

Bimetallic and cationic aluminum with N_3O_2 chelate ligands

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Abstract

The ligands aminobis(*N*-ethylenesalicylideneimine) (Salen N_3H_3) and aminobis(*N*-propylenesalicylideneimine) (Salpen N_3H_3) were used to form the bimetallic complexes Salen $N_3H\{AlMe_2\}_2$ (**1**), Salpen $N_3H\{AlMe_2\}_2$ (**2**), Salen $N_3H\{AlMeCl\}_2$ (**3**) and Salpen $N_3H\{AlMeCl\}$ (**4**). When extracted in THF **3** and **4** redistribute to form the ionic compounds [Salen $N_3H\{Al(THF)\}]^+ [AlMe_2Cl_2]^-$ (**5**) and [Salpen $N_3H\{Al(THF)\}]^+ [AlMe_2Cl_2]^-$ (**6**). The compounds were characterized by Mp analyses, ¹H-NMR and IR, and in the case of **2** and **6** by X-ray crystallography. Additionally, the potential of **5** and **6** to serve as propylene oxide polymerization catalysts was examined. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Bimetallic; Cationic; Chelate ligands

1. Introduction

The Salen¹ class of ligands have been of great use in the isolation of higher-coordinate monometallic Group 13 complexes. Some examples include those incorporating aluminum [1], gallium [2] and indium [3] alkyls and halides and aluminum amides [4], alkoxides [5], siloxides [6] and cations that are monometallic [7] and bimetallic [8]. Beyond their fundamental interest the cations have potential as initiators of cationic oligomerization of propylene oxide [7a]. A great deal of fundamental research remains to be conducted for combinations between chelate ligands and Group 13 elements. For example, bimetallic derivatives have not been well studied. The first bimetallic combination between the Group 13 elements and Salen ligands was Salpen(GaMe₂)₂ [9]. Although it was formed under forcing conditions, it was subsequently found that such complexes, including boron [10] and mixed-metal derivatives [11], were readily accessible. One motivation for continuing work on these bimetallic complexes is

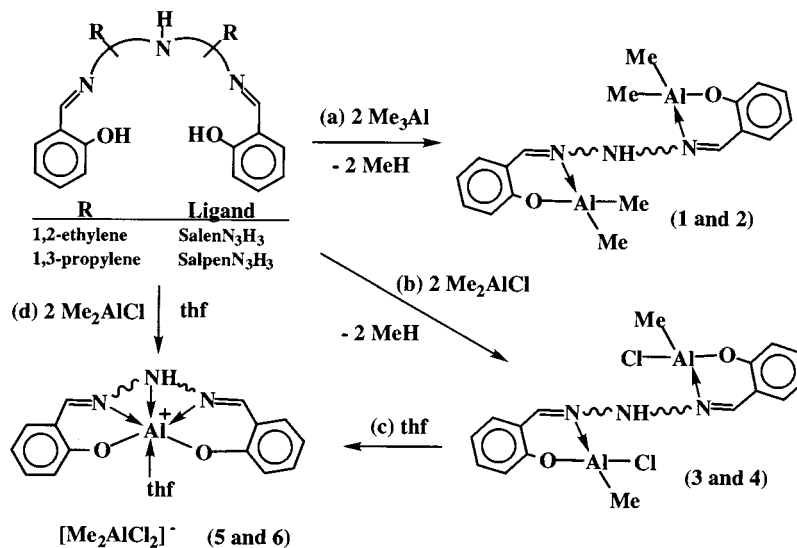
the possibility that they might be useful in the formation of two-point Lewis acidic complexes after chloride or alkyl abstraction. These complexes could be used as robust, inexpensive reagents for the hydrolysis of phosphate esters. This process is mediated by bimetallic complexes [12] in which the distance between the metals is of critical importance [13]. This is a property that would be easily manipulated in the Salen ligands.

The presence of the amine group in the related Salen N_3H_3 ligand (see Scheme 1) may lead to unusual complexes and behavior in contrast to the better-known Salen derivatives, where the ligand is generally innocent [1–8]. At the least, the amine group is of proven utility as an attachment point to polystyrene beads [14] or to biomolecules for imaging applications [15]. The majority of the work with this ligand has involved transition metals [16] and actinides [17]. In some instances, the metal complexes have utilized the water soluble ammonium chloride form of the ligand [18]. Overall, the combination of this ligand with the main group elements is an undeveloped field.

The present work will explore the use of the Salen N_3 ligand in forming aluminum complexes. Specifically, the bimetallic complexes $L\{AlMe_2\}_2$, $L\{AlMeCl\}$ and ion pairs $[L\{Al(THF)\}]^+ [AlMe_2Cl_2]^-$ with $L = SalenN_3$ and Salpen N_3 will be reported.

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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, SalenH₂.



Scheme 1. General syntheses of 1–4 (a and b) and the formation of the cations 5 and 6 (c).

2. Results and discussion

2.1. The bimetallics

2.1.1. Synthesis and spectroscopy

Compounds 1–4 are prepared by combining the SalenH₂ ligand with the appropriate Group 13 reagent in a 1:2 ligand-to-metal ratio. An alkane elimination leads to the formation of the complexes in good yields (Scheme 1(a) and (b)). The dialkyl derivatives, 1 and 2, are characterized by a single resonance in the ¹H-NMR for the methyl groups at δ –0.45 and –0.95 ppm, respectively. Further evidence for a symmetrical solution-state geometry is implied by the single imine resonances of the compounds at δ 7.95 ppm for each.

2.1.2. Structural characterization

A single-crystal X-ray analysis for compound 2 shows that the aluminum atoms adopt four-coordinate

distorted tetrahedral geometries (Fig. 1). The Al–O distances (~ 1.78 Å) are somewhat shorter than the Al–N distances (~ 1.96 Å) (Table 1). The primary deviation from tetrahedral geometry is found in the O–Al–N ($\sim 95.3^\circ$) and C–Al–C angles ($\sim 117^\circ$). A related, but more pronounced effect, occurs in the bimetallic complexes L{GaEt₂}₂ (L = Salen('Bu), Salpen('Bu), Salben('Bu) and Sallhen('Bu)), where the C–Ga–C angles are wider ($\sim 125^\circ$) and the N–Ga–O

Table 1
Bond lengths (Å) and angles (°) for 2 and 6

<i>SalpenN₃H</i> {AlMe ₂ } ₂ (2)			
Al(1)–O(1)	1.765(3)	Al(2)–O(2)	1.780(3)
Al(1)–N(1)	1.964(3)	Al(2)–N(2)	1.966(3)
Al(1)–C(21)	1.947(4)	Al(1)–C(22)	1.948(4)
Al(2)–C(23)	1.954(4)	Al(2)–C(24)	1.945(4)
O(1)–Al(1)–C(21)	113.5(2)	O(1)–Al(1)–C(22)	108.2(2)
C(21)–Al(1)–C(22)	117.3(2)	O(1)–Al(1)–N(1)	95.32(12)
C(21)–Al(1)–N(1)	107.3(2)	C(22)–Al(1)–N(1)	113.2(2)
O(2)–Al(2)–C(24)	108.9(2)	O(2)–Al(2)–C(23)	112.3(2)
C(24)–Al(2)–C(23)	118.5(2)	O(2)–Al(2)–N(2)	95.32(13)
C(24)–Al(2)–N(2)	111.1(2)	C(23)–Al(2)–N(2)	108.3(2)
<i>[SalpenN₃HAl(THF)]</i> ⁺ [<i>AlMe₂Cl</i>] ₂ [–] (6)			
Al(1)–O(1)	1.805(4)	Al(1)–O(2)	1.826(4)
Al(1)–O(3)	2.046(3)	Al(1)–N(1)	1.993(5)
Al(1)–N(2)	2.033(4)	Al(1)–N(3)	1.982(5)
O(1)–Al(1)–O(2)	173.0(2)	O(1)–Al(1)–N(3)	90.6(2)
O(2)–Al(1)–N(3)	89.8(2)	O(1)–Al(1)–N(1)	89.6(2)
O(2)–Al(1)–N(1)	90.3(2)	N(3)–Al(1)–N(1)	176.7(2)
O(1)–Al(1)–N(2)	95.6(3)	O(2)–Al(1)–N(2)	91.4(2)
N(3)–Al(1)–N(2)	86.8(2)	N(1)–Al(1)–N(2)	89.9(2)
O(1)–Al(1)–O(3)	86.4(2)	O(2)–Al(1)–O(3)	86.6(2)
N(3)–Al(1)–O(3)	92.2(2)	N(1)–Al(1)–O(3)	91.2(2)
N(2)–Al(1)–O(3)			

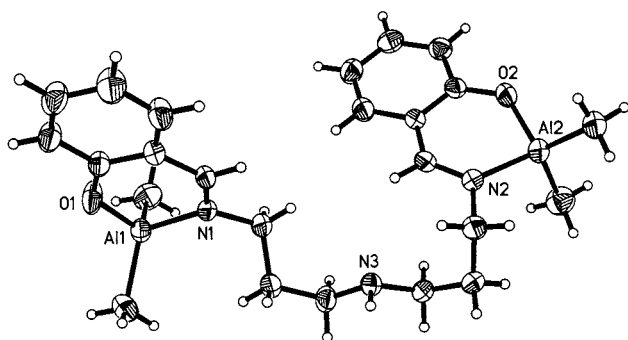


Fig. 1. Molecular structure of SalpenN₃H{AlMe₂}₂ (2).

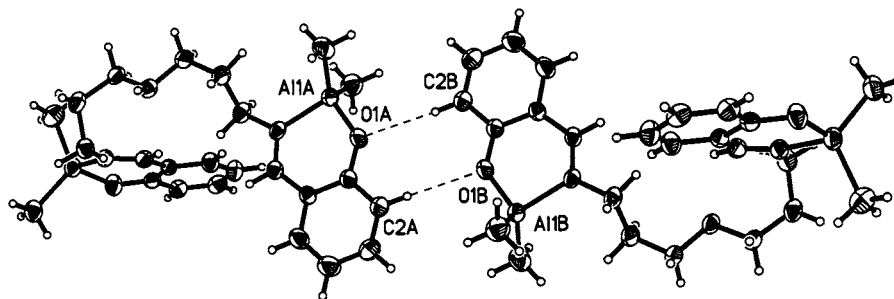


Fig. 2. The intermolecular hydrogen bonding observed for SalpenN₃H{AlMe₂}₂ (**2**).

correspondingly narrower ($\sim 92^\circ$) [10]. This may be interpreted as resulting from electronic rather than steric considerations. The N and O atoms of the Salen ligands can occupy tetrahedral sites around a coordinated metal. This is demonstrated in Salen[B(OMe)₂]₂ with a chelate O–B–N angle of $106.7(1)^\circ$ and a ligand O–B–O' angle of $112.7(1)^\circ$ [11]. Overall, the distortions seen within the bond angles of **2** can be explained by considering that the more electronegative atoms, N and O, attract more p-orbital character in their bonds and so produce more acute angles than the less electronegative constituents such as carbon. This occurrence is observed in other examples such as Cy₂GaBr(NH₂-Ph) (C–Ga–C = $124.9(4)^\circ$, Br–Ga–N = $95.8(2)^\circ$) [19] and Me₂InI(NH₂Bu) (C–In–C = $134.8(3)^\circ$, I–In–N = $90.4(1)^\circ$) [20]. It is interesting to note that the NH group does not coordinate the aluminum atoms despite its close proximity. Moreover, it is not involved in hydrogen-bonding interactions. The packing diagram does reveal a Ph–H...O hydrogen bonding interaction (~ 2.5 Å) between adjacent bimetallics (Fig. 2).

2.2. The cations

2.2.1. Synthesis and spectroscopy

Changing the solvent for the reaction in Scheme 1(d) from toluene to THF makes the formation of the ion-paired complexes **5** and **6** more favorable than that of the neutral bimetallics **3** and **4**. Alternatively, the cations can be prepared by dissolving **3** and **4** in THF (Scheme 1(c)). Although the NH group can be involved in coordinate covalent bonding (for example in SalenH₃U=O) [16a], it remains as the amine in **5** and **6**, as indicated by the NH absorbance at $\nu \sim 3200$ cm⁻¹ in the IR. The ¹H-NMR data is supportive of cations for **5** and **6**. There is only one Al–Me resonance, which can be attributed to the anion, and an integration for one coordinated THF. Both compounds have a single CH=N resonance.

2.2.2. Structural characterization

Compound **6** is structurally similar to the broad class of six-coordinate [SalenAl(base)₂]⁺ X⁻ cations, in

which the ligand occupies four sites and the bases two [7]. Thus, for **6** the aluminum atom is in an octahedral geometry with the THF molecule and the transannular amine occupying *trans* positions to one another (Fig. 3). As for the Salen complexes the imine nitrogens and two oxygens are co-planar. There are no substantial deviations from octahedral geometry; the greatest is the O(1)–Al(1)–O(2) angle at 173° . The solvent forms a longer bond to the aluminum atom (2.046(3) Å) than the ligand O atoms (~ 1.8 Å) in keeping with the difference between coordinate covalent, and covalent bonding, respectively. This trend, with very similar distances, is also observed in the [SalenAl(base)₂]⁺ cations [7].

3. Conclusions

This work represents a continuation of our pursuit of chelated cationic aluminum. Here we attempted to synthesize four-coordinate bimetallic dicationic species. The attempted reactions produced six-coordinate monometallic ion pairs instead.

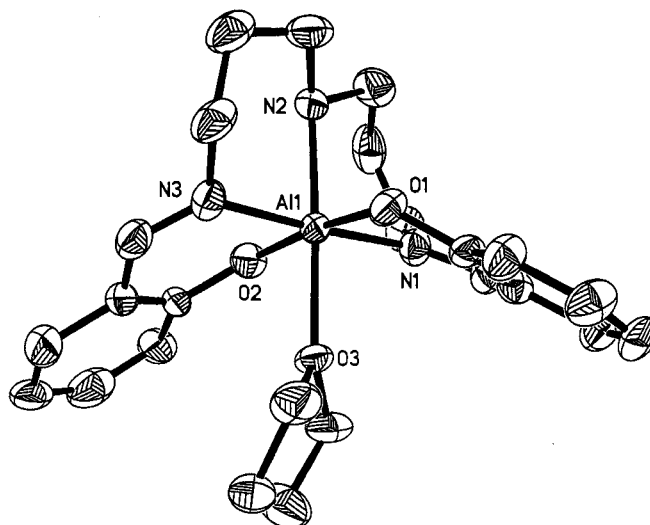


Fig. 3. Molecular structure of [SalpenN₃H{Al(THF)}]⁺ [AlMe₂Cl₂]⁻ (**6**).

Table 2
Crystallographic data for compounds **2** and **6**

Compound	2	6
Formula	C ₂₄ H ₃₅ Al ₂ N ₃ O ₂	C ₂₆ H ₃₇ Al ₂ Cl ₂ N ₃ O ₃
Formula weight	451.51	564.42
Crystal system	Triclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>Cc</i>
<i>a</i> (Å)	11.1959(9)	10.9230(8)
<i>b</i> (Å)	11.2533(9)	27.108(2)
<i>c</i> (Å)	12.1544(10)	10.1693(7)
α (°)	95.060(2)	90.00
β (°)	109.8710(10)	102.9740(10)
γ (°)	109.7490(10)	90.00
<i>V</i> (Å ³)	1319.3(2)	2934.2(4)
<i>Z</i>	2	4
<i>D</i> _{calc.} (Mg m ⁻³)	1.137	1.275
Temperature (K)	298	298
Crystal size (mm ³)	0.2 × 0.4 × 0.4	0.3 × 0.3 × 0.4
Color, habit	Pale yellow	Yellow
<i>F</i> (000)	484	1188
Absorption coefficient (mm ⁻¹)	1.901	0.312
θ range for data collection	1.83–20.00	1.50–20.00
Reflections collected	4014	4600
Independent reflections	2398 (<i>R</i> _{int} = 0.0630)	2442 (<i>R</i> _{int} = 0.0247)
Data/restraints/parameters	2398/0/284	2232/0/325
<i>R</i> ₁	0.0471	0.0462
<i>R</i> _{all}	0.0538	0.0481
Goodness-of-fit on <i>F</i> ²	0.626	0.786
Largest difference peak and hole (e Å ⁻³)	0.178 and –0.187	0.283 and –0.271

One potential application for these types of monometallic cations is as Lewis acid initiators for oxirane oligomerization. Both **5** and **6** are useful in this regard for the oligomerization of propylene oxide (PO). They produce PPO with a molecular weight ~ 700 and PDI = 1.5. Further studies are in progress to optimize the conditions for this polymerization and to determine the mechanism.

4. Experimental

4.1. 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-400 and -270 instruments operating at 270.17 and 400 MHz (¹H) and are reported relative to SiMe₄ using residual solvent as an internal referenced and are in ppm. Elemental analyses were obtained on a Perkin–Elmer 2400 analyzer. IR data were recorded as KBr pellets on a Matheson Instruments 2020 Galaxy Series spectrometer and are reported in cm⁻¹. The ligands were made from

the condensation of N(3-aminopropyl)-1,3-propylene (or ethylene) diamine and 2-hydroxy-benzaldehyde-(salicylaldehyde) through published methods [16]. Details on the spectroscopic properties of these and related ligands are also available [21]. X-ray data for **2** and **6** were collected on a Siemens SMART-CCD unit employing Mo–K α 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 2. In a typical polymerization, 20 ml of PO are condensed onto 2 mmol of the initiator and the solution allowed to stir at 25°C for 12 h before a standard work-up. The resulting oligomer was characterized by GPC.

4.1.1. SalenN₃H{AlMe₂}₂ (**1**)

To a solution of trimethylaluminum (0.695 g, 9.64 mmol) in toluene (15 ml) a solution of SalenN₃H₂ (1.500 g, 4.82 mmol) in toluene (20 ml) was added. The solution was stirred for 5 h. The solution was filtered and concentrated to 10 ml. Storage of the solution at –30°C for several days afforded a pale yellow solid, which was isolated by cannula filtration and thereafter dried under vacuum. Yield 1.81 g (89%). M.p. 105°C (dec.). ¹H-NMR (benzene-*d*₆, ppm): δ –0.45 (s, 12H, AlCH₃); 2.14 (t, 4H, CH₂NCH₂); 2.68 (t, 4H, C=NCH₂); 6.30–7.10 (m, 8H, C₆H₄); 7.78 (s, 2H, N=CH). IR (KBr, cm⁻¹): 3452 (br, w), 3273 (m), 3051 (w), 3016 (w), 2948 (m), 2923 (s), 2882 (m), 2847 (w), 1628 (s), 1549 (s), 1474 (s), 1455 (s), 1409 (m), 1341 (m), 1321 (s), 1249 (w), 1205 (m), 1188 (w), 1154 (m), 1127 (m), 1083 (w), 1071 (w), 1027 (m), 919 (m), 895 (w), 832 (m), 800 (w), 763 (s), 743 (w), 707 (m), 671 (s), 645 (m). Anal. Calc. for C₂₆H₃₇N₃O₃Al₂Cl₂: C, 62.40; H, 7.38. Found: C, 62.35; H, 7.38%.

4.1.2. SalpenN₃H{AlMe₂}₂ (**2**)

To a solution of trimethylaluminum (1.09 g, 11.8 mmol) in toluene (20 ml) a solution of SalpenN₃H₂ (2.00 g, 5.91 mmol) in toluene (20 ml) was added. The solution was stirred for 5 h. After filtration and concentration, pale yellow single crystals suitable for X-ray analysis were obtained in toluene at –30°C. The crystals were isolated by cannula filtration and the best ones were mounted in sealed capillaries for single-crystal analysis. Yield 2.64 g (99.2%). M.p. 73–76°C. ¹H-NMR (CDCl₃): δ –0.95 (s, 12H, AlCH₃); 1.71 (m, 4H, NCH₂CH₂CH₂N); 2.46 (m, 4H, CH₂NCH₂); 3.48 (t, C=NCH₂); 6.53–7.26 (m, 8H, C₆H₄); 7.94 (s, 2H, N=CH). IR (KBr, cm⁻¹): 3291 (m), 3054 (m), 3037 (m), 2930 (s), 2880 (s), 2838 (m), 2826 (m), 1624 (s), 1554 (s), 1478 (s), 1459 (s), 1438 (m), 1411 (m), 1352 (m), 1337 (s), 1318 (s), 1226 (m), 1206 (m), 1187 (m), 1153 (s), 1124 (m), 1055 (w), 1037 (w), 968 (w), 964 (w), 917 (m),

859 (w), 834 (w), 808 (w), 762 (s), 739 (w), 704 (s), 678 (s). Anal. Calc. for $C_{24}H_{35}N_3O_2Al_2$: C, 63.84; H, 7.81. Found: C, 63.75; H, 7.92%.

4.1.3. $SalenN_3H\{AlMeCl\}_2$ (**3**)

Dimethylaluminum chloride (0.594 g, 6.42 mmol) in toluene (20 ml) was added to a rapidly stirred solution of $SalenN_3H_2$ (1.00 g, 3.21 mmol) in toluene (20 ml) under nitrogen at 25°C. The solution was stirred for 5 h. After concentration and cannula filtration, a pale yellow solid was obtained. Yield 1.38 g (93%). M.p. 128°C (dec.). 1H -NMR ($CDCl_3$): δ -0.97 (s, 6H, $AlCH_3$); 2.87 (t, 4H, CH_2NCH_2); 3.81 (t, 4H, $C=NCH_2$); 6.25–7.30 (m, 8H, C_6H_4), 8.29 (2H, $N=CH$). IR (KBr, cm^{-1}): 3386 (s), 3244 (s), 3113 (m), 2961 (m), 2948 (m), 1633 (s), 1549 (s), 1478 (s), 1408 (w), 1320 (m), 126 (w), 1214 (w), 1185 (m), 1129 (w), 1032 (m), 907 (w), 803 (w), 762 (s), 669 (m), 633 (w), 553 (w), 502 (w). Anal. Calc. for $C_{26}H_{37}N_3O_3Al_2Cl_2$: C, 51.74; H, 5.43. Found: C, 51.60; H, 5.41%.

4.1.4. $SalpenN_3H\{AlMeCl\}_2$ (**4**)

Dimethylaluminum chloride (0.54 g, 5.88 mmol) in toluene (20 ml) was added to a rapidly stirred solution of $SalpenN_3H_2$ (1.00 g, 2.94 mmol) in toluene (20 ml) under nitrogen at 25°C. The solution was stirred for 5 h and a pale yellow solid yielded from the solution, which was filtered and dried under vacuum. Yield 1.41 g (97%). M.p. 108–111°C. 1H -NMR ($CDCl_3$): δ 0.20 (s, 6H, $AlCH_3$); 1.94 (m, 4H, $NCH_2CH_2CH_2N$); 3.15 (t, 4H, $NCH_2CH_2CH_2N$); 3.47 (t, 4H, $C=NCH_2$); 4.55 (s, 1H, NH); 7.25 (br, 8H, C_6H_4), 8.25 (s, 2H, $N=CH$). IR (KBr): 3362 (w), 3236 (m), 3062 (m), 2935 (s), 2289 (m), 1632 (s), 1549 (s), 1478 (m), 1318 (s), 1258 (w), 1206 (m), 1158 (m), 1045 (w), 905 (m), 803 (w), 772 (s), 669 (m), 553 (w). Anal. Calc. for $C_{22}H_{29}N_3O_2Al_2Cl_2$: C, 53.67; H, 5.94. Found: C, 53.60; H, 6.02%.

4.1.5. $[SalenN_3H\{Al(THF)\}]^+ [AlMe_2Cl_2]^-$ (**5**)

Dimethylaluminum chloride (0.480 g, 5.19 mmol) in THF (15 ml) was added to a rapidly stirred solution of $SalenN_3H_2$ (0.800 g, 2.57 mmol) in THF (15 ml) under nitrogen at 25°C. The solution was stirred for 5 h and after filtration and concentration a pale yellow solid was obtained from solution. Yield 1.21 g (87%). M.p. 101°C (dec.). 1H -NMR ($CDCl_3$): δ -0.98 (s, 6H, $AlCH_3$); 1.75 (m, 4H, THF); 3.73 (m, 4H, THF); 2.89 (t, 4H, CH_2NCH_2); 4.01 (t, 4H, $C=NCH_2$); 6.80 (m, 8H, C_6H_4), 8.18 (s, 2H, $N=CH$). IR (KBr): 3221 (m), 3057 (w), 2934 (s), 2887 (s), 2826 (w), 1630 (s), 1549 (s), 1477 (s), 1457 (s), 1407 (s), 1346 (m), 1322 (s), 1255 (w), 1207 (m), 1151 (s), 1130 (w), 1089 (w), 1041 (m), 994 (w), 918 (w), 861 (w), 805 (w), 757 (s), 669 (s), 631 (m). Anal. Calc. for $C_{24}H_{33}N_3O_3Al_2Cl_2$: C, 53.74; H, 6.20. Found: C, 53.71; H, 6.24%. A less direct synthesis involves the addition of THF (10 ml) to solid **3** (~2 mmol) with

stirring. The solid dissolved immediately and stirring was maintained for 1 h. After solvent removal the 1H -NMR data for the resulting white solid matched that of **5** above.

4.1.6. $[SalpenN_3H\{Al(THF)\}]^+ [AlMe_2Cl_2]^-$ (**6**)

Dimethylaluminum chloride (0.54 g, 5.88 mmol) in toluene (20 ml) was added to a rapidly stirred solution of $SalpenN_3H_2$ (1.00 g, 2.94 mmol) in toluene (20 ml) under nitrogen at 25°C. The solution was stirred for 5 h. After concentration and recrystallization in THF, colorless crystals were grown at -30°C and single crystals suitable for X-ray analysis were obtained. Yield 1.52 g (91%). M.p. 81–83°C. 1H -NMR ($CDCl_3$): δ 0.056 (s, 6H, $AlCH_3$); 1.83–1.85 (m, 8H, 4H from THF, 4H from $NCH_2CH_2CH_2N$); 3.46–3.76 (m, 12H, 4H from THF, 8H from $C=NCH_2$), 7.25 (m, 8H, C_6H_4), 8.21 (s, 2H, $N=CH$). IR (KBr): 3230 (m), 3113 (m), 2962 (s), 2891 (s), 1630 (s), 1551 (m), 1478 (m), 1406 (m), 1312 (m), 1262 (m), 1204 (m), 1151 (w) 1053 (s), 916 (w), 858 (m), 804 (m), 770 (m), 671 (s), 550 (w), 517 (m). Anal. Calc. for $C_{26}H_{37}N_3O_3Al_2Cl_2$: C, 55.32; H, 6.61. Found: C, 55.45; H, 6.53%. A less direct synthesis involves the addition of THF (15 ml) to solid **4** (~3 mmol) with stirring. The solid dissolved immediately and stirring was maintained for 1 h. After solvent removal the 1H -NMR data for the resulting white solid matched that of **6** above.

5. Supplementary material

Crystallographic data including full tables of bond lengths and angles, unit cell view and observed and calculated structure factors are available from the Cambridge Crystallographic Data Centre, CCDC nos. 134947 and 134948 for **2** and **6**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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