Use of the Salan Ligands To Form Bimetallic Aluminum Complexes

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The syntheses and characterization of two types of complexes having a metal−Salan ligand stoichiometry of 2:1 (where Salan = *N*,*N*′-bis(*o*-hydroxybenzyl)-1,2-diaminoethane (SaleanH$_4$), *N*,*N*′-bis(*o*-hydroxybenzyl)-1,2-diaminobenzene (SalophanH$_4$), and *N*,*N*′-bis(*o*-hydroxybenzyl)-1,2-diamino-(4,5-dimethyl)benzene (SalomphanH$_4$)) are reported. The first are designated type I and are of the general formula LHAlR(AlR$_2$), where L = Salean [R = Me (**1**), Et (**2**), ^{i}Bu (**3**)], Salophan [R = Me (**4**), Et (**5**), ^{i}Bu (**6**)], and Salomphan [R = Me (**7**), Et (**8**), ^{i}Bu (**9**)]. Formed by the thermolysis of RH from the type I complexes, the type II complexes are of the general formula [LAl(AlR$_2$)]$_2$, where L = Salophan [R = Me (**10**), ^{i}Bu (**11**)] and Salomphan [R = Me (**12**), ^{i}Bu (**13**)]. The type I complexes can be converted into the trimetallic derivatives SalanAlR(AlR$_2$)$_2$ (type III) through the addition of AlR$_3$ while the type II cannot. One structurally characterized trimetallic complex, SalophanAlEt(AlEt$_2$)$_2$ (**14**), serves as a representative of this successful transformation.

Introduction

The Salen[1] class of ligands (Figure 1a) has had an extensive[2] and continuing[3] history with the transition metals. Hydrogenation of the Salen ligand produces a new tetradentate ligand, known generally as Salan (Figure 1b).[4] While a number of transition metal derivatives of this ligand are known,[5] the corresponding chemistry with the main group elements remains relatively unexplored. Reported examples include complexes of Zn,[4] Al,[6] Ga[6b,7,9] and Sn.[8] The Salan ligands offer four potentially σ-bonding sites (two NH and two OH). Thus, they have also been conducive to the formation of anionic aluminum complexes with a ligand−metal ratio of 1:1 ([(SalanAl)Li(THF)$_2$]$_2$).[9] More commonly, however, trimetallic compounds of the general formula SalanMR(MR$_2$)$_2$ (where M = Al and Ga and R = Me and Et) have been reported.[6,7]

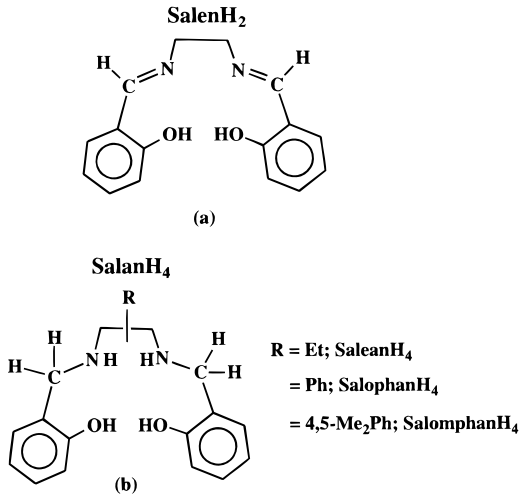

Figure 1. General depiction of SalenH$_2$ (a) and the SalanH$_4$ (b) ligands used in this study.

We have been exploring the unique chemistry of the Salan ligands with aluminum and gallium. The resulting complexes have predominantly been of a trimetallic formula (LMR(MR$_2$)$_2$) for which both cis and trans isomers have been identified.[6,7] Furthermore, the complexes exhibited unusual spectroscopic properties such as rigid solution-state geometries and anisotropic ring current effects. While both monomeric and trimetallic Salan complexes are known, those having a metal−ligand stoichiometry of 2:1 are extremely rare. The present manuscript describes a systematic exploration into complexes having this stoichiometry. It is part of a larger comprehensive program to develop the chemistry of the Salan ligands with the group 13 elements.

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(1) The term "Salen" is used to denote the class of ligands having the general formula shown in Figure 1a. Thus, the Acen ligand is placed into this class even though it is formally derived from 2-hydroxybenzaldehyde acetal.

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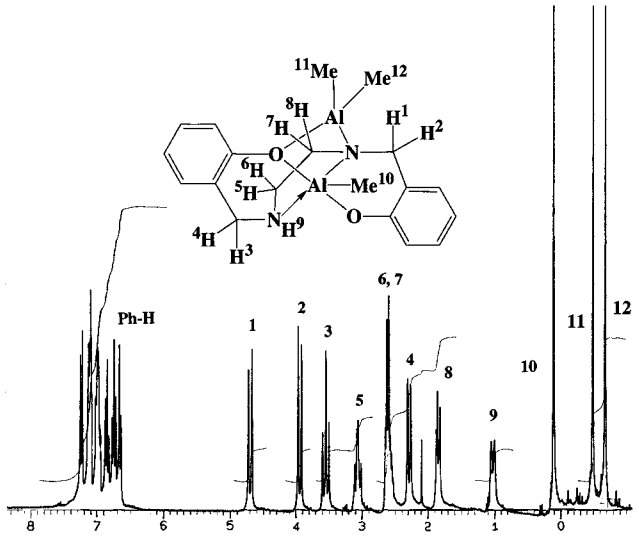


Figure 2. ^{1}H NMR spectrum of SaleanHAlMe(AlMe$_2$) (**1**).

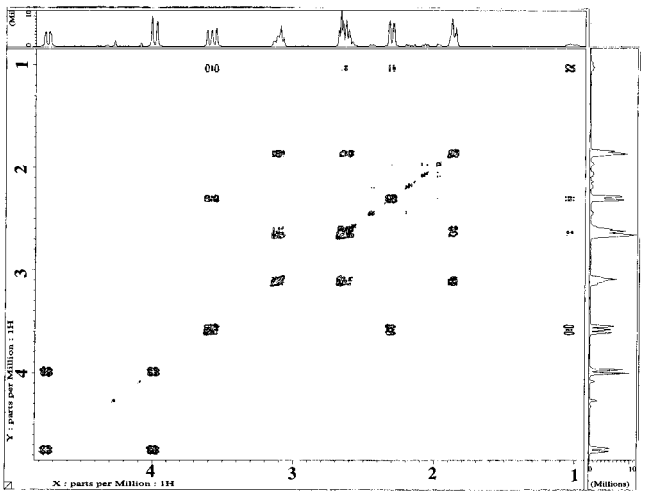


Figure 3. COSY spectrum of SaleanHAlMe(AlMe$_2$) (**1**).

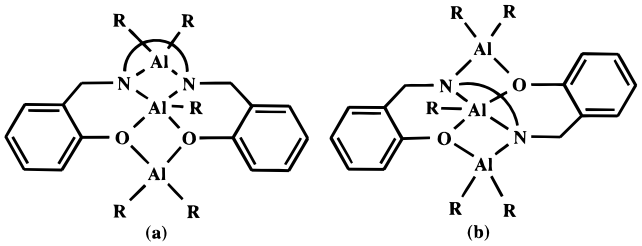


Figure 4. Generic examples of the cis (a) and trans (b) geometries for the Salan ligands.

Results and Discussion

Formation of the SalanHAlR(AlR$_2$) Derivatives. Initial attempts to prepare compounds **1**−**9** involved the addition of 2 mol of the aluminum reagent to the ligand followed by either stirring at 25 °C or reflux in toluene. In each case a mixture of products resulted. This was shown to include some of the trimetallic derivatives, SalanAlR(AlR$_2$)$_2$, and some of the targeted 2:1 product. Subsequently, we discovered that the reflux reactions also contained a modest amount of the fully condensed compounds, [SalanAl(AlR$_2$)]$_2$ (see below). After the reaction conditions were systematically varied, it was found that high yields of **1**−**9** could be obtained by refluxing the reaction mixture for not more than 10 min in toluene (eq 1).

$$\text{SalanH}_4 + 2\,\text{AlR}_3 \xrightarrow[\Delta,\ <10\ \text{min.}]{\text{Toluene}} \text{SalanHAlR(AlR}_2) + 3\,\text{HR} \qquad (1)$$

Salan; R = Salean; Me (1), Et (2), ^{i}Bu (3)
= Salophan; Me (4), Et (5), ^{i}Bu (6)
= Salomphan; Me (7), Et (8), ^{i}Bu (9)

Two spectroscopic features are readily apparent in **1**−**9**. The first is the presence of an NH stretch in the range of ν 3244−3291 cm^{-1}. The second is the extensive coupling present in the ^{1}H NMR spectrum. The trimetallic derivatives SalanMR(MR$_2$)$_2$ (where M = Al or Ga and R = alkyl) have been shown previously to possess rigid solution state geometries.[6,7] This is most apparent in AB-type coupling of the two benzylic methylenes. This leads to two doublets which is a signature for these compounds. Compounds **1**−**9** display similar behavior for one of the methylene groups. This group is observed as a set of doublets (1 and 2) for **1** (Figure 2). However, due to the presence of the NH group the other methylene is also coupled to the NH. This leads to the observed multiplets (3 and 4). Due to the asymmetry of the molecule this pattern is repeated for each of the hydrogens on the ligand backbone (5−8). The NH group appears as a broad multiplet (9). Irradiation and COSY NMR experiments were used to determine this pattern of coupling. The result of a COSY analysis for **1** is shown in Figure 3. Examination of the resonance assigned to the NH at δ 1.05 ppm shows that it is coupled to both of the methylene groups containing H3−H6. Furthermore there are three resonances that can be attributed to the AlMe groups (10−12).

The trimetallic group 13 Salan complexes adopt both cis and trans geometries (Figure 4a,b, respectively). These conformations can be defined relative to the positions of the N and O atoms (on the same side for cis and on opposite sides for trans). They may also be defined relative to the position of the ligand "backbone" (to one side of the central aluminum atom for cis and symmetrical with respect to the central aluminum atom for trans). This latter definition will be useful when discussing ligands such as open-chain amines possessing four nitrogen atoms. The arrangement for **1** is tentatively assigned a trans geometry based upon the fact that the majority of the Salean complexes of aluminum and gallium adopt this conformation.[6,7]

A similar pattern to what was observed for **1** is apparent in the ^{1}H NMR spectrum of SalomphanHAl^{i}Bu(Al^{i}Bu$_2$) (**9**) (Figure 5). The structure that is shown displays the ligand in a cis configuration. This follows the precedent set for the trimetallic derivatives for which it was shown that the aluminum complexes always adopt a cis geometry for the ligands Salpan (not used in the present study), Salophan, and Salomphan.

Closely related to **1**−**9** is the structurally characterized complex C$_8$H$_{19}$N$_4$(AlMe)(AlMe$_2$), shown in Figure 9a.[10] In the structure the ligand adopts a cis conformation around a central 5-coordinate aluminum in a tbp geometry. Due to the complexity inherent to the presence of both ethyl and propyl substituents the ^{1}H NMR spectrum cannot be interpreted in terms of a rigid solution-state geometry.

Thermolysis of the SalanHAlR(AlR$_2$) Derivatives. The NH group present on **4**, **6**, **7**, and **9** can be utilized in further reactivity. The first attempts to

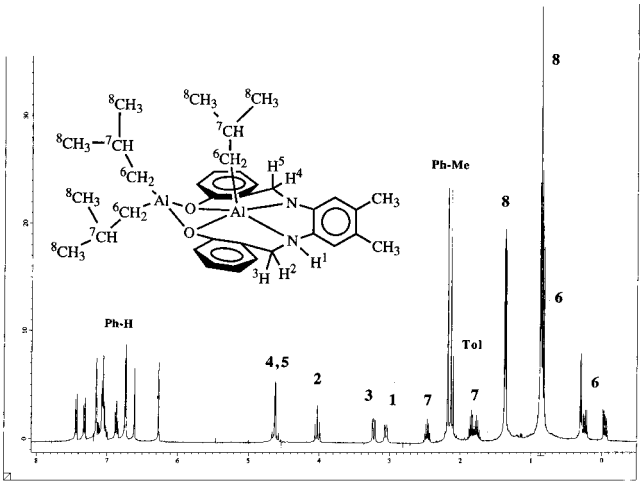


Figure 5. ^{1}H NMR spectrum of SalomphanHAl^{i}Bu(Al^{i}Bu$_2$) (**9**).

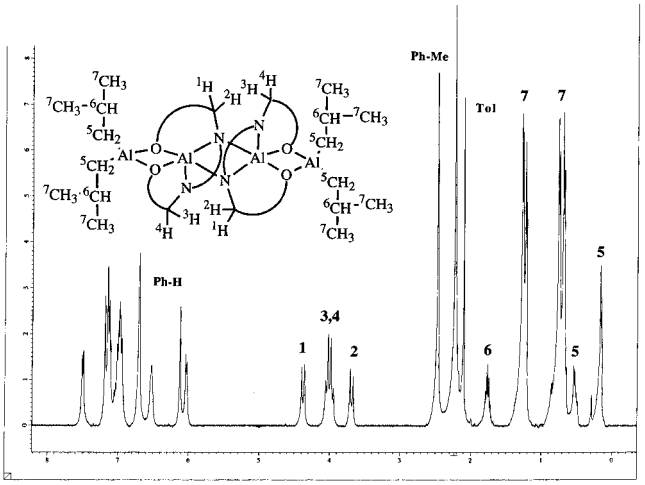


Figure 6. ^{1}H NMR spectrum of [SalomphanAl(Al^{i}Bu$_2$)]$_2$ (**13**).

prepare new complexes involved the reflux of the SalanHAlR(AlR$_2$) complexes in a concentration of 0.04 g/mL. This led to a mixture of products which included starting material. Reflux of the methyl or isobutyl derivatives incorporating the Salophan or Salomphan ligands for 1 day or more, at a concentration of 0.08 g/mL, leads to the formation of the condensation products, [SalanAl(AlR$_2$)]$_2$ (**10**−**13**; eq 2). Attempts to effect

$$\text{SalanHAlR(AlR}_2\text{)} \xrightarrow[\Delta\ >\ 20\ \text{h}]{\text{Toluene}} \text{[SalanAl(AlR}_2\text{)]}_2 + 2\text{HR} \qquad (2)$$

Salan; R = Salophan; Me (10), ^{i}Bu (11)
= Salomphan; Me (12), ^{i}Bu (13)

this transformation for the Salean derivatives were not successful. The NH proton on the complexes incorporating the ethylamine backbone are apparently not acidic enough to undergo alkane elimination reactions. Conducting the reaction in refluxing xylene led to decomposition of the compounds.

The spectroscopic data for these complexes differ from that of the starting materials in two significant ways. First, there is no evidence for the NH group (by NMR and IR spectroscopic techniques), and second, the central Al no longer possesses an alkyl group. A representative ^{1}H NMR spectrum for **13** is shown in Figure 6. There were resonances which could be attributed to two separate methylene groups (1−4). This

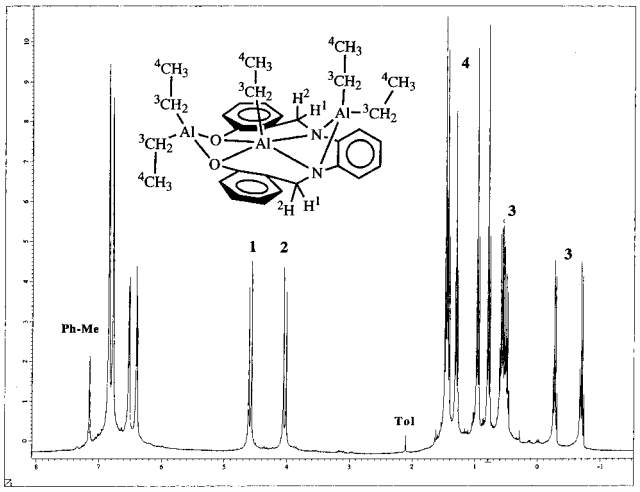


Figure 7. ^{1}H NMR spectrum of SalophanAlEt(AlEt$_2$)$_2$ (**14**).

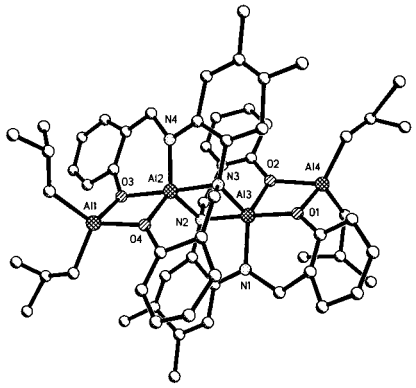


Figure 8. Molecular structure and atom-numbering scheme for [SalomphanAl(Al^{i}Bu$_2$)]$_2$ (**13**).

was the first evidence that the complex was dimeric and not a symmetrical monomer. Later, X-ray data confirmed this (see below). Furthermore, there are two Ph−Me resonances. The ^{i}Bu resonances are somewhat difficult to assign (5−7). But there are clearly at least two unique ^{i}Bu groups and, potentially, four. For comparison, the NMR spectrum of the symmetrical trimetallic, **14**, is shown in Figure 7. In this complex the presence of two doublets (1 and 2) indicates that there is only one methylene environment. Thus, the solution structures of **10**−**13** are apparently asymmetric and nonfluxional in solution. This is in agreement with the solid-state structure.

Structural Characterization of [SalomphanAl(Al^{i}Bu$_2$)]$_2$ (13). The molecular structure and atom-numbering scheme for **13** is shown in Figure 8.[11] There were serious disorder problems which hindered an acceptable refinement of the structure so the atoms are depicted as non-thermal ellipsoids (see X-ray Experimental Details). However, the overall morphological features of this molecule are clear. It adopts a dimeric structure with bridging nitrogens connecting two SalomphanAl(Al^{i}Bu$_2$) units. The framework of this dimer is composed of three four-membered rings (Al$_2$E$_2$ where E = O and N). This gives the molecule a helical twist with dihedral angles for the Al$_2$O$_2$ rings relative to the plane formed by the Al$_2$N$_2$ ring of 70.6° (Al(3), O(1), O(2),

(11) The best structure was obtained in the monoclinic space group *Cc*; a = 30.292(5) Å, b = 11.845(3) Å, c = 17.881(3) Å, β = 102.98(1)°, V = 6252(2) Å^3, and Z = 4, with 1713 observed reflections ($F > 5\sigma(F)$). R = 0.0659 and R_w = 0.0669.

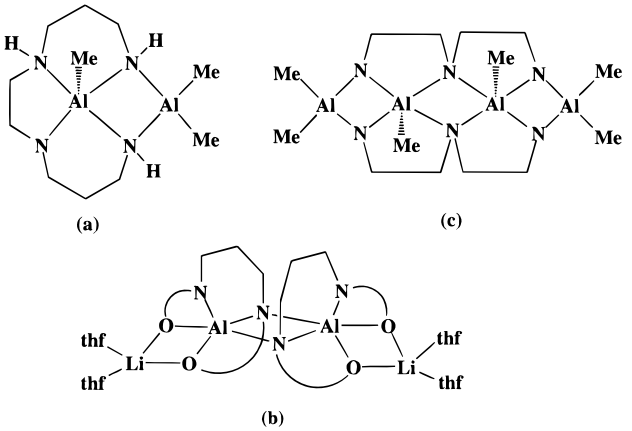
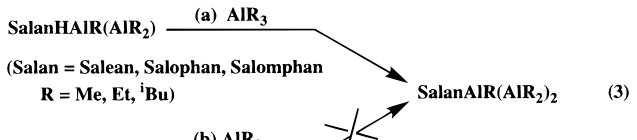


Figure 9. Other structurally characterized aluminum complexes incorporating multidentate ligands.

Al(4)) and −67.5° (Al(2), O(3), O(4), Al(1)). A similar situation was observed in the structure adopted by the anionic complex $[(SalpanAl)Li(THF)_2]_2$ which possesses dihedral angles of +50° and −53.2° (Figure 9b).[9]

Extended structures like this containing a five-coordinate aluminum atom have been reported previously with multidentate amine ligands complexed to group 13 moieties.[12] For example, the combination of Me_3Al with diethylaminetriamine results in the type of complex shown generally in Figure 9c.[13] In this complex there is a center of symmetry equating one-half of the molecule to the other. Thus, a helical twist to the central four-membered rings was not observed. A similar situation pertains to the complex $[(SalomphanAl)Li(THF)_2]_2$ which also possesses a center of symmetry.[9]

Conversion of Types I and II to Trimetallic Type III. In view of the fact that trimetallic species have been detected sporadically in the syntheses of 1:1 and 2:1 metal/ligand combinations, it was of interest to see if type I and II complexes could be intentionally converted into the corresponding type III trimetallic. Two sets of reactions were employed. The first involved the combination of the type I species with an extra 1 mol of AlR_3 (eq 3a). These reactions led to quantitative formation of the trimetallic, type III species. The second involved mixing the type II compounds (eq 3b) with 1 mol of AlR_3. These were conducted at 25 °C as well as in refluxing toluene. In this second set of reactions the final products were identified as unreacted starting material. Thus, it appears that a requirement for the conversion of the type I and II species is the presence of an available NH group. For the conversion of type I to type II this can be qualified further: the available NH group must also be acidic enough to participate in alkane elimination. Like the type II complexes, the trimetallic, type III complexes are unreactive. They do not undergo exchange of either AlR or R in solution.[7]



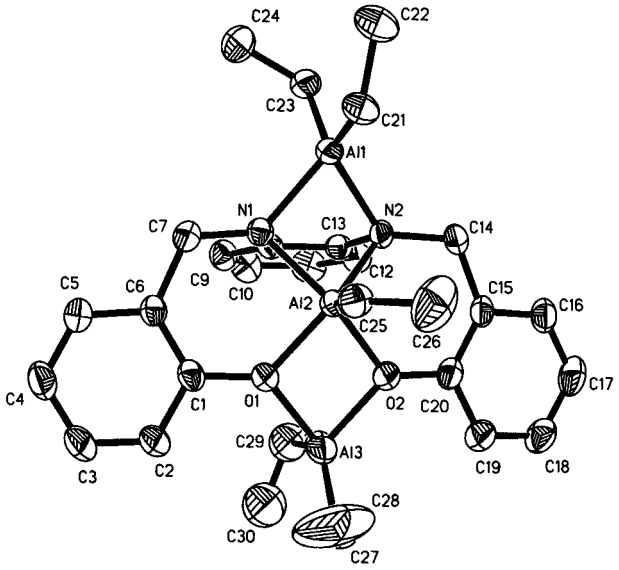


Figure 10. Molecular structure and atom-numbering scheme for $SalophanAlEt(AlEt_2)_2$ (**14**).

Molecular Structure of $SalophanAlEt(AlEt_2)_2$ (14). The molecular structure of **14** is shown in Figure 10. It consists of the Salophan ligand in a cis coordination mode to a central five-coordinate square pyramidal AlEt unit and to two terminal $AlEt_2$ units which adopt distorted tetrahedral geometries. The bond lengths and angles in this complex are very similar to previously reported trimetallic aluminum complexes with a cis ligand coordination. Comparison to the methyl analog, $SalophanAlMe(AlMe_2)_2$, shows that these parameters are essentially equivalent within the limits of experimental error. For the central five-coordinate aluminum atoms, the Al−N distances for the methyl and ethyl derivatives are an average of 1.99(1) Å while the Al−O distances are 1.888(3) Å. Any steric effect of the ethyl groups in **14** should act to perturb the terminal $AlEt_2$ groups. Examination of the N−Al−N and O−Al−O angles, however, shows that they are nearly identical to that observed for the methyl analog. Thus, a change from methyl to ethyl does not lead to any undue structural changes in the resulting trimetallic complex.

Conclusion

We are attempting to obtain a complete description of the reactivity of the Salan ligands with the group 13 elements. The work directed at aluminum is shown in Scheme 1. In previous publications we reported the synthesis and structures of a number of the trimetallic derivatives (type III).[6,7] In this publication we established the identity of two types of complexes having a metal-ligand stoichiometry of 2:1 (types I and II). In order to complete the broader goals of this project further research will be directed toward the preparation of the series of monometallic complexes (types IV and V).

Experimental Section

General Considerations. All manipulations were conducted using Schlenk techniques in conjunction to an inert-

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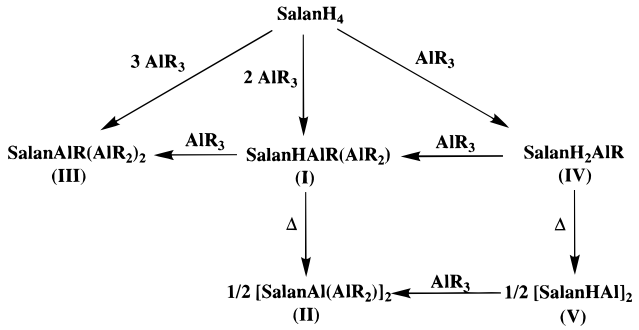
Scheme 1. Preparation and Interconversion of the Salan−Aluminum Complexes



atmosphere glovebox. All solvents were rigorously dried prior to use. The ligands SaleanH_4, SalophanH_4, and SalomphanH_4 were synthesized as previously described.[4] The synthesis and characterization of SalophanAlEt(AlEt_2)$_2$ (**14**) was reported previously.[6b] NMR data were obtained on JEOL-GSX-400 and -270 instruments at 270.17 (^{1}H) and 62.5 (^{13}C) MHz. Chemical shifts are reported relative to $SiMe_4$ and are in ppm. Elemental analyses were obtained on a Perkin-Elmer 2400 analyzer. Infrared data were recorded as KBr pellets on a Matheson Instruments 2020 Galaxy Series spectrometer and are reported in cm^{-1}.

SaleanHAlMe(AlMe_2) (1). SaleanH_4 (1.04 g, 3.8 mmol) was suspended in 10 mL of toluene and stirred while a solution of trimethylaluminum (0.550 g, 7.6 mmol) in 15 mL of toluene was added at 25 °C. The exothermic reaction was stirred for 30 min without heating and then brought to reflux for 10 min. Concentration to 10 mL and storage at −30 °C for 2 days yielded the title compound as a white precipitate (1.293 g, 92%): Mp 172−175 °C (dec); ^{1}H NMR (270 MHz, C_6D_6) δ −0.63 (s, 3H, AlCH_3), −0.48 (s, 3H, AlCH_3), 0.12 (s, 3H, AlCH_3), 1.05 (br d, 1H, NH), 1.88 (dd, 1H, NCH_2), 2.31 (dd, 1H, PhCH_2), 2.65 (m, 2H, NCH_2), 3.10 (m, 1H, NCH_2), 3.58 (app t, 1H, PhCH_2), 3.96 (d, 1H, PhCH_2), 4.73 (d, 1H, PhCH_2), 6.70−7.31 (m, 8H, Ph-*H*); ^{13}C NMR (100 MHz, C_6D_6) δ −11.5 (Al*C*H$_3$), −10.1 (Al*C*H$_3$), −7.0 (Al*C*H$_3$), 47.7 (Ph*C*H$_2$), 48.3 (N*C*H$_2$), 56.1 (Ph*C*H$_2$), 118.3 (Ph), 119.6, 122.0, 122.4, 125.1, 129.4, 130.2, 130.5, 132.5, 152.3, 153.2; IR (KBr) 3283, 2926, 2808, 1601, 1582, 1493, 1454, 1250, 1200, 1053, 883, 787, 692 cm^{-1}; MS (DIP/EI) *m*/*e* 368 (M$^+$), 353 (M$^+$ − CH$_3$), 337 (M$^+$ − H − 2CH$_3$), 295 (M$^+$ − CH$_3$ − H − AlMe$_2$). Anal. Calcd for $C_{19}H_{26}N_2O_2Al_2$: C, 61.96; H, 7.07. Found: C, 62.09; H, 7.01.

SaleanHAlEt(AlEt_2) (2). SaleanH_4 (2.55 g, 9.38 mmol) was suspended in 25 mL of toluene and stirred while a solution of triethylaluminum (2.30 g, 18.8 mmol, 93% pure) in 30 mL of toluene was added at 25 °C. The exothermic reaction was stirred for 10 min without heating and then brought to reflux for 5 min. Removal of volatiles, followed by dissolution of the white solid in hexanes, filtration, and storage at −30 °C, yielded the title compound as a white crystalline solid (3.142 g, 82%): Mp 130−135 °C; ^{1}H NMR (270 MHz, C_6D_6) δ −0.40 (q, 2H, AlCH_2), 0.11 (q, 2H, AlCH_2), 0.72 (q, 2H, AlCH_2), 1.04 (t, 3H, CH$_2$CH_3), 1.19 (t, 3H, CH$_2$CH_3), 1.21 (br m, 1H, NH), 1.66 (t, 3H, CH$_2$CH_3), 1.91 (m, 1H, NCH_2), 2.35 (dd, 1H, PhCH_2), 2.65 (m, 2H, NCH_2), 3.12 (app t, 1H, NCH_2), 3.70 (app t, 1H, PhCH_2), 3.99 (d, 1H, PhCH_2), 4.72 (d, 1H, PhCH_2), 6.68−7.25 (m, 8H, Ph-*H*); ^{13}C NMR (100 MHz, C_6D_6) δ −1.9 (Al*C*H$_2$), 1.2 (Al*C*H$_2$), 2.3 (Al*C*H$_2$), 8.5 (CH$_2$*C*H$_3$), 9.0 (CH$_2$*C*H$_3$), 10.5 (CH$_2$*C*H$_3$), 47.6 (Ph*C*H$_2$), 48.2 (N*C*H$_2$), 48.5 (N*C*H$_2$), 56.0 (Ph*C*H$_2$), 118.2 (Ph), 119.6, 121.9, 122.2, 124.8, 129.2, 129.9, 130.4, 132.1, 152.5, 153.2; IR (KBr) 3283, 2936, 2861, 1601, 1489, 1454, 1244, 1038, 883, 763, 663 cm^{-1}. Anal. Calcd for $C_{22}H_{32}N_2O_2Al_2$: C, 64.39; H, 7.80. Found: C, 64.80; H, 8.41.

SaleanHAl^{i}Bu(Al^{i}Bu$_2$) (3). SaleanH_4 (2.14 g, 7.87 mmol) was suspended in 50 mL of toluene and stirred while a solution of triisobutylaluminum (3.12 g, 15.7 mmol) in 50 mL of toluene was added at 25 °C. The exothermic reaction was stirred for 30 min without heating and then brought to reflux for 5 min. Removal of volatiles, followed by dissolution of the white solid in hexanes, filtration, and storage at −30 °C, yielded the title compound as a crystalline white solid (2.79 g, 72%): Mp 98−100 °C; ^{1}H NMR (270 MHz, C_6D_6) δ −0.25 (q, 1H, AlCH_2), 0.11 (q, 1H, AlCH_2), 0.20 (d, 2H, AlCH_2), 0.77 (app t, 2H, AlCH_2), 0.82 (d, 3H, CHCH_3), 0.86 (d, 3H, CHCH_3), 0.97 (d, 3H, CHCH_3), 1.06 (d, 3H, CHCH_3), 1.26 (br m, 1H, NH), 1.36 (t, 3H, CHCH_3), 1.83 (m, 2H, C*H*CH$_3$), 1.93 (dd, 1H, NCH_2), 2.37 (dd, 1H, PhCH_2), 2.47 (m, 1H, C*H*CH$_3$), 2.70 (m, 2H, NCH_2), 3.13 (m, 1H, NCH_2), 3.73 (app t, 1H, PhCH_2), 3.98 (d, 1H, PhCH_2), 4.71 (d, 1H, PhCH_2), 6.71−7.34 (m, 8H, Ph-*H*); ^{13}C NMR (100 MHz, C_6D_6) δ 21.3 (Al*C*H$_2$), 23.1 (Al*C*H$_2$), 24.8 (Al*C*H$_2$), 25.7 (CH*C*H$_3$), 26.4 (CH*C*H$_3$), 26.7 (CH*C*H$_3$), 27.6 (CH*C*H$_3$), 28.0 (CH*C*H$_3$), 28.6 (*C*HCH$_3$), 28.7 (*C*HCH$_3$), 28.8 (*C*HCH$_3$), 47.7 (Ph*C*H$_2$), 48.2 (N*C*H$_2$), 48.2 (N*C*H$_2$), 56.1 (Ph*C*H$_2$), 118.7 (Ph), 119.7, 121.9, 122.3, 124.9, 127.3, 129.1, 129.9, 130.2, 132.1, 152.5, 153.1; IR (KBr) 3289, 2944, 2861, 1601, 1491, 1456, 1244, 1040, 883, 760, 669 cm^{-1}. Anal. Calcd for $C_{28}H_{44}N_2O_2Al_2$: C, 68.02; H, 8.91. Found: C, 68.31; H, 9.02.

SalophanHAlMe(AlMe_2) (4). SalophanH_4 (1.25 g, 3.90 mmol) was suspended in 20 mL of toluene and stirred while a solution of trimethylaluminum (0.563 g, 7.82 mmol) in 20 mL of toluene was added at 25 °C. The exothermic reaction was stirred for 30 min without heating and then brought to reflux for 10 min. Removal of volatiles, followed by dissolution of the purple solid in toluene and storage at −30 °C, yielded the title compound as a purple solid (1.322 g, 82%): Mp 117−119 °C (dec); ^{1}H NMR (270 MHz, C_6D_6) δ −0.66 (s, 3H, AlCH_3), −0.44 (s, 3H, AlCH_3), 0.13 (s, 3H, AlCH_3), 2.83 (br d, 1H, NH), 3.06 (dd, 1H, PhCH_2), 3.66 (app t, 1H, PhCH_2), 4.42 (d, 1H, PhCH_2), 4.51 (d, 1H, PhCH_2), 6.48−7.30 (m, 12H, Ph-*H*); ^{13}C NMR (100 MHz, C_6D_6) δ −11.4 (Al*C*H$_3$), −6.8 (Al*C*H$_3$), −6.7 (Al*C*H$_3$), 49.6 (Ph*C*H$_2$), 53.3 (Ph*C*H$_2$), 109.9 (Ph), 113.2, 118.0, 119.1, 122.4, 122.6, 123.1, 124.0, 127.8, 128.4, 129.4, 129.8, 129.9, 130.2, 130.6, 150.5, 151.5, 152.8; IR (KBr) cm^{-1}. Anal. Calcd for $C_{23}H_{26}N_2O_2Al_2$: C, 66.35; H, 6.25. Found: C, 66.24; H, 6.40.

SalophanHAlEt(AlEt_2) (5). SalophanH_4 (1.75 g, 5.47 mmol) was suspended in 20 mL of toluene and stirred while a solution of triethylaluminum (1.37 g, 11.2 mmol, 93% pure) in 30 mL of toluene was added at 25 °C. The exothermic reaction was stirred for 10 min without heating and then brought to reflux for 5 min. Removal of volatiles, followed by dissolution of the purple solid in toluene and storage at −30 °C, yielded the title compound as a purple crystalline solid (2.17 g, 87%): Mp 134−135 °C (dec); ^{1}H NMR (270 MHz, C_6D_6) δ −0.02 (m, 2H, AlCH_2), 0.12 (dq, 2H, AlCH_2), 0.72 (q, 2H, AlCH_2), 1.02 (dt, 6H, CH$_2$CH_3), 1.62 (t, 3H, CH$_2$CH_3), 2.97 (dd, 1H, NH), 3.07 (dd, 1H, PhCH_2), 3.86 (app t, 1H, PhCH_2), 4.47 (d, 1H, PhCH_2), 4.55 (d, 1H, PhCH_2), 6.55−7.35 (m, 12H, Ph-*H*); ^{13}C NMR (100 MHz, C_6D_6) δ −1.7 (Al*C*H$_2$), −0.1 (Al*C*H$_2$), 2.5 (Al*C*H$_2$), 8.6 (CH$_2$*C*H$_3$), 8.8 (CH$_2$*C*H$_3$), 9.8 (CH$_2$*C*H$_3$), 49.7 (Ph*C*H$_2$), 53.7 (Ph*C*H$_2$), 110.0 (Ph), 113.3, 118.1, 119.1, 122.5, 122.6, 123.0, 124.1, 127.9, 129.8, 129.8, 129.9, 130.1, 130.7, 150.2, 151.7, 153.0; IR (KBr) 3291, 3059, 2932, 2859, 1605, 1493, 1453, 1333, 1246, 1196, 1111, 984, 920, 872, 794, 761, 634 cm^{-1}. Anal. Calcd for $C_{26}H_{32}N_2O_2Al_2$: C, 68.42; H, 6.99. Found: C, 68.60; H, 6.82.

SalophanHAl^{i}Bu(Al^{i}Bu$_2$) (6). SalophanH_4 (2.00 g, 6.25 mmol) was suspended in 30 mL of toluene and stirred while a solution of triisobutylaluminum (2.50 g, 12.6 mmol) in 50 mL of toluene was added at 25 °C. The exothermic reaction was stirred for 30 min without heating and then brought to reflux for 1 h. Removal of volatiles, followed by dissolution of the purple solid in hexanes and storage at −30 °C, yielded the title compound as a crystalline pink solid (2.152 g, 67%): Mp 134−142 °C (dec); ^{1}H NMR (270 MHz, C_6D_6) δ −0.98 (q, 1H, AlCH_2), 0.16 (q, 1H, AlCH_2), 0.27 (d, 2H, AlCH_2), 0.77 (dd, 2H, AlCH_2), 0.83 (dt, 12H, CHCH_3), 1.35 (dt, 6H, CHCH_3), 1.71 (m, 1H, C*H*CH$_3$), 1.82 (m, 1H, C*H*CH$_3$), 2.44 (m, 1H, C*H*CH$_3$), 3.03 (br d, 1H, NH), 3.17 (d, 1H, PhCH_2), 3.96 (app t, 1H, PhCH_2), 4.50

(d, 1H, PhCH_2), 4.57 (d, 1H, PhCH_2), 6.45−7.42 (m, 12H, Ph-H); ^{13}C NMR (100 MHz, C_6D_6) δ 25.7 (AlCH_2), 26.2 (AlCH_2), 26.3 (AlCH_2), 27.8 (CHCH_3), 27.8 (CHCH_3), 27.8 (CHCH_3), 28.0 (CHCH$_3$), 28.5 (CHCH$_3$), 28.6 (CHCH$_3$), 49.7 (PhCH_2), 53.9 (PhCH_2), 110.1 (Ph), 113.4, 118.6, 119.4, 122.5, 122.6, 122.8, 124.3, 128.2, 129.7, 129.9, 129.9, 130.1, 130.5, 150.3, 151.6, 153.0; IR (KBr) 3244, 2949, 2859, 1604, 1493, 1452, 1261, 1113, 1020, 797, 754, 669 cm^{-1}. Anal. Calcd for $C_{32}H_{44}N_2O_2Al_2$: C, 70.85; H, 8.12. Found: C, 71.21; H, 8.62.

SalomphanHAlMe(AlMe$_2$) (7). SalomphanH$_4$ (1.705 g, 4.90 mmol) was suspended in 30 mL of toluene and stirred while a solution of trimethylaluminum (0.711 g, 9.88 mmol) in 20 mL of toluene was added at 25 °C. The exothermic reaction was stirred for 30 min without heating and then brought to reflux for 8 h. Removal of volatiles, followed by dissolution of the purple solid in toluene and storage at −30 °C, yielded the title compound as a faintly purple solid (1.536 g, 71%): Mp 165−168 °C (dec); ^{1}H NMR (270 MHz, C_6D_6) δ −0.61 (s, 3H, AlCH_3), −0.42 (s, 3H, AlCH_3), 0.15 (s, 3H, AlCH_3), 2.16 (s, 3H, PhCH_3), 2.18 (s, 3H, PhCH_3), 2.86 (dd, 1H, NH), 3.12 (dd, 1H, PhCH_2), 3.77 (app t, 1H, PhCH_2), 4.50 (d, 1H, PhCH_2), 4.60 (d, 1H, PhCH_2), 6.26 (s, 1H, Ph-H), 6.55 (s, 1H, Ph-H), 6.65−7.29 (m, 8H, Ph-H); ^{13}C NMR (100 MHz, C_6D_6) δ −11.4 (AlCH$_3$), −6.7 (AlCH$_3$), −6.7 (AlCH$_3$), 18.7 (PhCH$_3$), 20.1 (PhCH$_3$), 49.8 (PhCH$_2$), 53.4 (PhCH$_2$), 111.4 (Ph), 118.1, 119.2, 120.3, 122.3, 122.5, 124.2, 124.3, 127.0, 128.6, 129.8, 130.2, 130.6, 137.3, 148.3, 151.5, 153.0; IR (KBr) 3234, 2933, 1607, 1506, 1493, 1454, 1400, 1275, 1245, 1198, 887, 760, 693 cm^{-1}. Anal. Calcd for $C_{25}H_{30}N_2O_2Al_2$: C, 67.57; H, 6.76. Found: C, 67.71; H, 6.57.

SalomphanHAlEt(AlEt$_2$) (8). SalomphanH$_4$ (2.00 g, 5.75 mmol) was suspended in 30 mL of toluene and stirred while a solution of triethylaluminum (1.41 g, 11.5 mmol, 93% pure) in 30 mL of toluene was added at 25 °C. The exothermic reaction was stirred for 10 min without heating and then brought to reflux for 5 min. Removal of volatiles, followed by dissolution of the purple solid in toluene and storage at −30 °C, yielded the title compound as a red-brown crystalline solid (2.336 g, 84%): Mp 98−102 °C (dec); ^{1}H NMR (270 MHz, C_6D_6) δ 0.04 (m, 2H, AlCH_2), 0.13 (m, 2H, AlCH_2), 0.73 (q, 2H, AlCH_2), 1.05 (t, 3H, CH$_2$CH$_3$), 1.07 (t, 3H, CH$_2$CH$_3$), 1.64 (t, 3H, CH$_2$CH$_3$), 2.16 (s, 3H, PhCH_3), 2.19 (s, 3H, PhCH_3), 3.01 (br d, 1H, NH), 3.17 (dd, 1H, PhCH_2), 3.93 (app t, 1H, PhCH_2), 4.56 (d, 1H, PhCH_2), 4.64 (d, 1H, PhCH_2), 6.25 (s, 1H, Ph-H), 6.58 (s, 1H, Ph-H), 6.68−7.31 (m, 8H, Ph-H); ^{13}C NMR (100 MHz, C_6D_6) δ −1.7 (AlCH$_2$), 0.1 (AlCH$_2$), 2.6 (AlCH$_2$), 8.6 (CH$_2$CH$_3$), 8.8 (CH$_2$CH$_3$), 9.9 (CH$_2$CH$_3$), 18.7 (PhCH$_3$), 20.1 (PhCH$_3$), 49.9 (PhCH$_2$), 53.9 (PhCH$_2$), 111.5 (Ph), 118.1, 119.2, 120.4, 122.4, 122.5, 124.1, 124.3, 127.4, 128.5, 129.8, 130.1, 130.7, 137.3, 148.4, 151.8, 153.1; IR (KBr) 3275, 3027, 2932, 2863, 1607, 1493, 1452, 1269, 1219, 1113, 756, 658 cm^{-1}. Anal. Calcd for $C_{28}H_{36}N_2O_2Al_2$: C, 69.14; H, 7.41. Found: C, 68.95; H, 7.53.

SalomphanHAl^{i}Bu(Al^{i}Bu$_2$) (9). SalomphanH$_4$ (1.76 g, 5.05 mmol) was suspended in 30 mL of toluene and stirred while a solution of triisobutylaluminum (2.00 g, 10.1 mmol) in 20 mL of toluene was added at 25 °C. The exothermic reaction was stirred for 30 min without heating and then brought to reflux for 1 h. Removal of volatiles, followed by dissolution of the purple solid in hexanes and storage at −30 °C, yielded the title compound as a crystalline pink solid (1.973 g, 69%): Mp 101−103 °C (dec); ^{1}H NMR (270 MHz, C_6D_6) δ 0.04 (q, 1H, AlCH_2), 0.24 (q, 1H, AlCH_2), 0.30 (d, 2H, AlCH_2), 0.83 (d, 2H, AlCH_2), 0.87 (t, 12H, CHCH_3), 1.37 (t, 6H, CHCH_3), 1.84 (m, 2H, CHCH$_3$), 2.14 (s, 3H, PhCH_3), 2.19 (s, 3H, PhCH_3), 2.47 (m, 1H, CHCH$_3$), 3.05 (br d, 1H, NH), 3.23 (br d, 1H, PhCH_2), 4.03 (app t, 1H, PhCH_2), 4.60 (d, 1H, PhCH_2), 4.61 (d, 1H, PhCH_2), 6.28 (s, 1H, Ph-H), 6.62 (s, 1H, Ph-H), 6.74−7.45 (m, 8H, Ph-H); ^{13}C NMR (100 MHz, C_6D_6) δ 18.7 (PhCH$_3$), 20.2 (PhCH$_3$), 21.2 (AlCH$_2$), 22.1 (AlCH$_2$), 25.0 (AlCH$_2$), 25.7 (CHCH$_3$), 26.3 (CHCH$_3$), 26.4 (CHCH$_3$), 27.8 (CHCH$_3$), 27.8 (CHCH$_3$), 27.9 (CHCH$_3$), 28.0 (CHCH$_3$), 28.5 (CHCH$_3$), 28.6 (CHCH$_3$), 49.8 (PhCH$_2$), 54.1 (PhCH$_2$), 111.6 (Ph), 118.7, 119.4, 120.6, 122.5, 122.5, 124.0, 124.2, 127.8, 128.3, 129.0, 129.7, 130.1, 130.5, 137.4, 148.2, 151.7, 153.1; IR (KBr) 3259, 2949, 2864, 1607, 1493, 1453, 1329, 1233, 887, 806, 760, 677 cm^{-1}. Anal. Calcd for $C_{34}H_{48}N_2O_2Al_2$: C, 71.58; H, 8.42. Found: C, 71.26; H, 8.31.

[SalophanAl(AlMe$_2$)]$_2$ (10). SalophanHAlMe(AlMe$_2$) (1.00 g, 2.40 mmol) was suspended in 10 mL of toluene and heated at reflux for 30 h. Removal of volatiles, followed by dissolution of the purple solid in toluene and storage at −30 °C, yielded the title compound as a white solid (0.701 g, 73%): Mp >260 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ −1.02 (s, 3H, AlCH_3), −0.36 (s, 3H, AlCH_3), 3.58 (dd, 1H, PhCH_2), 3.89 (d, 1H, PhCH_2), 3.97 (d, 1H, PhCH_2), 4.18 (d, 1H, PhCH_2), 6.14−7.38 (m, 12H, Ph-H); ^{13}C NMR (100 MHz, $CDCl_3$) δ −10.9 (AlCH$_3$), −6.4 (AlCH$_3$), 48.9 (PhCH$_2$), 55.9 (PhCH$_2$), 108.8 (Ph), 115.1, 117.2, 119.6, 122.5, 122.5, 123.5, 125.5, 126.0, 128.1, 128.9, 129.5, 130.5, 148.9, 151.0, 151.8; IR (KBr) 3062, 3038, 2926, 2804, 1585, 1491, 1329, 1248, 1194, 1016, 877, 797, 762, 702 cm^{-1}. Anal. Calcd for $C_{22}H_{22}N_2O_2Al_2$: C, 66.00; H, 5.50. Found: C, 66.41; H, 5.53.

[SalophanAl(Al^{i}Bu$_2$)]$_2$ (11). SalophanHAl^{i}Bu(Al^{i}Bu$_2$) (0.805 g, 1.49 mmol) was dissolved in 10 mL of toluene and heated at reflux for 48 h. Removal of volatiles, followed by dissolution of the purple solid in toluene and storage at −30 °C, yielded the title compound as a white solid (0.310 g, 43%): Mp >260 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ −0.16 (d, 2H, AlCH_2), 0.32 (dd, 1H, AlCH_2), 0.43 (dd, 1H, AlCH_2), 0.49 (d, 3H, CHCH_3), 0.55 (d, 3H, CHCH_3), 1.04 (d, 3H, CHCH_3), 1.09 (d, 3H, CHCH_3), 1.51 (m, 1H, CHCH$_3$), 2.01 (m, 1H, CHCH$_3$), 3.59 (d, 1H, PhCH_2), 3.84 (d, 1H, PhCH_2), 3.91 (d, 1H, PhCH_2), 4.18 (d, 1H, PhCH_2), 6.02−7.39 (m, 12H, Ph-H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.0 (AlCH$_2$), 24.8 (AlCH$_2$), 25.3 (CHCH$_3$), 26.0 (CHCH$_3$), 27.6 (CHCH$_3$), 28.1 (CHCH$_3$), 28.5 (CHCH$_3$), 48.9 (PhCH$_2$), 56.2 (PhCH$_2$), 108.9 (Ph), 115.1, 117.6, 119.9, 122.4, 122.6, 123.4, 125.4, 126.0, 128.0, 128.8, 129.0, 130.5, 148.9, 151.2, 151.8; IR (KBr) cm^{-1}. Anal. Calcd for $C_{28}H_{34}N_2O_2Al_2$: C, 69.42; H, 7.02. Found: C, 69.00; H, 6.83.

[SalomphanAl(AlMe$_2$)]$_2$ (12). SalomphanHAlMe(AlMe$_2$) (0.750 g, 1.32 mmol) was dissolved in 10 mL of toluene and heated at reflux for 30 h. Removal of volatiles, followed by dissolution of the purple solid in toluene and storage at −30 °C, yielded the title compound as a white solid (0.507 g, 75%): Mp > 260 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ −1.04 (s, 3H, AlCH_3), −0.42 (s, 3H, AlCH_3), 2.21 (s, 3H, PhCH_3), 2.31 (s, 3H, PhCH_3), 3.58 (dd, 1H, PhCH_2), 3.87 (d, 1H, PhCH_2), 3.98 (d, 1H, PhCH_2), 4.18 (d, 1H, PhCH_2), 5.93−7.38 (m, 10H, Ph-H); ^{13}C NMR (100 MHz, C_6D_6) δ −7.3, −4.0 (AlCH$_3$), 19.6, 19.9, 22.8 (Ph−CH$_3$), 48.9, 50.3 (PhCH$_2$), 110.9, 117.2, 119.5, 121.8, 123.3, 125.4, 128.3, 129.1, 138.0, 146.6, 151.1, 152.0 (Ph); IR (KBr) 3022, 2930, 1604, 1585, 1491, 1452, 1224, 1194, 1113, 891, 810, 754, 698, 640 cm^{-1}. Anal. Calcd for $C_{25}H_{30}N_2O_2Al_2$: C, 67.57; H, 6.76. Found: C, 67.55; H, 7.01.

[SalomphanAl(Al^{i}Bu)$_2$]$_2$ (13). SalomphanH$_4$ (2.50 g, 7.18 mmol) was suspended in 10 mL of toluene, and then triisobutylaluminum (2.85 g, 14.4 mmol) in 10 mL of toluene was added at 25 °C. The solid immediately went into solution combined with the vigorous evolution of gases. The faintly gray solution was then refluxed for 22 h, during which time the solution turned a deep purple. Removal of the volatiles under reduced pressure yielded a purple solid. Dissolution of the solid in 5 mL of toluene and cooling to −30 °C for 1 day yielded 2.62 g (71%) of a white solid. X-ray-quality crystals were obtained from a concentrated toluene solution stored at −30 °C for 1 week: Mp > 260 °C; ^{1}H NMR (270 MHz, C_6D_6) δ 0.15 (dd, J = 4, 8 Hz, 2H, AlCH_2), 0.51 (dd, J = 7, 15 Hz, 1H, AlCH_2), 0.67 (app dd, 1H, AlCH_2), 0.72 (dd, J = 6, 18 Hz, 6H, CHCH_3), 1.24 (dd, J = 6, 20 Hz, 6H, CHCH_3), 1.73−1.79 (m, 2H, CHCH$_3$), 2.23 (s, 3H, PhCH_3), 2.47 (s, 3H, PhCH_3), 3.68 (d, J = 15 Hz, 1H, PhCH_2), 3.96 (d, J = 14 Hz, 1H, PhCH_2), 4.03 (d, J = 14 Hz, 1H, PhCH_2), 4.37 (d, J = 15 Hz, 1H, PhCH_2), 6.02 (d, J = 7 Hz, 1H, Ph-H), 6.12 (s, 1H, Ph-H), 6.50−

Table 1. Summary of Crystal Data for SalophanAlEt(AlEt$_2$)$_2$ (14)

compd	**14**
formula	$C_{30}H_{41}Al_3N_2O_2$
fw	542.6
cryst system	triclinic
space group	$P\bar{1}$
a (Å)	10.165(3)
b (Å)	11.509(2)
c (Å)	13.607(3)
α (deg)	92.02(1)
β (deg)	100.17(2)
γ (deg)	103.59(2)
V (Å^3)	1518.2(6)
Z	2
D_{calc} (g/cm^3)	1.187
cryst size (mm)	0.8 × 0.6 × 0.3
temp (K)	298
2θ range (deg)	3.5−45
scan type	2θ−θ
scan speed (deg/min)	6−60
scan range (deg)	0.60
reflcns collcd	4799
indp reflcns	3986
obsd reflcns	2628
$F > X\,\sigma(F)$	4
no. of params	336
R	0.0577
R_w	0.0564
GOF	1.09
lar diff peak (e/Å^3)	0.34

6.54 (m, 1H, Ph-*H*), 6.70 (d, J = 2 Hz, 1H, Ph-*H*), 6.93−7.51 (m, 6H, Ph-*H*); ^{13}C NMR (100 MHz, C_6D_6) δ 20.0, 21.2 (Ph−*C*H$_3$), 25.6, 26.1, 28.1, 28.4, 28.5 (Al*Et*), 49.2, 56.3 (Ph*C*H$_2$), 110.9, 117.5, 119.8, 121.8, 122.5, 123.3, 124.0, 125.4, 130.5, 133.3, 134.7, 137.6 (*Ph*); IR (KBr) 3020, 2951, 2860, 1606, 1586, 1493, 1452, 1333, 1225, 1113, 891, 755, 683, 638, 579, 443 cm^{-1}. Anal. Calcd for $C_{60}H_{76}N_4O_4Al_4$: C, 70.31; H, 7.42; N, 5.47. Found: C, 70.67; H, 4.44; N, 5.41.

Conversion of SalanHAlR(AlR$_2$) to SalanAlR(AlR$_2$)$_2$. Two representative reactions were conducted as follows: 1. SaleanHAlMe(AlMe$_2$) (0.044 g, 0.119 mmol) was dissolved in 10 mL of toluene, with stirring, followed by the addition of a toluene solution (10 mL) of trimethylaluminum (0.012 g, 0.167 mmol). The resulting solution was allowed to stir at room temperature for 15 min followed by reflux for 2.5 h. The volatiles were then removed in vacuo to yield a white solid. ^{1}H NMR identified the solid as SaleanAlMe(AlMe$_2$)$_2$ in virtually quantitative yield (>95%).

2. SalophanHAlMe(AlMe$_2$) (1.095 g, 2.63 mmol) was dissolved in 10 mL of toluene and then combined with a toluene (20 mL) solution of AlMe$_3$ (0.208 g, 2.89 mmol). Gas evolution was witnessed, and the solution was heated to 60 °C for 15 min to yield a purple solution. The volatiles were removed in vacuo to yield a white crystalline solid which was identified by ^{1}H NMR as SalophanAlMe(AlMe$_2$)$_2$ in virtually quantitative yield (>95%).

Attempted Conversion of [SalanAl(AlR$_2$)]$_2$ to SalanAlR(AlR$_2$)$_2$. A representative reaction is as follows: [SalophanAl(AlMe$_2$)]$_2$ (0.300 g, 0.375 mmol) was suspended in 15 mL of toluene, trimethylaluminum (0.054 g, 0.75 mmol) was added neat at 25 °C, and the reaction was stirred at 25 °C for 24 h. The volatiles were removed in vacuo to leave a red solid which was taken up in C_6D_6. Examination by ^{1}H NMR revealed no presence of SalophanAlMe(AlMe$_2$)$_2$. An identical reaction, except carried out at reflux for 16 h, also did not produce the desired product, SalophanAlMe(AlMe$_2$)$_2$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for SalophanAlEt(AlEt$_2$)$_2$ (14)

Bond Lengths			
Al(1)-Al(2)	2.880 (2)	Al(2)-O(2)	1.890 (3)
Al(1)-N(1)	2.002 (4)	Al(2)-N(1)	2.001 (4)
Al(1)-N(2)	1.985 (4)	Al(2)-N(2)	2.000 (5)
Al(1)-C(21)	1.962 (5)	Al(2)-C(25)	1.947 (6)
Al(1)-C(23)	1.947 (6)	Al(3)-O(1)	1.834 (3)
Al(2)-Al(3)	2.890 (3)	Al(3)-O(2)	1.853 (4)
Al(2)-O(1)	1.887 (4)		

Bond Angles			
N(1)-Al(1)-N(2)	73.8(2)	N(1)-Al(2)-N(2)	73.5(2)
O(1)-Al(2)-O(2)	77.3(1)	O(1)-Al(3)-O(2)	79.5(2)
O(1)-Al(2)-N(1)	89.2(2)	Al(2)-O(1)-Al(3)	101.9(2)
O(2)-Al(2)-N(1)	137.8(2)	Al(2)-O(2)-Al(3)	101.1(2)
O(1)-Al(2)-N(2)	135.9(2)	Al(1)-N(1)-Al(2)	92.0(2)
O(2)-Al(2)-N(2)	88.7(2)		

X-ray Experimental Details. Data were collected on a Siemens P4 diffractometer using graphite-monochromated Mo Kα (0.710 73 Å) radiation. The check reflections, measured every 100 reflections, indicated a less than 5% decrease in intensity over the course of data collection for each compound, and hence, no correction was applied. 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 for **14**.

The structure solution of **13** was problematic for three reasons. First, there was a molecule of disordered toluene in the unit cell. Second, the ^{i}Bu groups (four of them) were disordered. These groups were refined using partial occupancy. Third, the phenyl rings possessed unrealistically low values for the thermal parameters. Early in the structure refinement these rings were refined using ideal positions. In the latter stages of the solution the R value was improved by allowing these rings to refine naturally.

The consequence of these three problems was that many of the non-hydrogen atoms would not refine anisotropically. The best final refinement was achieved with the monoclinic space group *Cc*. Repeated attempts to solve the structure in *C*2/*c* were unsuccessful. No undue relevance is claimed for any of the bond distance and angles within this structure. However, the overall arrangement of the atoms for **13** is clear from the present structure.

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Supporting Information Available: Unit cell diagrams and listings of X-ray experimental details, bond lengths and angles, anisotropic thermal parameters, and atomic coordinates and isotropic thermal parameters (23 pages). Ordering information is given on any current masthead page.

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