Bimetallic Aluminum and Gallium Chelates with N_2O_2 Ligands

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Received October 18, 1999

A wide range of bimetallic aluminum molecules are formed in combinations between Salen Schiff base ligands and either AlR_3 or AlR_2Cl. They are of the general formulas $L(AlR_2)_2$ and $L(AlRCl)_2$ with R = alkyl and L = Salen(^{t}Bu) ligand with relatively unusual "backbone" connections between the nitrogen atoms, 1,2-cyclohexylene (Salcen(^{t}Bu)), 1,4-butylene (Salben(^{t}Bu)), 1,5-pentylene (Salpten(^{t}Bu)), 1,6-hexylene (Salhen(^{t}Bu)), and 1,4-phenylene (1,4-Salophen(^{t}Bu)). Additionally, previously unknown ligands were employed with the "backbones" 1,4-bis(*p*-aminobenzyl)benzene (Salmaben(^{t}Bu)), 1-(*m*-aminobenzoyl)-4-(*m*-aminobenzyl)benzene (Salmabmaben(^{t}Bu)), and 4,4′-bis(*m*-aminobenzoyl)diphenylmethane (Salmadmen(^{t}Bu)). The ligands for these compounds were designed to feature two group 13 sites at long and varying distances from one another. The compounds were characterized by mp analyses, IR, and ^{1}H NMR, and X-ray structures were determined for the examples R,R′-Salcen(^{t}Bu){$AlMe_2$}$_2$ (**1**), Salben(^{t}Bu){$AlMe_2$}$_2$ (**2**), 1,4-Salophen(^{t}Bu){$GaEt_2$}$_2$ (**7**), R,R′-Salcen(^{t}Bu){AlMeCl}$_2$ (**11**), Salben(^{t}Bu){AlMeCl}$_2$ (**13**), and Salhen(^{t}Bu){AlMeCl}$_2$ (**14**).

Introduction

The Salen[1] class of ligands (Figure 1) has been of great utility in the isolation of higher-coordinate monometallic group 13 complexes. Some examples include those with aluminum,[2] gallium,[3] and indium[4] alkyls and halides and aluminum amides,[5] alkoxides,[6] siloxides,[7] and cations.[8] Beyond their fundamental interest the cations have potential as initiators in the cationic oligomerization of propylene oxide.[8a] A great deal of fundamental research remains to be conducted for combinations between the Salen ligands and the group 13 elements. For example, bimetallic derivatives have not been well-studied. The first bimetallic combination between the group 13 elements and Salen ligands, Salpen($GaMe_2$)$_2$, was formed under forcing conditions, perhaps giving the erroneous impression that the "open" bimetallic compound was difficult to prepare by comparison to the "closed" five-coordinate derivative (e.g., SalpenGaMe).[9] However, it was subsequently found that such complexes, including mixed-metal derivatives such as Salen($GaMe_2$)($AlMe_2$),[10] and boron derivatives Salen{$(BOR)_2$}$_2$ (R = alkyl)[11] were readily accessible simply by adding the reagents in the appropriate stoichiometry.

One motivation for continuing work on these bimetallic complexes is the possibility that they might be useful in the formation of two-point Lewis acidic complexes. For instance, these complexes could be used as robust, inexpensive reagents for the hydrolysis of phosphate esters. In living systems this process is mediated by bimetallic transition metal complexes in which the two metals act in a concerted fashion to bind and then promote the reactivity of the phosphate ester.[12] Model systems have employed transition metals as well as main group metals, and it has been determined that the distance between the metals is of critical importance.[13] This is a property that should be easily manipulated in the Salen ligands. The goal of the present work is to determine the range and limitations in the formation of bimetallic aluminum complexes with varying lengths of "backbone" connecting the two aluminum centers. Ultimately, these compounds will be explored as the first group 13 systems for phosphate ester hydrolysis.

Results and Discussion

Synthesis and Spectroscopy. Compounds **1**−**14** are prepared by combining the $SalenH_2$ ligand with the

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(1) "Salen" is the name that has historically been used to describe the entire class of such ligands possessing various diamino backbones. However, it is also the specific name of the ethyl derivative $SalenH_2$.

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10.1021/om990829q CCC: $19.00
Publication on Web 03/30/2000

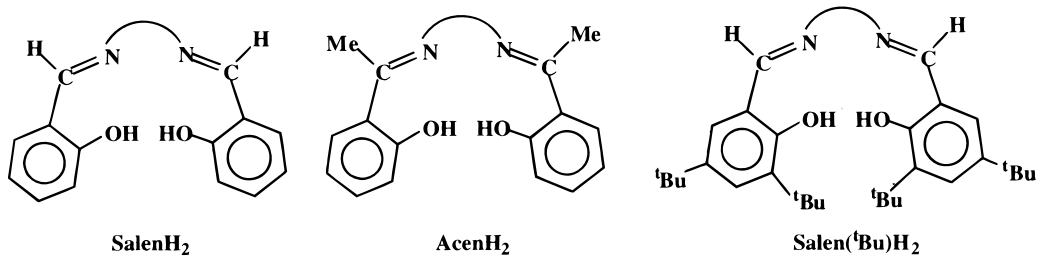
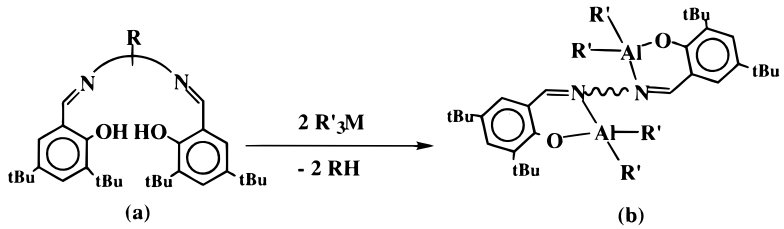


Figure 1. Members of the Salen class of ligands.

Scheme 1. General Syntheses and List of Ligands and Compounds



Ligand	R "backbone"
Salcen(tBu)H_2	1,2-cyclohexylene
Salben(tBu)H_2	1,4-butylene
Salpten(tBu)H_2	1,5-pentylene
Salhen(tBu)H_2	1,6-hexylene
1,4-Salophen(tBu)H_2	1,4-phenylene
Salmaben(tBu)H_2	1,4-bis{*m*-aminobenzyl)benzene (c)
Salmabmaben(tBu)H_2	1-(*m*-aminobenzoyl)-4-(*m*-aminobenzyl)benzene (d)
Salmadmen(tBu)H_2	4,4'-bis(*m*-aminobenzoyl)diphenylmethane (e)

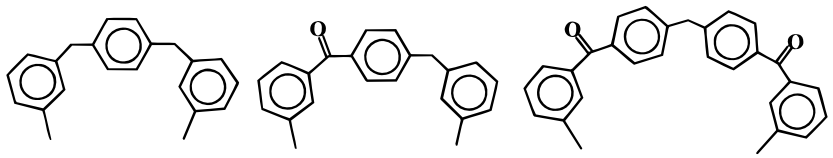


Table 1. Complete Listing of Compounds

Salcen(^{t}Bu)($AlMe_2$)$_2$ (**1**)	Salmaben(^{t}Bu)($AlMe_2$)$_2$ (**8**)
Salben(^{t}Bu)($AlMe_2$)$_2$ (**2**)	Salmabmaben(^{t}Bu)($AlMe_2$)$_2$ (**9**)
Salpten(^{t}Bu)($AlMe_2$)$_2$ (**3**)	Salmadmen(^{t}Bu)(AlMeCl)$_2$ (**10**)
Salhen(^{t}Bu)($AlMe_2$)$_2$ (**4**)	(R,R′Salcen(^{t}Bu)(AlMeCl)$_2$ (**11**)
Salhen(^{t}Bu)($AlEt_2$)$_2$ (**5**)	Salpen(^{t}Bu)(AlMeCl)$_2$ (**12**)
1,4-Salophen(^{t}Bu)($AlMe_2$)$_2$ (**6**)	Salben(^{t}Bu)(AlMeCl)$_2$ (**13**)
1,4-Salophen(^{t}Bu)($GaEt_2$)$_2$ (**7**)	Salhen(^{t}Bu)(AlMeCl)$_2$ (**14**)

appropriate group 13 reagent (Scheme 1). An alkane elimination leads to the formation of the complexes in good yields. A complete listing of the compounds is given in Table 1. With the exception of **1** and **9** the dialkyl derivatives have a single resonance in the ^{1}H NMR representing the group 13 alkyls. The Al−Me chemical shifts fall in the narrow range δ −0.7 to −0.8 ppm. For the gallium derivative, **7**, the Ga−CH_2 groups are more deshielded (δ +0.49 ppm) due to the more covalent nature of the Ga−C bond by comparison to the Al−C bonds.

Due to the geometric constraints of the R,R′-Salcen ligand, compound **1** is the only one in which the AlR_2 units cannot adopt equivalent trans geometries. The Me groups are consequently inequivalent, and two resonances are observed (δ −0.83 and −0.50 ppm). The ligand Salmabmaben(^{t}Bu) of compound **9** is asymmetric due to a C═O ligand connection on one side and a CH_2 connection on the other. This makes the two halves inequivalent, and two Al−Me resonances are observed (δ −0.80 and −0.75 ppm). The alkyl chloride derivatives **12**−**14** feature resonances corresponding to equivalent solution state environments for the akyls within each molecule (singlets ca. δ −0.5 ppm). For all but **9** there is only one imine resonance (ranging from δ 8.08 to 8.46 ppm) and two Ph−^{t}Bu resonances.

Excepting **9**, there is only one absorbance for the imine in the IR that falls in the narrow window 1610−1620 cm^{-1} for the aluminum derivatives. This implies that the donor action of the imine lone pair does not vary significantly throughout the series (even for **6** and **9**−**11**, which possess more electron-withdrawing phenyls adjacent to the imine functionality). This resonance in the gallium derivative **7** is only of marginally lesser value, 1602 cm^{-1}, and shifted in the direction expected for a weakened N═C bond. This may imply more covalency of the imine group toward Ga.

Structural Characterization. A single-crystal X-ray analysis for compounds **1**, **2**, **7**, **11**, **13**, and **14** (Figures 2−7, respectively) shows that the group 13 elements adopt a four-coordinate distorted tetrahedral geometry. The Al−O and Al−N distances for **1** and **2** are marginally shorter than for **7**, in keeping with the

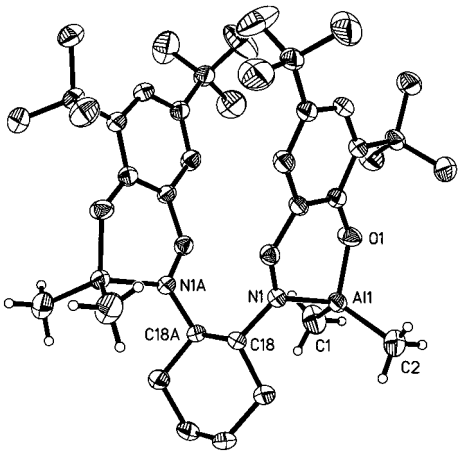


Figure 2. ORTEP (30%) view of Salcen(^{t}Bu)($AlMe_2$)$_2$ (**1**).

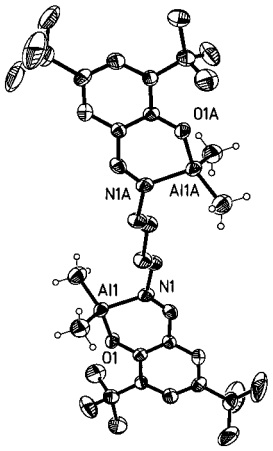


Figure 3. ORTEP (30%) view of Salben(^{t}Bu)($AlMe_2$)$_2$ (**2**).

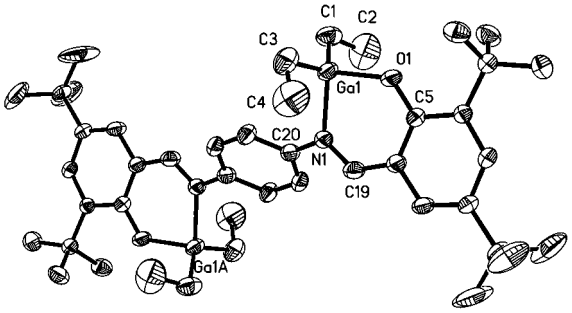


Figure 4. ORTEP (30%) view of 1,4-Salophen(^{t}Bu)($GaEt_2$)$_2$ (**7**).

slight increase in size on going from Al (0.53 Å) to Ga (0.61 Å) (see Table 2).[14] However, the O−Ga−N angle of **7** is more narrow (92.5(2)°) than the O−Al−N angles of **1** and **2** (∼94°). This is indicative of greater p-orbital character in the Ga−heteroatom bonds by comparison to Al. Consequently, the C−M−C angle is more obtuse for the Ga compound (127.7(3)°) than for the Al compounds (118.9(2)° and 115.6(3)°). The Al−O and Al−N distances in **11**, **13**, and **14** are shorter than seen in **1** and **2** due to the presence of the electron-withdrawing chloride atom. The reduced p-orbital character in these bonds causes a slight enlargement in the O−Al−N angles (in the range 96.0(4)−97.7(4)°). By comparison

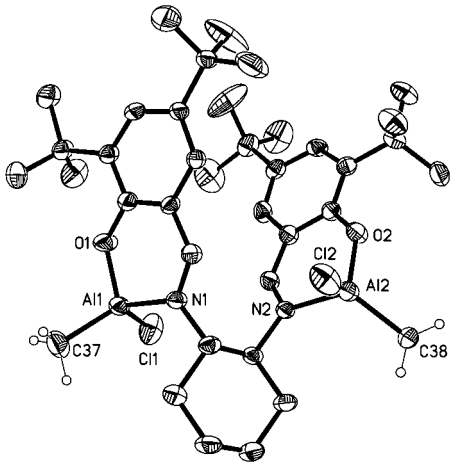


Figure 5. ORTEP (30%) view of Salcen(^{t}Bu)($AlMeCl$)$_2$ (**11**).

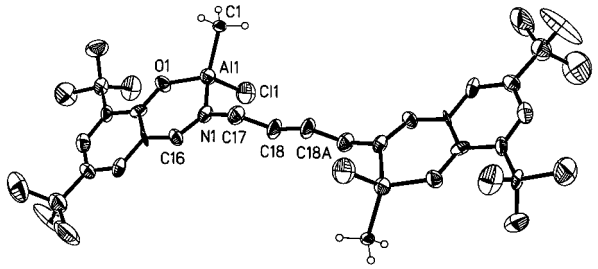


Figure 6. ORTEP (30%) view of Salben(^{t}Bu)($AlMeCl$)$_2$ (**13**).

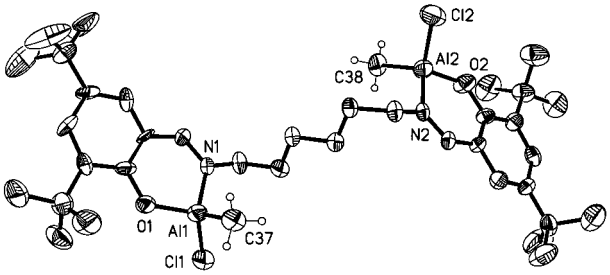


Figure 7. ORTEP (30%) view of Salhen(^{t}Bu)($AlMeCl$)$_2$ (**14**).

to the C−Al−C angles of **1** and **2**, the C−Al−Cl angles of **11**, **13**, and **14** are more narrowed (110.6(2)−114.0(2)°). It should be noted that the N and O atoms of the Salen ligands *can* occupy Td sites around a coordinated metal. This is demonstrated in Salen-$[B(OMe)_2]_2$ with a chelate O−B−N angle of 106.7(1)° and a ligand O−B−O′ angle of 112.7(1)°.[12] Overall, the distortions seen within the bond angles of these compounds can be explained by considering only electronic effects. The more electronegative atoms possess more p-orbital character in their bonds and so generally have more acute angles than for less electronegative constituents such as carbon. An example demonstrating that the steric influence of the ligand does not create these effects can be observed in the four-coordinate complexes $Cy_2GaBr(NH_2Ph)$ (C−Ga−C = 124.9(4)°; Br−Ga−N = 95.8(2)°)[15] and $Me_2InI(NH_2{}^tBu)$ (C−In−C = 134.8(3)°; I−In−N = 90.4(1)°),[16] which similarly dem-

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for 1, 2, 7, 11, 13, and 14

Salcen(^{t}Bu)(AlMe$_2$)$_2$ (**1**)			
Al(1)−O(1)	1.756(2)	Al(1)−N(1)	1.979(3)
Al(1)−C(2)	1.948(4)	Al(1)−C(1)	1.946(4)
O(1)−Al(1)−C(1)	108.4(2)	O(1)−Al(1)C(2)	112.0(2)
O(1)−Al(1)−N(1)	94.09(11)	C(1)−Al(1)−N(1)	111.0(2)
C(1)−Al(1)−C(2)	118.9(2)	C(2)−Al(1)−N(1)	109.6(2)
Salben(^{t}Bu)(AlMe$_2$)$_2$ (**2**)			
Al(1)−O(1)	1.754(4)	Al(1)−N(1)	1.952(5)
Al(1)−C(36)	1.943(7)	Al(2)−O(2)	1.759(4)
Al(2)−C(38)	1.943(7)	Al(2)−C(37)	1.946(7)
Al(1)−C(35)	1.944(7)	Al(2)−N(2)	1.958(5)
O(1)−Al(2)−C(35)	110.0(3)	O(1)−Al(1)−C(36)	113.9(3)
O(1)−Al(2)−N(2)	94.5(2)	C(35)−Al(1)−N(1)	112.3(3)
O(2)−Al(2)−C(38)	113.6(3)	O(2)−Al(2)−C(37)	110.0(3)
O(2)−Al(2)−N(2)	94.6(2)	C(38)−Al(2)−N(2)	108.8(3)
C(35)−Al(1)−C(36)	115.6(3)	C(36)−Al(1)−N(1)	108.7(3)
C(38)−Al(2)−C(37)	115.4(3)	C(37)−Al(2)−N(2)	112.6(3)
Salphen(^{t}Bu)(GaEt$_2$)$_2$ (**7**)			
Ga(1)−O(1)	1.876(4)	Ga(1)−N(1)	2.041(4)
Ga(1)−C(3)	1.960(7)	Ga(1)−C(1)	1.939(7)
O(1)−Ga(1)−C(1)	108.0(3)	O(1)−Ga(1)−C(3)	108.2(3)
O(1)−Ga(1)−N(1)	92.5(2)	C(1)−Ga(1)−N(1)	106.3(3)
C(1)−Ga(1)−C(3)	127.7(3)	C(3)−Ga(1)−N(1)	108.6(3)
Salcen(^{t}Bu)(AlMeCl)$_2$ (**11**)			
Al(1)−O(1)	1.732(4)	Al(1)−N(1)	1.951(4)
Al(1)−Cl(1)	2.131(2)	Al(2)−O(2)	1.745(4)
Al(2)−C(38)	1.945(7)	Al(2)−Cl(2)	2.139(2)
Al(3)−N(3)	1.954(4)	Al(3)−C(75)	1.935(6)
Al(4)−O(4)	1.734(4)	Al(4)−N(4)	1.950(4)
Al(4)−Cl(4)	2.138(2)	Al(1)−C(37)	1.931(6)
Al(2)−N(2)	1.943(4)	Al(3)−O(3)	1.732(4)
Al(3)−Cl(3)	2.143(2)	Al(4)−C(76)	1.938(5)
O(1)−Al(1)−C(37)	109.9(3)	O(1)−Al(1)−N(1)	96.1(2)
O(1)−Al(1)−Cl(1)	110.4(2)	C(37)−Al(1)−Cl(1)	114.0(2)
O(2)−Al(2)−N(2)	96.9(2)	C(38)−Al(2)−N(2)	108.8(3)
O(3)−Al(3)−C(75)	110.2(2)	O(3)−Al(3)−N(3)	96.1(2)
C(37)−Al(1)−N(1)	118.8(2)	N(1)−Al(1)−Cl(1)	106.06(14)
O(3)−Al(3)−Cl(3)	109.6(2)	C(75)−Al(3)−Cl(3)	113.6(2)
N(3)−Al(3)−Cl(3)	105.20(14)	C(37)−Al(2)−N(2)	112.6(3)
C(75)−Al(3)−N(3)	120.6(2)		
Salben(^{t}Bu)(AlMeCl)$_2$ (**13**)			
Al(1)−O(1)	1.734(7)	Al(1)−N(1)	1.936(8)
Al(1)−Cl(1)	2.113(4)	Al(1)−C(1)	1.932(7)
O(1)−Al(1)−C(1)	117.0(3)	O(1)−Al(1)−N(1)	96.0(4)
O(1)−Al(1)−Cl(1)	108.9(3)	C(1)−Al(1)−Cl(1)	110.6(3)
C(1)−Al(1)−N(1)	113.1(4)	Cl(1)−Al(1)−N(1)	110.4(3)
Salhen(^{t}Bu)(AlMeCl)$_2$ (**14**)			
Al(1)−O(1)	1.746(8)	Al(1)−N(1)	1.909(8)
Al(1)−Cl(1)	2.102(4)	Al(1)−C(37)	1.959(8)
Al(2)−O(2)	1.728(8)	Al(2)−C(38)	1.967(8)
Al(2)−Cl(2)	2.110(4)	Al(2)−N(2)	1.919(8)
Al(3)−N(3)	1.911(8)	Al(3)−C(57)	1.951(9)
Al(3)−Cl(3)	2.115(4)	Al(3)−O(3)	1.730(8)
O(1)−Al(1)−N(1)	97.7(4)	O(1)−Al(1)−C(37)	115.0(4)
C(37)−Al(1)−N(1)	114.7(4)	O(1)−Al(1)−Cl(1)	110.8(3)
Cl(1)−Al(1)−N(1)	105.0(3)	C(37)−Al(1)−Cl(1)	112.5(3)
O(2)−Al(2)−N(2)	96.8(4)	O(2)−Al(2)−C(38)	113.5(4)
C(38)−Al(2)−N(2)	116.8(4)	O(2)−Al(2)−Cl(2)	112.0(3)
Cl(2)−Al(2)−N(2)	105.1(3)	C(38)−Al(2)−Cl(2)	111.5(3)
O(3)−Al(3)−N(3)	97.1(5)	O(3)−Al(3)−C(57)	114.4(4)
C(57)−Al(3)−N(3)	114.9(4)	O(3)−Al(3)−Cl(3)	111.6(3)
Cl(3)−Al(3)−N(3)	104.8(4)	C(57)−Al(3)−Cl(3)	112.7(4)

onstrate obtuse C−M−C angles and more narrowed N−M−X angles than would be expected for an ideal Td geometry.

Conclusions

It has been demonstrated that a wide range of bimetallic aluminum compounds can be readily prepared in high yields. The only two ligands that appear unable to support the bimetallic formulation are Salophen and Salomphen which feature ortho imine groups. These ligands produce monometallic, five-coordinate compounds when combined with 2 equiv of a group 13 reagent (following the synthetic procedure in **1**, for example).[2−4] Further efforts are being directed toward the use of the bimetallic complexes Salen(AlRCl)$_2$ in the formation of bimetallic dicationic species, and their ultimate use in catalysis.

Experimental Section

General Considerations. All manipulations were conducted using Schlenk techniques in conjunction with an inert atmosphere glovebox. All solvents were rigorously dried prior to use. NMR data were obtained on JEOL-GSX-400 and -270 instruments operating at 270.17 and 399.78 MHz and are reported relative to SiMe$_4$ in ppm. Elemental analyses were obtained on a Perkin-Elmer 2400 analyzer and were satisfactory for all compounds. Infrared data were recorded as KBr pellets on a Matheson Instruments 2020 Galaxy Series spectrometer and are reported in cm^{-1}. The reagent 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde was prepared according to the literature.[17] The ligands were prepared by combining various diamines with the aldehyde following the literature precedent. The diamines for all but the ligands used for **9**−**11** could be purchased from commercial sources. The diamines used for **9**−**11** were prepared as described in the literature.[18] X-ray data for **1**, **2**, **7**, **8**, and **10**−**13** were collected on a Siemens SMART-CCD unit using Mo Kα radiation. The structures were refined using the Siemens software package SHELXTL 4.0. All of the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were put into calculated positions. Absorption corrections were not employed. Further details of the structure analyses are given in Table 2. Generally, higher than ideal *R* values are observed in these structures due to a combination of molecule size and the presence of groups, such as ^{t}Bu, having significant thermal motion.

Synthesis of (*R*,*R*)-Salcen(^{t}Bu)[AlMe$_2$]$_2$ (1). A solution of trimethylaluminum (0.26 g, 3.66 mmol) in toluene (15 mL) was added at room temperature to a stirred solution of (*R*,*R*)-Salcen(^{t}Bu)H$_2$ (1.00 g, 1.83 mmol) in toluene (20 mL). The resulting yellow solution was stirred for 5 h. After filtration and concentration, yellow crystalline solid yielded from solution (0.95 g,79%). Mp: 189−193 °C. ^{1}H NMR (CDCl$_3$): δ = −0.83 (s, 6H, AlCH$_3$), −0.50 (s, 6H, AlCH$_3$), 1.06 (s, 18H, CCH$_3$), 1.33 (s, 18H, CCH$_3$), 1.40 (m, 2H, CH$_2$), 1.95 (m, 4H, CH$_2$), 2.35 (m, 2H, CH$_2$), 3.57 (m, 2H, CH), 6.53 (d, 2H, PhH), 7.33 (d, 2H,PhH), 7.79 (s, 2H,N=CH). IR (KBr): 2941m, 2868m, 1610s, 1545s, 1462m,1432w, 1388w, 1356m, 1327m, 1257m, 1192s, 1145w, 1089m,1043w, 993w, 918w, 858m, 815w, 761w, 678m, 599w, 478w cm^{-1}. Anal. Calcd (found) for C$_{40}$H$_{64}$N$_2$O$_2$Al$_2$: C, 72.94 (72.71); H, 9.72 (9.53).

Synthesis of Salben(^{t}Bu)[AlMe$_2$]$_2$ (2). A solution of trimethylaluminum (0.18 g,2.46 mmol) in toluene (15 mL) was added at room temperature to a stirred solution of Salben(^{t}Bu)H$_2$ (0.64 g, 1.23 mmol) in toluene (20 mL). The resulting yellow solution was stirred for 5 h. After filtration and concentration, orange crystals were grown at −30 °C (0.70 g, 90%). Mp: 182−185 °C. ^{1}H NMR (CDCl$_3$): δ = −0.77 (s, 12H, AlCH$_3$), 1.27 (s, 18H, CCH$_3$), 1.39 (s, 18H, CCH$_3$), 1.79 (m, 4H, CH$_2$); 3.58 (m, 4H, CH$_2$); 6.99 (d, 2H, PhH), 7.51 (d, 2H, PhH), 8.08 (s, 2H, N=CH). IR (KBr): 2957m, 2874w, 1620s, 1545m, 1464m, 1438w, 1417w, 1388m, 1361m, 1321w, 1255w, 1176s,

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Table 3. Crystallographic Data for Structurally Characterized Compounds

	1	2	7	11	13	14
formula	$C_{54}H_{68}Al_2N_2O_2$	$C_{56}H_{68}Al_2N_2O_2$	$C_{24}H_{35}Al_2N_3O_2$	$C_{83}H_{124}Al_4Cl_4N_4O_4$	$C_{25}H_{32}AlClNO$	$C_{57}H_{90}Al_3Cl_3N_3O_3$
fw	807.04	831.06	451.51	1491.58	424.95	1052.61
cryst syst	orthorhombic	monoclinic	monoclinic	triclinic	orthorhombic	monoclinic
space group	*Pbcn*	$P2_1/c$	$P2_1/n$	$P\bar{1}$	*Pbca*	$P2_1/n$
a (Å)	16.8697(10)	11.4813(6)	10.6123(6)	15.8038(8)	11.2964(8)	17.7606(11)
b (Å)	21.6715(12)	11.7603(6)	31.008(2)	16.6905(9)	11.7863(9)	11.3327(7)
c (Å)	11.5654(6)	39.359(2)	11.7853(7)	18.7085 (13)	39.218(3)	32.867(2)
α (deg)	90	90	90	85.5680(10)	90	90
β (deg)	90	90.0370(10)	116.1050(10)	65.9390(10)	90	100.7390(10)
γ (deg)	90	90	90	84.9490(10)	90	90
V (Å^3)	4228.2(4)	5314.4(5)	3482.6(4)	4483.9(5)	5221.6(7)	6499.5(7)
Z	8	4	4	2	8	4
D(calcd) (Mg/m^3)	1.067	1.009	1.109	1.105	1.081	1.076
temperature (K)	298	298	298	298	298	298
cryst size (mm^3)	0.4 × 0.4 × 0.4	0.3 × 0.3 × 0.3	0.2 × 0.3 × 0.4	0.3 × 0.3 × 0.3	0.4 × 0.4 × 0.4	0.5 × 0.5 × 0.5
color, habit	pale yellow	pale yellow	pale yellow	yellow	pale yellow	yellow
F(000)	1520	1744	1244	1604	1816	2268
abs coeff (mm^{-1})	0.102	0.091	0.815	0.217	0.194	0.221
θ range for data collection	1.53−21.00	1.03−18.00	1.31−20.00	1.19−20.00	1.04−17.00	1.22−16.50
no. of reflns collected	13 052	11 681	10 238	13 533	9516	11 716
no. of ind reflns	2271 (R_{int} = 0.0482)	3635 (R_{int} = 0.0418)	3238 (R_{int} = 0.0630)	8039 (R_{int} = 0.0415)	1520 (R_{int} = 0.0865)	3443 (R_{int} = 0.0478)
no. of data/restraints/ params	2253/0/208	3598/0/513	3220/0/352	8003/0/892	1479/0/250	3395/0/618
R_1	0.0550	0.0714	0.0565	0.0620	0.0854	0.0747
R_{all}	0.0659	0.0850	0.0723	0.0780	0.01016	0.0987
goodness of fit on F^2	1.143	0.793	0.850	1.025	1.163	1.057
largest diff peak and hole (e/Å^3)	0.300 and −0.163	0.268 and −0.200	0.276 and −0.353	0.691 and −0.239	0.219 and −0.173	0.328 and −0.174

1039w, 914w, 852m, 785w, 760m, 684m, 601w, 545w, 472w cm^{-1}. Anal. Calcd (found) for $C_{38}H_{62}N_2O_2Al_2$: C, 72.15 (72.06); H, 9.81 (9.63).

Synthesis of Salpten(ᵗBu)[AlMe$_2$]$_2$ (3). A solution of trimethylaluminum (0.18 g, 2.46 mmol) in toluene (15 mL) was added at room temperature to a stirred solution of Salben(ᵗBu)H$_2$ (0.66 g, 1.23 mmol) in toluene (20 mL). The resulting yellow solution was stirred for 5 h. After filtration and concentration, orange crystals were grown at −30 °C (0.58 g, 73%). Mp: 143−146 °C. ^{1}H NMR ($CDCl_3$): δ = −0.76 (s, 12H, $AlCH_3$), 1.29 (s, 18H, CCH3), 1.38 (s, 18H, CCH_3), 1.50 (m, 2H, CH_2) 1.81 (m, 4H, CH_2) 3.56 (m, 4H, CH_2), 7.01 (d, 2H, PhH), 7.51 (d, 2H, PhH), 8.09 (s, 2H, N=CH). IR (KBr): 2943m, 2863w, 1620s, 1545m, 1462m, 1439w, 1415(w), 1392w, 1361m, 1325w, 1257w, 1192s, 1132w, 1076w, 1041w, 929w, 856m, 783w, 760m, 678s, 603w, 551w, 466w cm^{-1}. Anal. Calcd (found) for $C_{39}H_{64}N_2O_2Al_2$: C, 72.44 (72.25); H, 9.90 (9.75).

Synthesis of Salhen(ᵗBu)[AlMe$_2$]$_2$ (4). A solution of trimethylaluminum (0.26 g, 3.64 mmol) in toluene (15 mL) was added at room temperature to a stirred solution of Salhen(ᵗBu)H$_2$ (1.00 g, 1.82 mmol) in toluene (20 mL). The resulting yellow solution was stirred for 5 h. After filtration and concentration, yellow solid yielded from solution (1.0 g, 84%). Mp: 172−176 °C. ^{1}H NMR ($CDCl_3$): δ = −0.78 (s, 12H, $AlCH_3$), 1.28 (s, 18H, CCH_3), 1.38 (s, 18H,CCH_3), 1.40 (m, 4H, CH_2), 1.76 (m, 4H, CH_2), 3.54 (m, 4H, CH_2) 7.00 (d, 2H, PhH), 7.50 (d, 2H, PhH), 8.08 (s, 2H, N=CH). IR (KBr): 2962m, 2872w, 1620s, 1545m, 1465m,1440w, 1514w, 1361w, 1319w, 1259m, 1186m, 1078w, 1026w, 929w, 882w, 802w, 760w, 677m, 604w, 549w, 464w, cm^{-1}. Anal. Calcd (found) for $C_{40}H_{66}N_2O_2Al_2$: C, 72.94 (72.68); H, 10.03 (9.89).

Synthesis of Salhen(ᵗBu)[AlEt$_2$]$_2$ (5). A solution of triethylaluminum (0.39 g, 3.45 mmol) in toluene (15 mL) was added at room temperature to a stirred solution of Salhen(ᵗBu)H$_2$ (0.95 g, 1.72 mmol) in toluene (20 mL). The resulting yellow solution was stirred for 5 h. After filtration and concentration, yellow solid yielded from solution (0.91 g, 75%). Mp: 110−113 °C. ^{1}H NMR ($CDCl_3$): δ = −0.09 (m, 8H, $AlCH_2$), 0.98 (m, 12H, CH_3), 1.28 (s, 18H, CCH_3), 1.35 (s, 4H, CH_2), 1.41(m, 4H, CH_2), 1.76 (m, 4H, CH_2), 3.52 (m, 4H, CH_2), 6.98 (d, 2H, PhH), 7.50 (d, 2H, PhH), 8.11 (s, 2H, N=CH). IR (KBr): 2953m, 2858w, 1620s, 1554m, 1460m,1417w, 1359w, 1319m, 1257m, 1186w, 1030w, 995w, 852m, 783w, 758w, 650m, 522w, 493w cm^{-1}. Anal, Calcd (found) for $C_{44}H_{76}N_2O_2Al_2$: C, 73.94 (73.62); H, 10.36 (10.05).

Synthesis of 1,4-Salophen(ᵗBu)[AlMe$_2$]$_2$ (6). A solution of trimethylaluminum (0.21 g, 2.96 mmol) in toluene (15 mL) was added at room temperature to a stirred solution of Salomhen(1,4)(ᵗBu)H$_2$ (0.80 g, 1.48 mmol) in toluene (20 mL). The resulting yellow solution was stirred for 5 h. After filtration and concentration, yellow solid yielded from solution (0.80 g, 83%). Mp: 248−253 °C. ^{1}H NMR ($CDCl_3$): δ = −0.70 (s, 12H, $AlCH_2$), 1.26 (s, 18H, CCH_3), 1.45 (s, 4H, CH_2), 7.01 (d, 2H, PhH), 7.23 (d, 2H, PhH), 7.41 (d, 2H, PhH), 7.58 (d, 2H, PhH), 8.35 (s, 2H, N=CH). IR (KBr): 2960m, 2870w, 1610s, 1543m, 1502m,1462m, 1433m, 1386w, 1359m, 1321m, 1257m, 1134m, 1024w, 925w, 856m, 760w, 634w, 605w, 555w, 484w cm^{-1}. Anal. Calcd (found) for $C_{40}H_{58}N_2O_2Al_2$: C, 73.61 (73.34); H, 8.89 (8.61).

Synthesis of Salophen(1,4)(ᵗBu)[GaEt$_2$]$_2$ (7). A solution of triethylgallium (0.47 g, 2.96 mmol) in toluene (15 mL) was added at room temperature to a stirred solution of Salomhen(1,4)(ᵗBu)H$_2$ (0.80 g, 1.48 mmol) in toluene (20 mL). The resulting yellow solution was stirred for 5 h. After filtration and concentration, yellow crystals were grown at −30 °C (0.94 g, 64%). Mp: 193−196 °C. ^{1}H NMR ($CDCl_3$): δ 0.49 (s, 8H, $GaCH_2$), 1.04 (m, 12H, CH_2CH_3), 1.30 (s, 18H, CCH_3), 1.44 (s, 18H, CCH_3), 7.00 (d, 2H, PhH), 7.16 (d, 2H, PhH), 7.30 (d, 2H, PhH), 7.52 (d, 2H, PhH), 8.28 (s, 2H, N=CH). IR (KBr): 2922m, 2870w, 1602s, 1531m, 1498m, 1460m, 1428m, 1386w, 1359w, 1325m, 1168m, 1134m, 1007w, 1003m, 925w, 866m, 785w, 748w, 650m, 623w, 561w, 540w, 464w, 432w cm^{-1}. Anal. Calcd (found) for $C_{44}H_{66}N_2O_2Ga_2$: C, 66.54 (66.21); H, 8.31-(8.05).

Synthesis of Salmaben(ᵗBu){AlMe$_2$}$_2$ (8). To a solution of Salmaben(ᵗBu)H$_2$ (0.60 g, 0.83 mmol) in toluene (20 mL) was added a solution of trimethylaluminum (0.12 g, 1.67 mmol) in toluene (10 mL). The resulting solution was stirred for 5 h. After concentration and a hexane wash, a yellow solid was isolated (0.60 g, 87%). Mp: 174 °C (dec). ^{1}H NMR ($CDCl_3$): δ

−0.60 (s, 12H, AlCH3), 1.38 (s, 18H, CCH_3), 1.65 (s, 18H, CCH_3), 3.75 (s, 4H, $PhCH_2Ph$), 6.78−7.20 (m, 14H, PhH), 7.50 (s, 2H, PhH), 7.78 (s, 2H, NCH). IR: ν 2960 (s), 2928 (s), 2885 (m), 2869 (m), 1615 (s), 1592 (s), 1555 (m), 1538 (s), 1514 (m), 1460 (m), 1432 (s), 1383 (m), 1360 (m), 1320 (w), 1255 (m), 1229 (w), 1198 (m), 1179 (s), 1162 (w), 891 (w), 854 (m), 785 (m), 713 (m), 678 (s). Anal. Calcd for $C_{54}H_{70}Al_2N_2O_2$: C, 77.85 (77.82); H, 8.47 (8.53).

Synthesis of Salmabmaben(^{t}Bu){$AlMe_2$)$_2$ (9). To a solution of Salmabmaben(^{t}Bu)H_2 (1.0 g, 1.39 mmol) in toluene (15 mL) was added a solution of trimethylaluminum (0.20 g, 2.78 mmol) in toluene (10 mL). The resulting solution was stirred for 12 h. After concentration and a hexane wash added, a yellow solid was isolated at −30 °C (0.65 g, 55%). Mp: 126 °C (dec). ^{1}H NMR ($CDCl_3$): δ −0.80 (s, 6H, $AlCH_3$), −0.75 (s, $AlCH_3$), 1.26 (s, 18H, CCH_3), 1.39 (s, 18H, CCH_3), 4.11 (s, 2H, $PhCH_2Ph$), 7.0−7.80 (m, 16H, PhH), 8.22 (s, 1H, NCH), 8.31 (s, 1H, NCH). IR: ν 2958 (m), 2863 (w), 1615 (s), 1592 (s), 1556 (m), 1539 (s), 1463 (m), 1435 (s), 1387 (m), 1361 (w), 1317 (w), 1279 (m), 1256 (m), 1177 (s), 1134 (w), 1025 (w), 984 (w), 876 (w), 854 (m), 784 (m), 759 (m), 682 (s). 605 (m), 545 (m). Anal. Calcd for $C_{54}H_{78}Al_2N_2O_3$: C, 76.57 (76.52); H, 8.09 (8.14).

Synthesis of Salmadmen(^{t}Bu){$AlMe_2$)$_2$ (10). To a solution of Salmadmen(^{t}Bu)H_2 (0.75 g, 0.90 mmol) in toluene (20 mL) was added a solution of trimethylaluminum (0.13 g, 1.79 mmol) in toluene (10 mL). The resulting solution was stirred for 12 h. After concentration and wash with hexane, the solution was filtered and a yellow solid was isolated at −30 °C (0.50 g, 59%). Mp: 118 °C (dec). ^{1}H NMR ($CDCl_3$): δ −0.75 (s, 12H, $AlCH_3$), 1.25 (s, 18H, CCH_3), 1.40 (s, 18H, CCH_3), 4.18 (s, 2H, $PhCH_2Ph$), 7.00−7.80 (m, 16H, PhH), 8.32 (s, 2H, NCH). IR: ν 2992 (s), 2867 (w), 1620 (s), 1574 (s), 1465 (m), 1440 (s), 1357 (w), 1275 (m), 1259 (m), 1199 (w), 1168 (s), 1020 (w), 876 (m), 799 (w), 753 (w), 722 (w). 605 (w). Anal. Calcd for $C_{61}H_{72}Al_2N_2O_4$: C, 77.02 (77.11); H, 7.63 (7.58).

Synthesis of (*R*,*R*)-Salcen(^{t}Bu)[AlMeCl]$_2$ (11). A solution of dimethylaluminum chloride (0.34 g, 3.66 mmol) in toluene (15 mL) was added at room temperature to a stirred solution of (*R*,*R*)-Saltchen(^{t}Bu)H_2 (1.00 g, 1.83 mmol) in toluene (20 mL). The resulting yellow solution was stirred for 5 h. After filtration and concentration, yellow crystals were grown at −30 °C (0.88 g, 70%). Mp: 231−233 °C. ^{1}H NMR ($CDCl_3$): δ −0.43- (s, 6H, $AlCH_3$), 1.07 (s, 18H, CCH_3), 1.37 (s, 18H, CCH_3), 1.53 (m, 2H, CH_2), 1.98 (m, 4H, CH_2), 2.34 (m, 2H, CH_2), 4.06 (m, 2H, CH), 6.71 (d, 2H, PhH), 7.40 (d, 2H, PhH), 8.40 (s, 2H, N═CH). IR (KBr): 2972m, 2866m, 1612s, 1564s, 1465m, 1440m, 1390w, 1361w, 1321w, 1249m, 1199m, 1162w, 1087w, 1041w, 923w, 864m, 765w, 678m, 586w, 493w, 434w cm^{-1}. Anal. Calcd (found) for $C_{38}H_{58}N_2O_2Al_2Cl_2$: C, 65.24 (65.05); H, 8.29 (8.12).

Synthesis of Salpen(^{t}Bu)[AlMeCl]$_2$ (12). A solution of dimethylaluminum chloride (0.365 g, 3.95 mmol) in toluene (20 mL) was added to a rapidly stirred solution of Salpen- (^{t}Bu)H_2 (1.00 g, 1.97 mmol) in toluene (15 mL) in a drybox at 25 °C. The solution was stirred for 5 h. After filtration and recrystallization in toluene at −30 °C, single crystals suitable for X-ray analysis were obtained (1.15 g, 89%). Mp: 187−191 °C. ^{1}H NMR ($CDCl_3$, ppm): δ −0.62 (s, 6H, $AlCH_3$), 1.10 (s, 18H, CCH_3), 1.24 (s, 18H, CCH_3), 2.23 (m, 2H, NCH_2CH_2), 3.62 (m, 4H, NCH_2), 6.90 (m, 2H, PhH), 7.42 (d, 2H, PhH), 8.15 (d, 2H, HC═N). IR (KBr): 3089(w), 2998(m), 2961(vs), 2910(s), 2872(s), 1616(vs), 1546(s), 1462(s), 1441(s), 1421(s), 1394(m), 1361(s), 1338(m), 1313(m), 1279(m), 1257(s), 1241(m), 1217- (m), 1199(s), 1180(s), 1104(w), 1026(w), 897(w), 863(s), 797- (vw), 782(w), 766(m), 747(vw), 730(vw), 669(s), 616(w) cm^{-1}. Anal. Calcd (found): C, 63.72 (63.84); H, 8.25 (8.23).

Synthesis of Salben(^{t}Bu)[AlMeCl]$_2$ (13). A solution of dimethylaluminum chloride (0.355 g, 3.84 mmol) in toluene (20 mL) was added to a rapidly stirred solution of Salben- (^{t}Bu)H_2 (1.00 g, 1.92 mmol) in toluene (15 mL) in a drybox at 25 °C. The solution was stirred for 5 h. After filtration and recrystallization in toluene at −30 °C, single crystals suitable for X-ray analysis were obtained (1.17 g, 90%). Mp: 171−174 °C. ^{1}H NMR ($CDCl_3$): δ −0.46 (s, 6H, $AlCH_3$), 1.28 (s, 18H, CCH3), 1.45 (s, 18H, CCH_3), 1.94 (m, 4H, CH_2), 3.68 (m, 4H, CH_2), 7.09 (d, 2H, PhH), 7.58 (d, 2H, PhH), 8.23 (s, 2H, CH_2). IR (KBr): 2957m, 2881w, 1616s, 1556m, 1473m, 1440m, 1421w, 1390m, 1361w, 1257m, 1199m, 1026w, 927w, 862m, 765w, 677m, 580w, 489w, 435w cm^{-1}. Anal. Calcd (found) for $C_{36}H_{56}N_2O_2Cl_2Al_2$: C, 64.20 (64.03); H, 8.32 (8.02).

Synthesis of Salhen(^{t}Bu)[AlMeCl]$_2$ (14). A solution of dimethylaluminum chloride (0.29 g, 3.10 mmol) in toluene (15 mL) was added at room temperature to a stirred solution of Salhen(^{t}Bu)H_2 (0.85 g, 1.55 mmol) in toluene (20 mL). The resulting yellow solution was stirred for 5 h. After filtration and concentration, orange crystals were grown at −30 °C (0.75 g, 70%). Mp: 198−201 °C. ^{1}H NMR ($CDCl_3$): δ −0.46 (s, 6H, $AlCH_3$), 1.29 (s, 18H, CCH3), 1.42 (s, 18H, CCH_3), 1.53 (m, 4H, CH_2) 1.87 (m, 4H, CH_2), 3.68 (m, 4H, CH_2), 7.09 (d, 2H, PhH), 7.59 (d, 2H, PhH), 8.22 (s, 2H, N═CH). IR (KBr): 2953m, 2870w, 1612s, 1560m, 1465m,1421m, 1390w, 1363m,- 1309m, 1255m, 1197s, 1138w, 1074w, 995w, 860m, 765w, 680s, 588w, 489w, 437w cm^{-1}. Anal. Calcd (found) for $C_{38}H_{60}N_2O_2$- Cl_2Al_2: C, 65.05 (64.93); H, 8.56 (8.38).

Acknowledgment. This work was supported by the National Science Foundation NSF-CAREER award (CHE 9625376) and the donors of the Petroleum Research Fund (Grant 31901-AC3), administered by the American Chemical Society.

Supporting Information Available: Crystallographic data for compounds, **1**, **2**, **7**, **11**, **13**, and **14**, which include full tables of bond lengths and angles and unit cell views. Observed and calculated structure factor tables are available upon request. This material is available free of charge via the Internet at http://pubs.acs.org.

OM990829Q