Reactivity and Derivatization of Five-Coordinate, Chelated Aluminum

Miguel-Angel Munoz-Hernandez,[†] Timothy S. Keizer, Pingrong Wei, Sean Parkin, and David A. Atwood*

Department of Chemistry, The University of Kentucky, Lexington, Kentucky 40506-0055

Received July 17, 2001

The convenient five-coordinate starting materials, Salen(^{t}Bu)AlCl (Salen(^{t}Bu) = *N*,*N*′-alkylene (or arylene) bis (3,5-di-*tert*-butyl-2-hydroxybenzylideneamine) (**1**−**4**) can be used in a wide range of reactions to form five-coordinate aluminum compounds. Herein, these reagents were used to produce new five-coordinate azides, $LAlN_3$ (L = Salen(^{t}Bu) (**5**), Salpen(^{t}Bu) (**6**), and Salomphen(^{t}Bu) (**7**)) through trimethylsilylhalide elimination. The decomposition of the azides produce first hydroxide (LAlOH (L = Salen(^{t}Bu) (**8**)) and, subsequently in the presence of chlorotrimethylsilane, the siloxide compounds, $LAlOSiMe_3$ (L = Salen(^{t}Bu) (**9**), Salpen(^{t}Bu) (**10**), and Salomphen(^{t}Bu) (**11**)). Alkane elimination reactions may also be used to access this type of compound as evidenced by the formation of Salomphen(^{t}Bu)$AlOSiPh_3$ (**12**). Additionally, the first structurally characterized five-coordinate monomeric amide, Salcen(^{t}Bu)$AlN(SiMe_3)_2$ (**13**), can prepared by a salt elimination utilizing Salcen(^{t}Bu)AlCl (**4**). The compounds were characterized by spectroscopic methods (^{1}H and ^{27}Al NMR, MS, and IR) and, in the case of **2** (Salpen(^{t}Bu)AlCl), **3** (Salomphen(^{t}Bu)AlCl) **9**, **11**, **12**, and **13,** by X-ray analysis. Several of the compounds were explored as potential catalysts for the living polymerization of propylene oxide.

Introduction

In recent years there has been a resurgence of interest in Salen-main group compounds.[1] The Salen[2] ligands can be used as soluble platforms on which higher-coordinate main group chemistry may be conducted. This has been demonstrated in the formation of new five-coordinate compounds of aluminum,[3−6] gallium,[7] indium,[8] and a broad range of six-coordinate cations.[9] Beyond their fundamental interest and novelty, these compounds are finding applications in catalysis and synthesis. The cations, for example, appear to oligomerize propylene oxide through a cationic mechanism.[10] The neutral derivatives, by contrast, have been used in the living polymerization of propylene oxide and lactides.[11]

There remains, however, a great deal to be determined in the area of higher-coordinate group 13 complexes. Two issues, in particular, need to be addressed. The first is an understanding of the various geometries that can be obtained and whether the resulting compounds have similar properties to the better-known, three- and four-coordinate derivatives. The second is the range of the reactions these compounds can undergo. The present work will address these issues in the use of five-coordinate aluminum halide complexes in dehalosilylations, hydrolyses, HCl eliminations, and a salt elmination reaction, to prepare monomeric five-coordinate aluminum compounds with terminal azide, hydroxide, siloxide, and amido groups. Additionally, an exploration into the utility of these compounds as propylene oxide polymerization catalysts will be presented.

Results and Discussion

Five-Coordinate Aluminum Chlorides. Salen group 13 halides (SalenMX) are prepared in nearly quantitative yield by combining the ligand with a dialkyl group 13 halide in toluene.[6,7,8] The resulting complexes contain a five-coordinate aluminum atom that is either square pyramidal (sqp) or trigonal bipyramidal (tbp), depending on the nature of the connection between the two nitrogens of the ligand (the ligand "backbone"). With an ethyl, $(CH_2)_2$, or *o*-aryl backbone the complex adopts a sqp geometry. With more flexible backbones, $(CH_2)_n$ $n > 2$, a tbp geometry is obtained. This is a property of the ligands and observed in other derivatives, such as siloxides, and various compounds of Ga and In. These geometric preferences are exemplified in the structures of Salpen(^{t}Bu)AlCl (**2**) (tbp) and Salomphen(^{t}Bu)AlCl (**3**) (sqp) (Figures 1 and 2, respectively). The preference for a tbp geometry with the $(CH_2)_3$ backbone is probably due to the fact that a sqp geometry would cause the methylene hydrogens to be eclipsed. In the tbp geometry they are staggered.

However, the geometries in these types of compounds are generally not ideal for either tbp or sqp. For example, in **2**, one of the O−Al−N (eq) angles, expected to be 90°, is rather wide, 126.8(8)°. Similar deviations are found in the structure of **3**. For example, it contains an N−Al−O angle (O(1)−Al(1)−N(2),

---

* To whom correspondence should be addressed.

[†] Current Address: Universidad Autonoma del Estado de Morelos, Centro de Investigaciones Quimicas, Av. Universidad No. 1001, Col. Chamilpa, Cuernavaca, Morelos 62210.

(1) Harvey, M. J.; Atwood, D. A. *Chem. Rev.* **2001**, *101*, 37.

(2) "Salen" is the name that has historically been used to describe the entire class of such ligands possessing various diamino backbones. However, it is also the specific name of the ethyl derivative, $SalenH_2$.

(3) Dzugan, S. J.; Goedken, V. L. *Inorg. Chem*. **1986**, *25*, 2858. Leung, W.-H.; Chan, E. Y. Y.; Chow, E. K. F.; Williams, I. D.; Peng, S.-M. *J. Chem. Soc., Dalton Trans*. **1996**, 1229.

(4) Rutherford, D.; Atwood, D. *Organometallics* **1996**, *15*, 4417.

(5) Gurian, P. L.; Cheatham, L. K.; Ziller, J. W.; Barron, A. R. *J. Chem. Soc., Dalton Trans*. **1991**, 1449.

(6) Atwood, D. A.; Hill, M. S.; Jegier, J. A.; Rutherford, D. *Organometallics* **1997**, *16*, 2659.

(7) (a) Chong, K. S.; Rettig, S. J.; Storr, A.; Trotter, J. *Can. J. Chem*. **1977**, *55*, 2540. (b) Hill, M. S.; Atwood, D. A. *Eur. J. Inorg. Chem*. **1998**, 67.

(8) (a) Atwood, D. A.; Jegier, J. A.; Rutherford, D. *Bull. Chem. Soc. Jpn*. **1997**, *70*, 2093. (b) Hill, M. S.; Atwood, D. A. *Main Group Chem*. **1998**, *2*, 191.

(9) (a) Atwood, D. A.; Jegier, J. A.; Rutherford, D. *J. Am. Chem. Soc*. **1995**, *117*, 6779. (b) Davidson, M. G.; Lambert, C.; Lopez-Solera, I.; Raithby, P. R.; Snaith, R. *Inorg. Chem*. **1995**, *34*, 3765. (c) Atwood, D. A.; Jegier, J. A.; Rutherford, D. *Inorg. Chem*. **1996**, *35*, 63.

(10) Munoz-Hernandez, M.-A.; Keizer, T. S.; Yearwood, B.; Atwood, D. A. *Dalton Trans*., in press.

(11) Ovitt, R. M.; Coates, G. W. *J. Am. Chem. Soc.* **1999**, *121*, 4072−4073. Radano, Christopher P.; Baker, Gregory L.; Smith, III, Milton R. *J. Chem. Soc.* **2000**, *122*, 1552.

10.1021/ic010759r CCC: $20.00

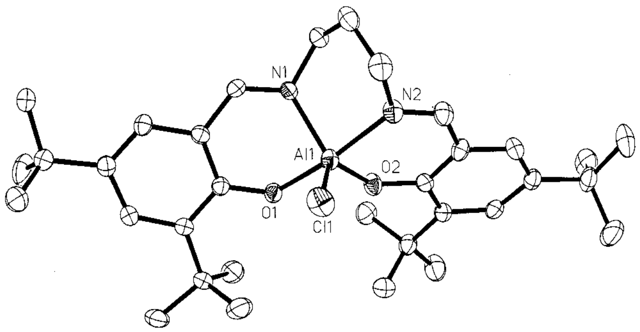


Figure 1. Ortep of Salpen(^{t}Bu)AlCl (**2**).

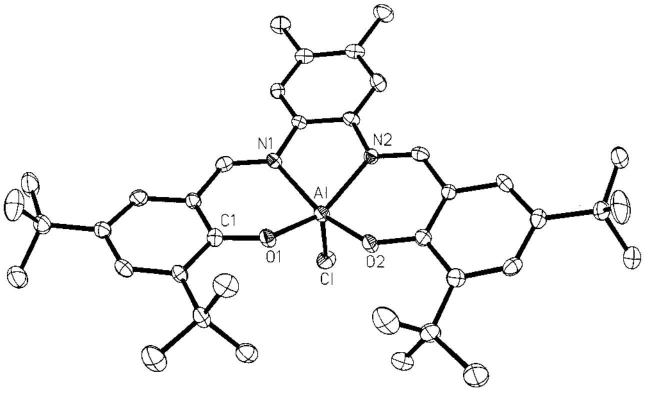
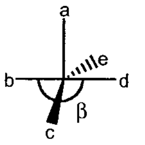


Figure 2. Ortep of Salomphen(^{t}Bu)AlCl (**3**).



$\tau = (\beta - \alpha)/60$

Figure 3. τ Diagram.

Table 1. τ Values for Compounds **2**, **3**, **9**, **11**, **12**, and **13**

compound	τ value
Salpen(^{t}Bu)AlCl (**2**)	0.77
Salomphen(^{t}Bu)AlCl (**3**)	0.18
Salomphen(^{t}Bu)AlOSiMe$_3$ (**9**)	0.46
Salomphen(^{t}Bu)AlOSiMe$_3$ (**11**)	0.15
Salen(^{t}Bu)AlOSiPh$_3$	0.40
Salpen(^{t}Bu)AlOSiPh$_3$	0.74
Salophen(^{t}Bu)AlOSiPh$_3$	0.17
Salomphen(^{t}Bu)AlOSiPh$_3$ (**12**)	0.17
Salcen(^{t}Bu)Al{N(SiMe$_3$)$_2$} (**13**)	0.55
(tbumSalcen)AlCl	0.37

147.08(12)°) that appears more appropriate for a tbp geometry rather than the sqp geometry it is assigned.

A quantitative measure has been devised to determine the extent to which observed geometries are more like tbp or sqp.[14] This measure, whose calculation is shown in Figure 3, produces a value, τ (Tau), that can be used to determine how closely a distorted compound approximates either a tbp or sqp geometry. α (c−e) and β (b−d) are the angles that are opposite each other in the *xy* plane, where a is in the *z* axis. By convention β is the most obtuse angle. The τ value ranges from 0 to 1. A value of zero identifies a compound as perfectly square pyramidal and a value of one as perfectly trigonal bipyramidal. The τ values assigned to compounds **2**, **3**, **9**, **11**, **12**, and **13** are listed in Table 1. From these numbers, it is readily observed that the compounds made from ligands containing an aryl group are only slightly distorted from sqp geometry. With a relatively long ligand backbone, **2** is able to achieve a marginally distorted tbp geometry. Those with two methylene units in the ligand backbone, **9** and (*tbum*Salcen)AlCl,[12] however, cannot be reasonably defined as having either geometry.

In square pyramidal **3**, the Al atom is perched 0.43 Å above the N_2O_2 plane. This distance increases with the size of the metal atom. It is 0.49 Å for Salophen(^{t}Bu)GaCl[3] and 0.61 Å for Salen(^{t}Bu)InCl.[4] The Al−Cl distances (~2.18 Å) are close to what is observed in related five-coordinate Ga compounds (~2.2 Å) and marginally shorter than observed for Salomphen(^{t}Bu)InCl, (2.327(2) Å). They are marginally longer than the distance observed in four coordinate derivatives, such as Mes$_2$AlCl(thf)[13] (1.993(7) Å).

Synthesis and Characterization of 5−7. The azides, Salen(^{t}Bu)AlN$_3$ (**5**), Salpen(^{t}Bu)AlN$_3$(**6**), and Salomphen(^{t}Bu)AlN$_3$ (**7**), are readily prepared in high yields by combining the appropriate Salen(^{t}Bu)AlCl reagent with SiMe$_3$N$_3$ in toluene (Scheme 1a). They can be isolated pure after solvent removal and washing with hexanes.

The asymmetric stretch of the azide group appears at υ 2114, 2128, and 2114 cm^{-1} and the symmetric stretch at υ 1421, 1462, and 1470 cm^{-1} for **5**, **6**, and **7**, respectively. These values compare closely to other molecules of general formula RAl(N$_3$) (R = chelating ligand) containing a terminal Al−N$_3$ unit (range of 2113−2129 cm^{-1}).[14] Bridging azides (through the α-N) appear at slightly higher values, as seen, for example, in [Me$_2$Al(N$_3$)]$_3$ (υ 2151 cm^{-1})[15] and [(piperidinyl)$_2$AlN$_3$]$_2$ (υ 2132 cm^{-1}).[16] Thus, the IR data supports the presence of terminal azides and the monomeric nature of **5**−**7**. However, the close occurrence of the terminal and bridging stretches precludes the use of these stretches in unambiguously determining structure. Indeed the values seen for terminal and bridging azides of indium overlap.[17]

The ^{27}Al NMR shifts for **5**, **6**, and **7** are more diagnostic for determining the degree of oligomerization. The shifts, δ 31.9−36.0 ppm ($w_{1/2}$ ranging between 1087 and 3263 Hz), fall within the range expected for five-coordinate complexes.[18] The ^{1}H NMR data for **5**−**7** contain two singlets for the ^{t}Bu-Ph groups, in the range δ 1.29−1.59 ppm, and one singlet for the proton on the imine carbon, from δ 8.26−8.92 ppm. Furthermore, the mass spectral data support the presence of monomeric compounds. The highest mass peaks detected could be attributed to monomer with one azide group.

Compounds **5**−**7** are air sensitive and hydrolyze readily to form aluminum hydroxides, Salen(^{t}Bu)AlOH (Scheme 1b). These compounds are, in turn, used without isolation in the formation of the siloxides. To confirm the presence of these hydroxides, one was isolated (Salen(^{t}Bu)AlOH (**8**)) and its characterization by mp, IR, ^{1}H NMR, and ^{27}Al NMR matched that previously reported.[4] The sensitivity to hydrolysis for **5**−**7**

---

(12) Taden, I.; Knag, H.; Massa, W.; Okuda, J. *J. Organomet. Chem.* **1997**, *540*, 189.

(13) Lalama, M. S.; Kampf, J.; Dick, D. G.; Oliver, J. P. *Organometallics* **1995**, *14*, 495.

(14) Muller, J.; Boese, R. *J. Mol. Struct*. **2000**, *520*, 215. Fischer, R. A.; Miehr, Herdtweck, E.; Mattner, M. R.; Ambacher, O.; Metzger, T.; Born, E.; Weinkauf, S.; Pulham, C. R.; Parsons, S. *Chem. Eur. J.* **1996**, *2*, 1353.

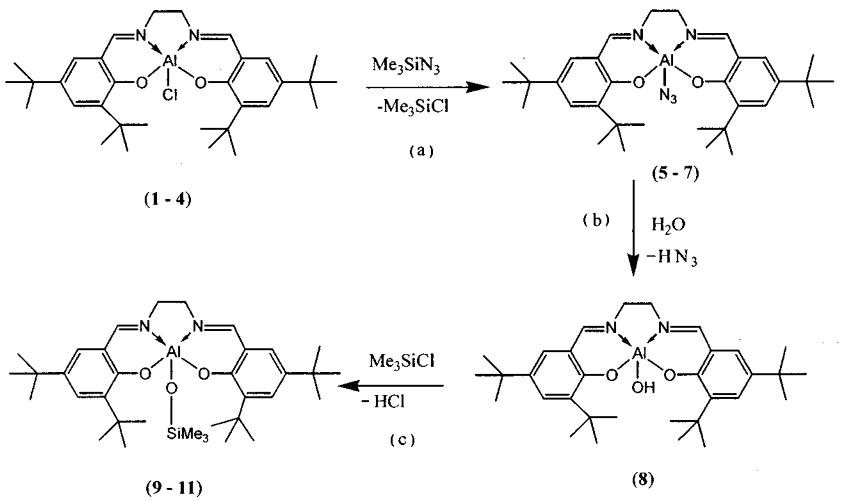
(15) Muller, J.; Dehnicke, K. *J. Organomet. Chem.* **1968**, *12*, 37.

(16) Silverman, J. S.; Carmalt, C. J.; Neumayer, D. A.; Cowley, A. H.; McBurnett, B. G.; Decken, A. *Polyhedron* **1998**, *17*, 977.

(17) Fischer, R. A.; Sussek, H.; Miehr, A.; Pritzkow, H.; Herdtweck, E. *J. Organomet. Chem.* **1997**, *548*, 73.

(18) Kidd, R. G. in *NMR of Newly Accessible Nuclei*; Laszlo, P., Ed., Academic Press: New York, 1983; Vol. 2, Chapter 3.

Scheme 1. General Syntheses of Five-Coordinate Aluminum Derivatives.



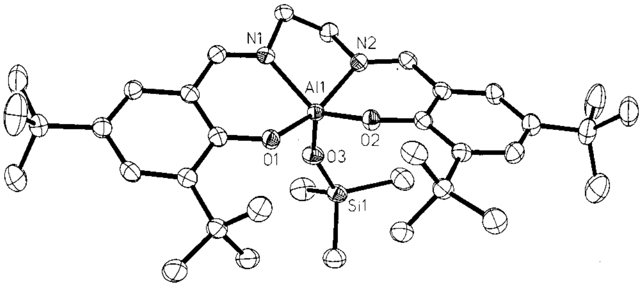


Figure 4. Ortep of Salen(^{t}Bu)AlOSiMe$_3$ (**9**).

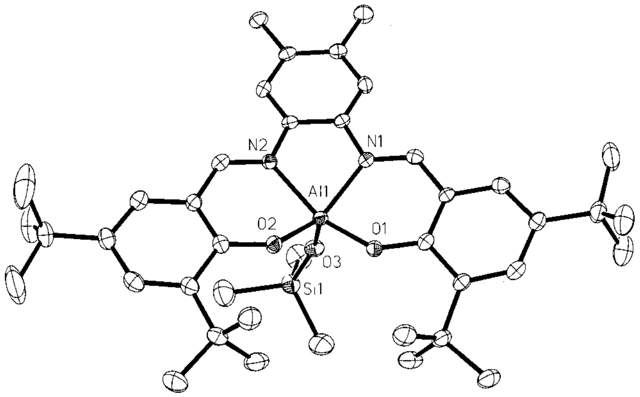


Figure 5. Ortep of Salomphen(^{t}Bu)AlOSiMe$_3$ (**11**).

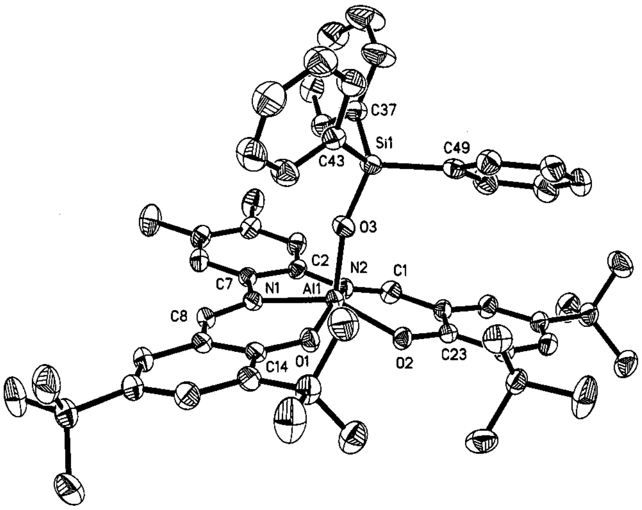


Figure 6. Ortep of Salomphen(^{t}Bu)AlOSiPh$_3$ (**12**).

can be loosely correlated to the geometry of the compound. The square pyramidal **7** is more sensitive than the trigonal bipyramidal **6**. For example, stirring **7** open to air for 12 h leads to complete conversion to the hydroxide (by ^{1}H NMR), while for **6**, this treatment leads to a 50:50 mixture of the azide and hydroxide.

Although the mechanism of this reaction has not been determined, it is likely to proceed through protonation of the azide on aluminum concurrent to the formation of a new Al−O bond.[19] Thus, **6** apparently impedes the protonation of the α-nitrogen of the azide more than **7**. Previously, it was demonstrated that the hydrolysis of amides was inhibited by the steric bulk of the amide.[4] This would support the idea that access to the nitrogen is important to the hydrolysis. Thus, there are both steric and geometric components to the mechanism of the hydrolyses.

Synthesis and Characterization of 9−12. In the presence of water or atmospheric moisture, the azides decompose to the respective hydroxides. These compounds, in turn, combine with the ClSiMe$_3$ present from the original azide synthesis and undergo an HCl elimination to form the siloxides, **9**−**11** (Scheme 1c). The compound incorporating the rigid aryl backbone (**11**) (Figure 5) undergoes this reaction much more readily than the compounds which contain an alkyl backbone (**9** (Figure 4) and **10**). Compound **12** was prepared by combining Ph$_3$SiOH with SalomphenAlR (R = alkyl), as reported previously (Figure 6).[6]

The ^{1}H NMR data for **9**−**11** are consistent with monomeric compounds in solution. The observed chemical shifts for the SiMe$_3$ range from δ −0.55 to 0.02 ppm. The ^{27}Al NMR shifts for each compound appear as a broad singlet in the range δ 30.5−73.2 ppm, where five-coordinate compounds are expected to appear. The highest mass peak in the mass spectral data could be attributed to a monomeric species.

Monomers were also observed for the crystal structures of **9**, **11**, and **12**. The structure of **12** follows the literature precedent for the analogous compounds, LAlOSiPh$_3$ (where L = Salen(^{t}Bu), Salpen(^{t}Bu), and Salophen(^{t}Bu)).[6] These compounds provide an interesting opportunity to compare how electronic effects influence the nature of the Al−O−Si linkage. For **9** and

---

(19) This is the general mechanism suggested for the hydrolysis of lower-coordinate group 13 compounds. McMahon, C. N.; Bott, S. G.; Barron, A. R. *Polyhedron* **1997**, *16,* 3407.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for the Structurally Characterized Compounds

Salpen(^{t}Bu)AlCl (**2**)			
Al(1)−O(1)	1.754(6)	O(1)−Al(1)−N(1)	89.5(3)
Al(1)−O(2)	1.815(6)	O(2)−Al(1)−N(1)	172.3(3)
Al(1)−N(2)	1.965(7)	N(2)−Al(1)−N(1)	85.3(3)
Al(1)−N(1)	2.031(8)	O(1)−Al(1)−Cl(1)	120.6(3)
Al(1)−Cl(1)	2.182(4)	O(2)−Al(1)−Cl(1)	95.9(2)
O(1)−Al(1)−O(2)	89.7(3)	N(2)−Al(1)−Cl(1)	112.9(3)
O(1)−Al(1)−N(2)	126.3(3)	N(1)−Al(1)−Cl(1)	91.0(2)
O(2)−Al(1)−N(2)	89.0(3)		
Salomphen(^{t}Bu)AlCl (**3**)			
Al(1)−O(1)	1.781(2)	O(1)−Al(1)−N(1)	88.84(12)
Al(1)−O(2)	1.789(2)	O(2)−Al(1)−N(1)	158.12(12)
Al(1)−N(2)	1.996(3)	N(2)−Al(1)−N(1)	78.96(12)
Al(1)−N(1)	2.002(3)	O(1)−Al(1)−Cl(1)	107.82(9)
Al(1)−Cl(1)	2.1753(14)	O(2)−Al(1)−Cl(1)	104.15(9)
O(1)−Al(1)−O(2)	90.57(11)	N(2)−Al(1)−Cl(1)	103.95(9)
O(1)−Al(1)−N(2)	147.08(12)	N(1)−Al(1)−Cl(1)	96.84(9)
O(2)−Al(1)−N(2)	89.89(12)	Al(1)−O(1)−Si(1)	163.53(13)
Salen(^{t}Bu)AlOSiMe$_3$ (**9**)			
Al(1)−O(3)	1.7173(14)	O(3)−Al(1)−N(1)	110.52(7)
Al(1)−O(2)	1.7940(13)	O(2)−Al(1)−N(1)	132.87(7)
Al(1)−O(1)	1.8094(13)	O(1)−Al(1)−N(1)	88.72(6)
Al(1)−N(1)	1.9902(16)	O(3)−Al(1)−N(2)	95.23(7)
Al(1)−N(2)	2.0212(16)	O(2)−Al(1)−N(2)	87.08(6)
O(3)−Al(1)−O(2)	115.47(7)	O(1)−Al(1)−N(2)	160.49(7)
O(3)−Al(1)−O(1)	103.27(7)	N(1)−Al(1)−N(2)	78.92(6)
O(2)−Al(1)−O(1)	90.47(6)	Al(1)−O(1)−Si(1)	152.92(9)
Salomphen(^{t}Bu)AlOSiMe$_3$ (**11**)			
Al(1)−O(3)	1.7126(16)	O(3)−Al(1)−O(1)	106.95(8)
Al(1)−O(2)	1.8015(15)	O(2)−Al(1)−O(1)	90.69(7)
Al(1)−O(1)	1.8046(15)	O(3)−Al(1)−N(1)	104.04(7)
Al(1)−N(1)	2.0182(18)	O(2)−Al(1)−N(1)	144.56(7)
Al(1)−N(2)	2.0351(18)	O(1)−Al(1)−N(1)	88.48(7)
O(3)−Al(1)−N(2)	98.11(7)	O(3)−Al(1)−N(2)	98.11(7)
O(2)−Al(1)−N(2)	87.98(7)	O(2)−Al(1)−N(2)	87.98(7)
O(1)−Al(1)−N(2)	153.73(8)	O(1)−Al(1)−N(2)	153.73(8)
N(1)−Al(1)−N(2)	77.74(7)	N(1)−Al(1)−N(2)	77.74(7)
O(3)−Al(1)−O2)	110.04(8)		
Salomphen(^{t}Bu)AlOSiPh$_3$(**12**)			
Al(1)−O(1)	1.804(2)	O(1)−Al(1)−N(2)	154.38(9)
Al(1)−O(2)	1.796(2)	O(2)−Al(1)−N(2)	87.82(9)
Al(1)−O(3)	1.715(2)	N(1)−Al(1)−N(2)	77.77(9)
Al(1)−N(1)	2.019(2)	O(1)−Al(1)−O(3)	107.12(9)
Al(1)−N(2)	2.029(2)	O(2)−Al(1)−O(3)	111.75(9)
O(1)−Al(1)−O(2)	91.12(9)	N(1)−Al(1)−O(3)	102.32(9)
O(1)−Al(1)−N(1)	88.54(9)	N(2)−Al(1)−O(3)	96.99(9)
O(2)−Al(1)−N(1)	144.38(9)	Al(1)−O(1)−Si(1)	163.53(13)
Salcen(^{t}Bu)Al{N(SiMe$_3$)$_2$} (**13**)			
Al(1)−O(1)	1.799(4)	O(1)−Al(1)−N(2)	126.4(2)
Al(1)−O(2)	1.824(4)	O(2)−Al(1)−N(2)	88.1(2)
Al(1)−N(1)	2.053(4)	N(1)−Al(1)−N(2)	76.3(2)
Al(1)−N(2)	2.018(4)	O(1)−Al(1)−N(3)	116.9(2)
Al(1)−N(3)	1.881(5)	O(2)−Al(1)−N(3)	101.4(2)
O(1)−Al(1)−O(2)	91.0(2)	N(1)−Al(1)−N(3)	97.7(2)
O(1)−Al(1)−N(1)	87.4(2)	N(2)−Al(1)−N(3)	115.8(2)
O(2)−Al(1)−N(1)	159.3(2)		

11, the groups on silicon are electron releasing, whereas for **12** and the others, the groups are electron withdrawing. The cone angles for these groups, using PMe$_3$ and PPh$_3$ as models for SiMe$_3$ and SiPh$_3$, are somewhat disparate, 118 and 145°, respectively.[20] However, there is little difference in either the Al−O (∼1.7 Å) or Si−O (∼1.6 Å) distances (see Table 2). In comparison, the Al−O−Si angles range from 152 to 156° for **9** and **11** and 158−167° for the −SiPh$_3$ compounds. Thus, the larger cone angle of the latter appears to induce a moderately more linear geometry. However, in four-coordinate derivatives, such as [(Ph$_3$SiO)$_2$Al(O^{t}Bu)]$_2$[21] and Al(OSiPh$_3$)$_3$(OEt$_2$),[22] the Al−O−Si angles are highly variable (153 and 178°) and not linked to steric or electronic effects. Additionally, the Al−O and Si−O distances in the four-coordinate derivatives are essentially the same as found in **9**, **11**, and **12**. Thus, coordination number does not affect the distances appreciably.

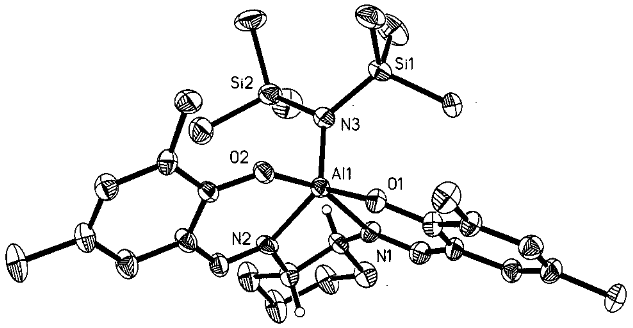


Figure 7. Ortep of Salcen(^{t}Bu)AlN(SiMe$_3$)$_2$ (**13**).

Synthesis and Characterization of 13. Compound **13** was prepared following the method previously outlined for the syntheses of other five-coordinate aluminum amides.[4] In this earlier report, it was noted that the amido compounds were extremely moisture sensitive and quickly decomposed to hydroxide and μ-oxo derivatives. However, it was found that high yields (∼90%) of **13** could be obtained by using standard inert-atmosphere techniques. The structure of **13** is shown in Figure 7. This is the first example of a structurally characterized five-coordinate aluminum amido compound. The bond distances the aluminum forms with the ligand oxygens and nitrogens are similar to that observed in four-coordinate derivatives, such as [H$_2$Al(O^{t}Bu)]$_2$ (Al−O = 1.81 Å)[23] and [Me$_2$Al{N(SiMe$_3$)Ph}]$_2$ (Al−N ∼2.0 Å).[24] Remarkably, the Al−N(SiMe$_3$)$_2$ distance is very short in **13** and comparable to lower coordinate aluminum amides, such as [MeAl{N(SiMe$_3$)Ph}$_2$] (Al−N = 1.83 Å).[24] The short distance in **13** may be attributed to a stronger electrostatic attraction between the Al and N atoms. The heightened air sensitivity of the compounds can be attributed to a strongly basic lone pair on the nitrogen. This also explains the stability differences between bulky amido groups and less sterically hindered amido groups.

Attempted Polymerization. It has been shown that the five-coordinate aluminum azide compounds [Salcen(^{t}Bu)AlN$_3$] will ring open and add the azide to an oxirane.[25] Lactides have also been shown to ring open and polymerize with a five-coordinate aluminum alkoxide, [*rac*-(Salbinap)Al^{i}OPr].[11] In light of this, and following our original discovery of oxirane oligomerization with cationic derivatives,[9a] we attempted the polymerization of propylene oxide with **5**, **7**, **8**, **9**, **11**, and **12**. It was found in all cases that the five-coordinate complexes, despite their anionic character, do not promote ring opening and polymerization. However, compound **5** does ring open and add azide catalytically to propylene oxide in the presence of Me$_3$SiN$_3$ to produce the silylated azido alcohol (Scheme 2). While this reaction has

---

(20) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; p 70.

(21) Veith, M.; Jarczyk, M.; Huch, V. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 117.

(22) Apblett, A. W.; Warren, A. C.; Barron, A. R. *Can. J. Chem.* **1992**, *70*, 771. Apblett, A. W.; Barron, A. R. *J. Cryst. Spectrosc. Res.* **1993**, *23*, 529.

(23) Veith, M.; Faber, S.; Wolfanger, H.; Huch, V. *Chem. Ber.* **1996**, *129*(4), 381−384.

(24) Waezsada, S. D.; Rennekamp, C.; Roesky, H. W.; Ropken, C.; Parisini, E. *Z. Anorg. Allg. Chem.* **1998**, *624*, 1987.

Scheme 2. Ring Opening of Propylene Oxide.

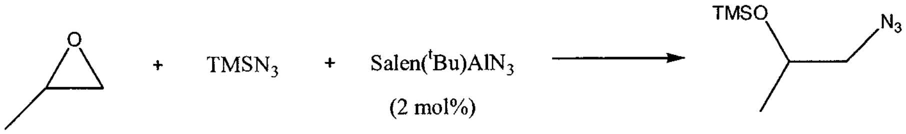


Table 3. Crystallographic Data

	Salpen(^{t}Bu)AlCl (**2**)	Salomphen(^{t}Bu)-AlCl (**3**)	Salen(^{t}Bu)-AlOSiMe$_3$ (**9**)	Salomphen(^{t}Bu)-AlOSiMe$_3$ (**11**)	Salomphen(^{t}Bu)-AlOSiPh$_3$ (**12**)	Salcen(^{t}Bu)Al-N(SiMe$_2$)$_2$ (**13**)
CCDC no						
color/shape	yellow needle	yellow needle	yellow plate	yellow plate	yellow plate	yellow plate
chem form	C67H98Al2Cl2N4O4	C45H58N2O2AlCl	C35H55AlN2O3Si	C41H59AlN2O3Si	C56H65AlN2O3Si	C49H78AlN3O2Si2
fw	1252.69	721.36	606.88	682.97	869.17	824.30
temp (K)	298(2)	173(1)	173(1)	173(1)	173(1)	298(2)
cryst syst	triclinic	monoclinic	monoclinic	monoclinic	monoclinic	orthorhombic
space group	*P*-1	$P2_1/n$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_12_12_1$
a (Å)	14.5977 (10)	19.256(3)	11.3420(10)	14.395(2)	19.2325 (11)	10.9002 (5)
b (Å)	15.0050 (11)	10.208(2)	18.764(3)	15.209(2)	14.2271 (8)	15.1173(8)
c (Å)	17.3345 (12)	21.640(3)	17.830(2)	18.297(2)	19.3777 (11)	31.5919(15)
α (°)	77.8900 (10)	−	−	−	−	−
β (°)	70.629 (2)	94.783(10)	104.500(10)	93.967(10)	109.529 (10)	−
γ (°)	85.725 (2)	−	−	−	−	−
Vol (Å^3)	3502.2 (4)	4238.9(12)	3673.7(8)	3996.2(9)	4997.2 (5)	5205.8(4)
Z	4	4	4	4	4	4
D (calcd)	1.188 Mg/m^3	1.130 Mg/m^3	1.097Mg/m^3	1.135 Mg/m^3	1.155 Mg/m^3	1.052 Mg/m^3
abs coeff	0.279 mm^{-1}	0.148 mm^{-1}	0.121 mm^{-1}	0.119 mm^{-1}	0.109 mm^{-1}	0.122 mm^{-1}
cryst size (mm)	0.50 × 0.30 × 0.10	0.28 × 0.08 × 0.04	0.32 × 0.28 × 0.20	0.50 × 0.20 × 0.05	0.55 × 0.21 × 0.12	0.50 × 0.20 × 0.10
diffractometer/scan	Siemens P-4	Nonius CCD	Nonius CCD	Nonius CCD	Nonius CCD	Siemens P-4
θ range for data collection	1.27−22.49	1.89−22.50	1.60−25.34	1.74−25.37	1.12−20.00	1.29−21.00
reflns meas	13280	10679	12973	14134	14703	17214
indep reflns (*R*int)	8620 (0.0622)	5529 (0.0662)	6715 (0.0354)	7323 (0.0425)	4634 (0.0281)	5558 (0.2094)
data/restraints/param	8620/740/740	5529/466/463	6715/0/380	7323/0/451	4634/0/568	5536/0/509
GOF on *F*^{2}	1.094	1.108	1.02	0.996	1.183	1.071
final *R* indices [*I* > 2ó(*I*)]	R = 0.1228	R = 0.0682	R = 0.0454	R = 0.0544	R = 0.0431	R = 0.0737
	wR2 = 0.2876	wR2 = 0.1294	wR2 = 0.1087	wR2 = 0.1151	wR2 = 0.1410	wR2 = 0.1360
R indices (all data)	R = 0.1671	R = 0.1064	R = 0.0718	R = 0.0870	R = 0.0488	R = 0.1295
	wR2 = 0.3175	wR2 = 0.1419	wR2 = 0.1203	wR2 = 0.1259	wR2 = 0.1472	wR2 = 0.1807

been demonstrated with other oxiranes,[25] it appears to not have been reported for propylene oxide until now. However, the conversion is only 38% for the present system, so it is likely to be of limited synthetic value under these conditions.

Conclusion

Many five-coordinate aluminum compounds can be obtained in good yield by using the Salen(^{t}Bu) ligands. We have demonstrated a wide range of different functional groups that can be substituted for the halide in the Salen(^{t}Bu)AlCl starting materials. In these compounds, the bonding of aluminum to the non-Salen nitrogen and oxygen atoms appears to be strongly electrostatic in nature. This is observed in very short Al−N and Al−O bond distances. None of the compounds were found to be useful as catalysts for the oligomerization or polymerization of propylene oxide.

Experimental Section

General Remarks. All glassware was rigorously cleaned and dried in an oven at 130 °C for 24 h prior to use. They were assembled hot and cooled under nitrogen. All of the manipulations of the air-sensitive compounds were conducted using standard benchtop inert atmosphere techniques in conjunction with an inert-atmosphere glovebox. The ligands[26] Salen(^{t}Bu)H$_2$, Salpen(^{t}Bu)H$_2$, and Salomphen(^{t}Bu)H$_2$ were synthesized according to the literature procedure. Salen(^{t}Bu)AlCl (**1**), Salpen(^{t}Bu)AlCl (**2**), Salomphen(^{t}Bu)AlCl (**3**), and Salcen(^{t}Bu)AlCl (**4**) was prepared as reported previously.[4] NMR data (^{1}H ^{27}Al) were obtained on JEOL-GSX-400 and 200 MHz instruments. Chemical shifts are reported relative to SiMe$_4$ for ^{1}H and AlCl$_3$ in D$_2$O for ^{27}Al and are in ppm. Infrared data were recorded as KBr pellets on a Matheson Instruments 2020 Galaxy Series spectrometer and are reported in cm^{-1}. EI (positive) (direct probe) spectra were acquired on a Kratos Concept IH at 70 eV. Elemental analyses were obtained on Elementar Vario EL III. X-ray data for **2** and **13** were collected on a Siemens P4 diffractometer in a sealed glass capillary tube under N$_2$ and those for **3**, **9**, **11**, and **12** on a Nonius CCD unit. Both employed Mo Kα radiation. The structures were refined using the Siemens software package SHELXTL 4.0. All of the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were put into calculated positions. Absorption corrections were not employed. Further details of the structure analyses are given in Table 3.

Salen(^{t}Bu)AlN$_3$ (5). To a stirring solution of Salen(^{t}Bu)AlCl (0.5 g, 0.91 mmol) in toluene (50 mL) was added Me$_3$SiN$_3$ (2 mL, 15.1 mmol). The reaction mixture was stirred under reflux for 5 h and then the volatiles were removed under vacuum. The remaining solid was redissolved in 30 mL of toluene, and the solution was cannula filtered. The solvent was removed under vacuum to leave a light green solid which was treated with hexanes (10 mL). Filtration and vacuum drying afforded Salen(^{t}Bu)AlN$_3$. Yield: 0.43 g (85%). Mp: 288 °C. ^{1}H NMR (CDCl$_3$): *δ* 1.29 [s, 18H, C(C*H*3)3], 1.53 [s, 18H, C(C*H*3)3], 3.76 [m, 2H, C*H*2], 4.14 [m, 2H, C*H*2], 7.04 [d, 2H, C6*H*2], 7.55 [d, 2H, C6*H*2], 8.38 [s, 2H, C*H*N]. ^{27}Al NMR (C$_6$D$_6$): *δ* 31.9 (w$_{1/2}$, 3263 Hz).

---

(25) Jacobsen, E. N. *Acc. Chem. Res.* **2000**, *33*, 421.
(26) Deng, L.; Jacobsen, E. N. *J. Org. Chem.* **1992**, *57*, 4320.

MS: 559(5%, $LAlN_3$), 517 (100%, $-N_3$). IR (cm^{-1}): 2955 (s), 2905 (m), 2870 (m), 2114 (s), 1636 (s), 1554 (s), 1470 (s), 1421 (s), 1388 (m), 1361 (m), 1335 (m), 1310 (m), 1280 (m), 1239 (m), 1200 (w), 1176 (s), 1137 (w), 1106 (w), 1061 (w), 993 (w), 929 (w), 867 (m), 845 (s), 816 (w), 774 (w), 761 (m), 713 (w), 661 (w), 634 (w), 605 (s). Anal. Calcd for $C_{32}H_{46}AlN_5O_2$: C, 68.65; H, 8.29; N, 12.52. Found: C, 69.59; H, 8.38; N, 10.10.

Salpen(^{t}Bu)AlN$_3$ (6). To a stirring solution of Salpen(^{t}Bu)AlCl (0.5 g, 0.88 mmol) in toluene (50 mL) was added Me_3SiN_3 (1.02 g, 8.87 mmol). The reaction mixture was stirred under reflux for 5 h and then the volatiles were removed under vacuum. The remaining solid was redissolved in toluene (30 mL), and the solution was cannula filtered. The solvent was removed under vacuum to leave a light green solid which was treated with 10 mL of hexanes. Filtration and vacuum drying afforded Salpen(^{t}Bu)AlN$_3$. Yield: 0.42 g (84%). Mp: 256−258 °C. ^{1}H NMR ($CDCl_3$): δ 1.39 [s, 18H, C(C*H3*)3], 1.79 [s, 18H, C(C*H3*)3], 1.86 [m, 2H, C*H2*], 2.74 [m, 2H, C*H2*], 3.18 [m, 2H, C*H2*], 7.04 [d, 2H, C6*H2*], 7.53 [d, 2H, C6*H2*], 8.26 [s, 2H, C*H*N]. ^{27}Al NMR (C_6D_6): δ 36.0 ($w_{1/2}$, 1263 Hz). MS: 573(5%, $LAlN_3$), 531(100%, $-N_3$). IR (cm^{-1}): 2959 (s), 2905 (m), 2868 (m), 2128 (s), 1620 (s), 1543 (s), 1462 (s), 1418 (m), 1362 (m), 1361 (m), 1314 (m), 1260 (m), 1179 (w), 1098 (w), 1065 (w), 845 (m), 785 (w), 752 (w), 560 (m), 567 (w), 457 (m). Anal. Calcd for $C_{33}H_{48}AlN_5O_2$: C, 69.07; H, 8.44; N, 12.21. Found: C, 69.27; H, 8.40; N, 10.72.

Salomphen(^{t}Bu)AlN$_3$ (7). To a stirring solution of Salomphen(^{t}Bu)AlCl (0.5 g, 0.80 mmol) in toluene (50 mL) was added Me_3SiN_3 (0.48 g, 4.2 mmol). The reaction mixture was stirred under reflux for 1.5 h, and the solution was cannula filtered. The solvent was removed under vacuum to leave a yellow/orange solid. Yield: 0.45 g (85%). Mp: 290−292 °C (dec). ^{1}H NMR ($CDCl_3$): δ 1.35 [s, 18H, C(C*H3*)3], 1.59 [s, 18H, C(C*H3*)3], 2.39 [s, 6H, PhC*H3*], 7.08 [d, 2H, Ph*H2*], 7.50 [s, 2H, Ph*H2*], 7.63 [d, 2H, Ph*H2*], 8.92 [s, 2H, C*H*N]. ^{27}Al NMR ($CDCl_3$): δ 31.9 ($w_{1/2}$, 1087 Hz). MS: 635(10%, $LAlN_3$), 593(100%, −N3). IR (cm^{-1}): 2964(s), 2923(m), 2875(w), 2114(s), 1619(s), 1592(m), 1554(m), 1540(s), 1470(m), 1442(w), 1420(w), 1387(w), 1360(m), 1255(w), 1198(w), 1181(m), 848(m), 787(w). Anal. Calcd for $C_{38}H_{50}AlN_5O_2$: C, 71.77; H, 7.93; N, 11.02. Found: C, 73.78; H, 8.13; N, 8.64.

Salen(^{t}Bu)AlOH (8). To a stirring solution of Salen(^{t}Bu)AlCl (0.5 g, 0.91 mmol) in toluene (50 mL) was added Me_3SiN_3 (2 mL, 15.1 mmol). The reaction mixture was stirred under reflux for 5 h and then the volatiles were removed under vacuum. The remaining solid was redissolved in 30 mL of toluene, and the solution was cannula filtered. The solution was open to the atmosphere and stirred for 48 h. The solvent was removed under vacuum to leave a pale yellow solid. Yield: 2.0 g (68%). Data reported in previous literature.[4]

Salen(^{t}Bu)AlOSiMe3 (9). To a stirring solution of Salen(^{t}Bu)AlCl (0.5 g, 0.91 mmol) in toluene (50 mL) was added Me_3SiN_3 (1.05 g, 9.1 mmol). The reaction mixture was stirred under reflux for 4 h and then open to air and stirred for 48 h at room temperature. The solvent was removed under vacuum to leave a yellow solid. Yellow X-ray quality crystals formed at room temperature in hexanes. Yield: 0.35 g (70%). Mp: 212−214 °C (dec). ^{1}H NMR (C_6D_6): δ 0.02 [s. 9H, Si(C*H3*)3], 1.35 [s, 18H, C(C*H3*)3], 1.85 [s, 18H, C(C*H3*)3], 2.6 [m, 2H, C*H2*], 3.28 [m, C*H2*] 6.89 [d, 2H, Ph*H2*], 7.45 [s, 2H, C*H*N] 7.78 [s, 2H, Ph*H2*]. 27Al NMR ($CDCl_3$): δ 30.5 ($w_{1/2}$, 833 Hz). MS: 606(80%, $LAlOSiMe_3$), 591(100%, −Me), 501(60%, $-N_3$). IR (cm^{-1}): 2953(s), 2901(m), 2868(m), 1651(m), 1623(s), 1557(m), 1539(m), 1471(m), 1443(m), 1418(m), 1390(w), 1362(w), 1337(w), 1308(m), 1256(m), 1203(w), 1177(m), 1055(m), 840(w), 752(w), 586(w). Anal. Calcd for $C_{35}H_{55}AlN_2O_3Si$: C, 69.26; H, 9.14; N, 4.62. Found: C, 68.78; H, 9.32; N, 4.48.

Salpen(^{t}Bu)AlOSiMe$_3$ (10). To a stirring solution of Salpen(^{t}Bu)AlCl (0.5 g, 0.88 mmol) in toluene (50 mL) was added Me_3SiN_3 (1.01 g, 8.8 mmol). The reaction mixture was stirred under reflux for 4 h and then opened to air and stirred for 48 h at room temperature. The solvent was removed under vacuum to leave a pale yellow solid. Yield: 0.41 g (75%). Mp: 220 °C(dec). ^{1}H NMR ($CDCl_3$): δ −0.25 [s. 9H, Si(C*H3*)3], 1.28 [s, 18H, C(C*H3*)3], 1.45 [s, 18H, C(C*H3*)3], 1.85 [m, 2H, C*H2*], 3.75 [m, 4H, C*H2*], 6.95 [d, 2H, Ph*H2*], 7.45 [s, 2H, Ph*H2*], 8.18 [s, 2H, C*H*N]. ^{27}Al NMR ($CDCl_3$): δ 34.4 ($w_{1/2}$, 3400 Hz). MS: 620(25%, $LAlOSiMe_3$), 605(30, −Me), 531(100%, −OSiMe$_3$). IR (cm^{-1}): 2953 (s), 2906 (s), 2868 (m), 1643 (s), 1619(s), 1606 (s), 1557 (m), 1541(m), 1477 (m), 1461 (s), 1439 (m), 1418 (w), 1392 (m), 1362 (w), 1344 (m), 1259 (m), 1242 (m), 1203 (m), 1178 (m), 1066 (s), 1040 (s), 830 (s), 749 (m), 592 (m), 568 (m). Anal. Calcd for $C_{36}H_{57}AlN_2O_3Si$: C, 69.63; H, 9.26; N, 4.51. Found: C, 71.86; H, 9.36; N, 4.25.

Salomphen(^{t}Bu)AlOSiMe$_3$ (11). To a stirring solution of Salomphen(^{t}Bu)AlCl (0.5 g, 0.80 mmol) in toluene (50 mL) was added Me_3SiN_3 (0.92 g, 8.0 mmol). The reaction mixture was stirred under reflux for 3 h. The solution was open to air and stirred for 15 h at room temperature. The solvent was removed under vacuum to leave a bright yellow solid. Yellow X-ray quality crystals form at room temperature in hexanes. Yield: 0.45 g (90%). Mp: 160 °C(dec). ^{1}H NMR ($CDCl_3$): δ −0.55 [s. 9H, Si(C*H3*)3], 1.32 [s, 18H, C(C*H3*)3], 1.57 [s, 18H, C(C*H3*)3], 2.4 [s, 6H, PhC*H3*], 7.10 [d, 2H, Ph*H2*], 7.45 [s, 2H, Ph*H2*], 7.59 [d, 2H, Ph*H2*], 8.82 [s, 2H, C*H*N]. ^{27}Al NMR (C_6D_6): δ 73.2 ($w_{1/2}$, 4258 Hz). M.S.: 682(40%, LAlOSiMe3), 667(50%, -Me), 593(100%, −OSiMe$_3$). IR (cm-1): 2964(s), 2924(s), 2883(m), 2867(m), 1622(s), 1594(m), 1552(m), 1539(s), 1505(w), 1472(m), 1420(w), 1388(w), 1360(m), 1254(m), 1193(w), 1180(m), 1064(s), 844(m), 832(m), 788(w), 753(w). Anal. Calcd for $C_{41}H_{59}AlN_2O_3Si$: C, 72.10; H, 8.71; N, 4.10. Found: C, 72.66; H, 8.68; N, 4.58.

R,R-Salcen(^{t}Bu)AlN(SiMe$_3$)$_2$ (13). To a stirring solution of R,R-Salcen(^{t}Bu)AlCl (0.61 g, 1.00 mmol) in THF (40 mL) was added LiN(SiMe$_3$)$_2$ (0.17 g, 1.00 mmol). The reaction mixture was stirred under reflux for 5 h then was left to reach room temperature and cannula filtered. The filtrate was concentrated (10 mL) and yellow crystals were deposited at 25 °C upon standing of the solution. Filtration and vacuum drying afforded R-Salcen(^{t}Bu)AlN (SiMe$_3$)$_2$. Yield 0.72 g (88%). Mp: 176 °C. ^{1}H NMR ($CDCl_3$): δ 0.66 [s, 18H, N(Si(CH_3)$_3$)$_2$], 1.24 [s, 18H, C(CH_3)$_3$], 1.30 [m, 4H, (CH_2)$_4$(CH)$_2$], 1.53 [s, 18H, C(CH_3)$_3$], 1.85 [m, 2H, (CH_2)$_4$(CH)$_2$], 2.10 [m, 2H, (CH_2)$_4$(CH)$_2$], 2.84 [m, 1H, (CH$_2$)$_4$(CH)$_2$], 4.32 [m, 1H, (CH$_2$)$_4$(CH)$_2$], 6.90 [d, 2H, C_6H_2], 7.42 [2, 2H, C_6H_2], 7.98 [s, 2H, C*H*N]. IR (cm^{-1}): 2918 (m), 2868 (w), 1656 (s), 1622 (m), 1552 (m), 1475 (m), 1440 (w), 1415 (w), 1390 (m), 1359 (w), 1313 (w), 1259 (m), 1203 (w), 1176 (w), 1093 (m), 1049 (m), 922 (m), 891 (w), 802 (w), 754 (w), 733 (w), 669 (w), 580 (w), 497 (w), 476 (w). Anal. Calcd for $C_{42}H_{70}AlN_3O_2Si_2$: C, 68.93; H, 9.57. Found: C, 68.72; H, 9.26.

Attempted Polymerization of Propylene Oxide. A bomb reactor was charged with 1.8 mmol of catalyst, 20 mL of CH_2Cl_2, and 180 mmol of propylene oxide. The reaction was stirred at 80 °C for 24 h. The reaction was quenched with acidic methanol and the solvent was removed. ^{1}H NMR was taken of the solid and showed no polypropylene oxide.

Ring Opening of Propylene Oxide. A 50 ml round-bottom flask was charged with 0.18 mmol of Salen(^{t}Bu)AlN$_3$ (**5**), 4.0 mL of Et_2O, 9.0 mmol of propylene oxide, and 9.45 mmol of Me_3SiN_3. The reaction was stirred for 24 h. The solvent was removed. Yield 0.6 g (38%). ^{1}H NMR($CDCl_3$): δ 0.12 [s, 9H, SiMe$_3$], 1.15[d, 3H, CH$_3$], 3.01[dd, 1H, CH$_2$], 3.18[dd, 1H, CH$_2$], 3.95[m, 1H, CH].

Acknowledgment. This work was supported by the National Science Foundation NSF-CAREER award (CHE 9625376) and the donors of the Petroleum Research Fund (Grant 31901-AC3), administered by the American Chemical Society. NMR instruments used in this research were obtained with funds from the CRIF program of the National Science Foundation (CHE 997841) and the Research Challenge Trust Fund of the University of Kentucky.

Supporting Information Available: Tables of bond lengths and angles in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC010759R