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FULL PAPER

Six-coordinate aluminium cations: synthesis, characterization and catalysis

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The present work details the synthesis and structural characterization of six-coordinate aluminium cations derived from the single starting material, Salen(^{t}Bu)AlCl **1** [Salen(^{t}Bu) = *N*,*N*′-ethylenebis(3,5-di-*tert*-butylsalicylideneimine)]. They are of formula [Salen(^{t}Bu)Al(base)$_2$]$^+$X$^-$ and contain various combinations of base and counter anion; H_2O, Cl^- **2**, MeOH, Cl^- **3**, MeOH, BPh_4^- **4**, MeOH, OTs^- **5**. With thf as base and OTs^- as the anion, the neutral complex, Salen(^{t}Bu)Al(thf)(OTs) **6** is obtained. MeOH can be added to **6** to displace the thf and produce **5**. In contrast the addition of acetophenone to **2** does not displace the H_2O but produces the hydrogen-bonded complex **2** · · · 2(acetophenone) **7**. All of the compounds were characterized spectroscopically and, in the case of **3**, **5** and **7**, by X-ray crystallography. Compounds **1**–**3** were examined for activity as oxirane polymerization catalysts.

Introduction

The Salen[1] class of ligands [Fig. 1(a)] have been of great utility in the isolation of higher-coordinate monometallic group 13 complexes. Some examples include those incorporating aluminium,[2] gallium[3] and indium[4] alkyls, amides,[5] alkoxides,[6] siloxides[7] and cations.[8] Beyond their fundamental interest the cations have potential as single-site catalysts for the polymerization of propylene oxide.[8a] This work supplements the established literature where bimetallic aluminium catalysts are used in living and "immortal" polymerizations of oxiranes and other monomers.[9] The Salen-supported cations are highly Lewis acidic, easy to synthesize, and can have their properties changed by simple changes of the ligand. Thus, they will clearly have other applications in catalysis and organic synthesis. However, one problem associated with traditional Salen derivatives is that they are usually insoluble in organic solvents. Use of the Acen ligand, with solubilizing Me groups [Fig. 1(b)] is not a sufficient solution to this problem. The most soluble of these ligands are the ones which possess *tert*-butyl groups at two positions on each of the phenol rings [Fig. 1(c)]. The present work will demonstrate that high yields of six-coordinate group 13 cations are accessible using these ligands and that they are soluble in a range of common solvents. They are of general formula, [Salen(^{t}Bu)Al(base)$_2$]$^+$X$^-$ where base = H_2O or MeOH and X is Cl^-, BPh_4^- or OTs^-. Some preliminary propylene oxide polymerizations will be presented. Overall, this study will provide a foundation for future homogeneous applications of these strongly Lewis acidic cations.

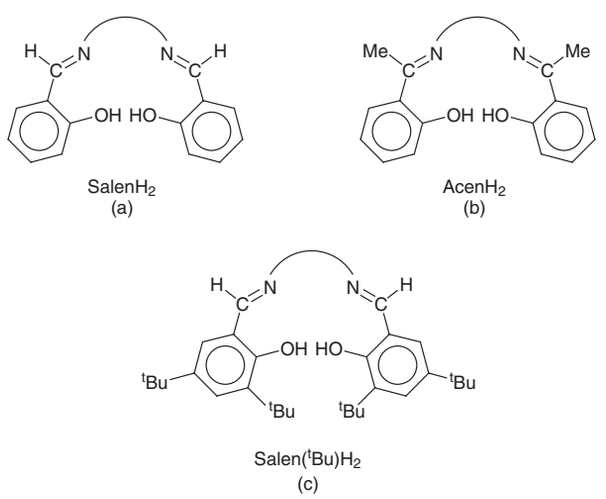
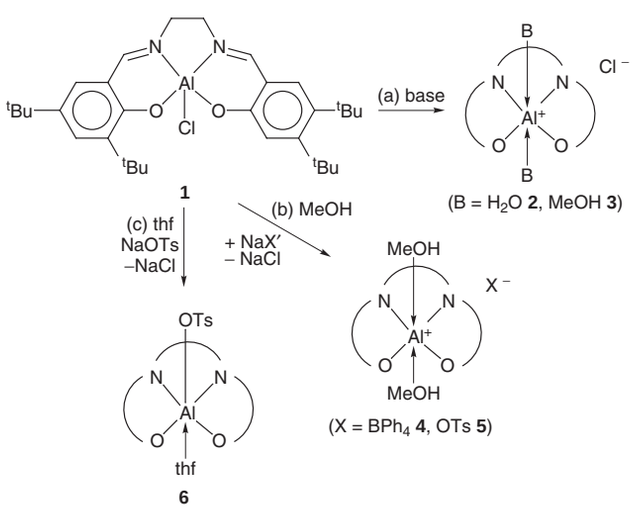


Fig. 1 General depiction of the types of Salen ligands mentioned in the text (a, b) and used in this study (c).

Results and discussion

Synthesis and spectroscopic characterization

The starting material for the preparation of the diverse cations is Salen(^{t}Bu)AlCl **1** which is readily obtained by combining an R_2AlCl reagent (R = Me, Et, ^{i}Bu) with the Salen(^{t}Bu)H_2 ligand. Subsequently, six-coordinate aluminium cations can be generated from **1** by either displacement of the halide with an appropriate base or by salt elimination. Thus, compounds **2** and **3** are prepared by combining **1** with H_2O and MeOH (Scheme 1a) while **4** and **5** result when $NaBPh_4$ or NaOTs are used with



Scheme 1 General syntheses relating to cationic **1**–**5** and neutral **6**.

MeOH as the solvent (Scheme 1b). When the latter reaction is conducted in thf the solvent is not of sufficient Lewis basicity to prevent the OTs^- group from coordinating and the neutral complex, **6**, is formed. The presence of one thf is confirmed in the ^{1}H NMR data and in the elemental analysis. This would imply that the ranking of base strength toward the cations is

Table 1 Data collection and processing parameters for **3**, **5** and **7**

	3	**5**	**7**
Formula	$C_{35}H_{58}N_2O_5AlCl$	$C_{44}H_{73}N_2O_{10}AlS$	$C_{52}H_{74}N_2O_7AlCl$
Formula weight	649.3	849.1	901.56
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	C_2/c	$P\bar{1}$	C_2/c
a/Å	39.740(4)	10.919(2)	30.477(2)
b/Å	7.396(1)	12.987(3)	11.3248(6)
c/Å	27.716(3)	18.310(6)	32.359(2)
α/°	—	78.47(2)	—
β/°	97.30(1)	87.70(1)	109.405(2)
γ/°	—	82.99(1)	—
V/Å^3	8079(2)	2524(1)	10534(1)
Z	8	2	8
μ/mm^{-1}	0.153	0.133	0.138
T/K	298	298	298
Unique data	5269	6578	15087
Obsd. [$F \geq 4\sigma(F)$]	3016	3673	4862
$R1$ (%)[a]	6.11	7.09	7.27
R all (%)	10.67	12.27	8.55

[a] $R = (\Sigma||F_o| - |F_c||)/\Sigma|F_o|$.

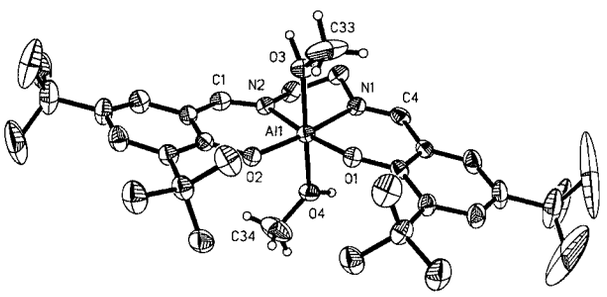


Fig. 2 ORTEP[15] view of the cation of [Salen(ᵗBu)Al(MeOH)$_2$]$^+$Cl$^-$ **3**.

MeOH > OTs$^-$ > thf. Addition of acetone or acetophenone to **2** results in the isolation of starting material: the water molecules are not displaced. Interestingly, the acetophenone molecules are found to be hydrogen bonded to the waters in forming compound **7** [eqn. (1)]. The Salen(ᵗBu) portion of the

$$[\text{Salen}(^t\text{Bu})\text{Al}(\text{H}_2\text{O})_2]^+\text{Cl}^-\ \mathbf{2} + 2(\text{acetophenone}) \xrightarrow{\text{thf}} [\text{Salen}(^t\text{Bu})\text{Al}(\text{H}_2\text{O}\cdots\text{acet})_2]^+\text{Cl}^-\ \mathbf{7} \quad (1)$$

^{1}H NMR spectra of **1**–**6** is very clean and indicative of a solution state structure in which the resonances attributed to the aryl portion of the molecules are either related by a C_2 symmetry axis or are coincident. For example, there is a singlet for each unique ᵗBu group (≈1.3 and 1.5 ppm) and one for the imines (≈8 ppm). The methylene units in the backbone are generally found as a single broad resonance except in the case of **1** (which is not C_2 symmetric) where there are two closely spaced multiplets and in **3** for which the resonances are two broad closely-spaced peaks. The O–H protons are observed in **2** but not for **3**, possibly due to hydrogen bonding with these groups in **3** (see below). The OH's are observed in the IR spectra of **2** and **3** (≈3400–3600 cm^{-1}).

Structural characterization

Crystals of **3**, **5** and **7** were formed from saturated solutions that were either left to stand in air (**3**) or cooled to −30 °C under anhydrous conditions (**5** and **7**). Single crystals of these compounds were cut to approximately cubic shapes for the collection of the X-ray data (Table 1). The structures of **3**, **5** and **7** are shown in Figs. 2–4, respectively. A summary of important bond lengths and angles for these compounds is given in Table 2.

In general, the structures consist of a central six-coordinate aluminium atom in a distorted O_h geometry with the Salen(ᵗBu) ligand occupying the four equatorial positions and the two solvent molecules in the axial positions. The equatorial angles are more obtuse for the oxygens [90.9(2) to 97.7(2)°] around aluminium and more acute for the nitrogens [80.4(2) to 81.3(2)°]. The O(ax)–Al–O(ax) angles are consequently bent slightly toward the open space between the oxygens and away

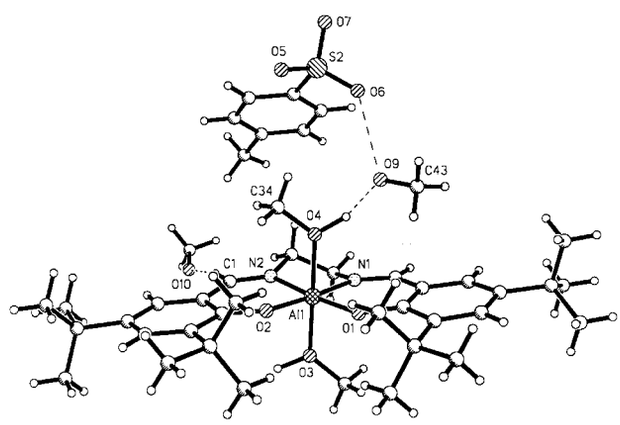


Fig. 3 Molecular structure and atom numbering scheme for [Salen(ᵗBu)Al(MeOH)$_2$]$^+$OTs$^-$·2MeOH **5**. A ball-and-stick model (generated from the X-ray data) is used for purposes of clarity.

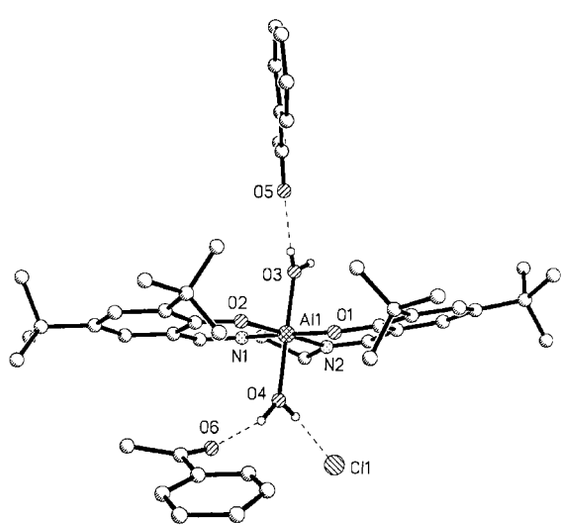


Fig. 4 Molecular structure and atom numbering scheme for the cation of [Salen(ᵗBu)Al(H$_2$O)$_2$]$^+$Cl$^-$·2(acetophenone) **7**. A ball-and-stick model (generated from the X-ray data) is used for purposes of clarity.

Table 2 Selected bond distances (Å) and angles (°) for **3**, **5** and **7**

[Salen(^{t}Bu)Al(MeOH)$_2$]Cl **3**

Al(1)–N(1)	1.991(5)	Al(1)–N(2)	1.999(4)	Al(1)–O(3)	1.963(4)
Al(1)–O(1)	1.794(4)	Al(1)–O(2)	1.795(4)	Al(1)–O(4)	1.980(4)

N(1)–Al(1)–N(2)	80.6(2)	N(1)–Al(1)–O(1)	90.9(2)
N(2)–Al(1)–O(1)	171.5(2)	N(1)–Al(1)–O(2)	171.8(2)
N(2)–Al(1)–O(2)	91.3(2)	O(1)–Al(1)–O(2)	97.2(2)
N(1)–Al(1)–O(3)	88.1(2)	N(2)–Al(1)–O(3)	87.1(2)
O(1)–Al(1)–O(3)	92.8(2)	O(2)–Al(1)–O(3)	91.7(2)
N(1)–Al(1)–O(4)	87.3(2)	N(2)–Al(1)–O(4)	87.6(2)
O(1)–Al(1)–O(4)	91.9(2)	O(2)–Al(1)–O(4)	92.2(2)
O(3)–Al(1)–O(4)	173.5(2)		

[Salen(^{t}Bu)Al(MeOH)$_2$]OTs·2MeOH **5**

Al(1)–N(1)	1.990(6)	Al(1)–N(2)	1.999(5)	Al(1)–O(3)	1.964(5)
Al(1)–O(1)	1.797(4)	Al(1)–O(2)	1.793(5)	Al(1)–O(4)	1.971(5)

N(1)–Al(1)–N(2)	81.3(2)	N(1)–Al(1)–O(1)	90.6(2)
N(2)–Al(1)–O(1)	171.8(2)	N(1)–Al(1)–O(2)	171.6(2)
N(2)–Al(1)–O(2)	90.4(2)	O(1)–Al(1)–O(2)	97.7(2)
N(1)–Al(1)–O(3)	88.3(2)	N(2)–Al(1)–O(3)	88.9(2)
O(1)–Al(1)–O(3)	92.0(2)	O(2)–Al(1)–O(3)	90.9(2)
N(1)–Al(1)–O(4)	89.1(2)	N(2)–Al(1)–O(4)	87.7(2)
O(1)–Al(1)–O(4)	91.2(2)	O(2)–Al(1)–O(4)	91.3(2)
O(3)–Al(1)–O(4)	175.9(2)		

[Salen(^{t}Bu)Al($H_2O\cdots$acetophenone)$_2$]Cl·2thf **7**

Al(1)–N(1)	1.995(4)	Al(1)–N(2)	1.981(4)	Al(1)–O(3)	1.942(3)
Al(1)–O(1)	1.801(3)	Al(1)–O(2)	1.795(3)	Al(1)–O(4)	1.955(3)

N(1)–Al(1)–N(2)	80.4(2)	N(1)–Al(1)–O(1)	172.8(2)
N(2)–Al(1)–O(1)	92.4(2)	N(1)–Al(1)–O(2)	91.2(2)
N(2)–Al(1)–O(2)	171.5(2)	O(1)–Al(1)–O(2)	96.1(1)
N(1)–Al(1)–O(3)	87.1(2)	N(2)–Al(1)–O(3)	85.8(1)
O(1)–Al(1)–O(3)	92.70(1)	O(2)–Al(1)–O(3)	93.0(1)
N(1)–Al(1)–O(4)	88.3(2)	N(2)–Al(1)–O(4)	88.4(1)
O(1)–Al(1)–O(4)	91.2(1)	O(2)–Al(1)–O(4)	92.3(1)
O(3)–Al(1)–O(4)	173.1(1)		

from the ligand backbone leading to angles less than ideal [173.1(1) to 175.9(2)°].

The axial Al–O distances ≈1.9 Å for all of the structures are substantially longer than those to the oxygens of the ligand [1.793(5) to 1.801(3) Å]. However, there is a slight difference between the Al–O (MeOH) distances of **3** and **5** [1.971(5) to 1.980(4) Å] when compared to the Al–O(H_2O) of **7** [1.942(3) and 1.955(3) Å] which can be attributed to the lessened steric requirements of H_2O by comparison to MeOH. These distances are similar to those of the non-*tert*-butylated Salen supported complexes, [SalenAl(base)$_2$]$^+X^-$.[8]

Hydrogen bonding

As noted earlier, it was surprising to discover that compound **3** contained no extraneous solvent molecules. Compound **5**, however, has an impressive range of hydrogen bonding as revealed in the crystal structure. There is an MeOH bridging between a coordinated MeOH and an OTs^- group with O···O distances of ≈2.5 and 2.7 Å, respectively. One of the OTs^- oxygens also makes a short contact with an imine hydrogen (H–C=N–) of an adjacent ligand (O···O ≈ 3.5 Å). Although not for the structure of **5**, intermolecular hydrogen bonding involving the imine groups has a structure-directing effect in the bimetallic borates, Salen{B(OR)$_3$}$_2$ (R = Me, Et).[10] For the borates the distances (C···O) are about 3.4 Å. In **7** the hydrogen bonding does not occur with the lattice solvent, thf (not unexpectedly) but, rather, with the added reagent, acetophenone. One acetophenone is paired with each coordinated water with O···O distances ≈ 2.8 Å. The chloride anion is also involved making a ≈3.2 Å contact with the remaining hydrogen of one of the waters.

Polymerizations

It has previously been shown that [SalenAl(MeOH)$_2$]$^+BPh_4^-$ polymerized propylene oxide while similar complexes coordinated by water or with Cl^- as the counteranion did not.[8a] This was also found to be true for the Salen(^{t}Bu) derivatives; **1** and **2** were inactive as catalysts while **3** produced low molecular weight oligomers (M_n = 427, PDI = 1.5; PDI = polydispersity index). While the mechanism for this oligomerization is not clear it is likely that it does not proceed through a cationic mechanism in which a proton from the MeOH groups initiates the reaction. If this were the case then the water supported cations would have been active catalysts.[11] Further work is being conducted to deduce the oxirane oligomerization mechanism.

Experimental

General considerations

All manipulations were conducted using Schlenk techniques in conjunction to 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 (^{1}H) and 400.25 MHz (^{27}Al) and 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.[12] X-Ray data for **3** and **5** were collected on a Siemens P-4 diffractometer and those for **7** on a Siemens SMART-CCD unit (F^2 data). Both employed Mo-Kα radiation. The struc-

tures were refined using the Siemens software package SHELXTL 4.0 and SHELXTL-PLUS.[13] All of the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were put into calculated positions. Absorption corrections were not employed. The *R* values for **5** and **7** were somewhat high due to the presence of both hydrogen-bonded and lattice solvent molecules. Further details of the structure analyses are given in Table 1.

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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.

Salen(^{t}Bu)AlCl 1

To a stirred solution of Salen(^{t}Bu)H_2 (32.01 mmol, 15.77 g) in toluene (100 mL) at −78 °C was added a solution of dimethylaluminium chloride (32.01 mmol, 2.961 g) in toluene (40 mL) also at −78 °C. The bright yellow suspension was stirred at this temperature and allowed to slowly warm to 25 °C. During this time the solid went into solution and a gas was evolved. A pale yellow precipitate began to form shortly after. The mixture was stirred for 18 hours, and the volatiles were removed under reduced pressure resulting in a nearly quantitative yield of a pale yellow powder. Mp >260 °C. ^{1}H NMR ($CDCl_3$): δ 1.29 [s, 18H, $C(CH_3)_3$], 1.53 [s, 18H, $C(CH_3)_3$], 3.74 (m, 2H, CH_2CH_2), 4.15 (m, 2H, CH_2CH_2), 7.03 (d, 2H, PhH), 7.55 (d, 2H, PhH), 8.37 (s, 2H, N=CH). IR ν/cm^{-1}: 2953m, 1624s, 1543s, 1398w, 1259s, 1094m, 816w, 608s, 444m. Analysis. Calc.: C, 69.50; H, 7.91. Found: C, 69.18; H, 8.02%.

[Salen(^{t}Bu)Al(H_2O)$_2$]Cl 2

To a stirring solution of Salen(^{t}Bu)AlCl (0.5 g, 0.9 mmol) in thf (20 mL) was added 10 mL of distilled water. The solution was filtered and left to evaporate at ambient temperature until light green crystals precipitated. The crystals were isolated by filtration and washed twice with diethyl ether. Yield 0.48 g (91%). Mp 298–301 °C. ^{1}H NMR ($CDCl_3$): δ 1.29 [s, 18H, $C(CH_3)_3$], 1.35 [s, 18H, $C(CH_3)_3$], 2.05 (s br, 4H, H_2O), 3.64 (s br, 4H, CH_2), 6.94 (d, 2H, C_6H_2), 7.44 (d, 2H, C_6H_2), 7.97 (s, 2H, CHN). IR ν/cm^{-1}: 3842w, 3838w, 3835w, 3670w, 2955s, 2908m, 2869m, 1631s, 1546m, 1471m, 1439m, 1326m, 1256m, 1187w, 1175m, 1064w, 927w, 860m, 756w. Analysis. Calc.: C, 69.48; H, 8.38. Found: C, 69.18; H, 8.02%.

[Salen(^{t}Bu)Al(MeOH)$_2$]Cl 3

To **1** (0.633 mmol, 0.350 g) was added MeOH (7 mL). The solid turned white and dissolved over 5 minutes. Slow evaporation of the solvent in air led to a nearly quantitative yield of pale yellow X-ray quality crystals. Over several weeks, the crystals desolvated yielding opaque yellow crystals. A quantitative yield of crystalline solid can be obtained by stirring **1** in MeOH for 3 hours and then removing the solvent under vacuum. Characterization data for single-crystalline material: Mp >260 °C. ^{1}H NMR ($CDCl_3$): δ 1.29 [s, 18H, $C(CH_3)_3$], 1.53 [s, 18H, $C(CH_3)_3$], 3.46 (s, 6H, CH_3OH), 3.79 [s (v br), 2H, CH_2CH_2], 4.12 [s (v br), 2H, CH_2CH_2], 7.04 (d, 2H, PhH), 7.55 (d, 2H, PhH), 8.38 (s, 2H, N=CH). IR ν/cm^{-1}: 3406w (br), 2955s, 2870m, 2779m, 1639s, 1554m, 1442m, 1311m, 1276m, 1174m, 1016m, 875m, 756m, 611m. Analysis. Calc.: C, 65.62; H, 8.59. Found: C, 65.78; H, 8.68%.

[Salen(^{t}Bu)Al(MeOH)$_2$]BPh_4 4

To **1** (2.71 mmol, 1.50 g) and sodium tetraphenylborate (2.71 mmol, 0.928 g) was added MeOH (20 mL). A yellow solid appeared and went back into solution. This yellow solution was stirred for 18 hours and allowed to stand for 24 hours during which time a small amount of white precipitate settled out of solution. The solution was filtered, concentrated to 15 mL, and cooled to −30 °C. After several days, pale yellow plates formed. These were isolated and dried under vacuum to yield 1.774 g (73%) of opaque yellow crystals. Mp 118–121 °C. ^{1}H NMR ($CDCl_3$): δ 1.31 [s, 18H, $C(CH_3)_3$], 1.46 [s, 18H, $C(CH_3)_3$], 2.93 (s, 6H, CH_3OH), 3.14 [s (br), 4H, CH_2CH_2], 6.71–7.66 (multiplets, 26H, PhH and N=CH). IR ν/cm^{-1}: 3437m (br), 3057m, 2956s, 2868w, 1626vs, 1543m, 1473s, 1311m, 1255s, 1176m, 1006m, 850m, 756m, 705s, 613s. Analysis. Calc.: C, 77.32; H, 8.42. Found: C, 77.32; H, 8.28%.

[Salen(^{t}Bu)Al(MeOH)$_2$]OTs 5

Method A: to **1** (1.808 mmol, 1.000 g) and sodium *para*-toluenesulfonate (1.808 mmol, 0.351 g) was added MeOH (20 mL). The mixture was stirred, and, after 3 minutes, the solids dissolved resulting in a yellow solution which was stirred for 24 hours. A small amount of white solid was removed by filtration and the solution cooled to −30 °C. After several days, single crystals of **5**·3MeOH suitable for X-ray diffraction were isolated. Yield is 0.626 g (41%). No attempt was made to optimize the yield. *Method B*: to **6** (below) (0.987 mmol, 0.750 g) was added MeOH (3 mL). After the solid had dissolved, the resulting solution was allowed to stand for 2 hours. The pale yellow solution was cooled to −30 °C. After several days, pale yellow crystals of **5**·3MeOH were isolated by filtration. Concentration of the filtrate and storage at −30 °C led to the isolation of a second batch of crystals. The crystals were dried under vacuum, yield 0.564 g (76% total). Mp 135–138 °C. ^{1}H NMR ($CDCl_3$): δ 1.20 [s, 18H, $C(CH_3)_3$], 1.36 [s, 18H, $C(CH_3)_3$], 3.03 (s, 6H, CH_3OH), 3.70 [s (br), 4H, CH_2CH_2], 6.77 (d, 2H, OTs PhH), 6.82 (d, 2H, ligand PhH), 7.15 (d, 2H, OTs PhH), 7.37 (d, 2H, ligand PhH), 7.96 (s, 2H, N=CH). IR ν/cm^{-1}: 3142m (br), 2955s, 2866m, 2779m, 1637s, 1550m, 1475m, 1444m, 1417m, 1338m, 1257s, 1172s, 1124m, 1012m, 860m, 682m, 611s. Analysis. Calc.: C, 65.37; H, 7.95. Found: C, 65.40; H, 8.17%.

Salen(^{t}Bu)AlOTs(thf) 6

To **1** (2.656 mmol, 1.469 g) and sodium *para*-toluenesulfonate (2.656 mmol, 0.52 g) was added thf (50 mL). The resulting hazy yellow solution was stirred for 6 hours and the colorless precipitate allowed to settle. The mixture was filtered and the resulting solution concentrated to approximately 15 mL. The solution was slowly cooled to −30 °C, and after several days, a mass of fine needles formed. These were isolated by filtration and dried under vacuum to give 0.985 g (49%) of pale yellow, opaque crystals. Removal of the volatiles from the filtrate afforded an additional 0.64 g of a yellow solid (combined yield 80%). Single crystals of **6**·thf were grown by slow evaporation of a thf solution. Mp >110–115 °C (decomp.). ^{1}H NMR ($CDCl_3$): δ 1.30 [s, 18H, $C(CH_3)_3$], 1.49 [s, 18H, $C(CH_3)_3$], 1.83 (m, 4H, thf), 3.73 (m, 4H, thf), 3.98 [s (v br), 4H, CH_2CH_2], 6.84 (d, 2H, OTs PhH), 7.03 (d, 2H, ligand PhH), 7.34 (d, 2H, OTs PhH), 7.50 (d, 2H, ligand PhH), 8.38 (s, 2H, N=CH). IR ν/cm^{-1}: 2958s, 2879m, 1629s, 1543s, 1419s, 1340m, 1265s, 1172s, 1118m, 1037m, 873m, 812m, 613s. Analysis. Calc.: C, 67.87; H, 8.08. Found: C, 67.47; H, 8.17%.

[Salen(^{t}Bu)Al{H_2O · · · acetophenone}$_2$] Cl 7

This compound can be isolated as a crystalline material. If sealed in a capillary the crystals are stable for several hours, long enough to be studied by X-ray diffraction. However, all other data, the ^{1}H NMR, IR, elemental analysis and Mp, are exactly the same as observed for **1** with the exception that trace acetophenone is present (as a singlet at δ 2.42, for example).

Attempted oligomerization of PO with 1

To **1** (0.832 mmol, 0.460 g) or **2** (0.832 mmol, 0.513 g) was added PO (286 mmol, 20 mL) *via* syringe. The resulting pale yellow solution was stirred for 48 hours during which time a yellow, needle-like precipitate formed. The excess monomer was removed under reduced pressure resulting in a yellow solid which was identified as unchanged starting material by ^{1}H NMR.

Oligomerization of PO with 3

To **3** (0.832 mmol, 0.750 g) was added PO (286 mmol, 20 mL) *via* syringe. The resulting pale yellow solution was stirred for 48 hours. The excess monomer was removed under reduced pressure resulting in a viscous yellow oil. This was dissolved in CH_2Cl_2 (100 mL) and washed with 0.1 M HCl (50 mL) resulting in an aqueous and an organic layer. The layers were separated, the aqueous layer was washed with an additional 50 mL of distilled water, and the layers were again separated. The combined organic layers were dried over $MgSO_4$ and the solvent removed under vacuum to yield a viscous 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 ($CDCl_3$). GPC data: $M_w = 600$, $M_n = 415$, $M_z = 849$. PDI = 1.45.

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References

1 "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, $SalenH_2$.
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Paper 9/02740H