DALTON
FULL PAPER

Six-coordinate aluminium cations: characterization, catalysis, and theory

Miguel-Angel Munoz-Hernandez,[a] Michael L. McKee,*[b] Timothy S. Keizer,[c] Burl C. Yearwood[c] and David A. Atwood*[c]

[a] *Universidad Autonoma del Estado de Morelos, Centro de Investigaciones Quimicas, Av. Universidad No. 1001, Col. Chamilpa, Cuernavaca, Morelos 62210, Mexico*
[b] *Department of Chemistry, Auburn University, Auburn, Alabama 36849-5312, USA*
[c] *Department of Chemistry, The University of Kentucky, Lexington, Kentucky 40506-0055, USA*

Received 30th May 2001, Accepted 22nd October 2001
First published as an Advance Article on the web 11th January 2002

The new thf supported cations, $[Salen(^tBu)Al(thf)_2]^+$ (**2**), $[Salpen(^tBu)Al(thf)_2]^+$ (**3**), $[Salben(^tBu)Al(thf)_2]^+$ (**4**) $[Salophen(^tBu)Al(thf)_2]^+$ (**5**) and $[Salomphen(^tBu)Al(thf)_2]^+$ (**6**), with BPh_4^- as the counter anion, have been prepared from salt elimination reactions with the respective Salen(^{t}Bu)AlCl reagent, including one that is new, Salben(^{t}Bu)AlCl (**1**). The cations were observed to polymerize propylene oxide. Based upon the results of experimental and theoretical work the mechanism appears to be one in which a carbocation is the propagating species although the PDI values are remarkably low, ≈1.2 in some cases. All of the potential catalysts were characterized spectroscopically and, in the case of **3**, by X-ray crystallography.

Introduction

Polyurethanes are of tremendous commercial value and have wide-ranging applications as flexible and rigid foams, coatings and elastomeric materials.[1] In many of these applications a key constituent of the urethane is a low molecular weight polyether or polyol. These polyols, such as poly(propylene oxide) (PPO) are soluble in water up to molecular weights of ≈760.[2] Furthermore, the physical properties of the hydrolytically stable urethanes may be controlled by changing the length of the incorporated polyol. Low MW polyols lead to hard plastics while high MW polyols lead to flexible elastomers.

The predominant catalyst for preparing polyols from the ring-opening of oxiranes such as propylene oxide (PO) is suprisingly simple: KOH. Unfortunately, the KOH ultimately must be removed from the polyol before being combined with the diisocyanates in forming the urethane polymer. Additionally, KOH promotes the formation of allyl alcohol which leads to monofunctional rather than the desired bifunctional polyol. Recently, this problem has been partially addressed by the introduction of a new catalyst, zinc hexacyanocobaltate.[3] However, the method of action of this catalyst is not clear and it is more complicated to use in comparison with KOH.

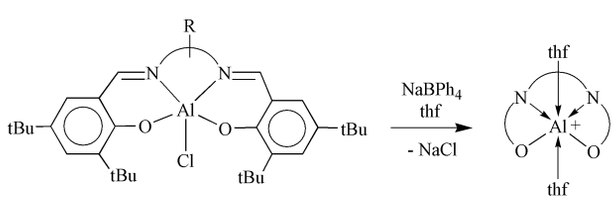
In an effort to find an ideal, commercially viable catalyst for polyol manufacture we have for some time been exploring the chemistry and potential utility of cationic aluminium complexes.[4] Six-coordinate cationic complexes supported by the Salen[5] class of ligands have emerged as potentially important catalysts in this regard.[6–9] They have the positive attributes of being robust, air stable, and relatively easy to synthesize.[10] By comparison, two-[11] three-[12] and four-coordinate[13] aluminium cations are highly air sensitive. Since the cations are Lewis acids a further potential advantage of this system is that they may potentially act as catalysts for joining the polyol and diisocyanate, and thus, obviate the need for tin–amine catalyst systems.

In previous studies we have shown that cations of the form, $[SalenAl(base)_2]^+X^-$ (where base = MeOH and X = Cl or BPh_4) catalyze the ring opening polymerization of PO to low molecular weight oligomers (≈700) with reasonable polydispersity index (PDI) values (≈1.5).[6,8] In an effort to examine this process further, and determine the role of the Lewis base donor molecules we have used the new thf supported cations, $[Salen(^tBu)Al(thf)_2]^+$ as catalysts for the formation of PPO (with BPh_4^- as the counter anion). Additionally, the mechanism of the catalysis will be explored through a theoretical study.

Results and discussion

Synthesis and spectroscopic characterization

The starting material for the preparation of the cations is of the simple formula LAlCl (where L = Salen(^{t}Bu), Salpen(^{t}Bu), Salben(^{t}Bu) (**1**) (first report here), Salophen(^{t}Bu) and Salomphen(^{t}Bu)). These are readily obtained by combining an R_2AlCl reagent (R = Me, Et, ^{i}Bu) with the Salen(^{t}Bu)H_2 ligand.[14] Subsequently, six-coordinate aluminium cations, **2**–**6**, can be generated by salt elimination with $NaBPh_4$ (Scheme 1). The



R	Cation	
$(CH_2)_2$	Salen(tBu)	(**2**)
$(CH_2)_3$	Salpen(tBu)	(**3**)
$(CH_2)_4$	Salben(tBu)	(**4**)
1,2-Ph	Salophen(tBu)	(**5**)
1,2 (4,5-Me_2)Ph	Salomphen(tBu)	(**6**)

Scheme 1 General syntheses of **2**–**6**.

Salen(^{t}Bu) portion of the ^{1}H NMR spectra of **2**–**6** contains only two resonances corresponding to each of the unique ^{t}Bu groups. This is indicative of a C_2-symmetric, monomeric, solution state structure. By comparison, the dimeric complex,

 DOI: 10.1039/b106003c

Table 1 Selected bond distances (Å) and angles (°) for [Salpen(^{t}Bu)Al(thf)$_2$]BPh$_4$·thf (**3**)

Al(1)–N(1)	2.004 (4)	Al(1)–N(2)	1.999 (4)	Al(1)–O(1)	1.799 (3)
Al(1)–O(2)	1.792 (3)	Al(1)–O(3)	2.052 (3)	Al(1)–O(4)	2.066 (3)
N(1)–Al(1)–N(2)	85.0 (2)			N(1)–Al(1)–O(1)	90.3 (1)
N(2)–Al(1)–O(1)	169.6 (2)			N(1)–Al(1)–O(2)	170.1 (2)
N(2)–Al(1)–O(2)	90.0 (4)			O(1)–Al(1)–O(2)	95.9 (1)
N(1)–Al(1)–O(3)	96.4 (1)			N(2)–Al(1)–O(3)	83.5 (1)
O(1)–Al(1)–O(3)	87.8 (1)			O(2)–Al(1)–O(3)	91.5 (1)
N(1)–Al(1)–O(4)	83.8 (1)			N(2)–Al(1)–O(4)	98.1 (1)
O(1)–Al(1)–O(4)	90.6 (1)			O(2)–Al(1)–O(4)	88.5 (1)
O(3)–Al(1)–O(4)	178.3 (1)				

[{Salpen(^{t}Bu)Al}$_2$]$^{2+}$[GaCl$_4^-$]$_2$, features four ^{t}Bu resonances.[15] There is only one imine resonance for **1** (δ 8.06) in keeping with the symmetric geometry. This resonance for **2**–**6** appears in the same region as the Ph–H resonances.

Structural characterization

Crystals of **3** were formed from saturated solutions that were stored at −30 °C under nitrogen. The structure of **3** is shown in Fig. 1 and important bond lengths and angles are given in

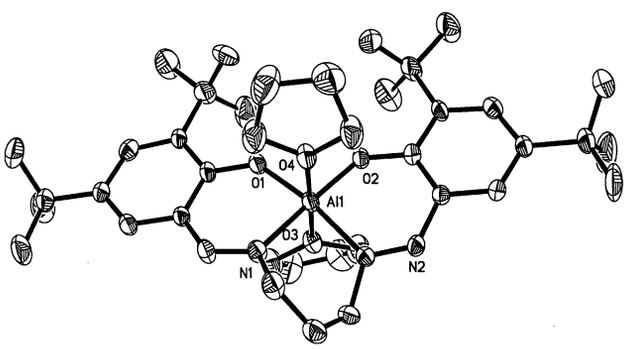


Fig. 1 ORTEP[28] view (30% ellipsoids) of [Salpen(^{t}Bu)Al(thf)$_2$]BPh$_4$ (**3**).

Table 1. The structure consists of a central six-coordinate aluminium atom in a distorted octahedral geometry with the Salpen(^{t}Bu) ligand occupying the four equatorial positions and the two thf molecules in the axial positions. The equatorial angles are moderately obtuse for the oxygens (95.9(1)°) around aluminium and more acute for the nitrogens (85.0(2)°). The O(ax)–Al–O(ax) angle is nearly linear (178.3(1)°). The axial Al–O distances are similar to the Al–N distances (≈2.0 Å) but longer than those to the oxygens of the ligand (≈1.8 Å).

Polymerizations

It has previously been shown that [SalenAl(MeOH)$_2$]$^+$X$^-$ complexes (with X = Cl or BPh$_4$) oligomerized propylene oxide while those coordinated by water did not. Although the mechanism for this oligomerization is not clear it is likely that it does not proceed *via* protonation from the MeOH group. The use of Brønsted-acidic compounds, including those incorporating aluminium are known.[16] If this mechanism was in effect in the present case then the water supported cations would have been active catalysts.[17] In order to avoid the complications and uncertainties associated with the presence of protic bases, the thf supported cations, **2** and **3** were examined. The results of the polymerizations, in either neat PO or with CH_2Cl_2 as solvent, proved to be superior to the previous studies. Molecular weights ranging from ≈400,000 for **2** and ≈180,000 for **3** were obtained. The PDI of the two catalysts differ. For **2**, the PDI of 1.32 is reasonable if a cationic mechanism is taking place. This appears to occur, for instance, in alumoxane catalyst systems.[18] The presence of CH_2Cl_2 does not have an appreciable impact on any of the polymerizations. However, the PDI of 1.16 for **3** is close to what is observed in "living" polymerization systems. This PDI, for example, is observed in the polymerization/oligomerization of cyclic ethers with Inoue's porphyrin systems[19] as well as with neutral SalenAlOR catalysts (with R = Me, ^{i}Pr[20] and SiPh$_3$[21]). The "living" systems appear to proceed through a single-site mechanism in which sequential monomers insert into the growing polymer chain

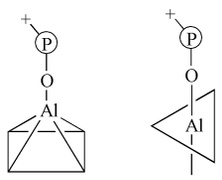


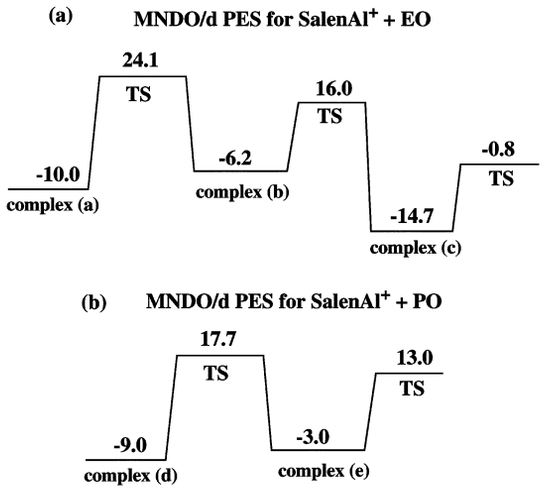
Fig. 2 Geometric differences between Salen(^{t}Bu)Al$^+$ (**2**) and Salpen(^{t}Bu)Al$^+$ (**3**) with growing polymer attached.

(Fig. 2a). This contrasts with the probable mechanism for the polymerization involving the cations, **2** and **3**. For these systems it is likely that the polymer grows through a cationic ring opening process (Fig. 2b). The low PDI values may be due to stabilization of the growing cationic end by the unreacted PO. Polymerizations were conducted at 8, 12, and 24 hours. The MW of the polymer increases with reaction time, but there was no linear correlation between M_n and the percent conversion. Increasing the reaction time past 24 hours did not result in an increase in polymer MW. These results suggest that the polymerization is not "living".

There is a structural difference between **2** and **3**. Previously it was shown that the Salen ligand supports a square pyramidal geometry (Fig. 3a) while the Salpen ligand creates a trigonal bipyramidal geometry around the central aluminium atom (Fig. 3b).[14,22] It is not clear, however, whether these geometries have an appreciable influence on the polymerization, in particular for the initial ring-opening step. In view of the uncertainty in how these cations polymerize PO a theoretical study was undertaken in order to elucidate the polymerization mechanism.

Theoretical study

The ring opening polymerization process was examined by the MNDO/d PES technique.[23,24] The steps in this process, using SalenAl$^+$ and PO, are shown in Fig. 4a–c. In the first step a Lewis acid–base complex is formed between the cation and monomer releasing 9 kcal mol^{-1} of energy (ΔH = −9.0 kcal mol^{-1}). From this point it requires 26.7 kcal to break the C–O bond of the monomer, 6.5 kcal mol^{-1} of which is recovered due to relief of ring strain. Thus, the energy required to form the first carbocation is 11.2 kcal mol^{-1} (ΔH = +11.2 kcal). A second monomer may then bind as indicated in Scheme 2. The process may be terminated by the release of a dioxane molecule with a total ΔH = −40 kcal mol^{-1}. Interestingly, the activation energy barrier for the ring-opening of either EO or PO decreases as the reaction center moves away from the aluminium. The calculated activation barrier for ring opening and reaction energies for complex formation is shown in Table 2.



Scheme 2 MNDO/d PES for $SalenAl^{+}$ and PO.

Since no cyclic species are observed in the GCMS it is likely that the cationic terminus of the growing polymer is stabilized by both the presence of excess monomer as well as contact with the counter anion. Anion stabilization is thought to occur in the cationic polymerization of other monomers, such as butadiene (with a two-coordinate cation as initiator).[11] However, this contact must be weak since the monomers are able to reach the active cationic site. There is apparently a subtle balance between reactivity and stabilization (and lessened reactivity) in this system as indicated by the high molecular weights that are obtained.

Conclusions

Cationic chelated aluminium complexes, supported by non-protic donor groups, are excellent initiators for the ring opening polymerization of propylene oxide. Although the mechanism is cationic it appears that the presence of excess monomer, and possibly the counter anion, stabilizes the cation to such an

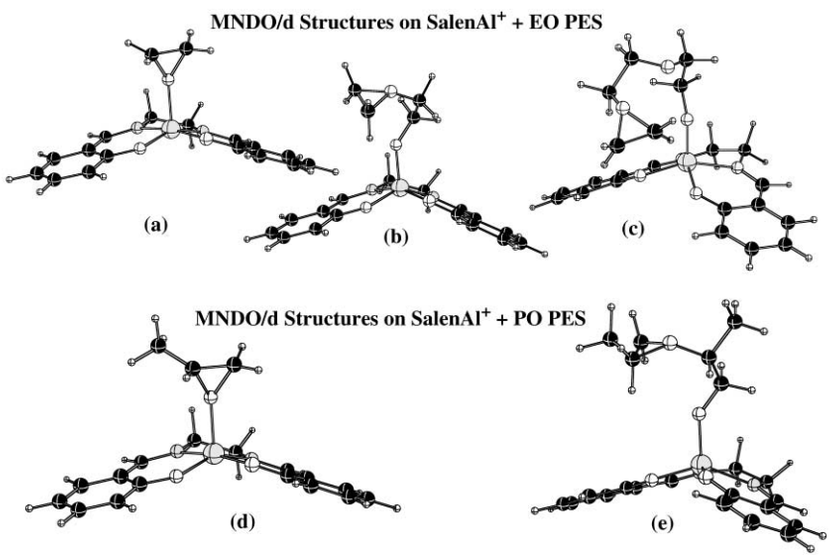


Fig. 3 Calculated structures modeling a potential polymerization mechanism.

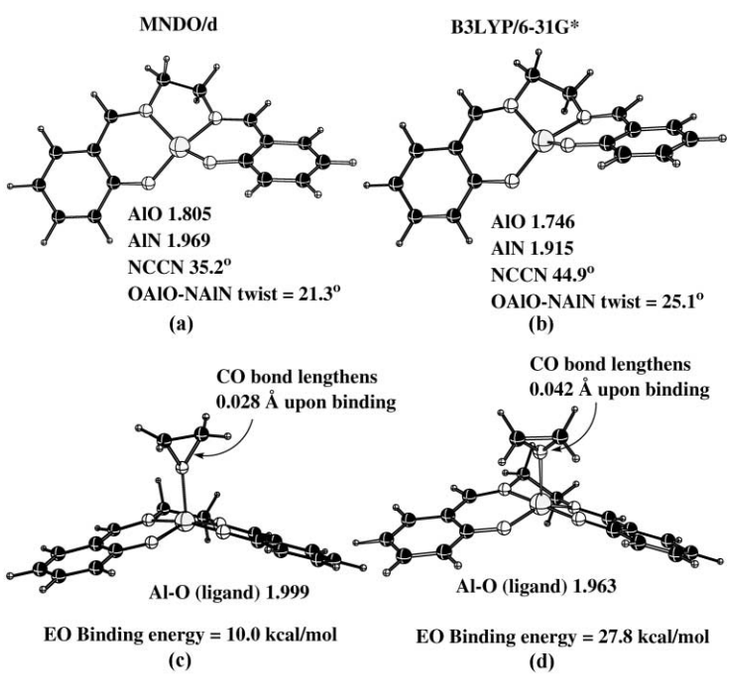


Fig. 4 Comparison of MNDO/d and B3LYP/6-31G techniques.

Table 2 Calculated activation barrier (kcal mol^{-1}) for ring opening and reaction energies (kcal mol^{-1}) for complex formation

Lewis acid[a]	Method	Oxirane		Methyloxirane	
		Ring-opening[c]	Complex	Ring-opening[c]	Complex
H^+	B3LYP/6-31G* + ZPC[b]			9.4	1.4
H^+	MP2/6-31G* + ZPC[b]			17.7	9.3
H^+	MNDO/d	19.3	5.0	14.5	−3.5
Al^+	B3LYP/6-31G* + ZPC	30.7	15.9		
Al^+	MP3/6-31G*//3-21G + ZPC[d]		32.9		
Al^+	MNDO/d	25.7	19.4	17.1	8.7
Sal-Al^+	MNDO/d	34.1	29.9	26.7	20.2
Sal-Al(unit)$^+$	MNDO/d	22.1	6.6	16.1	2.0
Sal-Al(unit)$_2^+$	MNDO/d	13.9	0.0[e]		
CH_3^+	MNDO/d	18.5	7.4	12.8	−1.4

[a] This is the species attached to the oxirane or methyloxirane. "Sal-Al(unit)$^+$" refers to the Salen–Al^+ complex with one or more units of the growing polymer attached. [b] Ref. 26. [c] Activation barrier for ring-opening. [d] Ref. 27. [e] In this complex, the terminal (charged) CH_2 group is interacting with (and stabilized by) the oxygen of the first unit (see Fig. 4).

extent that high molecular weight polymers, with remarkably low PDI values (≈1.2) can be obtained. Further work is being focused on how to control the MW of the polymers produced by these systems, with a view to obtaining low MW oligomers for use in polyurethane applications. Furthermore, as strong Lewis acidic complexes it is likely that these cations may find use in activating a wider range of electron rich substrates than just oxiranes.

Experimental

General considerations

All manipulations were conducted using Schlenk techniques in conjunction with an inert atmosphere glove box. All solvents were rigorously dried prior to use. NMR data were obtained on JEOL-GSX-270 and -400 instruments operating at 270.17 MHz (^{1}H) and 400.25 MHz are reported relative to $SiMe_4$ and are in ppm. Elemental analyses were obtained on a Perkin-Elmer 2400 Analyzer and were satisfactory for all compounds. Infrared data were recorded as KBr pellets on a Matheson Instruments 2020 Galaxy Series spectrometer and are reported in cm^{-1}. The reagent 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde was prepared according to the literature.[25] X-Ray data for **3** were collected on a Bruker SMART-CCD unit employing Mo-K_α radiation. The structure was refined using the Siemens software package SHELXTL 4.0[28] and SHELXTL-Plus.[28] All of the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were put into calculated positions. Absorption corrections were not employed. Space group assignment, $P2_12_12_1$, was based upon several factors. Firstly, systematic absences indicated the presence of screw axes down *a*, *b* and *c* only–there were no other absences. Secondly, normalized structure factor statistics were indicative of a non-centrosymmetric structure. Thirdly, the largest correlation coefficient matrix elements were all around −0.5, and were between *Uij* of the tertiary-butyl carbons. The structure refinement was unremarkable and the final geometry does not show any evidence of missed symmetry. Nevertheless, the crystals are probably inversion twinned, and were modeled as such with equal occupancy twin components. Furthermore, there is a molecule of thf in the crystal structure and the ^{t}Bu groups are disordered. Further details of the structure analyses are given in Table 3.

CCDC reference number 175835.

See http://www.rsc.org/suppdata/dt/b1/b106003c/ for crystallographic data in CIF or other electronic format.

The attempted polymerizations were carried out at ambient temperature and pressure. All studies were conducted using a similar procedure with propylene oxide freshly distilled from CaH_2. Polypropylene oxide (PPO) was characterized using Gel Permeation Chromatography using a Waters 510 HPLC pump and 746 Data Module against polystyrene standards.

Table 3 Summary of X-ray data for [Salpen(^{t}Bu)Al(thf)$_2$]BPh_4·thf (**3**)·thf

Color/shape	Yellow cube
Chemical formula	$C_{69}H_{92}AlBN_2O_5$
Formula weight	1067.24
Temperature/K	298(2)
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
a/Å	12.9154(8)
b/Å	14.2669(8)
c/Å	34.426(2)
Volume/Å^3	6343.4 (7)
Z	4
D_c/Mg m^{-3}	1.117
Absorption coefficient/mm^{-1}	0.081
Diffractometer	Bruker CCD
2θ range for data collection/°	1.18 to 20
Reflections measured	19406
Independent reflections	5920 (R_{int} = 0.0705)
Data/restraints/parameters	5920/0/703
Goodness of fit on F^2	0.808
Final *R* indices [$I > 2\sigma(I)$]	R = 0.0491, $wR2$ = 0.1453
R indices (all data)	R = 0.0561, $wR2$ = 0.1544

Syntheses

Salben(^{t}Bu)AlCl (1). Salben(^{t}Bu)H_2 (5.00 g, 9.60 mmol) was added to a rapidly stirred solution of Me_2AlCl (0.891 g, 9.62 mmol) in toluene (30 ml) under nitrogen in drybox at 25 °C. The solution was stirred for 2 h. After filtration, concentration and storage at −30 °C for 24 h, 5.02 g (90%) was obtained. Mp: 221 °C (decomp.) ^{1}H NMR ($CDCl_3$): δ 1.12 (m, 18H, CCH_3), 1.28 (d, 18H, CCH_3), 1.66 (m, 4H, CH_2), 3.43 (m, 4H, CH_2), 6.88 (d, 2H, PhH), 7.25 (d, 2H, PhH), 8.06 (s, 2H, CH=N); IR: *v* 3006 w, 2956 vs, 2908 s, 2867 s, 1633 s, 1617 vs, 1602 s, 1557 m, 1475 m, 1461 s, 1439 m, 1419 m, 1386 m, 1355 m, 1341 s, 1317 s, 1257 s, 1237 m, 1201 m, 1181 m, 1075 w, 878 w, 867 m, 846 m, 786 m, 761 m, 603 m, 569 w cm^{-1}; Analysis for $C_{34}H_{50}N_2O_2ClAl$. Calcd (found): C, 70.26 (70.02); H, 8.67 (8.59)%.

[Salen(^{t}Bu)Al(thf)$_2$]BPh_4 (2). To Salen(^{t}Bu)AlCl (4.00 g, 7.23 mmol) and sodium tetraphenyl borate (2.51 g, 7.35 mmol) was added thf (50 ml). The resulting turbid solution was refluxed for 12 h and was filtered under nitrogen. The solvent was removed under reduced pressure, yielding 5.93 g (84%) as a yellow solid. Mp: 197–202 °C. ^{1}H NMR ($CDCl_3$): δ 1.28 (s, 18H, $C(CH_3)_3$), 1.33 (s, 18H, $C(CH_3)_3$), 1.83 (m, 4H, thf), 2.74 (s (br), 2H, CH_2), 3.18 (s (br), 2H, CH_2), 3.71 (m, 4H, thf), 6.90–7.61 (m, 26H, PhH and N=CH). IR: *v* 3055 m, 2957 s, 2872 w, 1629 vs, 1556 m, 1508 w, 1446 m, 1315 m, 1276 m, 1176 m, 1047 s, 862 m, 734 s, 613 s cm^{-1}. Analysis for $C_{64}H_{82}N_2O_4AlB$, Calcd (found): C, 78.35 (78.44); H, 8.42 (8.29)%.

[Salpen(^{t}Bu)Al(thf)$_2$]BPh$_4$ (3). The procedure was as described for **2** with Salpen(^{t}Bu)AlCl (4.00 g, 7.01 mmol) and sodium tetraphenyl borate (2.48 g, 7.25 mmol) and thf (50 ml). Evaporation of the solvent produced a greenish yellow solid. Yield: 6.01 g (86%). Mp: 182 °C (decomp.). ^{1}H NMR ($CDCl_3$): δ 1.20 (s,18H, C(CH_3)$_3$), 1.45 (s,18H, C(CH_3)$_3$), 1.85 (m, 4H, thf), 2.85 (s(br), 2H, CH_2), 3.74 (m, 4H, thf), 6.91–7.61 (m, 24H, PhH and N=CH). IR: ν 3055 m, 2958 s, 2904 w, 2872 w, 1622 vs, 1545 m, 1477 m, 1421 s, 1354 m, 1315 w, 1261 m, 1180 m, 1072 m, 1016 w, 848 s, 744 m, 706 s, 605 s cm^{-1}. Analysis for $C_{65}H_{84}N_2O_4AlB$, Calcd (found): C, 78.45 (77.93); H, 8.51 (8.60)%.

[Salben(^{t}Bu)Al(thf)$_2$]BPh$_4$ (4). The procedure was as described for **2** with Salben(^{t}Bu)AlCl (1.29 g, 2.22 mmol) and sodium tetraphenyl borate (0.76 g, 2.22 mmol) in 50 ml thf. Yield: 1.91 g (85%). Mp: 80 °C(decomp.) ^{1}H NMR (THF-d^8): δ 1.28 (s, 18H, C(CH_3)$_3$), and 1.33 (s, 18H, C(CH_3)$_3$), 1.77 (t, 8H, thf), 3.61(t, 8H, thf), 6.67–7.51 (m, 26H, PhH and N=CH). IR: ν 3228 vw, 3127 w, 3052 m, 3036 m, 2958 vs, 2907 s, 2869 s, 1698 w, 1619 s,1599 s, 1555 s, 1546 s, 1518 w, 1473 s, 1441 s, 1420s, 1393s, 1360 m, 1340 m, 1316 m, 1258 s, 1237 m, 1203 m, 1178 m, 1138 w, 1073 w, 1027 w, 981 w, 964 w, 867 w, 849 w, 829 w, 814 w, 733 w, 721 w, 702 m, 682 w cm^{-1}; Analysis for $C_{66}H_{86}N_2O_4AlB$, Calcd (found): C, 78.55 (78.61); H, 8.59 (8.44)%.

[Salophen(^{t}Bu)Al(thf)$_2$]BPh$_4$ (5). The procedure was as described for **2** with Salophen(^{t}Bu)AlCl (4.00 g, 6.65 mmol) and sodium tetraphenyl borate (2.36 g, 6.690 mmol) in thf (50 ml). Yield: 5.58 g (81%). Mp: 122–127 °C. ^{1}H NMR ($CDCl_3$): δ 0.80 (s, 18H, C(CH_3)$_3$), 1.32 (s, 18H, C(CH_3)$_3$), 1.83 (m, 4H, thf), 6.85–7.44 (m, 30H, PhH and N=CH). IR: ν 3209 m, 3052 m, 2955 s, 2868 w, 1614 m, 1589 m, 1537 s, 1462 w, 1432 m, 1388 m, 1359 w, 1257 m, 1174 s, 1132 w, 1030 w, 846 m, 734 s, 705 s, 611 s cm^{-1}. Analysis for $C_{68}H_{82}N_2O_4AlB$, Calcd (found): C, 79.36 (78.88); H, 8.03 (7.97)%.

[Salomphen(^{t}Bu)Al(thf)$_2$]BPh$_4$ (6). The procedure was as described for **2** with Salomphen(^{t}Bu)AlCl (4.00 g, 6.32 mmol) and sodium tetraphenyl borate (2.25 g, 6.57 mmol) in thf (50 ml). Yield: 5.18 (78%). Mp: 92–97 °C. ^{1}H NMR ($CDCl_3$): δ 0.83 (s, 18H, C(CH_3)$_3$), 1.33 (s, 18H, C(CH_3)$_3$), 1.84 (m, 4H, thf), 2.16 (s, 3H, PhCH_3), 2.35 (s, 3H, PhCH_3), 3.72 (m, 4H, thf), 6.79–7.50 (m, 28H, PhH and N=CH). IR: ν 3225 w, 3055 w, 2960 s, 2872 w, 1618 m, 1593 m, 1552 s, 1477 m, 1435 m, 1384 w, 1255 s, 1174 s, 1112 w, 1030 m, 848 s, 734 s, 705 s, 642 s cm^{-1}. Analysis for $C_{70}H_{86}N_2O_4AlB$, Calcd (found): C, 79.52 (79.64); H, 8.20 (8.12)%.

Polymerization of propylene oxide (PO) using [Salen(^{t}Bu)Al(thf)$_2$]BPh$_4$ catalysts

Propylene oxide (PO) (142.9 mmol, 10 ml) freshly distilled from CaH_2 after stirring for 2 days, was added to the respective cations (1.0 g, 1.01 mmol) *via* syringe. The resulting pale yellow solution was stirred for 24 h. Polymerization was quenched using 2 ml of methanol mixed with a few drops of HCl. The polymer was extracted by dissolution in CH_2CH_2 (50 ml), then washing with 0.1 M HCl (25 ml), resulting in an aqueous and an organic layer. The organic layer was dried over $MgSO_4$, and the solvent removed under vacuum to yield a yellow oil with a precipitate (the precipitate may be $Al(OH)_3$–^{27}Al NMR showed a peak at approximately zero ppm, and mass spectrometry showed a peak at 78). Methanol (15 ml) was added, and the yellow solution decanted off. The methanol was allowed to evaporate, yielding a yellow oil. The oil was identified as an oligoether by the presence of multiplets centered at δ 1.20 and 3.45 in the ^{1}H NMR ($CDCl_3$).

Acknowledgements

This work was supported by the National Science Foundation NSF-Career Award. NMR instruments used in this research were obtained with funds from the CRIF program of the NSF (CHE 997841) and from the Research Challenge Trust Fund of the University of Kentucky. Computer time was provided by the Alabama Supercomputer Network.

References

1 M. Szycher, *Szycher's Handbook of Polyurethanes*, CRC Press, New York, 1999.
2 H. Ulrich, *Urethane Polymers in Encyclopedia of Polymer Science and Technology*, ed. J. I. Kroschwitz, Wiley, New York, 1985, vol. 24, p. 695.
3 G. H. Grosch, K. Harre, J. Erbes, R. Lorenz, S. Bauer, T. Ostrowski, E. Baum, D. Junge and E. M. Dexheimer, *PCT Int. Appl.* WO 0044813, 2000.
4 For a comprehensive listing of cationic Group 13 complexes see: D. A. Atwood, *Coord. Chem. Rev.*, 1998, **176**, 407.
5 "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.
6 D. A. Atwood, J. A. Jegier and D. Rutherford, *J. Am. Chem. Soc.*, 1995, **117**, 6779.
7 D. A. Atwood, J. A. Jegier and D. Rutherford, *Inorg. Chem.*, 1996, **35**, 63.
8 J. A. Jegier, M.-A. Munoz-Hernandez and D. A. Atwood, *J. Chem. Soc., Dalton Trans.*, 1999, 2583.
9 S. Liu, M.-A. Munoz-Hernandez and D. A. Atwood, *J. Organomet. Chem.*, 2000, **596**, 109.
10 M. G. Davidson, C. Lambert, I. Lopez-Solera, P. R. Raithby and R. Snaith, *Inorg. Chem.*, 1995, **34**, 3765.
11 M. Bochmann and D. M. Dawson, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 2226.
12 (*a*) M. P. Coles and R. F. Jordan, *J. Am. Chem. Soc.*, 1997, **119**, 8125; (*b*) E. Ihara, V. G. Young and R. F. Jordan, *J. Am. Chem. Soc.*, 1998, **120**, 8277; (*c*) C. E. Radzewich, M. P. Coles and R. F. Jordan, *J. Am. Chem. Soc.*, 1998, **120**, 9384; (*d*) C. E. Radzewich, I. A. Guzei and R. F. Jordan, *J. Am. Chem. Soc.*, 1999, **121**, 8673.
13 N. Emig, H. Nguyen, H. Krautscheid, R. Reau, J. B. Cazaux and G. Bertrand, *Organometallics*, 1998, **17**, 3599; M. Bruce, V. C. Gibson, C. Redshaw, G. A. Solan, A. J. P. White and D. J. Williams, *Chem. Commun.*, 1998, 2523.
14 D. Rutherford and D. A. Atwood, *Organometallics*, 1996, **15**, 4417.
15 M.-A. Munoz-Hernandez, B. Sannigrahi and D. A. Atwood, *J. Am. Chem. Soc.*, 1999, **121**, 6747.
16 T. Saegusa, T. Ueshima and S. Tomita, *Makromol. Chem.*, 1967, **107**, 131.
17 I. Kuntz, C. Cozewith, H. T. Oakley, G. Via, H. T. White and Z. W. Wilchinsky, *Macromolecules*, 1971, **4**, 4.
18 B. Wu, C. J. Harlan, R. W. Lenz and A. R. Barron, *Macomolecules*, 1997, **30**, 316.
19 T. Aida and S. Inoue, *Acc. Chem. Res.*, 1996, **29**, 39.
20 T. M. Ovitt and G. W. Coates, *J. Am. Chem. Soc.*, 1999, **121**, 4072; C. P. Radano, G. L. Baker and M. R. Smith III, *J. Am. Chem. Soc.*, 2000, **122**, 1552.
21 D. A. Atwood, US Patent Pending.
22 D. A. Atwood, M. S. Hill, J. A. Jegier and D. Rutherford, *Organometallics*, 1997, **16**, 2659.
23 Used as implemented in Unichem 3.0 and 4.0, Cray Research, Inc., 1994–1999 and Unichem 5.0, Oxford Molecular, Inc., 2000.
24 (*a*) W. Thiel and A. A. Voityuk, *Theor. Chim. Acta*, 1992, **81**, 391; W. Thiel and A. A. Voityuk, *Theor. Chim. Acta*, 1996, **93**, 315; W. Thiel and A. A. Voityuk, *Int. J. Quantum Chem.*, 1992, **44**, 807; W. Thiel and A. A. Voityuk, *THEOCHEM*, 1994, **313**, 141; W. Thiel and A. A. Voityuk, *J. Phys. Chem.*, 1996, **100**, 616.
25 G. Casiraghi, G. Casnati, G. Puglia, G. Sartori and G. Terenghi, *J. Chem. Soc., Perkin Trans. 1*, 1980, 1862.
26 J. M. Coxon, A. J. Thorpe and W. B. Smith, *J. Org. Chem.*, 1999, **64**, 9575.
27 J. Tortajada, A. Total, J. P. Morizur, M. O. Alcamí and M. Yáñez, *J. Phys. Chem.*, 1992, **96**, 8309.
28 C. K. Johnson, ORTEP, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976; G. M. Sheldrick, SHELXTL 4.0, Siemens Analytical X-Ray Instruments, Madison, WI, 1989; G. M. Sheldrick, SHELXTL-Plus, Siemens Analytical X-Ray Instruments, Madison, WI, 1989.