher catalytic activities but at the expense of the molecular weight distribution ($M_n = 25620$, $M_w/M_n = 2.34$). All neutral and cationic aluminum chloride derivatives **4**−**6** and **12**−**14** were inert toward (D,L)-lactide in a benzene solution at 80 °C. However, under the same reaction conditions, an aluminum alkoxide of type **16**, prepared in situ by reacting derivative **13** with PO at 80 °C [**13**/PO = 20], initiated the polymerization of (D,L)-lactide. After 5 days, a low molecular weight polymer ($M_n = 1476$) having a narrow molecular weight distribution ($M_w/M_n = 1.23$) was obtained in 46% yield. Polymers of higher molecular weight ($M_n = 18504$) can be produced by increasing the [(D,L)-lactide]/[catalyst] ratio, without significant modification of the molecular weight distribution ($M_w/M_n = 1.39$).

Conclusion

We have shown that diamidoamine ligands are particularly well adapted for the stabilization of neutral four-coordinated aluminum and gallium complexes **C** (Scheme 1) featuring various X substituents. Furthermore, these ligands can be modified in the coordination sphere of aluminum to give the first chiral cationic tetracoordinated aluminum derivatives **D**. In all cases, due to the formation of a rather rigid bicyclic core, these tridentate nitrogen donors enforce an approximately trigonal-monopyramidal coordination geometry. As a result of this unusual geometry, the empty axial coordination site is accessible for substrate binding. Initial results have shown that these Lewis acids are promising catalysts for the ring-opening polymerization of heterocycles. Notably, the presence of a free coordination site led to an original PO polymerization mechanism based upon repeated monomer coordination/migratory-insertion sequences analogous to those observed in classical transition-metal-mediated polymerizations.

Experimental Section

All experiments were performed under an atmosphere of dry argon. Melting points are uncorrected. ^{1}H, ^{13}C, ^{29}Si, and ^{27}Al NMR spectra were recorded on a Bruker AC200, WM250, or AMX400 spectrometer. ^{1}H, ^{13}C, and ^{29}Si chemical shifts are reported in ppm relative to Me_4Si as an external standard. ^{27}Al NMR downfield chemical shifts are expressed with a positive sign, in ppm, relative to external $Al(NO_3)_3$. Infrared spectra were recorded on a Perkin-Elmer FT-IR Spectrometer 1725 X. Conventional glassware was used. Propylene oxide was degassed to remove air, dried over sodium at room temperature, and distilled by vacuum distillation into a trap cooled with a liquid nitrogen bath. Commercial (D,L)-lactide was recrystallized from toluene and dried 24 h at 25 °C under reduce pressure (10^{-2} mmHg) before polymerization. Molecular weights (M_w and M_n) and polydispersities (M_w/M_n) of the polymers were determined by gel permeation chromatography (GPC) with respect to poly(ethylene glycol) and polystyrene standards for the samples of poly(propylene oxide) and poly[(D,L)-lactide], respectively. All samples were analyzed at 30 °C on a Waters high-speed liquid chromatograph equipped with a R 410 refractometer detector, using tetrahydrofuran as the eluent with a flow rate of 1 mL min^{-1}.

$(Me_3SiNHCH_2CH_2)_2NMe$ (2). To an ether solution (15 mL) of *N*-methyldiethylenetriamine (6.18 g, 52.7 mmol) at −40 °C was added dropwise 2 equiv of BuLi in hexanes. The solution was allowed to warm to room temperature and stirred for 1 h at room temperature. Neat trimethylsilyl chloride (13.6 mL, 107.1 mmol) was added at −40 °C. The solution was allowed to warm to room temperature, stirred overnight, and filtered, and the solvent was removed under vacuum. **2** was obtained by distillation as a colorless liquid (8.60 g, 62%): bp 55 °C (10^{-1} mmHg); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.02 (s, 18 H, CH_3Si), 0.95 (s br, 2 H, NH), 2.18 (s, 3 H, NCH_3), 2.33 (m, 4 H, CH_2), 2.76 (m, 4 H, CH_2); ^{13}C NMR ($CDCl_3$, 50.323 MHz) δ −0.18 (s, CH_3Si), 39.26 (s, CH_2), 42.23 (s, CH_3N), 61.23 (s, CH_2). Anal. Calcd for $C_{11}H_{31}N_3Si_2$: C, 50.51; H, 11.95; N, 16.06. Found: C, 50.68; H, 12.74; N, 16.37.

(*i*-$PrNHCH_2CH_2)_2NMe$ (3). To a water solution (200 mL) of acetic acid (100 mL), $CH_3CO_2Na{\cdot}3H_2O$ (28.0 g), and acetone (117 mL, 1.59 mol), *N*-methyldiethylenetriamine (6.18 g, 52.7 mmol) was added at room temperature. The solution was stirred for 1 h at room temperature, and $NaBH_4$ (46.8 g, 1.23 mol) was added, at 0 °C, in small portions over a period of 2 h. Sodium hydroxide (15%) was added until a pH of 12 was obtained, the aqueous phase wash extracted with ether (4 × 200 mL), and the ether fractions were combined and dried over Na_2SO_4. **3** was obtained by distillation as a colorless liquid (13.32 g, 66%): bp 49 °C (10^{-1} mmHg); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.95 (d, 12 H, $J_{HH} = 6.3$ Hz, CH_3CH), 1.35 (s br, 2 H, NH), 2.10 (s, 3 H, NCH_3), 2.38 (m, 4 H, CH_2), 2.57 (m, 4 H, CH_2), 2.67 (sept, 2 H, $J_{HH} = 6.3$ Hz, CH_3CH); ^{13}C NMR ($CDCl_3$, 50.323 MHz) δ 22.82 (s, CH_3CH), 42.14 (s, CH_2), 44.71 (s, CH_3N), 48.56 (s, CH_2), 57.23 (s, CH_3CH). Anal. Calcd for $C_{11}H_{27}N_3$: C, 65.62; H, 13.52; N, 20.87. Found: C, 65.79; H, 13.74; N, 20.37.

$[(Me_3SiNCH_2CH_2)_2NSiMe_3]AlCl$ (4). To a THF solution (100 mL) of *N*,*N*′,*N*″-tris(trimethylsilyl)diethylenetriamine (**1**)[9a] (3.34 g, 10.3 mmol), at −40 °C, was added dropwise 2 equiv of BuLi in hexanes. The solution was allowed to warm to room temperature and stirred for 2 h. A THF solution (100 mL) of $AlCl_3$ (1.38 g, 10.3 mmol) was added at −40 °C. The solution was allowed to warm to room temperature and stirred overnight, and the solvent was removed under vacuum. The residue was extracted with pentane (150 mL), and the solvent was removed in vacuo. **4** was obtained after sublimation under vacuum (100 °C, 10^{-1} mmHg) as colorless crystals suitable for a single-crystal X-ray diffraction study (2.06 g, 52% yield): mp 20−22 °C; ^{1}H NMR (C_6D_6, 400 MHz) δ 0.36 (s, 9 H, CH_3Si), 0.48 (s, 18 H, CH_3Si), 1.97 (ddd, 2 H, J_{HH} = 12.3, 5.3, and 5.3 Hz, CH_2), 2.42 (ddd, 2 H, J_{HH} = 12.3, 7.6, and 5.3 Hz, CH_2), 2.76 (ddd, 2 H, J_{HH} = 12.3, 5.3, and 5.3 Hz, CH_2), 2.92 (ddd, 2 H, J_{HH} = 12.3, 7.6, and 5.3 Hz, CH_2); ^{13}C NMR (C_6D_6, 100.630 MHz) δ −1.59 (s, CH_3Si), 1.40 (s, CH_3Si), 42.70 (s, CH_2), 54.22 (s, CH_2); ^{27}Al (C_6D_6, 104.273 MHz) +125 ($\nu_{1/2}$ = 5000 Hz). Anal. Calcd for $C_{13}H_{35}N_3AlClSi_3$: C, 41.08; H, 9.28; N, 11.05. Found: C, 41.22; H, 9.37; N, 11.00.

[($Me_3SiNCH_2CH_2$)$_2$NMe]AlCl (5). To a THF solution (100 mL) of *N*-methyl-*N′*,*N″*-bis(trimethylsilyl)diethylenetriamine (**2**) (7.23 g, 27.6 mmol), at −40 °C, was added dropwise 2 equiv of BuLi in hexanes. The solution was allowed to warm to room temperature and stirred for 2 h. A THF solution (50 mL) of $AlCl_3$ (3.53 g, 26.5 mmol) was added at −40 °C. The solution was allowed to warm to room temperature and stirred overnight, and the solvent was removed under vacuum. The residue was extracted with ether (150 mL), and the solvent was removed. **5** was obtained after sublimation under vacuum (100 °C, 10^{-1} mmHg) as colorless crystals suitable for a single-crystal X-ray diffraction study (6.44 g, 76% yield): mp 130 °C (dec); ^{1}H NMR (C_6D_6, 400 MHz) δ 0.41 (s, 18 H, CH_3Si), 1.95 (s, 3 H, CH_3N), 1.96 (dt, 2 H, J_{HH} = 11.7 and 5.6 Hz, CH_2), 2.27 (dt, 2 H, J_{HH} = 11.7 and 5.6 Hz, CH_2), 2.84 (dd, 4 H, J_{HH} = 5.6 and 5.6 Hz, CH_2); ^{13}C NMR (C_6D_6, 100.630 MHz) δ 1.19 (s, CH_3Si), 41.24 (s, CH_2), 42.01 (s, CH_3N), 58.37 (s, CH_2); ^{27}Al NMR (C_6D_6, 104.273 MHz) +121 ($\nu_{1/2}$ = 3100 Hz); ^{29}Si NMR (C_6D_6, 79.49 MHz) +1.46. Anal. Calcd for $C_{11}H_{29}N_3AlClSi_2$: C, 41.03; H, 9.08; N, 13.05. Found: C, 40.88; H, 9.01; N, 12.97.

[(*i*-PrNCH$_2$CH$_2$)$_2$NMe]AlCl (6). To a THF solution (100 mL) of *N*-methyl-*N′*,*N″*-bis(diisopropyl)diethylenetriamine (**3**) (3.91 g, 19.4 mmol), at −40 °C, was added dropwise 2 equiv of BuLi in hexanes. The solution was allowed to warm to room temperature and stirred for 2 h. A THF solution (50 mL) of $AlCl_3$ (2.67 g, 20.0 mmol) was added at −40 °C. The solution was allowed to warm to room temperature and stirred overnight, and the solvent was removed under vacuum. The residue was extracted with ether (150 mL), the solvent was removed, and **6** was obtained after sublimation under vacuum (90 °C, 10^{-1} mmHg) as a white powder (3.58 g, 70% yield): mp 63−65 °C; ^{1}H NMR (C_6D_6, 400 MHz) δ 1.42 (d, 6 H, J_{HH} = 6.3 Hz, CH_3CH), 1.44 (d, 6 H, J_{HH} = 6.3 Hz, CH_3CH), 2.00 (s, 3 H, CH_3N), 2.10 (dtr, 2 H, J_{HH} = 11.5 and 5.8 Hz, CH_2), 2.46 (dtr, 2 H, J_{HH} = 11.5 and 5.8 Hz, CH_2), 2.84 (dd, 4 H, J_{HH} = 5.8 and 5.8 Hz, CH_2), 3.18 (sept, 2 H, J_{HH} = 6.3 Hz, CH_3CH); ^{13}C NMR (C_6D_6, 100.630 MHz) δ 24.78 (s, CH_3CH), 25.60 (s, CH_3CH), 41.65 (s, CH_3N), 45.41 (s, CH_2), 50.80 (s, CH_3CH), 55.45 (s, CH_2); ^{27}Al NMR (C_6D_6, 104.273 MHz) +112 ($\nu_{1/2}$ = 400 Hz). Calcd for $C_{11}H_{25}N_3AlCl$: C, 50.47; H, 9.63; N, 16.05. Found: C, 50.34; H, 9.44; N, 16.24.

[($Me_3SiNCH_2CH_2$)$_2$NSiMe$_3$]GaCl (7). To a THF solution (50 mL) of *N*,*N′*,*N″*-tris(trimethylsilyl)diethylenetriamine (1.34 g, 4.2 mmol), at −40 °C, was added dropwise 2 equiv of BuLi in hexanes. The solution was allowed to warm to room temperature and stirred for 2 h. A THF solution (50 mL) of $GaCl_3$ (0.75 g, 4.3 mmol) was added at −40 °C. The solution was allowed to warm to room temperature and stirred overnight, and the solvent was removed under vacuum. The residue was extracted with pentane (50 mL), the solvent removed, and **7** obtained after sublimation under vacuum (95 °C, 10^{-1} mmHg) as a white powder (0.85 g, 48% yield): mp 62−64 °C; ^{1}H NMR (C_6D_6, 400 MHz) δ 0.18 (s, 9 H, CH_3Si), 0.46 (s, 18 H, CH_3Si), 1.98 (ddd, 2 H, J_{HH} = 12.2, 5.0, and 5.0 Hz, CH_2), 2.44 (ddd, 2 H, J_{HH} = 12.2, 7.4, and 5.2 Hz, CH_2), 2.94 (ddd, 2 H, J_{HH} = 12.2, 5.0, and 5.0 Hz, CH_2), 3.00 (ddd, 2 H, J_{HH} = 12.2, 7.4, and 5.2 Hz, CH_2); ^{13}C NMR (C_6D_6, 100.630 MHz) δ −1.42 (s, CH_3Si), 1.82 (s, CH_3Si), 44.20 (s, CH_2), 54.21 (s, CH_2); ^{29}Si NMR (C_6D_6, 79.49 MHz) −3.70, −3.05. Anal. Calcd for $C_{13}H_{35}N_3GaClSi_3$: C, 36.99; H, 8.36; N, 9.95. Found: C, 37.21; H, 8.44; N, 9.72.

{[($Me_3SiNCH_2CH_2$)$_2$NMe]InCl}$_2$ (8). To a THF solution (100 mL) of *N*-methyl-*N′*,*N″*-bis(trimethylsilyl)diethylenetriamine (2.57 g, 9.8 mmol), at −40 °C, was added dropwise 2 equiv of BuLi in hexanes. The solution was allowed to warm to room temperature and stirred for 2 h. A THF suspension (50 mL) of $InCl_3$ (2.21 g, 10.0 mmol) was added at room temperature, and the solution was refluxed for 10 h. The solvent was removed under vacuum, and the residue was extracted with toluene (70 mL). After filtration, the solution was concentrated under reduced pressure to approximately 30 mL. **8** was obtained from this solution, at −30 °C, as colorless crystals suitable for a single-crystal X-ray diffraction study (0.92 g, 23% yield): mp 124 °C (dec); ^{1}H NMR (C_6D_6, 400 MHz) δ 0.36−0.43 (s br, 18 H, CH_3Si), 1.80−1.90 (m, 2 H, CH_2), 1.90−1.95 (s br, 3 H, CH_3N), 2.09−2.15 (m, 2 H, CH_2), 2.80−3.00 (m, 4 H, CH_2). Anal. Calcd for $C_{11}H_{29}N_3InClSi_2$: C, 32.30; H, 7.15; N, 10.27. Found: C, 32.12; H, 7.02; N, 10.39.

[($Me_3SiNHCH_2CH_2$)($Me_3SiNCH_2CH_2$)NMe]AlMe$_2$ (9). To a toluene solution (100 mL) of *N*-methyl-*N′*,*N″*-bis(trimethylsilyl)diethylenetriamine (**2**) (3.51 g, 13.4 mmol), at −40 °C, was added dropwise 1 equiv of $AlMe_3$ in toluene. The solution was allowed to warm to room temperature and stirred overnight. The solution was concentrated under reduced pressure to approximately 30 mL. **9** was isolated by crystallization from this solution at −30 °C as a white powder (2.85 g, 67% yield): mp 10−12 °C; ^{1}H NMR (C_6D_6, 400 MHz) δ −0.36 (s, 6 H, CH_3Al), 0.25 (s, 9 H, CH_3Si), 0.47 (s, 9 H, CH_3Si), 2.10 (s, 3 H, CH_3N), 2.19 (m, 1 H, CH_2), 2.25 (ddd, 1 H, J_{HH} = 12.2, 10.5, and 5.2 Hz, CH_2), 2.62 (ddd, 1 H, J_{HH} = 12.2, 10.5, and 5.2 Hz, CH_2), 2.74 (ddd, 1 H, J_{HH} = 10.9, 10.9, and 6.3 Hz, CH_2), 2.84 (m, 1 H, CH_2), 3.01 (m, 1 H, CH_2), 3.13 (m, 1 H, CH_2), 3.16 (m, 1 H, CH_2), NH was not observed; ^{13}C NMR (C_6D_6, 100.630 MHz) δ −7.52, −7.18 (s, CH_3Al), 0.30 (s, CH_3Si), 0.92 (s, CH_3Si), 37.81 (s, CH_2), 39.41 (s, CH_3N), 41.75 (s, CH_2), 61.92 (s, CH_2), 62.10 (s, CH_2); ^{29}Si NMR (C_6D_6, 79.49 MHz) +4.00, 9.39. Anal. Calcd for $C_{11}H_{36}N_3AlSi_2$: C, 49.16; H, 11.42; N, 13.23. Found: C, 49.42; H, 11.84; N, 13.89.

[($Me_3SiNCH_2CH_2$)$_2$NMe]AlMe (10). A toluene solution (100 mL) of derivative **9** (4.25 g, 13.4 mmol) was heated at 80 °C overnight. The solvent was removed under vacuum, and derivative **10** was obtained after sublimation under vacuum (80 °C, 10^{-1} mmHg) as colorless crystals suitable for a single-crystal X-ray diffraction study (2.04 g, 50% yield): mp 67 °C; ^{1}H NMR (C_6D_6, 400 MHz) δ −0.32 (s, 3 H, CH_3Al), 0.39 (s, 18 H, CH_3Si), 1.82 (s, 3 H, CH_3N), 1.94 (ddd, 2 H, J_{HH} = 11.7, 6.8, and 5.1 Hz, CH_2), 2.32 (ddd, 2 H, J_{HH} = 11.3, 5.9, and 5.1 Hz, CH_2), 2.89 (ddd, 2 H, J_{HH} = 11.3, 5.9, and 5.1 Hz, CH_2), 2.98 (ddd, 2 H, J_{HH} = 11.7, 6.8, and 5.1 Hz, CH_2); ^{13}C NMR (C_6D_6, 100.630 MHz) δ 1.42 (s, CH_3Si), 1.78 (s, CH_3Al), 42.09 (s, CH_2), 42.22 (s, CH_3N), 59.76 (s, CH_2); ^{27}Al NMR (C_6D_6, 104.273 MHz) +150 ($\nu_{1/2}$ = 4300 Hz); ^{29}Si NMR (C_6D_6, 79.49 MHz) −0.80. Anal. Calcd for $C_{12}H_{32}N_3Al_2Si_2$: C, 47.79; H, 10.69; N, 13.93. Found: C, 47.63; H, 10.42; N, 13.97.

[($Me_3SiNCH_2CH_2$)$_2$NMe]AlH (11). To a THF solution (50 mL) of *N*-methyl-*N′*,*N″*-bis(trimethylsilyl)diethylenetriamine (**2**) (2.30 g, 8.8 mmol), at −40 °C, was added dropwise a THF suspension (70 mL) of $LiAlH_4$ (0.33 g, 8.8 mmol). The reaction mixture was allowed to warm to room temperature and stirred overnight. After filtration, the solvent was removed under vacuum. Derivative **11** was obtained after sublimation under vacuum (90 °C, 10^{-1} mmHg) as colorless crystals suitable for a single-crystal X-ray diffraction study (0.95 g, 38% yield): mp 15 °C; ^{1}H NMR (C_6D_6, 200 MHz) δ 0.43 (s, 18 H, CH_3Si), 1.88 (s, 3 H, CH_3N), 1.95 (ddd, 2 H, J_{HH} = 11.7, 6.6, and 5.2 Hz, CH_2), 2.29 (ddd, 2 H, J_{HH} = 12.1, 5.7, and 5.2 Hz, CH_2), 2.91 (ddd, 2 H, J_{HH} = 11.7, 5.7, and 5.3 Hz, CH_2), 2.97 (ddd, 2 H, J_{HH} = 12.1, 6.6, and 5.3 Hz, CH_2), 3.45 (s br, 1 H, AlH); ^{13}C

NMR (C_6D_6, 50.323 MHz) δ 1.53 (s, CH_3Si), 41.81 (s, CH_3N), 42.08 (s, CH_2), 59.45 (s, CH_2); ^{27}Al NMR (C_6D_6, 104.273 MHz) +133 ($\nu_{1/2} = 500$ Hz); ^{29}Si NMR (C_6D_6, 79.49 MHz) +0.06; IR (Toluene) 1811 cm^{-1} (AlH). Anal. Calcd for $C_{11}H_{30}N_3AlSi_2$: C, 45.95; H, 10.52; N, 14.61. Found: C, 45.63; H, 10.22; N, 13.97.

{[(Me$_3$SiNHCH$_2$CH$_2$)(Me$_3$SiNCH$_2$CH$_2$)NSiMe$_3$]AlCl}-{AlCl$_4$} (12). Addition, at −40 °C, of 1 equiv of HCl in ether to a toluene solution (3 mL) of aluminum chloride derivative **4** (0.19 g, 0.5 mmol) afforded a pale yellow precipitate. A homogeneous solution was obtained by addition, at −40 °C, of a toluene suspension (2 mL) of $AlCl_3$ (0.07 g, 0.5 mmol). The solution was allowed to warm to room temperature and stirred for 30 min. The solution was concentrated under reduced pressure to approximately 1 mL. **12** was isolated by crystallization from this solution, at −25 °C, as crystals suitable for a single-crystal X-ray diffraction study (0.23 g, 84% yield). According to NMR spectroscopy, **12** is a mixture of several diastereoisomers: ^1H NMR (C_6D_6, 400 MHz) δ 0.19, 0.21, 0.24, 0.27, 0.29, 0.34, 0.37, 0.41, 0.43, 0.45, 0.47, 0.48 (s, CH_3Si), 2.28, 2.67, 2.91, 3.04, 3.22, 3.29, 3.45, 3.88 (m, CH_2); ^{13}C NMR (C_6D_6, 100.630 MHz) δ −1.54, −1.57, −1.43, −1.29, −1.03, −0.88, 0.95, 1.01, 1.06, 1.35, 1.46 (s, CH_3Si), 40.18, 42.27, 42.66, 42.82, 43.02, 43.51, 45.63, 45.84, 49.26, 49.64, 50.63, 50.91, 52.03, 52.54, 54.35, 55.31, 56.07, 56.60 (s, CH_2). Anal. Calcd for $C_{13}H_{36}N_3Al_2Cl_5Si_3$: C, 28.39; H, 6.60; N, 7.64. Found: C, 28.09; H, 6.37; N, 7.52.

{[(Me$_3$SiNHCH$_2$CH$_2$)(Me$_3$SiNCH$_2$CH$_2$)NMe]AlCl}{AlCl$_4$} (13). Addition, at −40 °C, of 1 equiv of HCl in ether to a toluene solution (3 mL) of **5** (0.16 g, 0.5 mmol) afforded a pale yellow precipitate. A homogeneous solution was obtained by addition, at −40 °C, of a toluene solution (2 mL) of $AlCl_3$ (0.07 g, 0.5 mmol). The solution was allowed to warm to room temperature and stirred for 30 min. The solvent was removed under vacuum, and the residue was washed with pentane (2 × 5 mL). **13** was isolated as a white powder (0.20 g, 81% yield). According to NMR spectroscopy, several diastereoisomers are present: ^1H NMR (C_6D_6, 400 MHz) δ 0.28, 0.31, 0.36, 0.39 (s, CH_3Si), 1.94, 2.01 (s, CH_3N), 2.06 (m, CH_2), 2.12 (s, CH_3N), 2.24, 2.45, 2.63, 2.92 (m, CH_2); ^{13}C NMR (C_6D_6, 100.630 MHz) δ 1.07, 1.12, 1.15, 1.21 (s, CH_3Si), 41.33 (s, CH_2), 42.32 (s, CH_3N), 42.62 (s, CH_2), 42.67 (s, CH_3N), 42.89 (s, CH_2), 43.11 (s, CH_3N), 43.47, 45.62, 45.91, 52.12, 53.32, 55.72, 55.86 (s, CH_2); ^{27}Al (C_6D_6, 104.273 MHz) +110 ($\nu_{1/2} = 300$ Hz, AlN_3Cl), +107 ($\nu_{1/2} = 60$ Hz, $AlCl_4^-$); IR (Toluene) 3207 cm^{-1} (NH). Anal. Calcd for $C_{11}H_{30}N_3Al_2Cl_5Si_2$: C, 26.87; H, 6.15; N, 8.54. Found: C, 26.02; H, 5.87; N, 8.12.

{[(*i*-PrNHCH$_2$CH$_2$)(*i*-PrNCH$_2$CH$_2$)NMe]AlCl} {AlCl$_4$} (14). Addition, at −40 °C, of 1 equiv of HCl in ether to a toluene solution (3 mL) of aluminum chloride derivative **6** (0.13 g, 0.5 mmol) afforded a pale yellow precipitate. Very few crystals (mp 160 °C (dec)) of derivative **15** suitable for an X-ray diffraction study were obtained. A homogeneous solution was obtained by addition, at −40 °C, of a toluene solution (2 mL) of $AlCl_3$ (0.07 g, 0.5 mmol). The solution was allowed to warm to room temperature and stirred for 30 min. The solvent was removed under vacuum, and the residue was washed with pentane (2 × 5 mL). **14** was isolated as a white powder (0.20 g, 82% yield). According to multinuclear NMR spectroscopy, several diastereoisomers were present: ^1H NMR (C_6D_6, 400 MHz) δ 1.02, 1.17, 1.48, 1.52 (s, CH_3CH), 1.92 (s, CH_3N), 2.01 (m, CH_2), 2.17 (s, CH_3N), 2.39, 2.48, 2.70, 2.83 (m, CH_2), 3.23 (m, CH_3CH); ^{13}C NMR (C_6D_6, 100.630 MHz) δ 18.49, 20.96, 22.62, 23.85, 23.89, 24.08, 24.79, 25.67 (s, CH_3CH), 35.64, 38.27 (s, CH_2), 41.61, 42.82, 43.37 (s, CH_3N), 45.45, 45.74, 45.83 (s, CH_2), 46.14, 47.70, 49.48, 49.50, 50.88 (s, CH_3CH), 52.04, 52.21 (s, CH_2); ^{27}Al NMR (C_6D_6, 104.273 MHz) +120 ($\nu_{1/2} = 320$ Hz, AlN_3Cl), +107 ($\nu_{1/2} = 60$ Hz, $AlCl_4^-$); IR (Toluene) 3192 cm^{-1} (NH). Anal. Calcd for $C_{11}H_{22}N_3Al_2Cl_5$: C, 27.09; H, 5.37; N, 8.62. Found: C, 26.78; H, 5.00; N, 8.72.

Propylene Oxide Polymerization Procedure. The catalyst (0.4 mmol) was weighed into a Schlenk tube, equipped with magnetic stirring, under an argon atmosphere, then freshly dried propylene oxide (4.5 mL, 6.6 mmol) was added by syringe. The reaction vessel was immersed in a thermostatically controlled bath. After a predefined amount of time, the unreacted monomer was removed under reduced pressure (10^{-1} mmHg) at room temperature and methanol (20 mL) was added. The precipitate was eliminated by centrifugation, and the solvent was removed under vacuum. Samples of the poly(propylene oxide), which were obtained as almost colorless viscous liquids, were subjected to GPC and ^1H and ^{13}C NMR analysis.

(D,L)-Lactide Polymerization Procedures. (a) Derivatives **10** or **11** (0.2 mmol) and the (D,L)-lactide (1.20 g, 8.5 mmol) were weighed into a Schlenk tube, equipped with magnetic stirring, under a argon atmosphere. Benzene (30 mL) was added, and the reaction vessel was immersed in a thermostatically controlled bath. After a predefined amount of time, the reaction mixture was cooled to room temperature and the solvent was removed under vacuum. Wet THF (10 mL) was added, and the precipitate was eliminated by centrifugation. Samples of the poly[(D,L)-lactide, obtained as white solids, were subjected to GPC and ^1H and ^{13}C NMR analysis. **(b)** The cation **13** (0.08 g, 0.17 mmol) was weighed into a Schlenk tube, equipped with magnetic stirring, under a argon atmosphere, then freshly dried propylene oxide (0.2 mL, 0.3 mmol) was added, at room temperature, by a syringe. The reaction was allowed to stand for 5 h at 80 °C, then the unreacted PO was removed under reduced pressure (10^{-1} mmHg). A benzene solution (30 mL) of (D,L)-lactide (1.22 g, 8.5 mmol) was added at room temperature, and the reaction vessel was immersed in a thermostatically controlled bath. After a predefined amount of time, the solvent was removed under vacuum and the residue treated with THF. The precipitate was eliminated by centrifugation, and the solvent was removed under vacuum. The samples of poly[(D,L)-lactide] obtained as white solids, were subjected to GPC and ^1H and ^{13}C NMR analysis.

Solution and Refinement of Structures 5, 8, 10, 11, and 15. Crystal data for all structures are presented in Table 2. The data of the structures **8**, **10**, **11**, and **15** were collected on a STOE-IPDS diffractometer with Mo Kα (λ = 0.710 73 Å) radiation using φ-scans. The data for **5** were measured on an STOE-STADI IV diffractometer with Mo Kα (λ = 0.710 73 Å) radiation using $2\theta/\omega$ scans. The structures were solved by direct methods using *SHELXS-90*[25a] and refined with all data on F^2 with a weighting scheme of $\omega^{-1} = \sigma^2(F_o^2) + (g1\cdot P)^2 + (g2\cdot P)$ with $P = (F_o^2 + 2F_c^2)/3$ using *SHELXL-93*.[25b] All non-hydrogen atoms, except the carbon atoms C3 and C9 in structure **11**, were treated anisotropically. The hydrogen atoms H1 and H2 in structure **11** and H2 in structure **15** were located by difference Fourier maps. For the atom C2 in structure **5**, the atoms C2 and C3 in structure **10**, the atoms C2, C3, C8, and C9 in structure **11**, disorders in two positions were found and refined with occupancies of 0.5/0.5.

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Supporting Information Available: Tables of crystal and intensity collection data, position and thermal parameters, and interatomic distances and angles for derivatives **5**, **8**, **10**, **11**, and **15** (32 pages). Ordering information is given on any current masthead page.

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(25) (a) Sheldrick, G. M. *Acta Crystallogr., Sect A* **1990**, *46*, 467. (b) Sheldrick, G. M. *SHELXL-93, Program for Crystal Structure Refinement*; Universität Göttingen: Göttingen, Germany, 1993.