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The Use of Five-Coordinate Aluminum Alkyls To Prepare Molecules Containing a Single Al−O−Si Linkage

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The present work entails the synthesis and first structural characterization of complexes possessing a single Al−O−Si linkage. These are of the formula LAlOSiPh$_3$ (L = Salen(^{t}Bu) (*N*,*N*′-ethylenebis(3, 5-di-*tert*-butylsalicylideneimine)) (**11**); Salpen(^{t}Bu) *N*,*N*′-propylenebis-(3,5-di-*tert*-butylsalicylideneimine)) (**12**); Salophen(^{t}Bu) (*N*,*N*′-phenylenebis(3,5-di-*tert*-butylsalicylideneimine)) (**13**); and Salomphen(^{t}Bu) (*N*,*N*′-(3,4-dimethylphenylene)bis(3,5-di-*tert*-butylsalicylideneimine)) (**14**). They are formed by combining the novel five-coordinate aluminum alkyl starting materials L(^{t}Bu)AlR (where L = Salen(^{t}Bu), R = Me (**1**), Et (**2**), ^{i}Bu (**3**); Salpen(^{t}Bu), R = Me (**4**), Salophen(^{t}Bu) R = Me (**5**), Et (**6**), ^{i}Bu (**7**); and Salomphen, R = Me (**8**), Et (**9**), ^{i}Bu (**10**)) with Ph$_3$SiOH in toluene. All of the compounds were characterized spectroscopically and, in the case of **1**, **10**, **11**, **12**, and **13**, by X-ray crystallography.

Introduction

Aluminosilicates are ubiquitous in nature, and many new compositions have been, and continue to be, prepared synthetically.[1] They are of importance in a wide range of catalytic, synthetic and separation applications. There has been a drive recently to prepare soluble, molecular aluminosilicates that may act as building blocks to the solid-state material or as a means of modeling the behavior of the bulk material. This search has been partially realized in recent reports of soluble molecules having core structures similar to that of Linde type A zeolites.[2] Prior to this report, the most relevant compounds were cubic aluminosilsequioxanes[3] and tetrameric alkoxide siloxides.[4] These compounds are particularly important considering the fact that molecular group 13 silicates, in general, have not been extensively explored. Previously published works have described dimeric structures ([R$_2$M(μ-OSiR′$_3$)]$_2$),[5] examples containing acac supporting ligands,[6] those resulting from the insertion of a group 13 moiety into the Si−O bonds of siloxanes,[7] and homoleptic species, Al(OSiPh$_3$)$_3$·base.[8] Higher oligomers at the interface of molecules and materials constitute a unique and growing area of aluminosilicate chemistry.[9]

The present contribution to this area entails the synthesis and first structural characterization of complexes possessing a single Al−O−Si linkage. These are of the formula LAlOSiPh$_3$ (where L = Salen(^{t}Bu) (*N*,*N*′-alkylenebis(3,5-di-*tert*-butylsalicylideneimine). They are formed by combining the novel five-coordinate aluminum alkyl starting materials, LAlR, with Ph$_3$SiOH in toluene.

Results and Discussion

Five-Coordinate Aluminum Alkyls. Synthesis and Spectroscopic Characterization. The Salen(^{t}Bu) ligand can be envisioned as an extremely soluble "platform" upon which unique chemistry involving chelated metals may be conducted.[10,11] When the metal is coordinated in the N$_2$O$_2$ plane, six-coordinate complexes can be formed. When the metal is perched above this plane, only one additional coordination site is generally available. Since aluminum is a +3 metal, it was expected that a five-coordinate complex with the aluminum perched above the plane would result for the −AlR derivatives. This geometry was anticipated in the structure of SalpenAlEt[12] and in the recent characterization of Salcen(^{t}Bu)AlEt.[13]

Following procedures similar to those for the preparation of these two compounds, high yields of Me, Et, and

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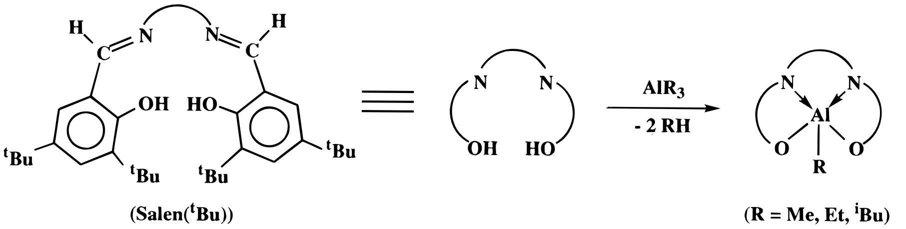
Scheme 1. General Syntheses of the Five-Coordinate Alkyl Derivatives (1−10)[a]



[a] The connection between the two nitrogens can be $(CH_2)_2$ (for Salen(^{t}Bu)), $(CH_2)_3$ (for Salpen(^{t}Bu)), C_6H_4 (for Salophen(^{t}Bu)), and 4,5-$(Me_2)C_6H_2$ (for Salomphen(^{t}Bu)).

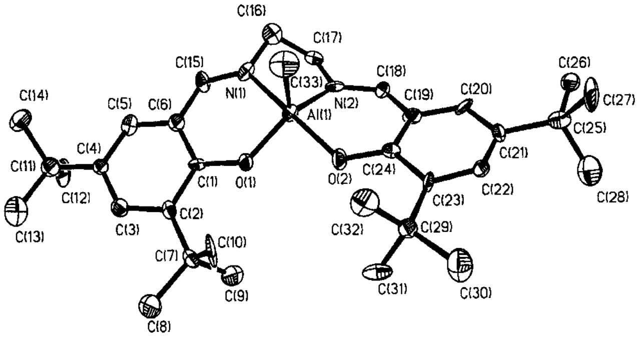


Figure 1. Molecular structure and atom numbering scheme for Salen(^{t}Bu)AlMe (**1**).

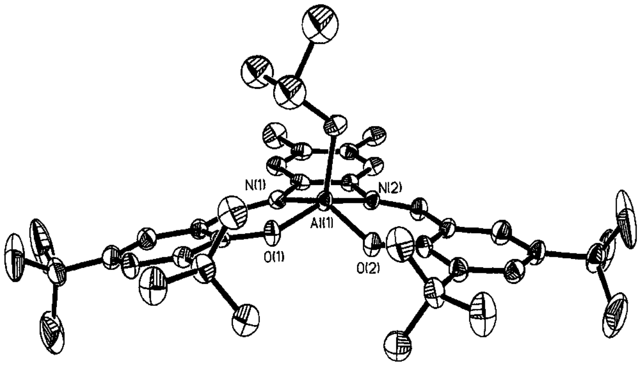


Figure 2. Molecular structure and atom numbering scheme for Salomphen(^{t}Bu)Al^{i}Bu (**10**).

^{i}Bu aluminum derivatives of Salen(^{t}Bu) (**1**−**3**), Salophen(^{t}Bu) (**5**−**7**), and Salopmphen(^{t}Bu) (**8**−**10**) can be obtained (Scheme 1). The Salpen(^{t}Bu) ligand is problematic in this regard. Reasonable yields of the Me derivative (**4**) can be obtained but none for either the Et or ^{i}Bu derivatives. For the heavier group 13 congeners (Ga and In), this ligand has demonstrated a tendency to form open, rather than closed, structures.[14]

The spectroscopic data for these complexes are consistent with monomeric chelated AlR units. For the methyl derivatives the chemical shifts demonstrate a slightly greater shielding when incorporated into a ligand possessing an aryl "backbone" (**1**, −1.11 ppm; **4**, −0.98 ppm; **5**, −1.22 ppm; **8**, −1.24 ppm). The same general trend holds for the ipso-carbon protons in the Et and ^{i}Bu derivatives. However, the values also compared closely to other related complexes containing a five-coordinate aluminum alkyl, such as SalanAlMe(AlMe$_2$)$_2$ (δ −0.35 ppm) and SalomphanAlMe(AlMe$_2$)$_2$ (δ −1.25 ppm).[15] In every case, there are two sharp singlets for the ^{t}Bu groups of the phenolic portion of the ligand.

Structural Characterization. In **1**, the central aluminum atom is in a geometry that is best described as distorted trigonal bipyramidal (Figure 1). The axial atoms, N(1) and O(2), form somewhat longer bonds to Al(1) (2.069(10) and 1.831(9) Å, respectively) than the equatorially disposed N(2) and O(1) (2.025(11) and 1.779(9) Å, respectively). The N(1)−Al(1)−O(2) angle is 158.7(5)°, while the N(2)−Al(1)−O(1) angle is 130.6(5)°. The remaining angles range from 76.4(4)° for N(1)−Al(1)−N(2) to 116.9(5)° for O(1)−Al(1)−C(33). In **10**, the central aluminum adopts a square pyramidal geometry in which the Al atom is located 0.54 Å above the N_2O_2 plane (Figure 2). The difference in geometries of **1** and **10** can be explained in terms of the greater flexibility of the ethyl backbone in **1** and the tendency for the hydrogens within this group to adopt a staggered conformation when possible. In comparison, SalenAlEt adopts a geometry that can best be described as one that is intermediary between that of **1** and **10**.[12] From these compounds, it is clear that the bulky Salen(^{t}Bu) ligands provide all of the usual attractive features of the Salen class of ligands but have the improved features of enhanced solubility. The existence of [Salpen(^{t}Bu)InOMe]$_2$ is an indication,[16] however, that the ^{t}Bu groups do not necessarily enforce the formation of a monomer.

The compound $(Me_3Al)_2$(diphos) serves as a useful representative of a four-coordinate Al−Me bond length (average = 1.96 Å).[17] The lengths in **1** (1.963(17) Å) and **10** (1.972(9) Å) do not differ from this value to any appreciable extent.

Molecules Possessing a Single Aluminosiloxane Linkage. Synthesis and Spectroscopic Characterization. Mixing of any of the alkyl derivatives **1**−**10** with Ph$_3$SiOH results in the formation of the novel aluminosiloxane monomers **11**−**14**. There was no apparent difference in reactivity or yield when using either the Me, Et, or ^{i}Bu derivatives. They are soluble in toluene and benzene and do not decompose on standing in air (in solution or as a solid) for several hours.

The ^{1}H NMR data for **11**−**14** are similar to what was observed for **1**−**10** with respect to chemical shifts associated with the ligand. However, an interesting feature is observed in the ^{1}H NMR of **11**. Three Si−Ph resonances can be discerned in the region of δ 7.0−7.4 ppm (Figure 1 in the Supporting Information). A view of the structure (Figure 3) shows that the three phenyl

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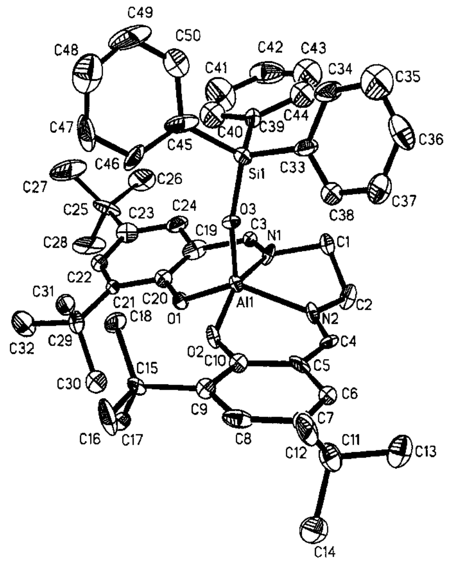
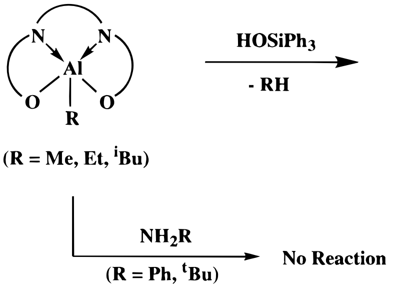


Figure 3. Molecular structure and atom numbering scheme for Salen(^{t}Bu)AlOSiPh$_3$ (**11**).

groups are found in unique environments. Most prominently, the phenyl group (C39...) situated at the concave side of the Al—O—Si bond is flattened relative to the other two phenyl groups. This feature is less well-defined in **12**—**14**. A related complex, AcacenTiOBPh$_3$, displays similar behavior.[18] The ^{29}Si chemical shifts fall in the narrow range of δ −28.77 to −29.99 ppm. These are similar to what was observed for Al(OSiPH$_3$)(thf) (−24.6 ppm) and Al(OSiPh$_3$)$_3$(H$_2$O)(thf)$_2$ (−25.7 ppm).[8a] For other molecular aluminosilicates where the Si has an RSiO$_3$ coordination environment the shifts are ≈ −60 ppm.[22]



In a previous review, it was predicted that "the reactvity of five-coodinate complexes would certainly be different than that of the four-coordinate derivatives."[19] However in the limited number of reactions of four- and five-coordinate aluminum alkyls with silanols there appears to be little difference. On the other hand, the formation of amides through alkane elimination proceeds readily for the four-coordinate derivatives but not at all for the five-coordinate ones. These must be formed through a salt elimination between the five-coordinate halide and the amido lithium derivative.[20]

Structural Characterization. The monomeric nature of **11**, **12**, and **14** in the solid state was confirmed by X-ray analyses. These structures clearly demonstrate how changing the ligand backbone changes the resulting coordination of the aluminum atom. In **11** (Figure 3), the ligand forms the basal coordination plane of a square pyramidal geometry about the aluminum. The aluminum atom is located 0.52 Å above the N$_2$O$_2$ plane. The apical site is occupied by the oxygen of the siloxane. However, the Al—O$_3$ (1.719(14) Å) distance is still substantially shorter than those to the ligand oxygens (1.807(16) and 1.820(19) Å). Compound **13** (Figure 2 in the Supporting Information) adopts the same structural arrangement. It also demonstrates a relatively short Al—O (apical) distance of 1.603(9) Å. The aluminum atom is perched at 0.48 Å above the N$_2$O$_2$ plane. In **12** (Figure 4), the geometry around the aluminum atom is best described as trigonal bipyramidal. The O1 and N2 atoms occupy the axial sites and form an angle of 169.5(1) Å. Atoms N1, O2, and O3 occupy equatorial sites and form angles that range from 99.0(1)° (O1—Al—O3) to 120.7(1)° (O2—Al—O3).

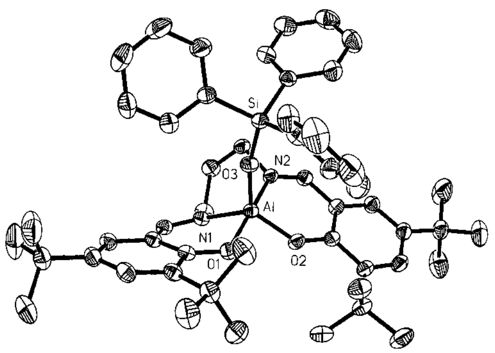


Figure 4. Molecular structure and atom numbering scheme for Salpen(^{t}Bu)AlOSiPh$_3$ (**12**).

These structures are unique because they are the first instances where a single Al—O—Si linkage has been structurally characterized. Molecules possessing this linkage have an almost overwhelming tendency to aggregate. This has its extreme manifestation in the bonding within zeolites. Indeed, the metrical parameters within **3** bear the most similarity to oligomeric aluminosilicates. For example, in the structure of [(2,6-Me$_2$C$_6$H$_3$)N(SiMe$_3$)SiO$_3$Al—dioxane]$_4$,[2c] which has the core structure of the Linde type-A zeolite, the Al—O—Si linkages average 140(5)°. For **11**—**13**, this angle is 157.9(14)°, 166.3(2)°, and 166.8(6)°, respectively. To the best of our knowledge, these are the widest Al—O—Si angles ever reported. The distances in the LTA complex range from 1.703(4) to 1.712(4)Å for Al—O bonds and 1.615(4) to 1.623(4)Å for the Si—O bonds. In **3**, the Al—O and Si—O distances fall within this range (1.719(14) and 1.608(13) Å, respectively). By comparison, the Al—O and Si—O distances for dimeric derivatives such as [Me$_2$AlOSiH$_2$(C$_2$H)]$_2$ are 1.85(1) and 1.651(2) Å, respectively.[4a]

Systems with Si—O bond lengths on the order of 1.6 Å are well-known to possess π-bonding. This is the case, for instance, in the silsesquioxane, (CySiO)$_7$O$_2$(μ^2-O$_3$)-AlO=PPh$_3$, for which the Si—O distances are 1.593−1.595 Å.[5] The obtuse Al—O—Si bond angles demonstrated by **11**—**13** are similar to the Al—O—C angle in Me$_2$(BHT)Al(PMe$_3$) (164.5(4)°) for which π bonding is supported by photoelectron spectroscopy.[21] In five-coordinate complexes like **11**—**14**, such π bonding might

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Table 1. Crystal Data for Salen(^{t}Bu)AlMe (1), Salomphen(^{t}Bu)Al^{i}Bu (10), Salen(^{t}Bu)AlOSiPh$_3$ (11), Salpen(^{t}Bu)AlOSiPh$_3$ (12), and Salophen(^{t}Bu)AlOSiPh$_3$ (13)

compd	**1**	**10**	**11**	**12**	**13**
formula	$C_{33}H_{49}N_2O_2Al$	$C_{49}H_{67}N_2O_2Al$	$C_{50}H_{61}N_2O_3SiAl$	$C_{58}H_{71}N_{2O3}Al_{Si}$	$C_{54}H_{61}N_2O_3AlSi$
fw	532.7	743.0	793.1	899.2	841.1
cryst syst	monoclinic	monoclinic	triclinic	triclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$	P-1	P-1	$P2_1/c$
a (Å)	10.057(3)	14.156(4)	10.837(3)	11.6224(6)	18.333(7)
b (Å)	18.962(3)	13.298(1)	14.055(4)	14.8998(8)	14.261(6)
c (Å)	17.595(2)	24.794(2)	17.027(4)	17.7648(9)	19.127(7)
α (deg)			96.03(2)	100.030(1)	
β (deg)	106.53(2)	97.44(2)	99.74(2)	104.931(1)	108.16(2)
γ (deg)			112.46(2)	109.485(1)	
V (Å^3)	3216.5(11)	4628.4(14)	2320.8(11)	2685.6(2)	4751(3)
Z	4	4	2	2	4
D_{calc} (g/cm^3)	1.100	1.066	1.135	1.112	1.176
cryst size (mm)	0.4 × 0.4 × 0.2	0.8 × 0.5 × 0.4	0.8 × 0.2 × 0.05	0.4 × 0.4 × 0.6	(0.3)3
scan range (deg)	0.45	0.60	0.47		0.60
no. of reflns collected	5413	7647	7207	15523	7158
no. of indep reflns	4199	6059	6026	15523	5833
no. of obsd reflns with $F > x\sigma F$; x	1155; 5	2376; 4	1496; 5	12244; 4	1955; 4
no. of params	343	484	424	586	550
R	0.0554	0.0612	0.0961	0.0646	0.0695
R_w	0.0599	0.0619	0.0108	0.0591	0.0765
GOF	2.85	2.45	4.37	1.16	1.07
diff peak (e/Å^{-3})	0.22	0.28	0.47	0.53	0.34

be envisioned to involve the participation of d orbitals on aluminum. However, at present, an Al−O−Si π-bonded system for these complexes is not proposed. Current research is directed toward gathering further evidence for this type of bonding and determining whether such bonding might also occur in five-coordinate, monomeric amides, phosphides, and arsenides.

Experimental Section

All manipulations were conducted under an inert atmosphere using a combination of drybox and Schlenk line techniques. Toluene was dried by refluxing over sodium−benzophenone prior to use. NMR data were obtained on Jeol instruments (270 or 400 MHz) at 270 Hz (^{1}H), 67.81 MHz (^{13}C), and 53.67 MHz (^{29}Si). Infrared data were obtained on a Galaxy FT-IR using KBr and are reported in cm^{-1}. Elemental analyses were conducted on a Perkin-Elmer 2400 unit. The results are listed in the Supporting Information. Compounds **1**−**10** were generally prepared and isolated as described for **1** with some minor variations as listed in the Supporting Information. In all cases, the spectroscopic data for the isolated solids matched that of the single-crystalline products.

Salen(^{t}Bu)AlMe (1). To a stirred toluene solution (30 mL) of Salen(^{t}Bu)H$_2$ (10.00 g, 20.29 mmol) was added Me$_3$Al (1.46 g, 20.29 mmol) in toluene (10 mL). The exothermic reaction was allowed to stir at 25 °C for 1 h before being refluxed for 2 h to yield a clear yellow solution. Removal of the solvent under vacuum yielded a yellow crystalline solid (yield 10.61 g, 98%): mp 213−218 °C; ^{1}H NMR (CDCl$_3$) δ −1.11 (s, 3H, $\mathrm{AlC}H_3$), 1.33 (s, 18H, $\mathrm{C(C}H_3)$), 1.53 (s, 18H, $\mathrm{C(C}H_3)$), 3.66 (m, 2H, $\mathrm{NC}H_2$), 3.94 (m, 2H, $\mathrm{NC}H_2$), 7.01 (d, 2H, $\mathrm{Ph}H$), 7.51 (d, 2H, $\mathrm{Ph}H$), 8.29 (s, 2H, $\mathrm{PhC}H$); IR 2949 vs (br), 2903 s (br), 2868 s (br), 1699 s, 1630 vs, 1541 s, 1420 s, 1179 s, 837 s, 750 s cm^{-1}.

Salen(^{t}Bu)AlEt (2). Reagents: Salen(^{t}Bu)H$_2$ (2.022 g, 4.10 mmol) and Et$_3$Al (1.0 M in hexane, 2.838 g, 4.10 mmol) (yield 1.585 g, 71%). **2**: mp 244−248 °C; ^{1}H NMR (CDCl$_3$) δ 0.14 (q, 2H, $\mathrm{AlC}H_2\mathrm{CH}_3$), 1.21 (t, 3H, $\mathrm{AlCH_2C}H_3$) 1.38 (s, 18H, $\mathrm{C(C}H_3)_3$), 1.86 (s, 18H, $\mathrm{C(C}H_3)_3$), 2.54 (m, 2H, $\mathrm{NC}H_2$), 3.01 (m, 2H, $\mathrm{NC}H_2$), 6.89 (d, 2H, $\mathrm{Ph}H$), 7.39 (d, 2H, $\mathrm{Ph}H$), 7.76 (s, 2H, $\mathrm{PhC}H$); IR 2955 vs, 2907 s, 2864 s, 1645 s, 1624 vs, 1541 s, 1443 s, 1414 s, 1310 s, 1256 s, 1175 s cm^{-1}.

Salen(^{t}Bu)Al^{i}Bu (3). Reagents: Salen(^{t}Bu)H$_2$ (1.552 g, 3.15 mmol) and ^{i}Bu$_3$Al (0.625 g, 3.15 mmol) (yield 1.395 g, 77%). **3**: mp 180−185 °C; ^{1}H NMR (C$_6$D$_6$) δ 0.17 (d, 2H, $\mathrm{AlC}H_2\mathrm{CH(CH_3)_2}$), 1.03 (d, 6H, $\mathrm{AlCH_2CH(C}H_3)_2$), 1.37 (s, 18H, $\mathrm{C(C}H_3)_3$), 1.87 (s, 18H, $\mathrm{C(C}H_3)_3$), 1.87 (m, coincident with $\mathrm{C(CH_3)_3}$ at 1.87, 1H, $\mathrm{AlCH_2C}H\mathrm{(CH_3)_2}$), 2.55 (m, 2H, $\mathrm{NC}H_2$), 3.08 (m, 2H, $\mathrm{NC}H_2$), 6.90 (d, 2H, $\mathrm{Ph}H$), 7.40 (s, 2H, $\mathrm{Ph}H$), 7.77 (d, 2H, $\mathrm{PhC}H$); IR 2957 vs (br), 2913 s (br), 2863 s (br), 1645 s, 1620 vs, 1541 s, 1256 s, 1175 s, 837 s, 752 s, 575 s cm^{-1}.

Salpen(^{t}Bu)AlMe (4). Reagents: Salpen(^{t}Bu)H$_2$ (1.323 g, 2.61 mmol) and Me$_3$Al (0.201, 2.79 mmol) (yield 0.942 g, 66%). **4**: mp 256 °C dec; ^{1}H NMR (CDCl$_3$) δ −0.98 (s, 3H, $\mathrm{AlC}H_3$), 1.28 (s, 18H, $\mathrm{C(C}H_3)_3$), 1.45 (s, 18H, $\mathrm{C(C}H_3)_3$), 2.13 (m, 2H, $\mathrm{C}H_2$), 3.61, 3.78 (m, 4H, $\mathrm{NC}H_2$), 6.97 (d, 2H, $\mathrm{Ph}H$), 7.45 (d, 2H, $\mathrm{Ph}H$), 8.15 (s, 2H, $\mathrm{PhC}H$); IR 2957 vs, 2903 s, 2870 s, 1624 vs, 1555 s, 1460 s, 1416 s, 1316 s, 1260 s, 1177 s, 1098 w, 843 s, 750 w, 650 s, 565 w cm^{-1}.

Salophen(^{t}Bu)AlMe (5). Reagents: Salophen(^{t}Bu)H$_2$ (0.706 g, 1.31 mmol) and Me$_3$Al (0.101 g, 1.40 mmol) (yield 0.696 g, 91.5%). **5**: mp 271−274 °C dec; ^{1}H NMR (CDCl$_3$) δ −1.22 (s, 3H, $\mathrm{AlC}H3$), 1.33 (s, 18H, $\mathrm{C(C}H_3)_3$), 1.55 (s, 18H, $\mathrm{C(C}H_3)_3$), 7.14 (d, 2H, $\mathrm{Ph}H$), 7.37 (m, 2H, $\mathrm{Ph}H$), 7.58 (d, 2H, $\mathrm{Ph}H$), 7.68 (m, 2H, $\mathrm{Ph}H$), 8.79 (s, 2H, $\mathrm{PhC}H$); IR 2958 vs (br), 2922 s, (br), 2868 s (br), 1616 s, 1535 vs, 1471 s, 1386 m, 1359 m, 1261 m, 1180 m, 1101 m, 1030 m, 841 m, 752 s, 621 m, 585 m, 547 m, 454 m cm^{-1}.

Salophen(^{t}Bu)AlEt (6). Reagents: Salophen(^{t}Bu)H$_2$ (2.30 g, 4.26 mmol) and Et$_3$Al (0.48g, 4.26 mmol) (yield 1.44g, 57%). **6**: mp 258 °C dec; ^{1}H NMR (CDCl$_3$) δ −0.43 (q, 2H, $\mathrm{AlC}H_2$-$\mathrm{CH_3}$), 0.58 (t, 3H, $\mathrm{AlCH_2C}H_3$, 1.35 (s, 18H, $\mathrm{C(C}H_3)_3$), 1.58 (s, 18H, $\mathrm{C(C}H_3)_3$), 7.15 (d, 2H, $\mathrm{Ph}H$), 7.40 (m, 2H, $\mathrm{Ph}H$), 7.60 (d, 2H, $\mathrm{Ph}H$), 7.68 (m,2H,$\mathrm{Ph}H$), 8.81 (s, 2H, $\mathrm{PhC}H$); IR 2958 vs, 2935s, 2901 s, 1614 vs, 1583 s, 1535 s, 1469 s, 1384 s, 1359 s, 1261 s, 1201 s, 1178 s, 1095 w, 1026 w, 869 m, 841 m, 750 s, 607 m, 580 m cm^{-1}.

Salophen(^{t}Bu)AliBu (7). Reagents: Salophen(^{t}Bu)H$_2$ (2.30g, 4.26 mmol) and ^{i}Bu$_3$Al (0.845g, 4.26 mmol) (yield 1.58g, 60%). **7**: mp 208 °C dec; ^{1}H NMR (CDCl$_3$) δ −0.35 (d, 2H, $\mathrm{AlC}H_2\mathrm{CH(CH_3)_2}$), 0.50 (d, 3H, $\mathrm{AlCH_2CH(C}H_3)_2$, 1.38 (s, 18H, $\mathrm{C(C}H_3)_3$), 1.56 (s, 18H, $\mathrm{C(C}H_3)_3$), 7.14 (d, 2H, $\mathrm{Ph}H$), 7.40 (m, 2H, $\mathrm{Ph}H$), 7.59 (d, 2H, $\mathrm{Ph}H$), 7.66 (m, 2H, $\mathrm{Ph}H$), 8.77 (s, 2H, $\mathrm{PhC}H$); IR 2955 vs, 2906s, 2860 s, 1620 vs, 1583 s, 1502, 1469 s, 1386s, 1359 s, 1262 s, 1202s, 1180 s, 1022 m, 872 w, 802 m, 744 s, 657 w, 640 m, 559 m, 547 m, 495 w, 435 w cm^{-1}.

Salomphen(^{t}Bu)AlMe (8). Reagents: Salomphen(^{t}Bu)H$_2$ (1.187 g, 2.09 mmol) and Me$_3$Al (0.150 g, 2.09 mmol) (yield 0.79 g, 62%). **8**: mp 257−259 °C; ^{1}H NMR (CDCl$_3$) δ −1.24 (s, 3H, $\mathrm{AlC}H_3$), 1.31 (s, 18H, $\mathrm{C(C}H_3)_3$), 1.56 (s, 18H, $\mathrm{C(C}H_3)_3$), 2.37 (s, 6H, $\mathrm{PhC}H_3$), 7.15−7.57 (m, 6H, $\mathrm{Ph}H$), 8.75 (s, 2H,

Table 2. Bond Lengths (Å) and Angles (deg) for Salen(^{t}Bu)AlMe (1) and Salomphen(^{t}Bu)AliBu (10)

1		**10**	
Bond Lengths (Å)			
Al(1)−O(1)	1.799(9)	Al(1)−O(1)	1.809(6)
Al(1)−O(2)	1.831(9)	Al(1)−O(2)	1.825(5)
Al(1)−N(1)	2.069(10)	Al(1)−N(1)	2.033(6)
Al(1)−N(2)	2.025(11)	Al(1)−N(2)	2.056(6)
Al(1)−C(33)	1.963(17)	Al(1)−C(39)	1.972(9)
O(1)−C(1)	1.320(13)	O(1)−C(1)	1.311(9)
O(2)−C(24)	1.309(13)	O(2)−C(30)	1.321(9)
N(1)−C(15)	1.282(14)	N(1)−C(15)	1.309(10)
N(1)−C(16)	1.454(17)	N(1)−C(16)	1.437(9)
N(2)−C(17)	1.455(16)	N(2)−C(21)	1.420(9)
N(2)−C(18)	1.297(15)	N(2)−C(24)	1.297(15)
Angles (deg)			
O(1)−Al(1)−O(2)	91.7(4)	O(1)−Al(1)−O(2)	90.1(2)
O(1)−Al(1)−N(1)	87.4(4)	O(1)−Al(1)−N(1)	87.7(2)
O(2)−Al(1)−N(1)	158.7(5)	O(2)−Al(1)−N(1)	142.2(3)
O(1)−Al(1)−N(2)	130.6(5)	O(1)−Al(1)−N(2)	150.5(3)
O(2)−Al(1)−N(2)	88.3(4)	O(2)−Al(1)−N(2)	87.1(2)
N(1)−Al(1)−N(2)	76.4(4)	N(1)−Al(1)−N(2)	76.9(2)
O(1)−Al(1)−C(33)	116.9(5)	O(1)−Al(1)−C(39)	110.2(3)
O(2)−Al(1)−C(33)	103.0(5)	O(2)−Al(1)−C(39)	107.4(3)
N(1)−Al(1)−C(33)	96.3(5)	N(1)−Al(1)−C(39)	108.6(3)
N(2)−Al(1)−C(33)	111.1(6)	N(2)−Al(1)−C(39)	98.5(3)
Al(1)−O(1)−C(1)	134.7(8)	Al(1)−O(1)−C(1)	136.2(5)
Al(1)−O(2)−C(24)	126.5(9)	Al(1)−O(2)−C(30)	132.3(5)
Al(1)−N(1)−C(15)	125.9(9)	Al(1)−N(1)−C(15)	126.4(5)
Al(1)−N(1)−C(16)	113.4(7)	Al(1)−N(1)−C(16)	115.3(4)

PhC*H*); IR 2959 vs (br), 2868 s, 1618 vs, 1593 vs, 1537 vs, 1472 s, 1385 s, 1254 s, 1177 s, 845 s, 789 s, 752 w, 625 s cm^{-1}.

Salomphen(^{t}Bu)AlEt (9). Reagents: Salomphen(^{t}Bu)H$_2$ (1.760 g, 3.09 mmol) and ^{i}Bu$_3$Al (0.35 g, 3.09 mmol) (yield 0.38 g, 20%). **9**: mp 254−56 °C dec; ^{1}H NMR (CDCl$_3$) δ −0.49 (q, 2H, AlCH_2CH$_3$), 0.54 (t, 3H, AlCH$_2$CH_3) 1.33 (s, 18H, C(CH_3)$_3$), 1.55 (s, 18H, C(CH_3)$_3$), 2.36 (s, 6H, PhCH_3), 7.13 (d, 2H, Ph*H*), 7.45 (s, 2H, Ph*H*), 7.55 (d, 2H, Ph*H*), 8.76 (s, 2H, PhC*H*); IR 2960 vs (br), 2914 s, 2858 s, 1618 vs, 1589 s, 1535 s, 1471 s, 1357 m, 1257 s, 1176 s, 1087 s, 1022 m, 844 s, 800 s, 752 s, 586 m, 559 w cm^{-1}.

Salomphen(^{t}Bu)Al^{i}Bu (10). Reagents: Salomphen(^{t}Bu)-H$_2$ (0.769 g, 1.35 mmol) and ^{i}Bu$_3$Al (0.268 g, 1.35 mmol) (yield 0.35 g, 40%). **10**: mp 197−199 °C dec; ^{1}H NMR (CDCl$_3$) δ −0.39 (d, 2H, AlCH_2CH(CH$_3$)$_2$), 0.49 (d, 6H, AlCH$_2$CH(CH_3)$_2$) 1.33 (s, 18H, C(CH_3)$_3$), 1.52 (s, 18H, C(CH_3)$_3$), 2.37 (s, 6H, PhCH_3), 7.13−7.56 (m, 6H, Ph*H*), 8.73 (s, 2H, PhC*H*); IR 2959 vs (br), 2864 s, 1622 vs, 1593 s, 1537 s, 1470 s, 1256 s, 1177 s, 845 s, 789 s, 554 s cm^{-1}.

Salen(^{t}Bu)AlOSiPh$_3$ (11). Ph$_3$SiOH (1.337 g, 4.84 mmol, 98% pure) was added to a toluene solution (20 mL) of **1** (2.526 g, 4.741 mmol) at 25 °C. The exothermic reaction produced a cloudy mixture and became a clear yellow solution and then a yellow precipitate. After being stirred at 25 °C for 2 h, the mixture was filtered via cannula to yield a light yellow crystalline solid (3.595 g, 96%). X-ray quality crystals were obtained by slow evaporation of a CH$_2$Cl$_2$ solution at 25 °C: mp 268−269 °C dec; ^{1}H NMR (CDCl$_3$) δ 1.33 (s, 18H, C(CH_3)$_3$), 1.53 (s, 18H, C(CH_3)$_3$), 3.45 (m, 2H, NCH_2), 3.55 (m, 2H, NCH_2) 6.93 (d, 2H, Ph*H*), 7.20 (m, 15H, SiPh*H*), 7.53 (d, 2H, Ph*H*); ^{29}Si NMR (CDCl$_3$) δ −29.99; IR 2961 vs (br), 2917 s (br), 2873 s (br), 1647 s, 1622 vs, 1543 vs, 1445 s, 1428 s, 1389 s, 1308 s, 1258 s, 1177 s, 1111 vs, 1065 s, 708 vs, 583 s, 515 vs cm^{-1}.

Salpen(^{t}Bu)AlOSiPh$_3$ (12). This compound was synthesized employing the same general method as for **11** from Ph$_3$-SiOH (0.51 g, 1.83 mmol) and **4** (1.0 g, 1.83 mmol) in toluene (10 mL) producing a pale green solution. Stirring was continued for 12 h, at which point removal of the solvent under vacuum produced a pale yellow glass. Recrystallization from a hexane/toluene (3:1) solution at 25 °C yielded pale yellow/green rectangular crystals suitable for single-crystal X-ray analysis (1.25 g, 85%): mp 150−151 °C; ^{1}H NMR (CDCl$_3$) δ

Table 3. Bond Lengths (Å) and Angles (deg) for Salen(^{t}Bu)AlOSiPh$_3$ (11), Salpen(^{t}Bu)AlOSiPh$_3$ (12), and Salophen(^{t}Bu)AlOSiPh$_3$ (13)

11		**12**		**13**	
Bond Lengths (Å)					
Al(1)−O(1)	1.807(16)	Al(1)−O(1)	1.828(1)	Al(1)−O(1)	1.794(8)
Al(1)−O(2)	1.820(19)	Al(1)−O(2)	1.764(2)	Al(1)−O(2)	1.806(9)
Al(1)−N(1)	1.963(25)	Al(1)−N(1)	1.987(1)	Al(1)−N(1)	2.007(13)
Al(1)−N(2)	2.057(24)	Al(1)−N(2)	2.037(1)	Al(1)−N(2)	2.026(10)
Al(1)−O(3)	1.719(14)	Al(1)−O(3)	1.726(2)	Al(1)−O(3)	1.702(9)
Si(1)−O(3)	1.608(13)	Si(1)−O(3)	1.597(2)	Si(1)−O(3)	1.603(9)
Si(1)−C(33)	1.874(29)	Si(1)−C(34)	1.867(3)	Si(1)−C(37)	1.871(15)
Si(1)−C(39)	1.864(33)	Si(1)−C(40)	1.888(1)	Si(1)−C(43)	1.885(13)
Si(1)−C(45)	1.846(39)	Si(1)−C(46)	1.878(3)	Si(1)−C(49)	1.875(15)
O(1)−C(20)	1.333(30)	O(1)−C(1)	1.319(4)	O(1)−C(14)	1.332(15)
O(2)−C(10)	1.374(30)	O(2)−C(21)	1.334(4)	O(2)−C(23)	1.307(14)
N(1)−C(1)	1.508(33)	N(1)−C(15)	1.292(4)	N(1)−C(7)	1.450(18)
N(1)−C(3)	1.260(31)	N(1)−C(16)	1.476(4)	N(1)−C(8)	1.307(15)
N(2)−C(17)	1.457(40)	N(2)−C(18)	1.458(3)	N(2)−C(1)	1.308(15)
N(2)−C(4)	1.263(38)	N(2)−C(19)	1.280(4)	N(2)−C(2)	1.420(19)
Angles (deg)					
N(1)−Al(1)−N(2)	79.5(9)	N(1)−Al(1)−N(2)	83.7(1)	N(1)−Al(1)−N(2)	79.0(9)
O(1)−Al(1)−O(2)	88.9(8)	O(1)−Al(1)−O(2)	90.7(1)	O(1)−Al(1)−O(2)	88.9(8)
O(1)−Al(1)−N(1)	87.9(8)	O(1)−Al(1)−N(1)	88.2(1)	O(1)−Al(1)−N(1)	88.2(4)
O(2)−Al(1)−N(1)	159.3(7)	O(2)−Al(1)−N(1)	125.2(1)	O(2)−Al(1)−N(1)	155.0(5)
O(1)−Al(1)−N(2)	135.6(8)	O(1)−Al(1)−N(2)	169.5(1)	O(1)−Al(1)−N(2)	145.1(5)
O(2)−Al(1)−N(2)	88.6(9)	O(2)−Al(1)−N(2)	88.6(1)	O(2)−Al(1)−N(2)	88.5(4)
N(1)−Al(1)−O(3)	97.2(8)	N(1)−Al(1)−O(3)	113.5(1)	N(1)−Al(1)−O(3)	96.7(5)
N(2)−Al(1)−O(3)	107.4(8)	N(2)−Al(1)−O(3)	90.4(1)	N(2)−Al(1)−O(3)	102.9(4)
O(1)−Al(1)−O(3)	116.4(8)	O(1)−Al(1)−O(3)	99.0(1)	O(1)−Al(1)−O(3)	110.8(4)
O(2)−Al(1)−O(3)	102.6(9)	O(2)−Al(1)−O(3)	120.7(1)	O(2)−Al(1)−O(3)	107.3(5)
O(3)−Si(1)−C(33)	109.0(10)	O(3)−Si(1)−C(34)	109.0(1)	O(3)−Si(1)−C(43)	111.4(6)
O(3)−Si(1)−C(39)	109.9(11)	O(3)−Si(1)−C(40)	112.1(1)	O(3)−Si(1)−C(37)	108.9(6)
C(33)−Si(1)−C(39)	112.0(14)	C(34)−Si(1)−C(40)	108.5(1)	C(37)−Si(1)−C(43)	107.8(6)
O(3)−Si(1)−C(45)	109.7(13)	O(3)−Si(1)−C(46)	109.2(1)	O(3)−Si(1)−C(49)	108.6(5)
C(33)−Si(1)−C(45)	107.8(14)	C(34)−Si(1)−C(46)	108.3(1)	C(37)−Si(1)−C(49)	109.5(6)
C(39)−Si(1)−C(45)	108.4(14)	C(40)−Si(1)−C(46)	109.7(1)	C(43)−Si(1)−C(49)	110.6(7)
Al(1)−O(3)−Si(1)	157.9(14)	Al(1)−O(3)−Si(1)	166.3(2)	Al(1)−O(3)−Si(1)	166.8(6)

1.36 (s, 18H, C(C*H*$_3$)$_3$), 1.43 (s, 18H, C(C*H*$_3$)$_3$), 1.84 (m, 1H, C*H*$_2$(CH$_2$)$_2$), 1.98 (m, 1H, C*H*$_2$(CH$_2$)$_2$), 3.22, 3.58 (m, 4H, NC*H*$_2$), 7.02−7.54 (m, 23H, Ph*H*), 8.05 (s, 2H, PhC*H*); ^{29}Si NMR (CDCl$_3$) δ −29.22; IR 2957 vs (br), 2903 s, (br), 1645 s, 1620 vs, 1541 m, 1462 s, 1417 m, 1313 s, 1257 s, 1176 m, 1111 vs, 1070 vs, 841 m, 740 m, 702 vs, 580 s, 509 vs, 464 m cm^{-1}.

Salophen(^{t}Bu)AlOSiPh$_3$ (13). This compound was synthesized employing the same general method as for **11** from Ph$_3$SiOH (0.36 g, 1.29 mmol) and **5** (0.75 g, 1.29 mmol). Recrystallization from hexane/toluene (3:1) at 25 °C yielded bright yellow rectangular crystals suitable for single-crystal X-ray analysis (0.92 g, 85%): mp 294−297 °C; ^{1}H NMR (CDCl$_3$) δ 1.40 (s, 18H, C(C*H*$_3$)$_3$), 1.62 (s, 18H, C(C*H*$_3$)$_3$), 6.97−7.68 (m, 23H, Ph*H*), 8.68 (s, 2H, PhC*H*); ^{29}Si NMR (CDCl$_3$) δ −28.77; IR 2958 vs (br), 2910 s (br), 2868 s, 1614 vs, 1583 s, 1537 vs, 1471 s, 1386 s, 1359 s, 1261 m, 1201 m, 1182 m, 1111 vs, 1070 vs, 842 m, 788 w, 742 m, 704 s, 586 m, 513 s cm^{-1}.

Salomphen(^{t}Bu)AlOSiPh$_3$ (14). This compound was synthesized employing the same general method as for **11** from Ph$_3$SiOH (0.178 g, 0.645 mmol) and **8** (0.385 g, 0.632 mmol). The reaction was allowed to stir at 25 °C for 5 h yielding a clear orange solution. The solvent was removed under vacuum to yield an orange crystalline solid (0.45 g, 82%): mp 296−299 °C; ^{1}H NMR (CDCl$_3$) δ 1.35 (s, 18H, C(C*H*$_3$)$_3$), 1.61 (s, 18H, C(C*H*$_3$)$_3$), 2.35 (s, 6H, PhC*H*$_3$), 6.89−7.63 (m, 21H, Ph*H*), 8.64 (s, 2H, PhC*H*); ^{29}Si NMR (CDCl$_3$) δ −29.15; IR 2963 vs (br), 2868 s, 1620 vs, 1593 s, 1537 vs, 1470 s, 1393 vs (br), 1256 s, 1181 s, 1111 vs, 1074 vs, 843 s, 789 s, 708 s, 513 s cm^{-1}.

X-ray Experimental Data. Details of the crystal data and a summary of data collection parameters for the complexes are given in Tables 1−3. Data were collected at ambient temperature on a Siemens P4 diffractometer for **1** and **10** and on a SMART CCD unit for **11**−**13**. Both utilized graphite-monochromated Mo Kα (0.710 73 Å) radiation. All calculations were performed on a personal computer using the Siemens software package, SHELXTL-Plus. The structures were solved by direct methods and successive interpretation of difference Fourier maps, followed by least-squares refinement. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included in the refinement in calculated positions using fixed isotropic parameters.

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Supporting Information Available: Tables of bond lengths and angles, positional parameters, anisotropic thermal parameters, and unit cell views, elemental analyses, a figure of the ^{1}H NMR spectrum of **11**, and a view of the structure of **12** (72 pages). Ordering information is given on any current masthead page.

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