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Syntheses and reactions of Saltren–Group 13 complexes

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Abstract

Neutral Group 13 combinations with the Saltren ligand (tris(((2-hydroxybenzyl)amino)ethyl)amine)) have been prepared and their reactivity explored. The majority of the compounds are of formula Saltren$(MR_2)_3$ where M = B; R = OMe (**1**), OEt (**2**), O^{n}Pr (**3**); M = Al; R = Me (**4**), Et (**5**), ^{i}Bu (**6**) and R = Et for M = Ga (**7**) and In (**8**). Mono-, $[\text{SaltrenHAlMe}]_n$ (**9**), and tetra-metallic, Saltren$(AlMe_2)_3$–$AlMe_3$ form when one and four equivalents of $AlMe_3$ are added to the ligand. Compound **9** can be converted to **4** by the addition of two or three additional molecules of $AlMe_3$. Compounds **1** and **4** form unique zwitterionic compounds, $[\text{SaltrenH}_3\{M(OSiPh_3)_3\}_3]$ (M = B (**11**) and Al (**12**) when combined with six equivalents of Ph_3SiOH. Attempts to prepare those of formula Saltren$\{MR(OSiPh_3)\}_3$ where M = B and Al led to an inseparable mixture of compounds. All of the compounds were characterized by standard techniques and, in the case of **1**, **4**, **7** and **12**, by X-ray crystallography. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Saltren; Group 13; Reactivity

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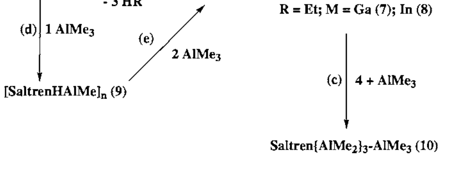
1. Introduction

The SalenH_2(*N*,*N*′alkylene (or arylene) bis(salicylideneimine)) ligands have been used extensively to support various Group 13 bonding schemes. Depending on the metal, ligand, and stoichiometry, a diverse range of structural types can be isolated. Predominant among these are complexes having a 1:1 metal–ligand stoichiometry {e.g. SalenMR (R = alkyl [1,2], halide or amide [3], alkoxide [4], siloxide [2] and $[\text{SalenM(-base)}_2]^+$ [5]} and those having a 2:1 metal–ligand stoichiometry (e.g. Salen$(MR_2)_2$) {where M = B (R = aryl [6] or alkoxide [7]), Al [8], Ga [9], In [10] (R = alkyl)}. It would be interesting to discover whether the same types of compounds might be accessible with other multidentate ligands, such as the SaltrenH_3(tris(((2-hydroxybenzyl)amino)ethyl)amine)) class. The use of these and related ligands in the preparation of charged Group 13 complexes, generally with a 1:1 metal–ligand stoichiometry, has already been demonstrated [11]. The present study is focused on the preparation of neutral combinations between the SaltrenH_3 ligand and the Group 13 elements.



Scheme 1. General syntheses of compounds **1–10**.

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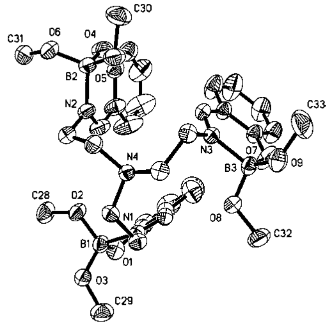


Fig. 1. Molecular structure and atom numbering scheme for Saltren{B(OMe)$_2$}$_3$ (**1**).

2. Results and discussion

2.1. Saltren–Group 13 alkyls

A homologous series of bimetallic Saltren derivatives can be prepared by combining the Group 13 reagent with the ligand in toluene. In order to obtain the boron derivatives an alcohol elimination reaction must be utilized since an alkane elimination route with BR$_3$ is not effectual (Scheme 1). The alcohol elimination has been used previously to prepare boron derivatives of various aminophenols [12] and Salen [7]. Alkane elimination reactions are, however, useful for the Al, Ga and In derivatives (Scheme 1b). The spectroscopic data for **1**–**8** are consistent with the maintenance of a single environment for the MR$_2$ units. There is one resonance for these groups and only one resonance for the imine CH group. Thus, the 'arms' of the ligand are equivalent in solution.

Compounds **1**, **4** and **7** were characterized by X-ray crystallography. Thus, a comparison can be made in the behavior of the Saltren ligand through the series B, Al and Ga (Figs. 1–3, respectively). Compounds **1** and **4** display structures that have approximate C_3 symmetry (space group $R\bar{3}$ for **4**). In this arrangement, the MR$_2$ groups are directed away from the center of the molecule minimizing any contacts of these groups with the ligand. In contrast, the gallium derivative appears more randomly oriented with two of the GaEt$_2$ groups facing one another. The M–O(ligand) (1.487(5), 1.724(7) and 1.875(8) Å) and M–N distances (1.619(5), 1.960(7), 2.025(7) Å) increase through the series $B < Al < Ga$ in keeping with the increasing size of the atoms. Overall, these distances compare closely with those of the related bimetallic Salen derivatives of formula, Salen(MR$_2$)$_2$.

In each of the structures, the central nitrogen of the ligand is arranged so that the lone electron pair is pointed inward. However, it can still be used to coordinate an external molecule of AlMe$_3$ to form a tetrametallic derivative (Scheme 1c). This is demonstrated by addition of AlMe$_3$ to **4** in the formation of **10**. The

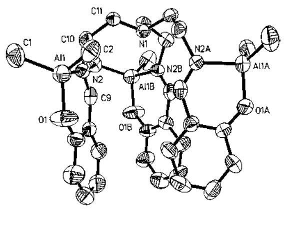


Fig. 2. Molecular structure and atom numbering scheme for Saltren{AlMe$_2$}$_3$ (**4**).

^{1}H-NMR displays two sharp singlets for the Al–Me groups (AlMe$_2$, −0.72, AlMe$_3$, −0.92 ppm).

When one equivalent of AlMe$_3$ is combined with the SaltrenH$_3$ ligand a white solid precipitates (Scheme 1d). An elemental analysis corresponds to the formula [SaltrenHAlMe]$_n$ (**9**) which is presumably polymeric. Similar products, for instance, are obtained when AlMe$_3$ is combined with ethylenediamine [13]. Combining **9** with 2 mol of AlMe$_3$, either at ambient temperature or with reflux in toluene, leads to high yields of **4**. It is notable that a molecule of formula [SaltrenAlMe(AlMe$_2$)]$_n$ is not isolated. This may indicate that the Saltren ligand is not suitable for the formation of aggregated compounds. Indeed, all of the previously reported compounds have been monomeric (with either one or two ligands around a central metal) [11].

2.2. Saltren–Group 13 siloxides

There are relatively few molecular borosiloxanes and aluminosiloxanes despite the fact that aluminosilicates are one of the most prevalent materials on the earth. This is due principally to the fact that the M–O–Si unit tends to oligomerize. This tendency can be overcome by the use of sterically encumbered ligands (such as the use of 2,6-(^{i}Pr)$_2$C$_6$H$_5$N(SiMe$_3$)Si(OH)$_3$ in the formation of mineral-like aluminosilicates [14]) and often in conjunction with chelating ligands. This has been demonstrated with acac (Al(OSiPh$_3$)$_2$(acac) (**13**) [15]) and salen ligands (SalenAlOSiPh$_3$ (**14**) [2]). In these compounds and elsewhere, the Ph$_3$SiO ligand has been of particular utility {see, for instance, [(Ph$_3$SiO)$_2$Al(μ-O^{t}Bu)]$_2$ (**15**) [16]}.

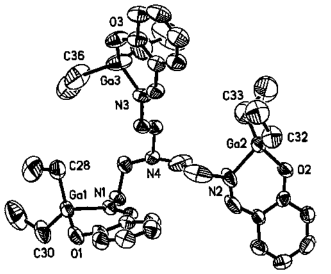


Fig. 3. Molecular structure and atom numbering scheme for Saltren{GaEt$_2$}$_3$ (**7**).

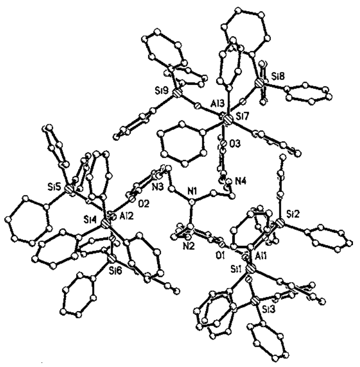
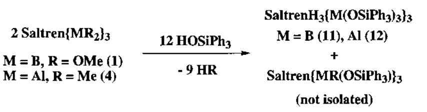


Fig. 4. Molecular structure and atom numbering scheme for $SaltrenH_3\{Al(OSiPh_3)_3\}_3$ (**12**).

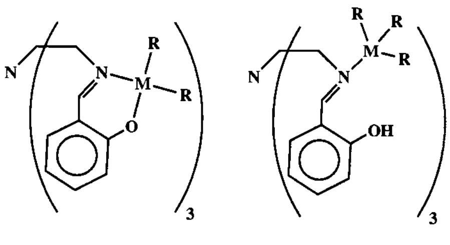
Thus, triphenylsilanol was viewed as a good ligand for making Saltren–Group 13 siloxides. Accordingly, the combination of six equivalents of the silanol with **1** and **4** was conducted with the expectation that the compounds, $Saltren\{M(OSiPh_3)_2\}_3$ might form. Surprisingly, the isolated products are the Lewis acid–base complexes $SaltrenH_3\{M(OSiPh_3)_3\}_3$ [with M = B (**11**) and Al (**12**)]. The molecular structure of **12** is shown in Fig. 4. The formation of **11** and **12** cannot be explained by considering only the steric requirements of the Ph_3SiO ligand (Scheme 2). In compound **1**, for example, the chelate angle, O–Al–N is 94.4(3)° and the Me–Al–Me′ angle 116.0(3)°. In **13** these two angles are 115° (between the Ph_3SiO groups) and 98° (the 'bite' angle of the acac ligand). Thus, it would appear that two of the Ph_3SiO groups could easily fit around an aluminum atom having two of its coordination sites taken up by the Saltren ligand. A general depiction of compounds **1**–**12** is shown in Fig. 5 .

The Al–O distances in **12** range from 1.694(11) to 1.800(11) Å. Those to the Saltren ligand are consistently shorter than those to the Ph_3SiO ligands. These latter distances compare closely with those observed for the $(Ph_3SiO)_3Al$–base {base = THF (**16**) [17], H_2O (**17**) [18] and Et_2O (**18**) [18]} series of compounds. The Al–O–Si angles for **12** as well as the majority of the compounds reported in the literature span a fairly wide range. For instance, in **12** they are 153.8(7) to 170.9(8)° and in **15** they are 153.5(2) and 177.6(2)°.

The tris mono-siloxy derivatives $Saltren\{MR(OSiPh_3)\}_3$ (M = B; R = OMe and M = Al, R = Me) could not be prepared by the addition of three equivalents of $HOSiPh_3$ to **1** or **4**. When these reactions are conducted a mixture of products results.



Scheme 2. General synthesis of compounds **11** and **12**.



(a) (b)

Fig. 5. General depiction of compounds **1**–**10** (a) and **11** and **12** (b).

3. Experimental section

3.1. 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-400 and -270 instruments at 270.17 (^1H) MHz. Chemical shifts are reported relative to $SiMe_4$ 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} (see Section 4). The $SaltrenH_3$ ligand was prepared according to the literature [11]. X-ray data were collected on a Siemens CCD diffractometer using graphite monochromated Mo–K_α (0.71073 Å) radiation. All calculations were performed on a PC using the Siemens software package, SHELXTL-Plus. Selected bond lengths and angles for complexes **1**, **4**, **7** and **12** are listed in Table 1, while details of the crystal data and a summary of data collection parameters for the complexes are given in Table 2.

3.2. *Saltren[B(OMe)$_2$]$_3$ (**1**)*

To a stirred toluene solution (25 ml) of $SaltrenH_3$ (1.00 g, 2.15 mmol) was added trimethylborate (0.67 g, 6.46 mmol). The resulting solution was refluxed for 6 h. After filtration and concentration, pale yellow crystals were grown at −30°C (0.85 g, 61%). M.p. 184°C. ^1H-NMR (270 MHz, $CDCl_3$): δ 2.91 (br, 6H, NCH_2), 3.29 (s, 18H, OCH_3), 3.81 (br, 6H, NCH_2), 5.50 (d, 3H, Ph*H*), 6.32 (t, 3H, Ph*H*), 7.03 (d, 3H, Ph*H*), 7.43 (t, 3H, Ph*H*), 8.59 (s, 3H, NC*H*). Analysis for $C_{33}H_{45}N_4O_9B_3$: Calc.: C 58.82, H 6.67. Found: C 59.14, H 7.07%.

3.3. *Saltren[B(OEt)$_2$]$_3$ (**2**)*

The same procedure for **1** was followed with $SaltrenH_3$ (1.00 g, 2.15 mmol) and triethylborate (0.94 g, 6.46 mmol): yellow solid (1.0 g, 63%). M.p. 113°C.

Table 1
Selected bond lengths (Å) and angles (°) for 1, 4, 7 and 12

$\text{Saltren}\{\text{B(OMe)}_2\}_3$ (1)					
B(1)–O(3)	1.404(5)	O(3)–B(1)–O(2)	112.4(3)	O(6)–B(2)–N(2)	110.4(3)
B(1)–O(2)	1.422(5)	O(3)–B(1)–O(1)	110.6(3)	O(5)–B(2)–N(2)	105.7(3)
B(1)–O(1)	1.487(5)	O(2)–B(1)–O(1)	112.5(3)	O(4)–B(2)–N(2)	108.1(3)
B(1)–N(1)	1.619(5)	O(3)–B(1)–N(1)	110.8(3)	O(8)–B(3)–O(9)	110.7(3)
B(2)–O(6)	1.413(5)	O(2)–B(1)–N(1)	104.3(3)	O(8)–B(3)–O(7)	111.3(4)
B(2)–O(5)	1.418(5)	O(1)–B(1)–N(1)	105.9(3)	O(9)–B(3)–O(7)	110.8(3)
B(2)–O(4)	1.489(5)	O(6)–B(2)–O(5)	113.4(4)	O(8)–B(3)–N(3)	106.2(3)
B(2)–N(2)	1.588(5)	O(6)–B(2)–O(4)	108.5(3)	O(9)–B(3)–N(3)	109.8(3)
B(3)–O(8)	1.408(5)	O(5)–B(2)–O(4)	110.6(3)	O(7)–B(3)–N(3)	107.9(3)
B(3)–O(9)	1.412(5)				
B(3)–O(7)	1.456(5)				
B(3)–N(3)	1.616(5)				
$\text{Saltren}\{\text{AlMe}_2\}_3$ (4)					
Al(1)–O(1)	1.724(7)	O(1)–Al(1)–C(1)	114.4(3)	C(2)–Al(1)–N(2)	111.5(3)
Al(1)–C(1)	1.944(8)	O(1)–Al(1)–C(2)	111.4(3)	C(3)–O(1)–Al(1)	132.5(7)
Al(1)–C(2)	1.948(7)	C(1)–Al(1)–C(2)	116.0(3)	C(9)–N(2)–Al(1)	121.0(5)
Al(1)–N(2)	1.960(7)	O(1)–Al(1)–N(2)	94.4(3)	C(10)–N(2)–Al(1)	120.7(6)
O(1)–C(3)	1.306(9)	C(1)–Al(1)–N(2)	107.0(3)		
$\text{Saltren}\{\text{GaEt}_2\}_3$ (7)					
Ga(1)–O(1)	1.875(8)	O(1)–Ga(1)–C(28)	109.8(4)	O(2)–Ga(2)–N(2)	93.0(4)
Ga(1)–C(28)	1.926(11)	O(1)–Ga(1)–C(30)	108.0(5)	C(34)–Ga(2)–N(2)	112.5(7)
Ga(1)–C(30)	1.970(11)	C(28)–Ga(1)–C(30)	124.1(6)	C(32)–Ga(2)–N(2)	104.3(6)
Ga(1)–N(1)	2.025(7)	O(1)–Ga(1)–N(1)	92.6(4)	C(38)–Ga(3)–O(3)	107.2(7)
Ga(2)–O(2)	1.863(8)	C(28)–Ga(1)–N(1)	107.1(4)	C(38)–Ga(3)–N(3)	105.5(10)
Ga(2)–C(34)	1.92(2)	C(30)–Ga(1)–N(1)	110.7(4)	O(3)–Ga(3)–N(3)	92.9(4)
Ga(2)–C(32)	1.958(12)	O(2)–Ga(2)–C(34)	111.2(6)	C(38)–Ga(3)–C(36)	130.3(10)
Ga(2)–N(2)	1.994(10)	O(2)–Ga(2)–C(32)	108.7(5)	O(3)–Ga(3)–C(36)	105.9(6)
Ga(3)–C(38)	1.52(3)	C(34)–Ga(2)–C(32)	122.9(6)	N(3)–Ga(3)–C(36)	108.7(6)
Ga(3)–O(3)	1.875(9)				
Ga(3)–N(3)	2.007(9)				
Ga(3)–C(36)	2.02(2)				
$\text{SaltrenH}_3\{\text{Al(OSiPh}_3)_3\}_3$ (12)					
Al(1)–O(6)	1.700(11)	O(6)–Al(1)–O(5)	113.0(6)	O(12)–Al(3)–O(10)	112.8(5)
Al(1)–O(5)	1.694(11)	O(6)–Al(1)–O(4)	114.9(5)	O(11)–Al(3)–O(3)	108.1(5)
Al(1)–O(4)	1.719(10)	O(5)–Al(1)–O(4)	112.1(5)	O(12)–Al(3)–O(3)	106.7(5)
Al(1)–O(1)	1.794(10)	O(6)–Al(1)–O(1)	108.4(5)	O(10)–Al(3)–O(3)	100.1(5)
Al(2)–O(8)	1.688(10)	O(5)–Al(1)–O(1)	108.6(5)	Si(1)–O(4)–Al(1)	153.8(7)
Al(2)–O(9)	1.696(11)	O(4)–Al(1)–O(1)	98.6(5)	Si(2)–O(5)–Al(1)	165.6(7)
Al(2)–O(7)	1.716(10)	O(8)–Al(2)–O(9)	113.3(6)	Si(3)–O(6)–Al(1)	169.3(7)
Al(2)–O(2)	1.790(11)	O(8)–Al(2)–O(7)	114.3(5)	Si(4)–O(7)–Al(2)	154.7(6)
Al(3)–O(11)	1.701(10)	O(9)–Al(2)–O(7)	112.9(5)	Si(5)–O(8)–Al(2)	173.6(7)
Al(3)–O(12)	1.696(10)	O(8)–Al(2)–O(2)	108.2(5)	Si(6)–O(9)–Al(2)	170.9(8)
Al(3)–O(10)	1.718(10)	O(9)–Al(2)–O(2)	107.4(6)	Si(7)–O(10)–Al(3)	159.7(7)
Al(3)–O(3)	1.800(11)	O(7)–Al(2)–O(2)	99.5(5)	Si(8)–O(11)–Al(3)	167.4(7)
Si(1)–O(4)	1.611(10)	O(11)–Al(3)–O(12)	112.7(5)	Si(9)–O(12)–Al(3)	168.0(7)
Si(2)–O(5)	1.604(11)	O(11)–Al(3)–O(10)	115.2(5)		
Si(3)–O(6)	1.604(11)				
Si(4)–O(7)	1.598(10)				
Si(5)–O(8)	1.597(11)				
Si(6)–O(9)	1.594(11)				
Si(7)–O(10)	1.600(10)				
Si(8)–O(11)	1.601(10)				
Si(9)–O(12)	1.603(10)				

^{1}H-NMR (270 MHz, $CDCl_3$): δ 1.15 (m, 18H, OCH_2CH_3), 2.95 (br, 6H, NCH_2), 3.56 (m, 12H, OCH_2), 3.86 (br, 6H, NCH_2), 5.49 (d, 3H, Ph*H*), 6.30 (t, 3H, Ph*H*), 7.00 (d, 3H, Ph*H*), 7.42 (t, 3H, Ph*H*), 8.66 (s, 3H, NC*H*). Analysis for $C_{39}H_{57}N_4O_9B_3$: Calc.: C 61.81, H 7.52. Found: C 61.81, H 7.74%.

3.4. *Saltren[B(O^{n}Pr)$_2$]$_3$ (**3**)*

The same procedure for **1** was followed with SaltrenH$_3$ (1.00 g, 2.15 mmol) and tri-*n*-propylborate (1.22 g, 6.46 mmol): yellow solid (0.88 g, 49%). M.p. 45°C. ^{1}H-NMR (270 MHz, $CDCl_3$): δ 0.85 (m, 18H,

Table 2
Summary of data collection and structure solution parameters

Compound	**(1)**	**(4)**	**(7)**	**(12)**
Formula	$C_{33}H_{45}B_3N_4O_9$	$C_{11}H_{15}AlN_{1.33}O$	$C_{39}H_{57}Ga_3N_4O_3$	$C_{204}H_{178}Al_3N_4O_{12}Si_9$
Formula weight	674.16	208.89	839.05	3353.05
Crystal system	Monoclinic	Trigonal	Triclinic	Triclinic
Space group	$P2_1/c$	$R-3$	$P-1$	$P-1$
a (Å)	16.595(1)	14.446(1)	10.1989(7)	19.796(1)
b (Å)	11.6424(7)	14.446(1)	14.482(1)	21.339(1)
c (Å)	18.708(1)	35.016(5)	16.368(1)	25.486(1)
α (°)	90	90	70.472(1)	102.011(1)
β (°)	91.458(1)	90	79.414(1)	97.891(1)
γ (°)	90	120	69.825(1)	116.111(1)
V (Å^3)	3613.4(4)	6329(1)	2132.3(3)	9127.6(9)
Z	4	18	2	2
$F(000)$	1432	2004	872	3518
$D_{\mathrm{calc.}}$ (g cm^{-3})	1.239	0.987	1.307	1.220
Crystal size (mm^3)	0.2 × 0.4 × 0.7	0.4 × 0.4 × 0.4	0.3 × 0.3 × 0.3	0.4 × 0.4 × 0.4
Colour, habit	Pale yellow, needle	Pale yellow, cube	Pale yellow, cube	Pale yellow, cube
Temperature (K)	298	298	298	298
Absorption coefficient (mm^{-1})	0.088	0.120	0.919	0.200
θ range for data collection (°)	1.23–22.50	1.73–16.47	1.32–17.50	1.11–19.00
Reflections collected	13267	4045	4846	24252
Independent reflections	4661 ($R_{\mathrm{int}} = 0.0551$)	762 ($R_{\mathrm{int}} = 0.0457$)	2671 ($R_{\mathrm{int}} = 0.0752$)	14150 ($R_{\mathrm{int}} = 0.0381$)
Data/restraints/parameters	7634/0/442	707/0/130	2655/0/442	14083/0/2078
R_1	0.0659	0.0687	0.0550	0.0755
R_{all}	0.0922	0.1247	0.0617	0.0944
Goodness-of-fit on F^2	0.994	1.069	1.027	1.049
Largest difference peak and hole	0.140, −0.168	0.444, −0.413	0.313, −0.685	0.692, −0.438

CH2CH_3), 1.50 (m, 12H, OCH_2CH_2), 2.93 (br. 6H, NCH_2), 3.45 (m, 12H, OCH_2), 3.83 (br, 6H, NCH_2), 5.53 (d, 3H, Ph*H*), 6.26 (m, 3H, Ph*H*), 6.90 (d, 3H, Ph*H*), 7.39 (m, 3H, Ph*H*), 8.52 (s, 3H, NC*H*). Analysis for $C_{45}H_{69}N_4O_9B_3$: Calc.: C 64.20, H 8.19. Found: C 63.83, H 8.46%.

3.5. *Saltren[AlMe$_2$]$_3$* ***(4)***

Trimethylaluminum (0.47 g, 6.46 mmol) in 20 ml of toluene was added to a rapidly stirred solution of SaltrenH$_3$ (1.00 g, 2.15 mmol) in toluene (20 ml) at 25°C. The vigorous exothermic reaction was allowed to stir for 5 h, and the volatiles removed under reduced pressure. Recrystallization from a hexane/toluene (5:1) solution yielded yellow crystals suitable for single-crystal X-ray analysis (1.30 g, 96%). M.p. 90°C. ^{1}H-NMR (270 MHz, CDCl$_3$): 0 −0.74 (s, 18H, $AlCH_3$), 2.89 (t, 6H, NCH_2), 3.57 (t, 6H, NCH_2), 6.65 (t, 3H, Ph*H*), 6.78 (d, 3H, Ph*H*), 6.85 (d, 3H, Ph*H*), 7.41 (t, 3H, Ph*H*), 7.89 (s, 3H, NC*H*). Analysis for $C_{33}H_{45}N_4O_3Al_3$: Calc.: C 63.28, H 7.18. Found: C 63.15, H 7.04%.

3.5.1. *Alternate synthesis of* **4**

Trimethylaluminum (0.18 g, 2.50 mmol) in toluene (20 ml) was added to a rapidly stirred suspension of **9** (0.65 g, 1.25 mmol) in toluene (30 ml) at 25°C. The mixture was stirred at reflux for 3 h, resulting in a clear yellow solution and then filtered. The volatiles were removed under reduced pressure. Recrystallization from a hexane/toluene (5:1) yielded Saltren[Me$_2$Al]$_3$ (**4**) (0.60 g) as determined by ^{1}H-NMR.

3.6. *Saltren[AlEt$_2$]$_3$* ***(5)***

Prepared as for **4** with triethylaluminum (0.74 g, 6.46 mmol), toluene (20 ml) and SaltrenH$_3$ (1.00 g, 2.15 mmol) in toluene (20 ml) yielding a yellow solid (1.4 g, 91%). M.p. 75°C. ^{1}H-NMR (270 MHz, CDCl$_3$): δ −0.08 (m, 12H, $AlCH_2$), 0.96 (m, 18H, $AlCH_2CH_3$), 2.94 (br, 6H, NCH_2), 3.57 (br, 6H, NCH_2), 6.72 (m, 9H, Ph*H*) 6.89 (m, 3H, Ph*H*), 8.01 (s, 3H, NC*H*). Analysis for $C_{39}H_{57}N_4O_3Al_3$: Calc.: C 65.94, H 8.02. Found: C 65.67, H 7.95%.

3.7. *Saltren[Al(^{i}Bu)$_2$]$_3$* ***(6)***

Prepared as for **4** with tri-iso-butylaluminum (1.28 g, 6.46 mmol) in toluene (20 ml) and SaltrenH$_3$ (1.00 g, 2.15 mmol) in toluene (20 ml) to yield a yellow solid (1.1 g, 58%). M.p. 60°C. ^{1}H-NMR (270 MHz, CDCl$_3$): δ −0.01 (m, 12H, $AlCH_2$), 0.90 (m, 36H, $CH(CH_3)_2$), 1.80 (m, 6H, CH_2CH), 2.92 (t, 6H, NCH_2), 3.55 (t, 6H, NCH_2), 6.72 (t, 3H, Ph*H*), 6.87 (d, 3H, Ph*H*), 7.00 (d, 3H, Ph*H*), 7.41 (t, 3H, Ph*H*), 7.98 (s, 3H, NC*H*). Analysis for $C_{51}H_{81}N_4O_3Al_3$: Calc.: C 69.72, H 9.22. Found: C 69.58, H 9.11%.

*3.8. Saltren[GaEt$_2$]$_3$ (**7**)*

Prepared as for 4 with triethylgallium (1.35 g, 8.62 mmol) in toluene (20 rnL) and SaltrenH$_3$ (1.00 g, 2.15 mmol) in toluene (20 ml) to yield yellow crystals (1.1 g, 61%). M.p. 83°C. ^{1}H-NMR (270 MHz, CDCl$_3$): δ 0.41 (m, 12H, GaCH_2), 1.03 (m, 18H, CH$_2$CH_3), 2.85 (t, 6H, NCH_2), 3.63 (t, 6H, NCH_2), 6.59 (m, 3H, PhH), 6.84 (m, 6H, PhH), 7.75 (m, 3H, PhH), 7.85 (s, 3H, NCH). Analysis for $C_{39}H_{57}N_4O_3Ga_3$: Calc.: C 55.85, H 6.79. Found: C 55.97, H 6.56%.

*3.9. Saltren[InEt$_2$]$_3$ (**8**)*

Prepared as for **4** with triethylindium (1.31 g, 6.46 mmol) in toluene (20 ml) and SaltrenH$_3$ (1.00 g, 2.15 mmol) in toluene (20 ml) to yield a yellow solid, (1.9 g 91%). M.p. 187°C. ^{1}H-NMR (270 MHz, DMSO): δ 0.45 (m, 12H, InCH_2), 1.10 (m, 18H, CH$_2$CH_3), 2.85 (br, 6H, NCH_2), 3.60 (br, 6H, NCH_2), 6.45 (t, 3H, PhH), 6.61 (d, 3H, PhH), 7.15 (m, 6H, PhH), 8.22 (s, 3H, NCH). Analysis for $C_{39}H_{57}N_4O_3In_3$: Calc.: C 48.09, H 5.85. Found: C 48.03, H 5.44%.

*3.10. [SaltrenH(AlMe)]$_n$ (**9**)*

Trimethylaluminum (0.23 g, 3.23 mmol) in 20 ml of toluene was added to a rapidly stirred solution of SaltrenH$_3$ (1.50 g, 3.23 mmol) in toluene (20 ml) at 25°C. The addition took place over 3–5 min, resulting in a yellow solution and pale yellow solid. The mixture was allowed to stir for 5 h at 25°C, and then filtered. The solid was dried in vacuo, yielding 1.0 g, 93%. M.p. > 260°C. Analysis for $C_{28}H_{31}N_4O_3Al$: Calc.: C 67.42, H 6.22. Found: C 66.99, H 5.92%.

*3.11. Saltren[AlMe$_2$]$_3$[AlMe$_3$] (**10**)*

Trimethylaluminum (0.62 g, 8.62 mmol) in 20 ml of toluene was added to a rapidly stirred solution of SaltrenH$_3$ (1.00 g, 2.15 mmol) in toluene (20 ml) at 25 _C. The vigorous exothermic reaction was allowed to stir for 5 h, and the volatiles removed under reduced pressure. Recrystallization from a hexane/toluene (5:1) solution yielded a yellow solid (1.2 g, 80%). M.p. 80°C. ^{1}H-NMR (270 MHz, CDCl$_3$): δ -0.92 (s, 9H, AlCH_3), -0.72 (s, 18H, AlCH_3), 2.94 (t, 6H, NCH_2), 3.62 (t, 6H, NCH_2), 6.82 (t, 3H, PhH), 6.96 (m, 6H, PhH), 7.44 (t, 3H, PhH), 8.00 (s, 3H, NCH). Analysis for $C_{36}H_{54}N_4O_3Al_4$: Calc.: C 61.91, H 7.73. Found: C 61.52, H 7.47%.

*3.12. SaltrenH$_3$[B(OSiPh$_3$)$_3$]$_3$ (**11**)*

To a solution of Saltren[B(OMe)$_2$]$_3$ (0.70 g, 1.03 mmol) in toluene (30 ml) was added triphenylsilanol (1.70 g, 6.18 mmol). The resulting solution was refluxed for 5 h. Removal of solvent under vacuum followed by recrystalization from CH$_2$Cl$_2$ solution yielded a yellow solid (1.4 g, 47%). M.p. 144°C. ^{1}H-NMR (270 MHz, CDCl$_3$): δ 2.60 (m, 6H, NCH_2), 3.05 (m, 6H, NCH_2), 5.75 (m, 3H, PhH), 6.33 (m, 3H, PhH), 6.48 (m, 3H, PhH), 7.07–7.42 (br, 138H, PhH), 7.57 (m, 3H, NCH). Analysis for $C_{189}H_{165}N_4O_{12}Si_9B_3$: Calc.: C 76.57, H 5.56. Found: C 76.23, H 5.40%.

*3.13. SaltrenH$_3$[Al(OSiPh$_3$)$_3$]$_3$ (**12**)*

Prepared as for **11** with Saltren[AlMe$_2$]$_3$ (0.63 g, 1.00 mmol) in toluene (30 ml) and triphenylsilanol (1.66 g, 6.00 mmol) to yield orange crystals at -30°C (1.3 g, 44%). M.p. 173°C. ^{1}H-NMR (270 MHz, CDCl$_3$): δ 0.93 (m, 6H, NCH_2), 2.20 (m, 6H, NCH_2), 5.02 (m, 3H, PhH), 5.88 (m, 3H, PhH), 6.73–7.51 (br, 141H, PhH), 11.70 (m, 3H, NCH). Analysis for $C_{189}H_{165}N_4O_{12}Si_9Al_3$: Calc.: C 75.33, H 5.47. Found: C 75.14, H 5.28%.

4. Supplementary material available

Tables of atomic coordinates and equivalent isotropic thermal parameters, hydrogen atom parameters, anisotropic thermal parameters and bond lengths and angles for **1**, **4**, **7** and **12** are available on request from the authors.

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References

[1] S.J. Dzugan, V.L. Goedken, Inorg. Chem. 25 (1986) 2858.
[2] D.A. Atwood, M.S. Hill, J.A. Jegier, D. Rutherford, Organometallics 16 (1997) 2659.
[3] D. Rutherford, D.A. Atwood, Organometallics 15 (1996) 4417.
[4] P.L. Gurian, L.K. Cheatham, J.W. Barron, A.R. Ziller, J. Chem. Soc. Dalton Trans. (1991) 1449.
[5] (a) D.A. Atwood, J.A. Jegier, D. Rutherford, J. Am. Chem. Soc. 117 (1995) 6779. (b) M.G. Davidson, C. Lambert, I. Lopez-Solera, P.R. Raithby, R. Snaith, Inorg. Chem. 34 (1995) 3765. (c) D.A. Atwood, J.A. Jegier, D. Rutherford, Inorg. Chem. 35 (1996) 63.
[6] D.A. Atwood, J.A. Jegier, M.P. Remington, D. Rutherford, Aust. J. Chem. 49 (1996) 1333.
[7] P. Wei, D. Atwood, Inorg. Chem. 36 (1997) 4060.

[8] M.S. Hill, P. Wei, D.A. Atwood, Polyhedron 17 (1998) 811.

[9] K.S. Chong, S.J. Rettig, A. Storr, J. Trotter, Can. J. Chem. 55 (1977) 2540.

[10] D. Rutherford, J.A. Jegier, D.A. Atwood, Bull. Chem. Soc. Jpn. 70 (1997) 2093.

[11] (a) S. Liu, S.J. Rettig, C. Orvig, Inorg. Chem. 31 (1992) 5408. (b) E. Wong, P. Caravan, S. Liu, S.J. Rettig, C. Orvig, Inorg. Chem. 35 (1996) 715. (c) P. Caravan, C. Orvig, Inorg. Chem. 36 (1997) 236.

[12] P. Wei, D. Atwood, Inorg. Chem. (1998) submitted.

[13] Z. Jiang, L.V. Interrante, Chem. Mater. 2 (1990) 439.

[14] (a) M.L. Montero, I. Uson, H.W. Roesky, Angew. Chem. Int. Ed. Engl. 33 (1994) 2103. (b) M.L. Montero, A. Voigt, M. Teichert, I. Uson, H.W. Roesky, Angew. Chem. Int. Ed. Engl. 34 (1995) 2504.

[15] J.H. Wengrovius, M.F. Garbauskas, E.A. Williams, R.C. Going, P.E. Donahue, J.F. Smith, J. Am. Chem. Soc. 108 (1986) 982.

[16] M. Veith, M. Jarczyk, V. Huch, Angew. Chem. Int. Ed. Engl. 36 (1997) 117.

[17] A.W. Apblett, A.C. Warren, A.R. Barron, Can. J. Chem. 70 (1992) 771.

[18] A.W. Apblett, A.R. Barron, J. Cryst. Spect. Res. 23 (1993) 529.