

Syntheses and reactions of Saltren–Group 13 complexes

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Abstract

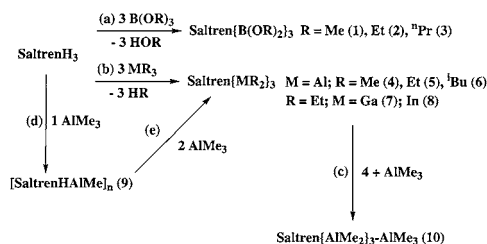
Neutral Group 13 combinations with the Saltren ligand (tris(((2-hydroxybenzyl)amino)ethyl)amine)) have been prepared and their reactivity explored. The majority of the compounds are of formula Saltren(MR₂)₃ where M = B; R = OMe (1), OEt (2), OⁿPr (3); M = Al; R = Me (4), Et (5), ⁱBu (6) and R = Et for M = Ga (7) and In (8). Mono-, [SaltrenHAlMe]_n (9), and tetra-metallic, Saltren(AlMe₂)₃–AlMe₃ form when one and four equivalents of AlMe₃ are added to the ligand. Compound 9 can be converted to 4 by the addition of two or three additional molecules of AlMe₃. Compounds 1 and 4 form unique zwitterionic compounds, [SaltrenH₃{M(OSiPh₃)₃}₃] (M = B (11) and Al (12) when combined with six equivalents of Ph₃SiOH. Attempts to prepare those of formula Saltren{MR(OSiPh₃)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

1. Introduction

The SalenH₂(*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 [SalenM(base)₂]⁺ [5]} and those having a 2:1 metal–ligand stoichiometry (e.g. Salen(MR₂)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 SaltrenH₃(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 SaltrenH₃ ligand and the Group 13 elements.



Scheme 1. General syntheses of compounds 1–10.

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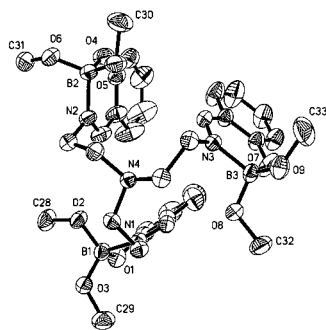


Fig. 1. Molecular structure and atom numbering scheme for Saltren{B(OMe)₂}₃ (**1**).

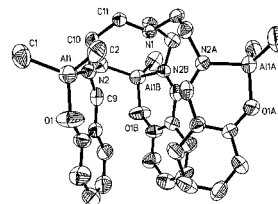
2. Results and discussion

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 BR₃ 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 MR₂ 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 C₃ symmetry (space group $R\bar{3}$ for **4**). In this arrangement, the MR₂ 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 GaEt₂ 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(MR₂)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 AlMe₃ to form a tetrametallic derivative (Scheme 1c). This is demonstrated by addition of AlMe₃ to **4** in the formation of **10**. The



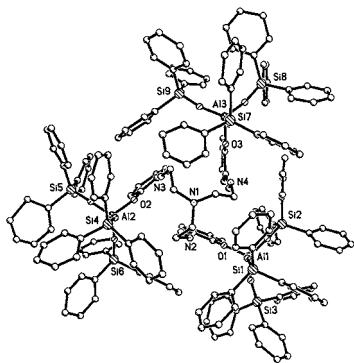
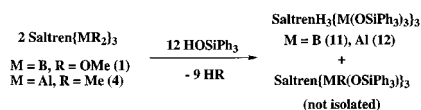


Fig. 4. Molecular structure and atom numbering scheme for SaltrenH₃{Al(OSiPh₃)₃}₃ (**12**).

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(OSiPh₃)₂}₃ might form. Surprisingly, the isolated products are the Lewis acid–base complexes SaltrenH₃{M(OSiPh₃)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 Ph₃SiO 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 Ph₃SiO groups) and 98° (the 'bite' angle of the acac ligand). Thus, it would appear that two of the Ph₃SiO 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 Ph₃SiO ligands. These latter distances compare closely with those observed for the (Ph₃SiO)₃Al–base {base = THF (**16**) [17], H₂O (**17**) [18] and Et₂O (**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(OSiPh₃)₃}₃ (M = B; R = OMe and M = Al, R = Me) could not be prepared by the addition of three equivalents of HOSiPh₃ to **1** or **4**. When these reactions are conducted a mixture of products results.



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

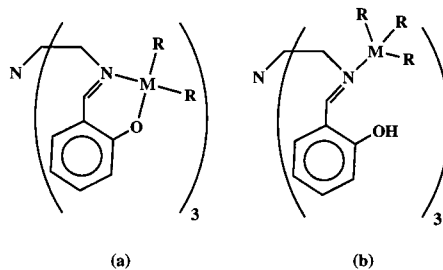


Fig. 5. General depiction of compounds **1**–**10** (a) and **11** and **12** (b).

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 SiMe₄ 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 SaltrenH₃ 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 SaltrenH₃ (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, CDCl₃): δ 2.91 (br, 6H, NCH₂), 3.29 (s, 18H, OCH₃), 3.81 (br, 6H, NCH₂), 5.50 (d, 3H, PhH), 6.32 (t, 3H, PhH), 7.03 (d, 3H, PhH), 7.43 (t, 3H, PhH), 8.59 (s, 3H, NCH). Analysis for C₃₃H₄₅N₄O₉B₃: 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 SaltrenH₃ (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

Saltren{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)				
Saltren{AlMe₂}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)		
Saltren{GaEt₂}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)				
SaltrenH₃{Al(OSiPh₃)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)				

¹H-NMR (270 MHz, CDCl₃): δ 1.15 (m, 18H, OCH₂CH₃), 2.95 (br, 6H, NCH₂), 3.56 (m, 12H, OCH₂), 3.86 (br, 6H, NCH₂), 5.49 (d, 3H, PhH), 6.30 (t, 3H, PhH), 7.00 (d, 3H, PhH), 7.42 (t, 3H, PhH), 8.66 (s, 3H, NCH). Analysis for C₃₉H₅₇N₄O₉B₃: Calc.: C 61.81, H 7.52. Found: C 61.81, H 7.74%.

3.4. Saltren[B(OⁿPr)₂]₃ (3)

The same procedure for **1** was followed with SaltrenH₃ (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. ¹H-NMR (270 MHz, CDCl₃): 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 ₃ N ₄ O ₉	C ₁₁ H ₁₅ AlN _{1.33} O	C ₃₉ H ₅₇ Ga ₃ N ₄ O ₃	C ₂₀₄ H ₁₇₈ Al ₃ N ₄ O ₁₂ Si ₉
Formula weight	674.16	208.89	839.05	3353.05
Crystal system	Monoclinic	Trigonal	Triclinic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>R</i> –3	<i>P</i> –1	<i>P</i> –1
<i>a</i> (Å)	16.595(1)	14.446(1)	10.1989(7)	19.796(1)
<i>b</i> (Å)	11.6424(7)	14.446(1)	14.482(1)	21.339(1)
<i>c</i> (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)
<i>V</i> (Å ³)	3613.4(4)	6329(1)	2132.3(3)	9127.6(9)
<i>Z</i>	4	18	2	2
<i>F</i> (000)	1432	2004	872	3518
<i>D</i> _{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 (<i>R</i> _{int} = 0.0551)	762 (<i>R</i> _{int} = 0.0457)	2671 (<i>R</i> _{int} = 0.0752)	14150 (<i>R</i> _{int} = 0.0381)
Data/restraints/parameters	7634/0/442	707/0/130	2655/0/442	14083/0/2078
<i>R</i> ₁	0.0659	0.0687	0.0550	0.0755
<i>R</i> _{all}	0.0922	0.1247	0.0617	0.0944
Goodness-of-fit on <i>F</i> 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

CH₂CH₃), 1.50 (m, 12H, OCH₂CH₂), 2.93 (br. 6H, NCH₂), 3.45 (m, 12H, OCH₂), 3.83 (br. 6H, NCH₂), 5.53 (d, 3H, PhH), 6.26 (m, 3H, PhH), 6.90 (d, 3H, PhH), 7.39 (m, 3H, PhH), 8.52 (s, 3H, NCH). Analysis for C₄₅H₆₉N₄O₉B₃: Calc.: C 64.20, H 8.19. Found: C 63.83, H 8.46%.

3.5. Saltren[AlMe₂]₃ (4)

Trimethylaluminum (0.47 g, 6.46 mmol) in 20 ml of toluene was added to a rapidly stirred solution of SaltrenH₃ (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. ¹H-NMR (270 MHz, CDCl₃): 0 – 0.74 (s, 18H, AlCH₃), 2.89 (t, 6H, NCH₂), 3.57 (t, 6H, NCH₂), 6.65 (t, 3H, PhH), 6.78 (d, 3H, PhH), 6.85 (d, 3H, PhH), 7.41 (t, 3H, PhH), 7.89 (s, 3H, NCH). Analysis for C₃₃H₄₅N₄O₃Al₃: 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[Me₂Al]₃ (4) (0.60 g) as determined by ¹H-NMR.

3.6. Saltren[AlEt₂]₃ (5)

Prepared as for 4 with triethylaluminum (0.74 g, 6.46 mmol), toluene (20 ml) and SaltrenH₃ (1.00 g, 2.15 mmol) in toluene (20 ml) yielding a yellow solid (1.4 g, 91%). M.p. 75°C. ¹H-NMR (270 MHz, CDCl₃): δ – 0.08 (m, 12H, AlCH₂), 0.96 (m, 18H, AlCH₂CH₃), 2.94 (br. 6H, NCH₂), 3.57 (br. 6H, NCH₂), 6.72 (m, 9H, PhH) 6.89 (m, 3H, PhH), 8.01 (s, 3H, NCH). Analysis for C₃₉H₅₇N₄O₃Al₃: 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 SaltrenH₃ (1.00 g, 2.15 mmol) in toluene (20 ml) to yield a yellow solid (1.1 g, 58%). M.p. 60°C. ¹H-NMR (270 MHz, CDCl₃): δ – 0.01 (m, 12H, AlCH₂), 0.90 (m, 36H, CH(CH₃)₂), 1.80 (m, 6H, CH₂CH), 2.92 (t, 6H, NCH₂), 3.55 (t, 6H, NCH₂), 6.72 (t, 3H, PhH), 6.87 (d, 3H, PhH), 7.00 (d, 3H, PhH), 7.41 (t, 3H, PhH), 7.98 (s, 3H, NCH). Analysis for C₅₁H₈₁N₄O₃Al₃: Calc.: C 69.72, H 9.22. Found: C 69.58, H 9.11%.

3.8. *Saltren*[GaEt₂]₃ (**7**)

Prepared as for **4** with triethylgallium (1.35 g, 8.62 mmol) in toluene (20 mL) and *Saltren*H₃ (1.00 g, 2.15 mmol) in toluene (20 mL) to yield yellow crystals (1.1 g, 61%). M.p. 83°C. ¹H-NMR (270 MHz, CDCl₃): δ 0.41 (m, 12H, GaCH₂), 1.03 (m, 18H, CH₂CH₃), 2.85 (t, 6H, NCH₂), 3.63 (t, 6H, NCH₂), 6.59 (m, 3H, PhH), 6.84 (m, 6H, PhH), 7.75 (m, 3H, PhH), 7.85 (s, 3H, NCH). Analysis for C₃₉H₅₇N₄O₃Ga₃: Calc.: C 55.85, H 6.79. Found: C 55.97, H 6.56%.

3.9. *Saltren*[InEt₂]₃ (**8**)

Prepared as for **4** with triethylindium (1.31 g, 6.46 mmol) in toluene (20 mL) and *Saltren*H₃ (1.00 g, 2.15 mmol) in toluene (20 mL) to yield a yellow solid, (1.9 g, 91%). M.p. 187°C. ¹H-NMR (270 MHz, DMSO): δ 0.45 (m, 12H, InCH₂), 1.10 (m, 18H, CH₂CH₃), 2.85 (br, 6H, NCH₂), 3.60 (br, 6H, NCH₂), 6.45 (t, 3H, PhH), 6.61 (d, 3H, PhH), 7.15 (m, 6H, PhH), 8.22 (s, 3H, NCH). Analysis for C₃₉H₅₇N₄O₃In₃: Calc.: C 48.09, H 5.85. Found: C 48.03, H 5.44%.

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

Trimethylaluminum (0.23 g, 3.23 mmol) in 20 mL of toluene was added to a rapidly stirred solution of *Saltren*H₃ (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 C₂₈H₃₁N₄O₃Al: Calc.: C 67.42, H 6.22. Found: C 66.99, H 5.92%.

3.11. *Saltren*[AlMe₂]₃[AlMe₃] (**10**)

Trimethylaluminum (0.62 g, 8.62 mmol) in 20 mL of toluene was added to a rapidly stirred solution of *Saltren*H₃ (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. ¹H-NMR (270 MHz, CDCl₃): δ –0.92 (s, 9H, AlCH₃), –0.72 (s, 18H, AlCH₃), 2.94 (t, 6H, NCH₂), 3.62 (t, 6H, NCH₂), 6.82 (t, 3H, PhH), 6.96 (m, 6H, PhH), 7.44 (t, 3H, PhH), 8.00 (s, 3H, NCH). Analysis for C₃₆H₅₄N₄O₃Al₄: Calc.: C 61.91, H 7.73. Found: C 61.52, H 7.47%.

3.12. *Saltren*H₃[B(OSiPh₃)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 recrystallization from CH₂Cl₂ solution yielded a yellow solid (1.4 g, 47%). M.p. 144°C. ¹H-NMR (270 MHz, CDCl₃): δ 2.60 (m, 6H, NCH₂), 3.05 (m, 6H, NCH₂), 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 C₁₈₉H₁₆₅N₄O₁₂Si₉B₃: Calc.: C 76.57, H 5.56. Found: C 76.23, H 5.40%.

3.13. *Saltren*H₃[Al(OSiPh₃)₃]₃ (**12**)

Prepared as for **11** with *Saltren*[AlMe₂]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. ¹H-NMR (270 MHz, CDCl₃): δ 0.93 (m, 6H, NCH₂), 2.20 (m, 6H, NCH₂), 5.02 (m, 3H, PhH), 5.88 (m, 3H, PhH), 6.73–7.51 (br, 141H, PhH), 11.70 (m, 3H, NCH). Analysis for C₁₈₉H₁₆₅N₄O₁₂Si₉Al₃: 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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