Chem. Rev. **2001,** *101,* 37−52

Group 13 Compounds Incorporating Salen Ligands

David A. Atwood* and Melanie J. Harvey

Department of Chemistry, The University of Kentucky, Lexington, Kentucky 40506-0055

Received March 9, 2000

Contents

I. Introduction

The condensation of an amine with an aldehyde, forming what is called a Schiff base, is one of the oldest reactions in chemistry.[1] Schiff base ligands coordinate to a metal through the imine nitrogen and another group, usually oxygen, situated on the original aldehyde. When a diamine was first combined with 2 equiv of salicylaldehyde, the Salen ligands came into being.[2] The ligands feature two covalent and two coordinate covalent sites situated in a planar array. This makes the ligands ideal for the equatorial coordination of transition metals, leaving the two axial sites open for ancillary ligands. They are very much like porphyrins in this regard, but unlike porphyrins the salen ligands are easy to prepare and inexpensive.[3] Evidence for the tremendous amount of transition-metal chemistry that has been conducted is demonstrated by the fact that the first reviews in this area were published in 1966.[4] By incorporating additional groups around the phenol portion of the ligand, such as ^{t}Bu, the ligands can be made highly soluble in aryl and alkyl solvents. This form of the ligand, Salen(^{t}Bu), has been used to great effect in Mn derivatives for olefin epoxidations.[5] Incorporation of hydrophilic groups may also lead to ligands that are soluble in water and alcohols. The malleability inherent to the salen ligands has led to their extensive use in transition-metal chemistry, particularly in modeling enzymes and in catalysis.[5] More recent applications include use as metal-containing liquid-crystalline polymers,[6] as nonradioactive models for Tc,[7] as anitviral agents,[8] and in asymmetric catalysis.[9] However, only sporadic reports of main-group−salen complexes have appeared. Most notably, complexes of Zn[10] and Li[11] have been reported. Despite the similarity between the group 13 elements and the trivalent transition metals, very little work has been done in this area until recent times.

The purpose of this review is to evaluate the salen−group 13 chemistry that is known in order to provide guidance and encouragement for continuing investigations by other researchers. This includes both fundamental studies as well as the identification of new applications in catalysis and synthesis.

II. Monometallic Compounds (Having a 1:1 Metal to Ligand Stoichiometry)

A. Alkyls and Halides

1. Synthesis and Spectroscopic Characterization.

Salen−group 13 alkyl complexes are conveniently prepared by combining the ligand with a trialkyl group 13 reagent in non-oxygenated solvents at ambient temperatures (Scheme 1). The choice of solvent depends on which Salen ligand is being used, but toluene generally works well. High yields of five-coordinate alkyl derivatives of aluminum (**1**−**18**),[12−15] gallium (**19**−**22**),[16] and indium (**23**−**31**)[17−19] can be accessed in this way (Table 1), particularly with Salen(^{t}Bu)H_2, Salophen(^{t}Bu)H_2, and Salomphen(^{t}Bu)-H_2. The Salpen(^{t}Bu) ligand is problematic in this regard. Along with other ligands such as Salben and Salpten, it tends to form open bimetallic complexes (see below). Thus, only Salpen(^{t}Bu)AlMe (**12**) and Salpen(^{t}Bu)InEt (**29**) are known.

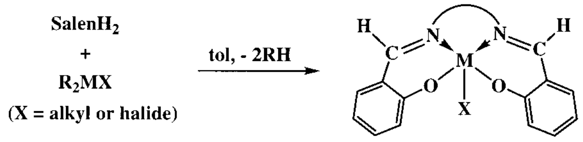
Salen−group 13 halide compounds, SalenMX, are prepared similarly with R_2AlCl as the group 13 reagent.[15,20,21] In some instances, it is necessary to conduct the initial addition of the group 13 reagent to the ligand at a lower temperature in order to prevent HCl elimination and subsequent contamination of the desired compound with SalenMR. Both

10.1021/cr990008v CCC: \$36.00

David Allan Atwood was born in 1965 in Urbana, IL, while his father Jerry Atwood was in graduate school at the University of Illinois. At an early age David moved to Tuscaloosa, AL, where he grew up and ultimately attended college. After graduation from the University of Alabama he moved to Austin, TX, to attend graduate school at the University of Texas. In the spring of 1992 he graduated with his Ph.D. degree in Inorganic Chemistry under the skillful guidance of Richard A. Jones. From UT he moved as an Assistant Professor to North Dakota State University as part of their new Center for Main Group Chemistry. In 1998 David Atwood joined the Chemistry Department at the University of Kentucky faculty as an Associate Professor. His research is designed to address both fundamental and applied aspects of the main-group metals. This includes work on chelated group 13 compounds, molecular routes to metal oxide materials, and the design and use of ligands to remove heavy metals from the environment.

Melanie Jean Harvey was born in 1974 in Oklahoma City, OK. She received her B.A. degree in Chemistry in 1996 from Anderson University, Anderson, IN. She attended graduate school at Vanderbilt University in Nashville, TN. Under the direction of Timothy Hanusa, she studied the effects of bulky ligands on the reactivity of organoalkaline-earth complexes. After completing her Ph.D. in Inorganic Chemistry, she moved to Lexington, KY, to begin postdoctoral studies with David A. Atwood. She is the recipient of a University of Kentucky Postdoctoral Fellowship for Women.

Scheme 1. General Syntheses of the Five-Coordinate Alkyl and Halide Derivatives[a]



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

Table 1. Salen−Group 13 Alkyls and Halides

compound	ref	compound	ref
SalenAlMe (**1**)	42	SalomphenInMe (**26**)	17
Salen(Cl)AlMe (**2**)	15	Salen(^{t}Bu)InMe (**27**)	18
AcenAlMe (**3**)	15	Salen(^{t}Bu)InEt (**28**)	18
SalcenAlMe (**4**)	61	Salpen(^{t}Bu)InEt (**29**)	18
SalenAlEt (**5**)	12	Salophen(^{t}Bu)InEt (**30**)	18
AcenAlEt (**6**)	12	Salomphen(^{t}Bu)InEt (**31**)	18
SalpenAlEt (**7**)	12	SalenAlCl (**32**)	15
SalophenAlEt (**8**)	12	Salen(Cl)AlCl (**33**)	15
Salcen(^{t}Bu)AlEt (**9**)	14	AcenAlCl (**34**)	15
Salen(^{t}Bu)AlMe (**10**)	13	Salen(^{t}Bu)AlCl (**35**)	20
Salen(^{t}Bu)AlEt (**11**)	13	Salpen(^{t}Bu)AlCl (**36**)	20
Salpen(^{t}Bu)AlMe (**12**)	13	Salophen(^{t}Bu)AlCl (**37**)	20
Salophen(^{t}Bu)AlMe (**13**)	13	Salomphen(^{t}Bu)AlCl (**38**)	20
Salophen(^{t}Bu)AlEt (**14**)	13	Acen(^{t}Bu)AlCl (**39**)	20
Salophen(^{t}Bu)AliBu (**15**)	13	Salcen(^{t}Bu)AlCl (**40**)	21
Salomphen(^{t}Bu)AlMe (**16**)	13	Salophen(^{t}Bu)GaCl (**41**)	16
Salomphen(^{t}Bu)AlEt (**17**)	13	Salomphen(^{t}Bu)GaCl (**42**)	16
Salomphen(^{t}Bu)AliBu (**18**)	13	Salen(^{t}Bu)InCl (**43**)	16
Salomphen(^{t}Bu)GaMe (**19**)	16	Salpen(^{t}Bu)InCl (**44**)	18
Salen(^{t}Bu)GaEt (**20**)	16	Salophen(^{t}Bu)InCl (**45**)	18
Salophen(^{t}Bu)GaEt (**21**)	16	Salomphen(^{t}Bu)InCl (**46**)	18
Salomphen(^{t}Bu)GaEt (**22**)	16	Salen(^{t}Bu)InBr (**47**)	18
AcenInMe (**23**)	17	Salpen(^{t}Bu)InBr (**48**)	18
SalenInMe (**24**)	17	Salophen(^{t}Bu)InBr (**49**)	18
SalophenInMe (**25**)	17	Salomphen(^{t}Bu)InBr (**50**)	18

the alkyl and halide compounds can be isolated by precipitation after concentration of the solution, or crystallization, after cooling to −30 °C for a few days. Often the compounds incorporating the non-*tert*-butylated ligand precipitated immediately upon formation. While this leads to a high-yield synthesis, it hampers solution-state characterizations. Thus, the preponderance of NMR data focuses on compounds incorporating the *tert*-butyl derivative of this ligand. In the syntheses there was no evidence for the rearrangement of the parent SalenMX compounds into cation−anion pairs (such as [Salen(^{t}Bu)In$^+$][Salen(^{t}Bu)InX$_2^-$]). This has been observed to occur with pyrazolylborates and porphyrins.[22]

The spectroscopic data for these complexes are consistent with monomeric chelated metal−alkyl or −halide units. In the ^{1}H NMR one resonance is observed for the group 13 alkyls. For the Al−Me derivatives, the chemical shifts demonstrate a slightly greater shielding when incorporated into a ligand possessing an aryl "backbone" (Salen(^{t}Bu)AlMe (**10**) (Figure 2), −1.11 ppm;[13] Salpen(^{t}Bu)AlMe (**12**), −0.98 ppm; Salophen(^{t}Bu)AlMe (**13**) −1.22 ppm; Salomphen(^{t}Bu)AlMe (**16**), −1.24 ppm). The same general trend holds for the ipso-carbon protons in the Et and ^{i}Bu derivatives. It should be noted, however, that 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).[23] Indeed, these values also do not differ from analogous four-coordinate derivatives.

By comparison, the methyl resonances of gallium and indium derivatives appear at lower field. For instance, the Me resonance of Salomphen(^{t}Bu)GaMe (**19**) is −0.59 ppm[16] and that of Salen(^{t}Bu)InMe (**27**) is −0.31 ppm.[18] Moreover, these are at a significantly

Table 2. Selected Structural Data for Salen–Group 13 Alkyl and Halide Compounds

compound	geometry	M–R or Cl	M–O	M–N	O–M–O	N–M–N	O–M–N[†]
			Alkyls				
5	sqp	1.966(7)	1.800(5) 1.829(5)	2.013(6) 2.027(6)	88.4(3)	79.3(3)	151.1(3)
10	tbp	1.96(1)	1.799(9) 1.831(9)	2.07(1) 2.03(1)	91.7(4)	76.4(4)	158.7(5)
18	sqp	1.972(9)	1.809(6) 1.825(5)	2.033(5) 2.056(6)	90.1(2)	76.9(2)	150.5(3)
19	sqp	1.939(5)	1.901(3) 1.909(3)	2.064(4) 2.105(4)	86.4(1)	76.0(1)	148.8(2)
20	sqp	1.95(1)	1.900(8) 1.932(9)	2.09(1) 2.06(1)	86.6(4)	77.5(5)	153.2(4)
21	sqp	2.019(8)	1.905(2) 1.907(3)	2.107(3) 2.072(3)	86.9(1)	76.4(1)	147.6(1)
22	sqp	1.970(9)	1.913(4) 1.910(4)	2.091(5) 2.109(5)	87.2(2)	75.9(2)	146.3(2)
27	sqp	2.135(4)	2.095(2) 2.099(2)	2.257(3) 2.242(3)	89.11(8)	72.9(1)	139.4(1)
30	sqp	2.135(6)	2.092(2)	2.266(2)	86.2(1)	71.7(1)	130.85(8)
			Halides				
36	tbp	2.176(9)	1.77(2) 1.79(2)	1.99(2) 2.00(2)	89.1(7)	86.6(9)	172.1(8)
40	sqp	2.181(5)	1.81(1) 1.770(8)	1.98(1) 1.98(1)	91.1(4)	78.2(5)	154.1(5)
41	sqp	2.199(3)	1.862(6) 1.881(6)	2.045(7) 2.016(7)	87.4(3)	78.6(4)	153.8(3)
43	sqp	2.327(2)	2.045(5) 2.051(4)	2.193(6) 2.196(5)	95.7(2)	74.9(2)	152.3(2)
48	tbp	2.5087(6)	2.060(3) 2.079(3)	2.218(3) 2.213(4)	88.8(1)	84.7(1)	160.2(1) †

Most obtuse angle.

higher field than comparable four-coordinate derivatives such as observed in $Me_3Ga{-}L$ (with L = thf (−0.3 ppm),[24] $NH(^iPr)_2$ (0.33 ppm),[25] and PPh_3 (0.17 ppm)[26]), $[Me_2In(P^tBu_2)]_2$ (0.29 ppm),[27] $[Me_2InI(NH_2{}^tBu)]$ (0.22 ppm),[28] and $[Me_3InN(SnMe_3)_3]$ (0.25 ppm)[29]. The ligands have less influence on chemical shifts in the indium compounds. For instance, the resonances of the ipso-carbons of the InEt derivatives of Salpen(^{t}Bu) (**29**) and Salophen(^{t}Bu) (**30**) are the same (0.68 ppm).

In general, ^{27}Al NMR shifts vary according to coordination number.[30] For Salen-chelated aluminum, those containing four-coordinate aluminum appear at ~160 ppm, five-coordinate at ~50−100 ppm, and six-coordinate at ~0 ppm. The resonances observed for **35**−**38** in the range 43−57 ppm are consistent with five-coordinate solution-state species.

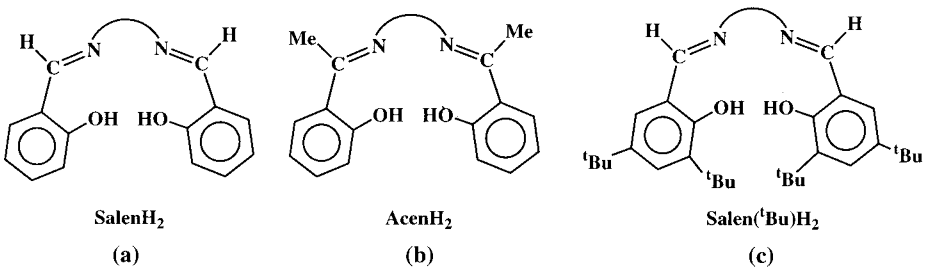
2. Structural Characterization.

The compounds contain a five-coordinate group 13 atom (Al, Ga, In) that is either trigonal bipyramidal (tbp) or square pyramidal (sqp) depending on the nature of the connection between the two nitrogens of the ligand (the ligand "backbone"). With more flexible backbones, $(CH_2)_n$ $n > 2$, a tbp geometry is obtained (Table 2), probably due to the fact that a sqp geometry would cause the methylene hydrogens to be eclipsed. In the tbp geometry they are staggered. With an ethyl, $(CH_2)_2$, or *o*-aryl backbone the metal adopts a sqp geometry. This ligand−geometry correlation is a fundamental property of the Salen ligands and is observed in all of the other derivatives (see below). For example, this rule is followed for Salpen(^{t}Bu)AlCl (**36**) (tbp) (Figure 3)[31] and Salomphen(^{t}Bu)GaEt (**22**) (sqp) (Figure 4).[16]

Compound **36** contains a central Al in a distorted tbp geometry. The amount of the distortion can be measured using the geometric calculation, $\tau = (\beta - \alpha)/60$.[32] The τ value ranges from 0 (perfectly square pyramidal) to 1 (perfectly trigonal bipyramidal). Alpha and beta are the angles that are opposite each other in the *xy* plane (with the Al−R group oriented along the *z*-axis). For **36**, the τ value is 0.76, clearly indicating more tbp character. By comparison, a more distorted tbp geometry is observed in Salen(^{t}Bu)AlMe (**10**) (Figure 4),[13] which has a τ value of 0.47.

In the square pyramidal compounds the τ values are much closer to zero (0.20 for Salomphen(^{t}Bu)GaMe (**19**) and 0.17 for Salophen(^{t}Bu)GaEt (**21**)). In these compounds the central metal is perched above the N_2O_2 plane at a distance that reflects the size of the atom (five-coordinate ionic radii are Al, 0.62 Å; Ga, 0.69 Å; and In, 0.85 Å). The Al atom in the alkyl derivate, Salomphen(^{t}Bu)Al(^{i}Bu) (**18**), is displaced by 0.54 Å, while in the chloride derivative, Salcen(^{t}Bu)AlCl (**40**), the atom is 0.43 Å above the N_2O_2 plane. The Ga derivatives have comparable displacements for alkyl derivatives, **19**−**22**, ~0.6 Å, and a halide, Salophen(^{t}Bu)GaCl (**41**), 0.49 Å. By comparison to Al and Ga, the In atoms are perched much further above the N_2O_2 plane at a distance of ~0.6 Å for Salpen(^{t}Bu)InCl (**42**) and Salpen(^{t}Bu)InBr (**43**), 0.86 Å for Salen(^{t}Bu)InMe (**27**), and 0.89 Å for Salophen(^{t}Bu)InEt (**30**). Overall, this is a feature that the Salen ligands share with the analogous porphyrin derivatives which feature out-of-plane distances in the range of 0.78−0.98 Å.[33]

The Al−C bond lengths in SalenAlMe (**1**) (1.963(17) Å) and Salen(^{t}Bu)AlMe (**10**) (1.972(9) Å) do not differ from those found in traditional four-coordinate

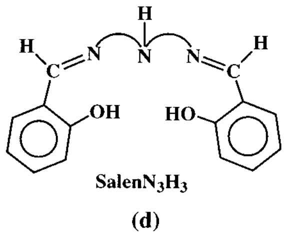


SalenH$_2$ (a)

AcenH$_2$ (b)

Salen(^{t}Bu)H$_2$ (c)

Ligand	R "backbone"
SalenH$_2$	1,2-ethylene
SalpenH$_2$	1,2-propylene
SalbenH$_2$	1,4-butylene
SalptenH$_2$	1,5-pentylene
SalhenH$_2$	1,6-hexylene
SalcenH$_2$	1,2-cyclohexylene
1,4-SalophenH$_2$	1,4-phenylene
SalmabenH$_2$	1,4-bis{*m*-aminobenzyl)benzene (e)
SalmabmabenH$_2$	1-(*m*-aminobenzoyl)-4-(*m*-aminobenzyl)benzene (f)
SalmadmenH$_2$	4,4'-bis(*m*-aminobenzoyl)diphenylmethane (g)



SalenN$_3$H$_3$ (d)

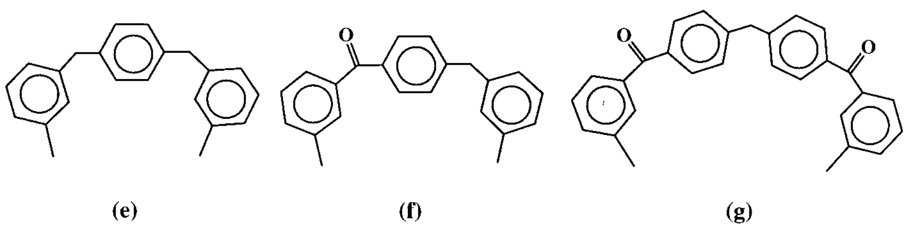


Figure 1. Various ligands that are included as "Salen" ligands. They primarily differ in two ways: in the type of connection, or backbone, between the nitrogen atoms and in the constiuents on the phenol portion of the ligand.

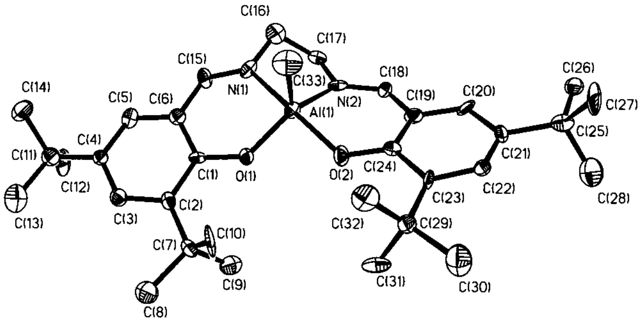


Figure 2. ORTEP view of Salen(^{t}Bu)AlMe (**10**).-

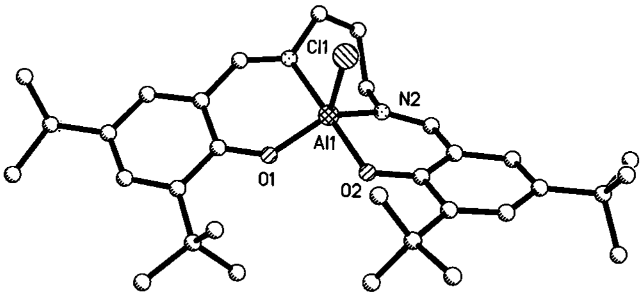


Figure 3. Molecular structure and simplified atom numbering scheme for Salpen(^{t}Bu)AlCl (**36**).

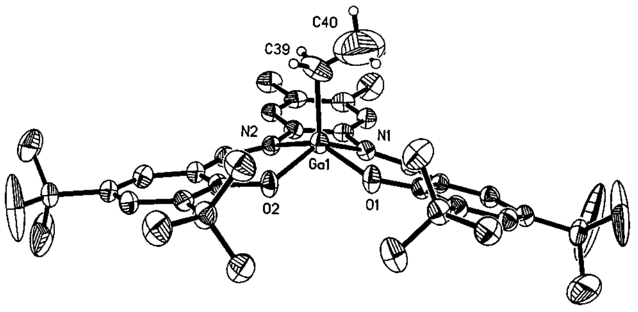


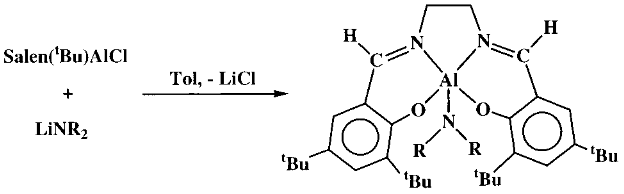
Figure 4. ORTEP view of Salomphen(^{t}Bu)GaEt (**22**).

compounds, such as $(Me_3Al)_2$(diphos) Al−C$_{Ave}$ = 1.96 Å.[34] The Ga−C distances are similar but cover a wider range (1.939(5)−2.019(8) Å). As expected, the In−C distances are significantly longer, 2.135 Å, but similar to the In−C distances in the five-coordinate oxime complex $[InMe_2(ON{=}CHC_5H_4N)]_2$ (2.153(27) and 2.165(25) Å).[35] The same trend appears in the M−X bonds, where Al−Cl and Ga−Cl are similar (~2.19 Å) but shorter than for In−Cl (~2.3).

B. Amides

The combination of a SalenAlCl starting material with a lithium amide leads to the formation of a unique class of five-coordinate aluminum amides (Scheme 2).[20] These are the first compounds to possess terminal amido groups on a five-coordinate aluminum atom. The yellow and orange compounds are highly moisture sensitive and hydrolyze much more rapidly than related four-coordinate derivatives (of the general formula $[R_2AlNR'_2]_n$).[31−34] This can be attributed to the strong Lewis-basic nature of the free nitrogen lone pair of electrons in the five-coordinate derivatives. By comparison, the lone pair is employed in coordinate covalent bonding in the four-coordinate compounds. The hydrolysis is slowed by the presence

Scheme 2. Formation of Terminal Five-Coordinate Aluminum Amides



of bulky groups such that the least moisture-sensitive are those containing the 2,6(^{i}Pr)$_2$–Ph (DIPP) ligand, Salen(^{t}Bu)Al{NH(Dipp)} (**53**). To completely characterize the compounds, they must be handled rapidly under dry nitrogen and preferably at low temperatures. The ^{1}H NMR data indicate that the ligands are symmetric and that there is a single resonance in the ^{27}Al NMR in the five-coordinate range, 40–57 ppm. These data confirm the monomeric nature of **51**–**59**. Further support for the existence of monomeric amides was provided in the crystal structure of Salcen(^{t}Bu)Al{N(SiMe$_3$)$_2$} (**59**) (Figure 5).[36] The central Al atom is in a distorted sqp geometry. The amide group occupies the apical position at a distance of 1.881(5) Å. This is shorter than the Al–N distances in compounds containing bridging amido groups (for instance, [(Me$_3$Si)$_2$AlNH$_2$]$_2$,1.955(2) Å);[37] [Me$_2$Al{N(H)-NMe$_2$}]$_2$, 1.958(3) Å;[38] and [MeAlNR]$_{4,6}$ (R = 4-F–C$_6$H$_2$), 1.909(3)–1.952(3) Å).[39] It is most comparable to that found in the imido derivative [Cp*AlNSiPh$_3$]$_2$ (shortest distance = 1.835(2) Å).[40]

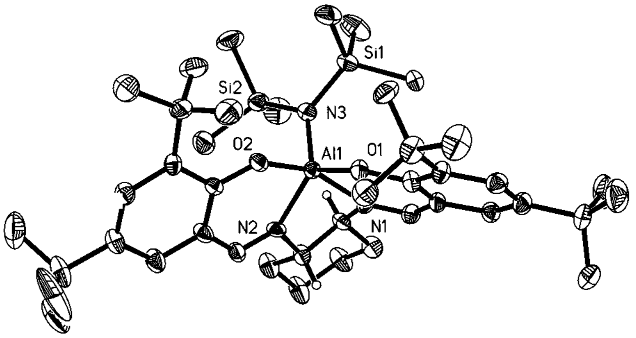


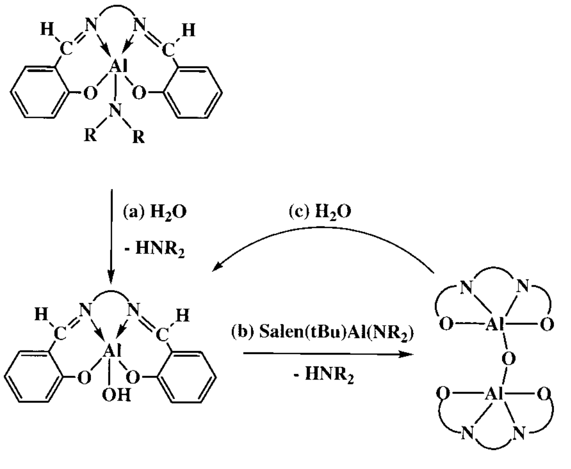
Figure 5. ORTEP view of Salcen(^{t}Bu)Al{N(SiMe$_3$)$_2$} (**59**).

C. Hydroxide and μ-Oxo Compounds

Any of the amide compounds can be used as a sacrificial reagent in the hydrolytic formation of Salen(^{t}Bu)AlOH (**60**) in high yield (Scheme 3).[20] The key to the synthesis is to make sure the compound is exposed to moist air for an extended period of time. Upon the basis of the spectroscopic data, a symmetric solution-state geometry, and a ^{27}Al resonance at 41 ppm, the compound is apparently a monomer in solution. This is a rare[41] example of a group 13 metal with a terminal hydroxy group.

In the presence of unreacted amide, **60** forms the μ-oxo species, {Salen(^{t}Bu)Al}$_2$O (**61**).[20] This same type of reaction (between SalenAlR and the non-*tert*-butylated version of **60**) was shown previously to form the analogous Salen derivative, {SalenAl}$_2$O (**62**).[42] The structure of **61** is shown in Figure 6. The O–Al–O angle is remarkably obtuse, 159.5(5)°, slightly more than that in structurally characterized **62** (152.0(3)°). Fe(III) analogues feature comparable angles,[43] while {SalenRe(O)}$_2$O is linear.[7] The Al atoms in the structures are in a sqp geometry. Despite the apparent larger steric bulk of **61**, the Al–O distances, 1.696(3) Å, are actually shorter than those in **62**, 1.705(5) Å. This may be attributed to a greater degree of sp hybridization in a more linear Al–O–Al linkage. Compound **61** quantitatively reverts back to **60** upon exposure to atmospheric moisture (Scheme 3).

Scheme 3. Formation of Aluminum Hydroxides (a and c) and a Bridged Oxo Compound (b)



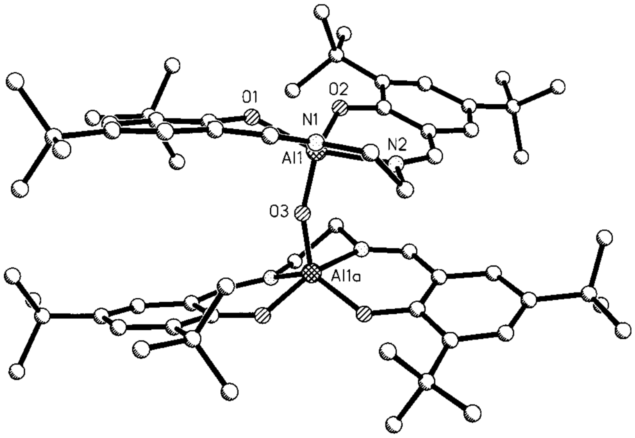


Figure 6. Molecular structure and atom-numbering scheme for {Salen(^{t}Bu)Al}$_2$O (**61**).

D. Alkoxides

Combination of a SalenAlR reagent with an alcohol leads to an alkane elmination and the formation of alkoxide derivatives. The first compound to be prepared in this manner, SalenAlOMe (**63**), was thought to be monomeric.[44] Subsequently, it was shown that **63** was, in fact, dimeric,[15] although in MeOH the unique solvated alkoxide, Salen(^{t}Bu)AlOMe(MeOH) (**65**),[45] can be isolated. In the structure of **65** the Al–O bond in the coordinated solvent (2.381(9) Å) is easily distinguished from that of the covalent alkoxide (1.792(5) Å).

The use of the non-*tert*-butlyated Salen ligand allows the formation of dimers in a manner similar to conventional lower-coordinate alkoxides (in general like [R$_2$Al(μ-OR)]$_2$ (where R = alkyl, etc.)). Accordingly, [AcenAl(μ-OMe)]$_2$ (**64**)[15] and [SalpenIn(μ-

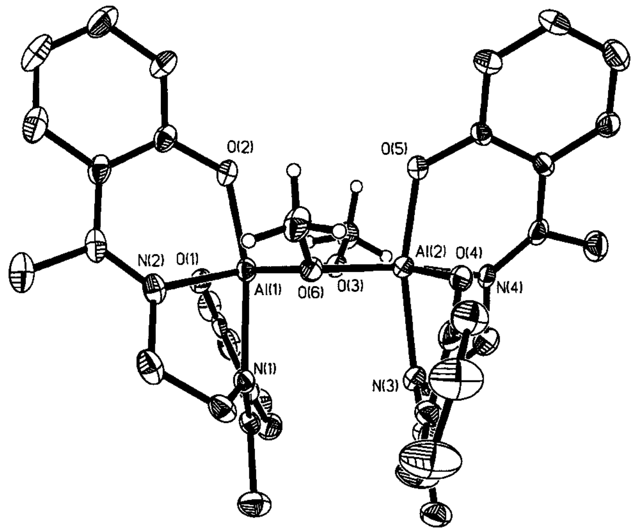


Figure 7. ORTEP view of [AcenAl(μ-OMe)]$_2$ (**64**).

OMe)]$_2$ (**77**)[17] are also dimeric (the structure of **64** is shown in Figure 7). The aluminum atoms in the dimeric structures adopt distorted octahedral geometries (see Table 4). Due to the constraints imposed by the ligand, the most obtuse angles are ~168°. Even with the *tert*-butyl substitution, the Salen ligand with the propylene backbone is flexible enough to allow dimerization. This is seen, for example, in [Salpen(^{t}Bu)In(μ-OMe)]$_2$ (**78**). Like **77**, the geometry around the indium is distorted O_h.

When the alkoxide is anything other than a methyl group, the resulting compounds are monomeric.[35] This has been demonstrated in Salen(^{t}Bu)AlOEt (**66**) and [SalenAl{O(2,4,6-Me$_3$Ph)}] (**72**).[41] All of the known carboxylate derivatives are monomeric as well (compounds **73**−**76**). A wider range of alkoxide derivatives are available for indium (**77**−**79**) apparently due to the greater lability of the ligands on this metal by comparison to aluminum and gallium. In addition to compounds [{(SalpenIn)(μOMe)}$_2$] (**77**)[17] and [Salpen(^{t}Bu)In(μ-OMe)]$_2$ (**78**), the isomer where both ligands bridge the two indium atoms can also be formed, {(μ-Salpen)In(μ-OMe)}$_2$ (**79**). However, the geometry and distances around the indium atom in this structure change little from those observed in **77** and **78**. In reactions intended to produce SalpenInMe, a dimer containing three ligands and two metals was isolated ([{SalpenIn}$_2$(μ-Salpen)]; **80**). The range of alkoxide structures that may be adopted with the Salen ligands is summarized in Figure 8. Chiral alkoxides have been reported as living polymerization catalysts for lactides but have not been fully characterized.[46,47]

E. Siloxides

Mixing of any of the alkyl aluminum derivatives (**1**−**10**) with Ph$_3$SiOH, followed by reflux in toluene, results in the formation of the novel aluminosiloxane monomers (**81**−**84**) (Scheme 4).[13] An indium derivative, Salen(^{t}Bu)In(OSiPh$_3$) (**85**), can be prepared similarly, but it is necessary to subject the reaction mixture to a prolonged reflux (>80 h).[18] For the aluminum compounds there was no apparent difference in reactivity or yield when using either the Me, Et, or ^{i}Bu derivatives. The products are soluble in toluene and benzene and do not decompose on standing in air, either in solution or as a solid, for several hours. The ^{29}Si chemical shifts for **81**−**84** fall in the narrow range of δ −28.77 to −29.99 ppm, close to that observed for Al(OSiPH$_3$)$_3$(thf) (−24.6 ppm).[48]

The monomeric nature of **81**−**84** in the solid state was confirmed by X-ray analyses. The structures of **82** and **84** are shown in Figures 9 and 10, respectively. They clearly demonstrate how changing the ligand backbone changes the resulting coordination of the aluminum atom. In **81** the geometry around the aluminum atom is best described as trigonal bipyramidal and is a result of the flexibility inherent to the −(CH$_2$)$_3$− backbone. The O1 and N2 atoms occupy the axial sites and form an angle of 169.5(1)°. 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). In **84** the ligand, with a rigid *o*-phenylene backbone, forms the basal coordination plane of a square pyramidal geometry about the aluminum. The aluminum atom is located 0.53 Å above the N_2O_2 plane. The apical site is occupied by the oxygen of the siloxane. However, the Al−O3 distance (1.715(2) Å) is still substantially shorter than those to the ligand oxygens (1.804(2) and 1.796-

Table 3. Group 13 Amides, Alkoxides, Siloxides, and Related Compounds

compound	ref	compound	ref
Salen(^{t}Bu)Al(NH^{t}Bu) (**51**)	20	AcenAlO(2,6-Me$_2$-4-Cl)Ph (**69**)	15
Salen(^{t}Bu)Al(NHPh) (**52**)	20	[SalenAlOPh] (**70**)	42
Salen(^{t}Bu)Al{NH(Dipp)} (**53**)	20	[SalenAlO(4-^{t}Bu-Ph)] (**71**)	42
Salen(^{t}Bu)Al(NMe$_2$) (**54**)	20	[SalenAlO(2,4,6-Me$_3$-Ph)] (**72**)	42
Salen(^{t}Bu)Al(NEt$_2$) (**55**)	20	[SalenAl(O$_2$CMe)] (**73**)	42
Salen(^{t}Bu)Al{N(SiMe$_3$)$_2$} (**56**)	20	[SalenAl(O$_2$CPh)] (**74**)	42
Acen(^{t}Bu)Al(NHPh) (**57**)	20	[SalenAl(acac)] (**75**)	42
Acen(^{t}Bu)Al{N(SiMe$_3$)$_2$} (**58**)	20	SalenAl[2-OPh{C(O)Me}] (**76**)	42
Salcen(^{t}Bu)Al{N(SiMe$_3$)$_2$} (**59**)	20	[{(SalpenIn)(μOMe)}$_2$] (**77**)	17
Salen(^{t}Bu)AlOH (**60**)	20	[Salpen(^{t}Bu)In(μ-OMe)]$_2$ (**78**)	17
{SalenAl}$_2$O (**62**)	42	[{(μ-Salpen)In(μ-OMe)}$_2$] (**79**)	17
{Salen(^{t}Bu)Al}$_2$O (**61**)	20	[{SalpenIn(μSalpen)}$_2$] (**80**)	17
[SalenAl(μ-OMe)]$_2$ (**63**)	15	Salen(^{t}Bu)Al(OSiPh$_3$) (**81**)	13
[AcenAl(μ-OMe)]$_2$ (**64**)	15	Salpen(^{t}Bu)Al(OSiPh$_3$) (**82**)	13
Salen(^{t}Bu)AlOMe(MeOH) (**65**)	45	Salophen(^{t}Bu)Al(OSiPh$_3$) (**83**)	13
Salen(^{t}Bu)AlOEt (**66**)	45	Salomphen(^{t}Bu)Al(OSiPh$_3$) (**84**)	13
SalenAlO(2,6-Me$_2$-4-Cl)Ph (**67**)	15	Salen(^{t}Bu)In(OSiPh$_3$) (**85**)	18
SalenClAlO(2,6-Me$_2$-4-Cl)Ph (**68**)	15		

Table 4. Selected Bond Lengths and Angles for Amides, Alkoxide, Siloxides, and Related Compounds

compound	geometry	M−N or O (ligand)	M−O (Salen)	M−N (Salen)	O−M−O (Salen)	N−M−N (Salen)	O−M−N†
			Amide				
59	sqp	1.881(5)	1.799(9)	2.07(1)	91.0(2)	76.3(2)	159.3(2)
			1.831(9)	2.03(1)			
μ-oxo **61**	sqp	1.705(5)	1.836(5)	2.024(6)	89.0(2)	78.3(2)	152.0(3)
			1.809(5)	2.013(6)			
62	sqp	1.696(3))	1.821(6)	2.008(5)	90.2(3)	77.7(3)	158.2(3)
			1.793(6)	2.035(7)			
			Alkoxides				
63	Oh	1.87(1)	1.887(9)	2.04(1)	94.5(5)	77.1(6)	166.6(6)
			1.83(1)	2.05(1)			
65	Oh	1.792(5)	1.810(4)	2.004(5)	95.2(2)	79.6(2)	162.1(2)
		2.381(9)	1.802(5)	1.987(5)			
66	sqp	1.737(2)	1.812(2)	2.017(2)	91.34(7)	78.49(8)	161.96(8)
			1.789(2)	1.988(2)			
72	sqp (distorted)	1.737(3)	1.787(3)	1.994(2)	89.1(1)	78.8(1)	136.5(1)
			1.798(2)	2.000(3)			
77	Oh	2.152(6)	2.133(7)	2.222(8)	91.4(2)	85.5(2)	167.3(2)
			2.085(7)	2.263(7)			
78	Oh	2.154(4)	2.089(4)	2.291(6)	93.1(2)	82.1(2)	162.2(2)
			2.127(4)	2.227(5)			
79	Oh	2.141(3)	2.107(4)	2.252(4)	97.4(2)	171.5(2)	94.5(1)
80	Oh	2.263(6)	2.114(5)	2.222(8)	88.4(2)	82.7(2)	160.6(3)
		2.122(5)	2.088(5)	2.263(7)			
			Siloxides				
81	sqp	1.72(1)	1.81(2)	1.96(3)	88.9(8)	79.5(9)	159.3(7)
			1.82(2)	2.06(2)			
82	tbp	1.726(2)	1.828(1)	1.987(1)	90.7(1)	83.7(1)	169.5(1)
			1.764(2)	2.037(1)			
83	sqp	1.702(9)	1.794(8)	2.01(1)	88.9(8)	79.0(9)	155.0(5)
			1.806(9)	2.03(1)			
84	sqp	1.715(2)	1.804(2)	2.019(2)	91.12(9)	77.77(9)	154.38(9)
			1.796(2)	2.029(2)			

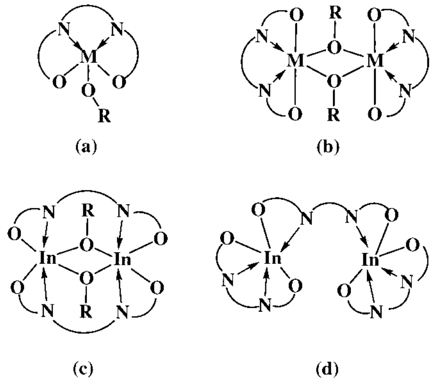
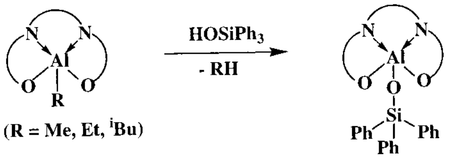


Figure 8. Known types of alkoxide derivatives (a−c) and a related structure (d).

Scheme 4. Formation of Terminal Aluminum Siloxides



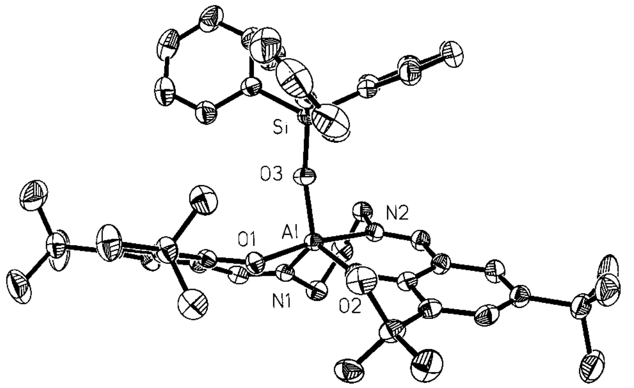


Figure 9. ORTEP view of Salpen(^{t}Bu)Al(OSiPh$_3$) (**82**).

(2) Å). Compounds **81** and **83** adopt the same structural arrangement as **84** with relatively short Al−O (apical) distances of ~1.7 Å. The aluminum atoms are perched at 0.48 and 0.52 Å above the N_2O_2 plane, respectively.

These structures are unique because they are the first instances that a single Al−O−Si linkage has been structurally characterized. Molecules possessing this linkage have an almost overwhelming tendency to aggregate as manifested in the bonding within zeolites. By comparison to **81**−**84**, the structure of [(2,6-$Me_2C_6H_3$)N(SiMe$_3$)SiO$_3$Al-dioxane]$_4$,[49] which has the core structure of the Linde type A zeolite, contains Al−O−Si linkages averaging 140(5)°.[50] For **81**−**84** these angles are 157.9(14)°, 166.3(2)°, 166.8(6)°, and 163.5 (1)°, respectively. These are more comparable to other compounds containing three Ph$_3$SiO− units with Al−O−Si angles of 150−160°.[51,52] The most linear angle (177.6(2)°) is observed for one of the Al−O−Si units in [{Ph$_3$SiO}$_2$Al(^{t}Bu)]$_2$.[53] The distances in the LTA complex (mentioned above)[49] 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 **81**−**84** the Al−O and Si−O distances fall within this range (Table 4). By comparison, the Al−O and Si−O distances for dimeric derivatives such as [Me$_2$AlOSiH$_2$-

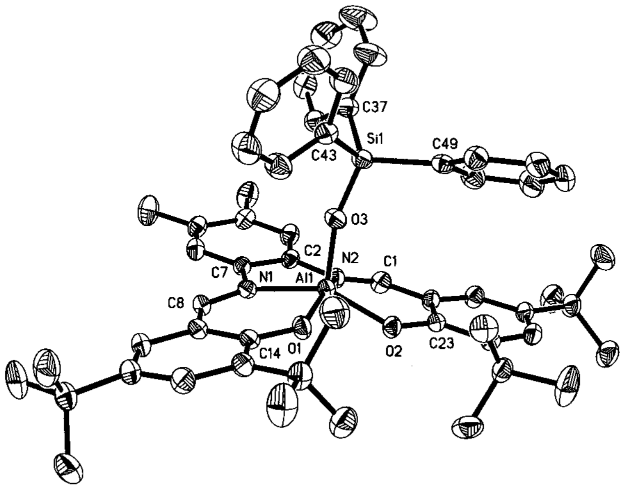


Figure 10. ORTEP view of Salomphen(^{t}Bu)Al(OSiPh$_3$) (**84**).

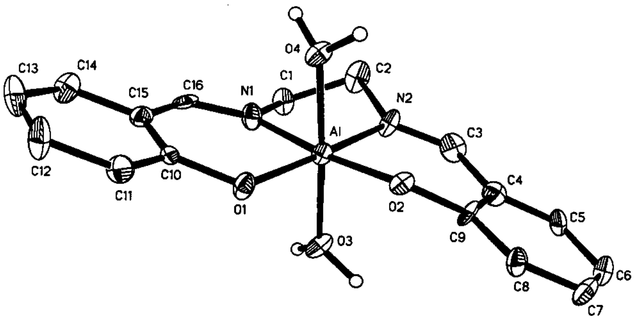


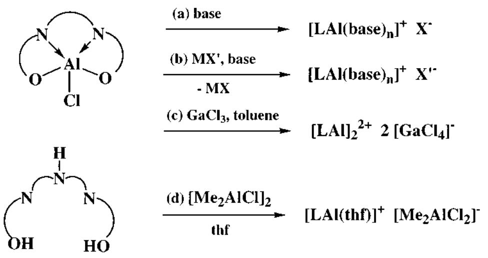
Figure 11. ORTEP view of the cation of [SalenAl(H$_2$O)$_2$]$^+$ Cl$^-$ (**86**).

(C$_2$H)]$_2$ are 1.85(1) and 1.651(2) Å, respectively.[54]

F. Cations

A wide variety of six-coordinate cations[55] can be prepared through several convenient methods.[15,56,57] One of the more simple is the dissolution of a SalenAlCl reagent in a Lewis-basic solvent (Scheme 5a). This reaction leads to the formation of cations of the type [SalenAl(base)$_2$]$^+$Cl$^-$. The bases that are able to promote displacement of the halide may be protic (H$_2$O, MeOH)[15,53] or nonprotic (Ph$_3$P=O,[57] thf,[58] HMPA[59]). Additionally, chiral derivatives are accessible.[60,61] The diaquo cation, [SalenAl(H$_2$O)$_2$]$^+$, of (**86**) is shown in Figure 11 (Cl$^-$ is the counteranion). The efficacy of the nonprotic reagents implies that hydrogen bonding is not a critical feature of the displacement. The counteranion can be changed to BPh$_4^-$ through a salt elimination reaction (Scheme 5b).[62] The ^{27}Al NMR of these cations appear as singlets in the range 2–10 ppm. The X-ray structures of the cations are very similar. All feature shorter Al–O bonds to the ligand than to the coordinated bases (Table 5). The shortest Al–O(base) distances are observed in the complexes with the least steric encumberance.

Scheme 5. Currently Available Routes to the Formation of Salen-Supported Cations



For many applications it would be preferable to have a solvent-free cation. This can be achieved by removing the chloride of a SalenAlCl reagent with GaCl$_3$ in toluene (Scheme 5c).[63] The first compound to be isolated was a bimetallic dication (a molecular structure is shown in Figure 12). The dimer is formed through intramolecular solvation. As for [Salpen(^{t}Bu)In(μ-OMe)]$_2$ (**78**), the propyl backbone is flexible enough to allow dimerization (**108**). The dehalogenation of Salomphen(^{t}Bu)AlCl, a complex in which the backbone should be rigid, also produced a dimer, [{Salomphen(^{t}Bu)$_3$Al}$_2$]$^{2+}$2[GaCl$_4$]$^-$ (**109**) (Figure 13). Dimerization is allowed by the ejection of one of the ^{t}Bu groups from the ligand (hence the (^{t}Bu)$_3$ designation). Although rare, such a Friedel–Crafts dealkylation is not unprecedented.[64] It would be interesting to understand the process by which these cations form and whether some type of four-coordinate square pyramidal aluminum cation may be involved; it seems logical that such a species is formed during the reaction.

A fourth preparative route that may be used specifically for the SalenN$_3$ ligands involves the addition of 2 equiv of R$_2$AlX to the ligand in thf (Scheme 5d).[65] When conducted in toluene, this reaction produces the neutral bimetallics (described below). Although the NH group in these compounds can be involved in coordinate covalent bonding (this is seen, for example, in SalenN$_3$U=O), it remains as

Table 5. Cationic Aluminum Chelates

compound	ref	compound	ref
[SalenAl(H$_2$O)$_2$]$^+$ Cl$^-$ (**86**)	15	[Salen(^{t}Bu)Al(H$_2$O)$_2$]$^+$ Cl$^-$ (**99**)	62
[Salen(Cl)Al(H$_2$O)$_2$]$^+$ Cl$^-$ (**87**)	15	[Salen(^{t}Bu)Al(H$_2$O)$_2${C(O)Ph}]$^+$ Cl$^-$ (**100**)	62
[AcenAl(H$_2$O)$_2$]$^+$ Cl$^-$ (**88**)	15	[Salen(^{t}Bu)Al(MeOH)$_2$]$^+$ Cl$^-$ (**101**)	62
[SalenAl(MeOH)$_2$]$^+$ Cl$^-$ (**89**)	15	[Salen(^{t}Bu)Al(MeOH)$_2$]$^+$ BPh$_4^-$ (**102**)	62
[Salen(Cl)Al(MeOH)$_2$]$^+$ Cl$^-$ (**90**)	15	[Salen(^{t}Bu)Al(MeOH)$_2$]$^+$ OTs$^-$ (**103**)	62
[AcenAl(MeOH)$_2$]$^+$ Cl$^-$ (**91**)	15	Salen(^{t}Bu)AlOTs(thf) (**104**)	62
[SalenAl(MeOH)$_2$]$^+$BPh$_4$ (**92**)	15	Salcen(^{t}Bu)AlOTs (**105**)	61
[Salen(Cl)Al(MeOH)$_2$]$^+$ BPh$_4^-$ (**93**)	15	Salcen(^{t}Bu)Al(MeOH)$_2$]$^+$ Cl$^-$ (**106**)	60
[AcenAl(MeOH)$_2$]$^+$ BPh$_4^-$ (**94**)	15	Salcen(^{t}Bu)Al(thf)$_2$]$^+$ BPh$_4^-$ (**107**)	61
[SalenAl(thf)$_2$]$^+$ [AlCl$_4$]$^-$ (**95**)	59	[Salpen(^{t}Bu)4Al]$_2^{2+}$ 2[GaCl$_4$]$^-$ (**108**)	63
[SalenAl(hmpa)$_2$]$^+$ Cl$^-$ (**96**)	59	[Salomphen(^{t}Bu)$_3$Al]$_2^{2+}$ 2[GaCl$_4$]$^-$ (**109**)	63
[SalenAl(hmpa)$_2$]$^+$ I$^-$ (**97**)	59	[SalenN$_3$Al(thf)]$^+$ [AlMe$_2$Cl$_2$]$^-$ (**110**)	65
[SalenAl(hmpa)$_2$]$^+$ [CF$_3$SO$_3$]$^-$ (**98**)	59	[SalpenN$_3$Al(thf)]$^+$ [AlMe$_2$Cl$_2$]$^-$ (**111**)	65

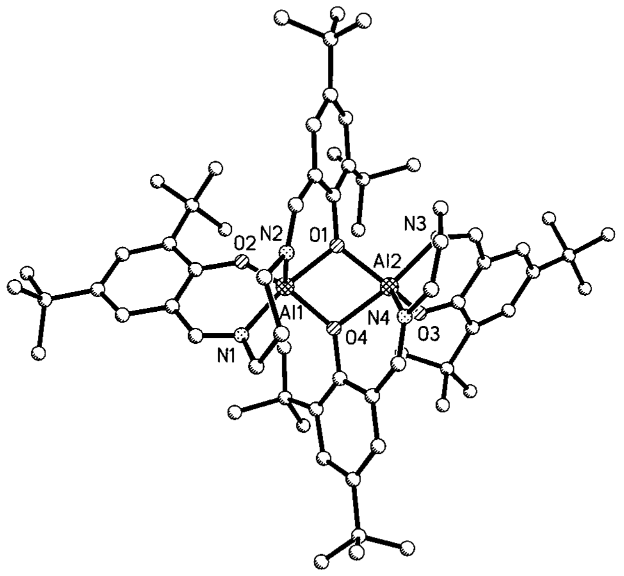


Figure 12. ORTEP view of the cation of [Salpen(^{t}Bu)Al]$_2^{2+}$ 2 GaCl$_4^-$ (**108**).

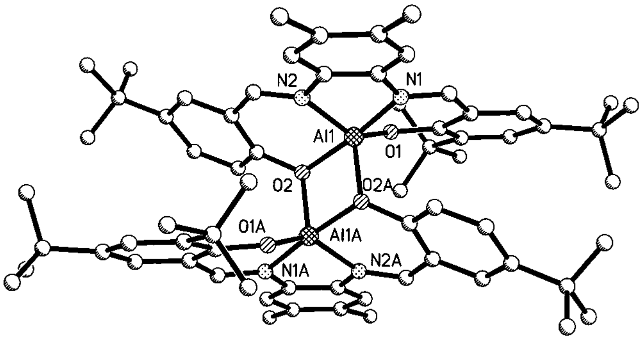


Figure 13. ORTEP view of the cation of [Salomphen(^{t}Bu)$_3$Al]$_2^{2+}$ 2 GaCl$_4^-$ (**109**).

the free amine in **110** and **111**, as indicated by the NH absorbance at $\upsilon \sim 3200$ cm^{-1} in the IR. Compound **111** is structurally similar to the six-coordinate [SalenAl(base)$_2$]$^+$X$^-$ described above.[15] Thus, for **111** the aluminum atom is in an octahedral geometry with the thf molecule and the transannular amine occupying trans positions to one another. The solvent forms a longer bond to the aluminum atom (2.046(3) Å) than do the ligand O atoms (~1.8 Å) in keeping with the difference between coordinate covalent and covalent bonding, respectively. This trend, with very similar distances, is also observed in the [SalenAl(base)$_2$]$^+$ cations.[15]

Several varieties of six-coordinate cations can be prepared from the five-coordinate halides described above through several different methods (Scheme 5a–d). A summary of the known cations is shown in Figure 15. Generally, three variables may be manipulated in these cations; ligand, counteranion, and coordinating solvent. For aluminum there appears to be no limit to the types of cations that may be accessed. Surprisingly, the analogous gallium cations have yet to be prepared by any route despite the apparent close similarity between Al(III) and Ga(III). The only member of this group is [{Salomphen(^{t}Bu)Ga(MeOH)}$_2$(μ-Cl)]$^+$[BPh$_4$]$^-$, which was adventitiously isolated in an attempt to prepare [Salomphen(^{t}Bu)Ga(MeOH)$_2$]$^+$[BPh$_4$]$^-$.[16] A low-quality crystal structure reveals that the gallium atoms are coplanar with the salen ligand and that the chlorine is equally shared (~2.0 Å) by the cationic halves, with a Ga–Cl–Ga angle of 149°. There are no reports whatsoever of salen-supported indium cations.

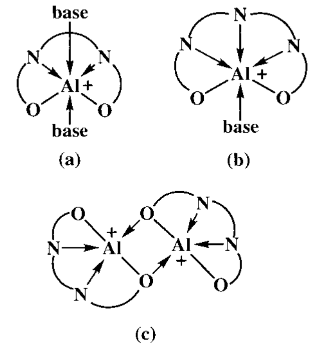


Figure 14. Overview of the three types of cations supported by the Salen (and related) ligands.

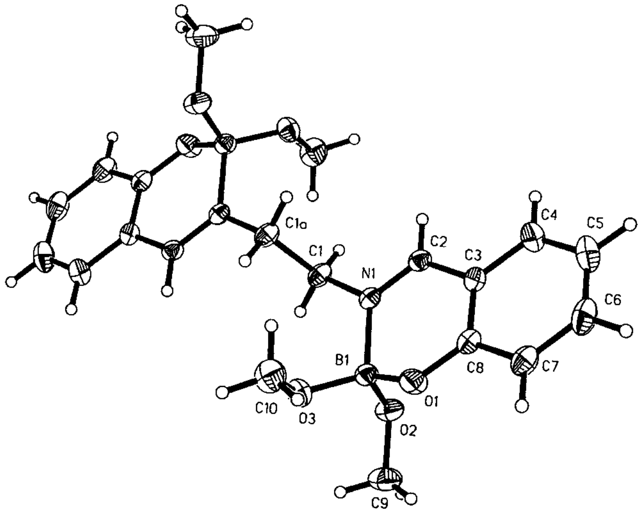


Figure 15. ORTEP view of Salen{B(OMe$_2$)}$_2$ (**113**).

III. Bimetallic Compounds (Having a 2:1 Metal to Ligand Stoichiometry).

A. Boron

Due to the strong, covalent nature of the B–C bond, alkane eliminations (with BR$_3$, for instance) are not useful in preparing chelated boron complexes. However, alcohol eliminations work well provided the reaction is heated for a reasonable period of time. The choice of alkyl group on the borate (whether Me, Et,

Table 6. Selected Bond Lengths and Angles for the Cationic Complexes

cation	Al–O	Al–N	Al–B	O–Al–O	N–Al–N	B–Al–B
86	1.82	1.98	1.95	94.8(4)	80.5(4)	176.0(3)
92	1.80	1.98	1.99	92.3(2)	81.6(2)	175.8(2)
94	1.79	1.98	1.96	93.3(4)	83.1(4)	176.1(3)
95	1.79	1.99	2.00	not reported		
96	1.82	2.00	1.93			
97	1.82	2.02	1.92			
98	1.81	2.00	1.90			
101	1.79	2.00	1.97	97.2(2)	80.6(2)	173.5(2)
103	1.80	1.99	1.97	97.7(2)	81.3(2)	175.9(2)
107	1.78	1.98	2.04	96.2(2)	81.2(2)	178.3(2)

Table 7. Bimetallic Aluminum, Gallium, and Indium Compounds

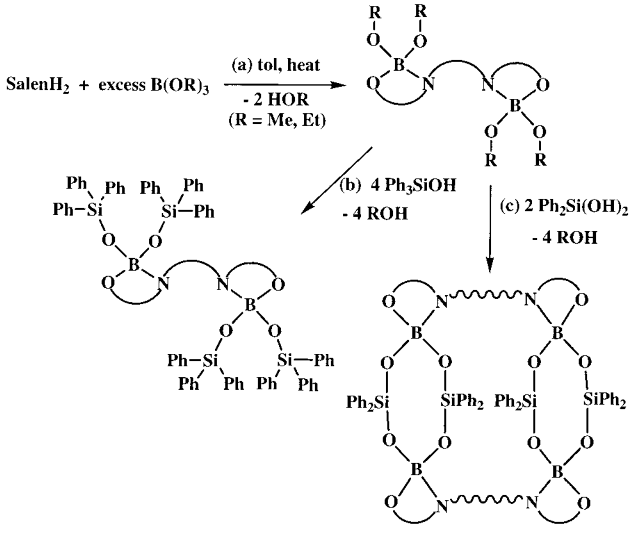
compound	ref	compound	ref
Acen{B(Ph)$_2$}$_2$ (**112**)	69	Salpten(^{t}Bu)(AlMe$_2$)$_2$ (**142**)	76
Salen{B(OMe)$_2$}$_2$ (**113**)	66	Salhen(^{t}Bu)(AlMe$_2$)$_2$ (**143**)	76
Salen{B(OEt)$_2$}$_2$ (**114**)	66	Salhen(^{t}Bu)(AlEt$_2$)$_2$ (**144**)	76
Salen(^{t}Bu){B(OMe)$_2$}$_2$ (**115**)	66	1,4-Salophen(^{t}Bu)(AlMe$_2$)$_2$ (**145**)	76
Salen(^{t}Bu){B(OEt)$_2$}$_2$ (**116**)	66	1,4-Salophen(^{t}Bu)(GaEt$_2$)$_2$ (**146**)	76
Salpen{B(OMe)$_2$}$_2$ (**117**)	66	Salmaben(^{t}Bu)(AlMe$_2$)$_2$ (**147**)	76
Salpen{B(OEt)$_2$}$_2$ (**118**)	66	Salmabmaben(^{t}Bu)(AlMe$_2$)$_2$ (**148**)	76
Salpen(^{t}Bu){B(OMe)$_2$}$_2$ (**119**)	66	Salmadmen(^{t}Bu)(AlMe$_2$)$_2$ (**149**)	76
Salben(^{t}Bu){B(OEt)$_2$}$_2$ (**120**)	66	Salcen(^{t}Bu)(AlMeCl)$_2$ (**150**)	76
Salben{B(OMe)$_2$}$_2$ (**121**)	66	Salpen(^{t}Bu)(AlMeCl)$_2$ (**151**)	76
Salben{B(OEt)$_2$}$_2$ (**122**)	66	Salben(^{t}Bu)(AlMeCl)$_2$ (**152**)	76
Salben(^{t}Bu){B(OMe)$_2$}$_2$ (**123**)	66	Salhen(^{t}Bu)(AlMeCl)$_2$ (**153**)	76
Salben(^{t}Bu){B(OEt)$_2$}$_2$ (**124**)	66	SalenN$_3$(AlMe$_2$)$_2$ (**154**)	65
Salpten{B(OMe)$_2$}$_2$ (**125**)	66	SalpenN$_3$(AlMe$_2$)$_2$ (**155**)	65
Salpten{B(OEt)$_2$}$_2$ (**126**)	66	SalenN$_3$(AlMeCl)$_2$ (**156**)	65
Salpten(^{t}Bu){B(OMe)$_2$}$_2$ (**127**)	66	SalpenN$_3$(AlMeCl)$_2$ (**157**)	65
Salpten(^{t}Bu){B(OEt)$_2$}$_2$ (**128**)	66	Salen(GaMe$_2$)$_2$ (**158**)	74
Salhen{B(OMe)$_2$}$_2$ (**129**)	66	Salen(^{t}Bu)(GaEt$_2$)$_2$ (**159**)	75
Salhen{B(OEt)$_2$}$_2$ (**130**)	66	Salpen(^{t}Bu)(GaEt$_2$)$_2$ (**160**)	75
Salhen(^{t}Bu){B(OMe)$_2$}$_2$ (**131**)	66	Salben(^{t}Bu)(GaEt$_2$)$_2$ (**161**)	75
Salhen(^{t}Bu){B(OEt)$_2$}$_2$ (**132**)	66	Salhen(^{t}Bu)(GaEt$_2$)$_2$ (**162**)	75
SalenN$_3$H{B(OMe)$_2$}$_2$ (**133**)	66	Salen(^{t}Bu)H{GaMe$_2$} (**163**)	75
Salben{B(OSiPh$_3$)$_2$}$_2$ (**134**)	67	Salen(^{t}Bu)H{GaEt$_2$} (**164**)	75
Salen(^{t}Bu){B(OSiPh$_3$)$_2$ (**135**)	67	Salpen(^{t}Bu)H{GaEt$_2$} (**165**)	75
Salben(^{t}Bu){B(OSiPh$_3$)$_2$}$_2$ (**136**)	67	Salen(^{t}Bu){(AlMe$_2$)(GaEt$_2$)} (**166**)	75
SalenN$_3$H{B(OSiPh$_3$)$_2$}$_2$ (**137**)	67	Salen(^{t}Bu){(AlEt$_2$)(GaEt$_2$)} (**167**)	75
[Salpten(^{t}Bu){B(μ-O$_2$SiPh$_2$)}$_2$]$_2$ (**138**)	67	Salpen(^{t}Bu){(AlMe$_2$)(GaEt$_2$) (**168**)	75
[SalenN$_3$H{B(μ-O$_2$SiPh$_2$)}$_2$]$_2$ (**139**)	67	Salpen(^{t}Bu){(AlEt$_2$)(GaEt$_2$)} (**169**)	75
Salcen(^{t}Bu)(AlMe$_2$)$_2$ (**140**)	76	Salpen{InMe$_2$}$_2$ (**170**)	17
Salben(^{t}Bu)(AlMe$_2$)$_2$ (**141**)	76	Salpen{InEt$_2$}$_2$ (**171**)	17

Table 8. Selected Bond Lengths and Angles for the Bimetallic Compounds

compound	M−O	M−N	M−R (or OR)	O−M−N	R−M−R
112	1.47(2)	1.65(1)	1.63	105.3(9)	116(1)
113	1.495(2)	1.615(2)	1.495(2) 1.426(2)	106.7(1)	112.7(1)
116	1.49(1)	1.60(2)	1.42(2)	105.2(9)	113(1)
118	1.480(6)	1.616(6)	1.409(6) 1.435(6)	105.5(4)	113.0(4)
119	1.498(7)	1.600(7)	1.411(7) 1.414(7)	106.4(4)	112.0(5)
125	1.475(8)	1.622(8)	1.413(8) 1.442(8)	106.6(4)	106.6(5)
130	1.49(1)	1.62(2)	1.41(2) 1.42(2)	105(1)	107(1)
134	1.481(4)	1.618(5)	1.418(4) 1.429(4)	105.5(3)	113.3(3)
135	1.479(6)	1.635(6)	1.411(6) 1.431(6)	104.9(4)	114.8(4)
138	1.47(1)	1.64(1)	1.42(1)	105.0(7)	115.7(8)
140	1.756(2)	1.979(3)	1.948(4) 1.946(4)	94.1(1)	118.9(2)
141	1.754(4)	1.952(5)	1.943(7) 1.944(7)	94.5(2)	115.6(3)
146	1.876(4)	2.041(4)	1.960(7) 1.939(7)	92.5(2)	127.7(3)
150	1.732(4)	1.951(4)	1.931(6) (Cl) 2.121(2)	96.1(2)	114.0(2)
152	1.734(7)	1.936(8)	1.932(7) (Cl) 2.113(4)	96.0(4)	110.6(3)
157	1.746(8)	1.909(8)	1.959(8) (Cl) 2.102(4)	97.7(4)	110.8(3)
158	1.869(2)	2.026(3)	1.948(6) 1.950(5)	94.0(1)	124.6(4)
159	1.874(5)	2.010(6)	1.98(1) 1.99(1)	92.4(2)	124.1(5)
160	1.863(6)	2.024(6)	1.95(1)	92.5(2)	126.4(5)
161	1.88(1)	2.02(1)	1.95(2) 1.96(2)	91.0(6)	125.8(8)
163	1.886(4)	2.013(5)	1.949(7) 1.956(7)	91.5(2)	124.6(3)
164	1.871(8)	2.03(1)	1.97(2) 1.89(2)	92.3(4)	123.4(8)

^{n}Pr, ^{n}Bu) apparently has no influence on the outcome of the reaction. This was the route used to prepare a range of bimetallic borates supported by the Salen[66,67] and related Schiff base[68] ligands. Combinations of salen ligands and borate starting materials readily lead to bimetallic compounds, even under conditions of excess ligand. This is attributed to the fact that boron prefers a four-coordinate, tetrahedral geometry. With only one exception, aryl or alkyl boranes did not form compounds with the salen ligands. Compound Acen{B(Ph)$_2$}$_2$ (**112**) was apparently formed from the photolytic and atmospheric decomposition of [AcenAl(MeOH)$_2$]$^+$ BPh$_4^-$ (**94**).[69] Although the compound was structurally characterized (see Table 8), it could not be reproduced. However, using the route outline in Scheme 6a with borate starting materials, good yields of a large number of compounds (**113**−**133**) could be isolated. A crystal struc-

Scheme 6. Syntheses of Borates (a), Siloxides (b), and Those with a "Drum-Like" Framework (c)



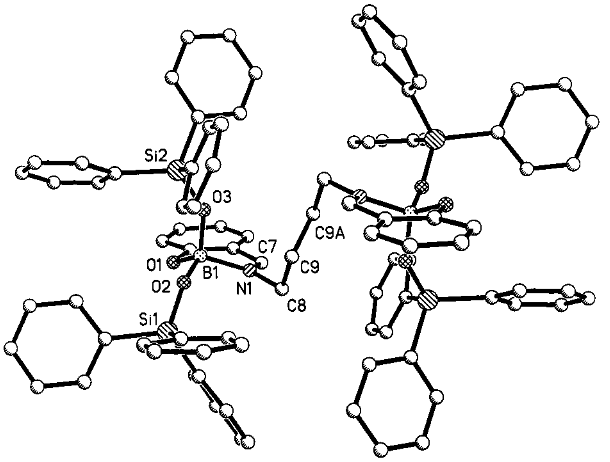


Figure 16. Molecular structure of Salben{B(OSiPh$_3$)$_2$}$_2$ (**134**).

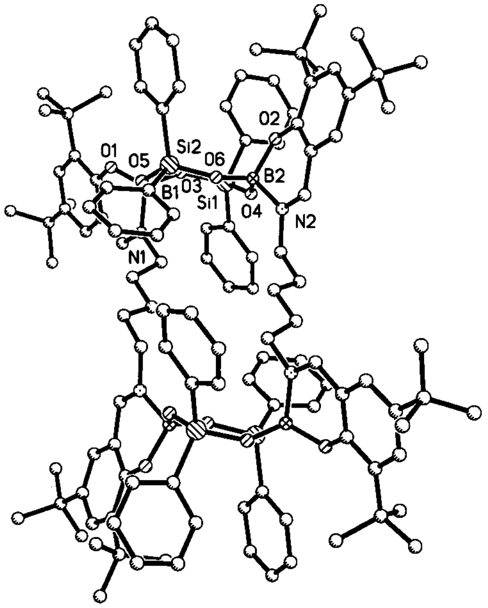


Figure 17. Molecular structure of [Salpten(^{t}Bu){B(μ-O$_2$-SiPh$_2$)}$_2$] (**138**).

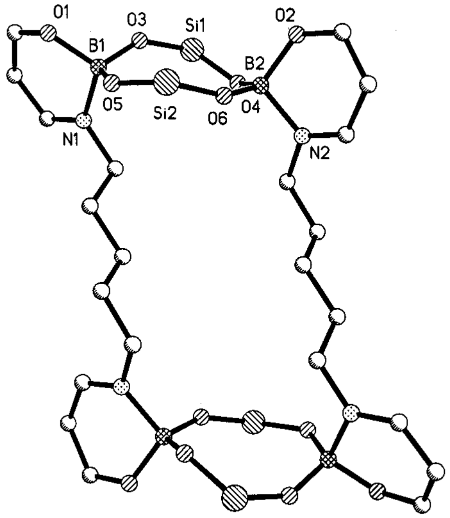


Figure 18. Skeletal structure of [Salpten(^{t}Bu){B(μ-O$_2$-SiPh$_2$)}$_2$] (**138**).

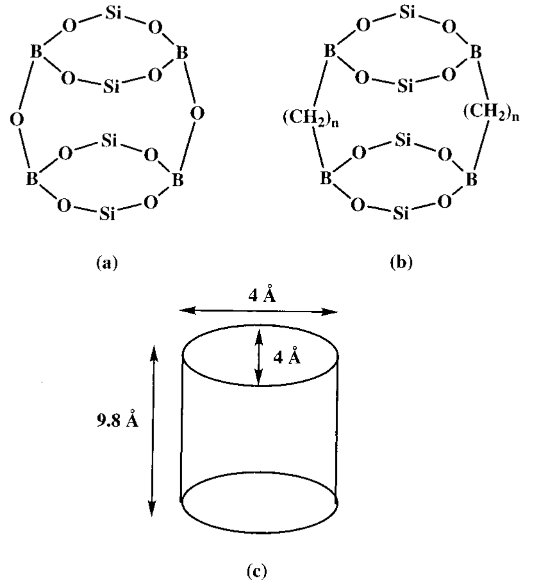


Figure 19. Comparison between the inorganic core of borosilicates (a) and that of **136** (b) which adopts the shape of a drum (c).

ture of Salen{B(OMe)$_2$}$_2$ (**113**) is representative of the group (Figure 15).

In previous work involving the Saltren ligand (tris-(((2-hydroxybenzyl)amino)ethyl)amine), attempts to synthesize the bis-siloxides (Saltren{B(OSiPh$_3$)$_2$}$_2$ were unsuccessful.[70] Rather, these reactions resulted in a complex, SaltrenH$_3${B(OSiPh$_3$)$_3$}$_3$, where the ligand acts as a Lewis base toward the neutral boron fragment. Thus, it was interesting to find that high yields of the bis-siloxides (**134**−**137**) were readily available for various Salen ligands (Scheme 6(b)). One example, Salben{B(OSiPh$_3$)$_2$}$_2$ (**134**), is shown in Figure 16. There are no inter- or intramolecular hydrogen bonds in compounds **134** and **135**. The three phenyl groups of the Ph$_3$SiO− unit effectively shield the siloxy-oxygen atom and prevent any intermolecular or intramolecular contacts.

The combination of Ph$_2$Si(OH)$_2$ with Salpten(^{t}Bu)-{B(OMe)$_2$}$_2$ (**127**) or SalenN$_3$H{B(OMe)$_2$}$_2$ (**133**) leads to [Salpten(^{t}Bu){B(μ-O$_2$SiPh$_2$)}$_2$]$_2$ (**138**) (shown in Figure 17) and [SalenN$_3$H{B(μ-O$_2$SiPh$_2$)}$_2$]$_2$ (**139**).[65] In aluminum derivatives containing the RSi(OH)$_3$ group, the (OH)SiO$_2$ unit bridges two metals[71] rather than chelating just one (Figure 19a).[72] The phosphonate (RPO(OH)$_2$) derivatives of the group 13 elements have similar structures.[73] In each case eight-membered rings form that contain the group 13 element, two oxygens, and the heteroatom (either Si or P). This arrangement is important in that it is also found in group 13 silicate and phosphate solid-state materials. This type of bonding is also observed for **138** and **139** (The framework of **138** is shown in Figure 18). However, unlike the previously reported examples, the eight-membered (BO$_2$Si)$_2$ units in these compounds are unique in that they are connected to one another by the length of the ligand backbone rather than an oxygen (Figure 19b). The framework of **138** can be represented by a cylinder that is 9.8 Å long (the average of the Si1−Si2a and Si2−Si1a distances), 4 Å wide (the Si1−Si2 distance), and 4 Å deep (the B1−B2 distance) (Figure 19c). A crude estimate of the volume within this cavity would then

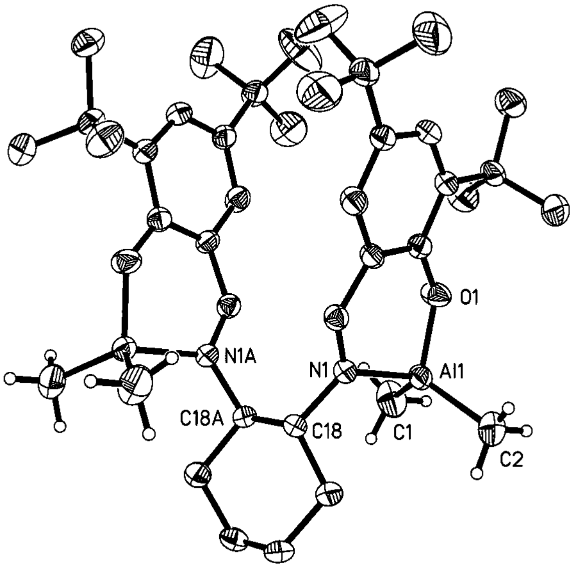


Figure 20. ORTEP view of Salcen(^{t}Bu){AlMe$_2$}$_2$ (**140**).

be 157 Å^3. The volume may be varied by changing the length of the ligand backbone.

B. Aluminum, Gallium, and Indium

Bimetallic compounds (**140**−**171**) are readily prepared by combining the SalenH$_2$ ligand with 2 equiv of the appropriate group 13 reagent (shown generally in Scheme 7)[74,75,76] Trialkyl- or dialkylhalide group 13 reagents can be used with equal facility provided the solvent is noncoordinating. The choice of ligand is only limited in that those with a 1,2-aryl backbone cannot be used (SalophenH$_2$ or SalomphenH$_2$, for example) since they favor monometallic compounds regardless of the reaction stoichiometry (see Section II above). A complete listing of the compounds is given in Table 8.

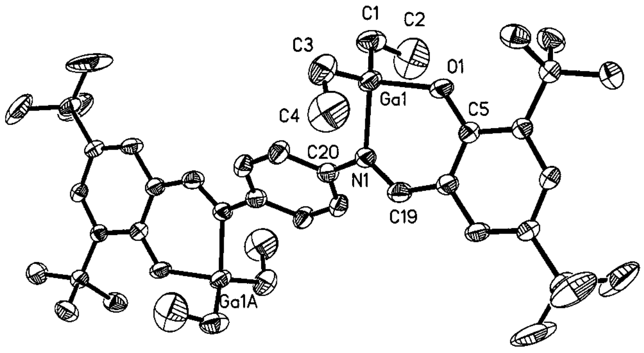


Figure 21. ORTEP view of 1,4-Salophen(^{t}Bu){GaEt$_2$}$_2$ (**146**).

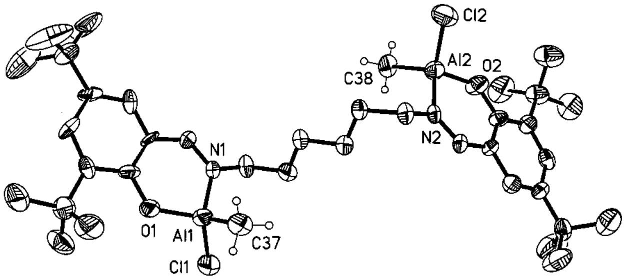
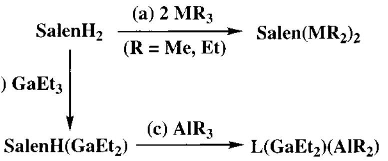


Figure 22. ORTEP view of Salhen(^{t}Bu){AlMeCl}$_2$ (**153**).

Many of the compounds have been examined with X-ray analysis (see Table 8). Representative examples of a dialkyl aluminum (Salcen(^{t}Bu){AlMe$_2$}$_2$ (**140**), a dialkyl gallium 1−4-Salophen(^{t}Bu){GaEt$_2$}$_2$ (**146**), and an alkylhalide aluminum Salhen(^{t}Bu){AlMeCl}$_2$ (**153**) are shown in Figures 20−22, respectively. In each the group 13 element adopts a four-coordinate distorted tetrahedral geometry. The Al−O and Al−N distances for **140** are marginally shorter than for **146**, in keeping with the slight increase in size on going from Al (0.53 Å) to Ga (0.61 Å) (see Table 8).[77] However, the O−Ga−N angle of **146** is more narrow (92.5(2)°) than the O−Al−N angles of **140** (~ 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 Al (118.9(2)°). These distortions are not caused by the ligand. The N and O atoms of the Salen ligands *can* occupy two T$_d$ sites around a coordinated metal as demonstrated in Salen[B(OMe)$_2$]$_2$ (**113**) with a chelate O−B−N angle of 106.7(1)° and a ligand O−B−O′ angle of 112.7(1)°. Overall, the distortions seen within the bond angles of the bimetallics can be explained by considering only electronic effects. The more electronegative atoms possess more p-orbital character in their bonds and, thus, 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$_2$GaBr(NH$_2$Ph) (C−Ga−C = 124.9(4)°; Br−Ga−N = 95.8(2)°)[78] and Me$_2$InI(NH$_2$^{t}Bu) (C−In−C = 134.8(3)°; I−In−N = 90.4(1)°),[79] which similarly demonstrate obtuse C−M−C angles and more narrowed N−M−X angles than would be expected for an ideal T$_d$ geometry.

Scheme 7



Three very unusual monometallic “open” compounds of the general form SalenH(GaR$_2$) (**164** and **165**) are prepared in high yield by the addition of GaEt$_3$ to the ligand at 25 °C (Scheme 7b). Remarkably, they can be refluxed in toluene for up to 4 h without effecting ring closure. The previous isolation of SalenH(GaMe$_2$) (**163**), which was originally reported as the monoalkyl derivative, is implied in the isolation of **164** and **165**. Under these conditions the same reaction with either aluminum or indium reagents would instantly lead to ring closure and formation of the five-coordinate monometallic derivatives (in fact, this would occur without heating). Thus, the R$_2$Ga− unit appears to be remarkably stable in relation to the aluminum and indium derivatives. This finding follows earlier work, which demonstrated that Me$_2$Ga$^+$ does not decompose in aqueous sulfuric acid.[80] The bonding of gallium in this circumstance is more like that of boron.

These monometallics can be used to form unique bimetallic derivatives containing two different metals. This is achieved by forming either **164** or **165** in situ, followed by addition of AlR_3. The mixed-metal compounds of the form Salen($GaEt_2$)(AlR_2) (**166**−**169**) can be made in this manner. The compounds are readily characterized by their distinctive ^{1}H NMR in which there are two sets of resonances that can be ascribed to each of the MR_2 groups. Moreover, at ambient temperatures there is no evidence for either metal or alkyl exchange in solution. A similar observation (that of a "rigid" solution state geometry) has been made for group 13 derivatives of the reduced Salen ligand, Salan.[81]

IV. Hydrogen Bonding

Hydrogen bonding is often an organizing force in the packing of Salen−group 13 compounds in the solid state. These bonds form through two main contacts on the Salen ligand: the imine hydrogen, which is the contact most often observed, and the hydrogens in the ligand backbone that are α to the nitrogen atoms (or, simply, the methylene hydrogens). These two sites make intermolecular and intramolecular contacts with a variety of electron-rich targets. A common one is the counteranion in cationic aluminum compounds. It is observed,with C···X distances of 3.4−3.7 Å (H···X distances ∼ 2.5 Å), in compounds of the form $[SalenAl(base)_2]^+X^-$ (compounds **95**−**98**). Hydrogen bonding to protic Lewis-basic groups, as in ion pairs of the form $[SalenAl(base)_2]^+ X^-$ (where base = H_2O, MeOH; compounds **86**−**94**)), take precedence, however, over contacts to the ligand.

A unique situation is found in the structure of Salen(^{t}Bu)InMe (**27**), where a methylene hydrogen makes an unusual and short contact (C···O = 3.4 Å) with the oxygen of an adjacent Salen ligand to form a dimer. A related contact is between a Salen oxygen and an aryl proton (C···O ∼ 3.4 Å) in Salhen{$B(OMe)_2$}$_2$ (**129**). These are the only two examples where the oxygen of a Salen ligand is employed in a hydrogen bond.

Another type of contact occurs between the imine and an oxygen of a borate (with a C···O distance close to 3.4 Å in all cases) in molecules of the form Salen{$B(OR)_2$}$_2$ (compounds **113**−**133**). In a rare case this contact was intramolecular (Salen(^{t}Bu){$B(OEt)_2$}$_2$ (**116**)), but most often the bonding is intermolecular.

As the length of the ligand backbone increases, the packing diagrams are observed to demonstrate layered structures. For the structures currently available the transition to this type of structure occurs for the pentyl backbone, Salpten{$B(OMe)_2$}$_2$ (**125**), which forms a two-dimensional layered structure. The extreme manifestation of this backbone effect occurs in Salhen{$B(OMe)_2$}$_2$ (**129**). Each molecule is oriented in an extended trans configuration (Figure 23) which maintains a staggered arrangement for the methylenes making up the backbone. The bimetallic units orient themselves such that the packing diagram consists of an infinite spiral of molecules. Hydrogen bonding in bis-formamides connected by alkyl chains has been demonstrated to be related to the number of methylenes in the alkyl.[82] Maximal hydrogen bonding was found for even-numbered alkyls. This is apparently not the case for the present compounds as both the pentyl and hexyl derivatives feature similar extended structures.

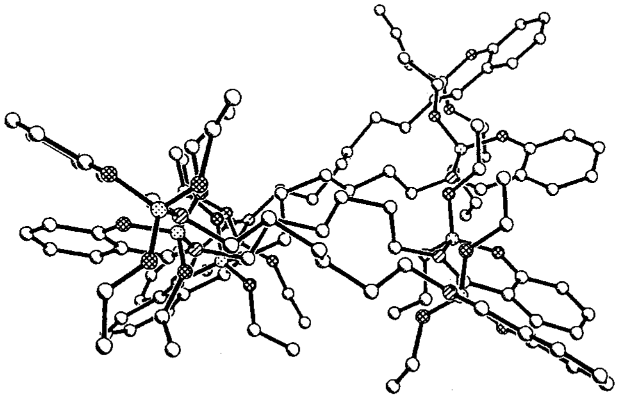


Figure 23. The helical packing of Salhen{$B(OMe)_2$}$_2$ through hydrogen bonding.

V. Applications

Early on we discovered that neutral five-coordinate Salen−aluminum compounds[83] and the related six-coordinate cationic aluminum[84] were useful as catalysts for the polymerization of oxiranes.[55] These applications had precedence in the efforts of Spassky[85] and in the substantial work of Inoue.[86] Although Spassky's work indicated an activity of the SalenAlCl in the oligomerization, based upon our subsequent work on cation formation, it is likely that the active species was cationic. Indeed, in a recent synthetic and theoretical examination of propylene oxide polymerization it was demonstrated the cation induces ring opening and that the anion was not involved.[58] A standard cationic mechanism was in operation. This contrasts with the work of Inoue on related bimetallic systems where living polymerizations of oxiranes was achieved.[87]

It is likely that a broader range of applications will be found for the aluminum cations. The fact that they are robust, highly soluble, highly acidic Lewis acids should make them ideal for use under a wide range of conditions. One recent development along these lines is the use of the chiral cation, $[Salcen(^tBu)Al(MeOH)_2]^+Cl^-$ (**106**) as a phospho-transfer catalyst.[60]

Some additional catalytic reactions that these cations might be useful for include Meerwein−Ponndorf−Verley reductions (MPV),[88] Friedel−Crafts reactions,[89] Oppenaur oxidation, Tishchenko reactions,[90] the ene reaction,[91] mixed-aldol condensation,[92] Diels−Alder reactions,[93] dipolar cycloadditions, Claisen rearrangements,[94] and the cyclotrimerization of isocyanates to isocyanurates.[95] In each case the cation would act as a soluble Lewis acid that binds through either one or two of the coordination sites.

More recently, applications involving five-coordinate siloxides, $SalenAlOSiPh_3$ (compounds **81**−**84**), and alkoxides have have been developed much more extensively. In addition to our own work on propylene oxide,[96] there are two reports of catalytic stereospecific lactide polymerization.[97] In these systems the siloxide or alkoxide acts as a ring-opening anion and subsequent monomers insert into the Al−O bond. This process may then become living under the appropriate conditions. Of related interest, Salen(^{t}Bu)AlMe has been used as an initiator (after conversion to an enolate through insertion of methyl methacrylate into the Al−C bond) for methyl methacrylate polymerization.[98]

In a study of metal-catalyzed Strecker reactions it was found that the aluminum analogue, Salcen(^{t}Bu)AlCl (**40**), performed better than transition-metal compounds.[21] In general, the use of group 13 compounds in applied chemistry has been slight in comparison to Salen-supported transition-metal compounds for which an extensive applied chemistry has been developed. The majority of these applications are made possible by the presence of d orbitals on the transition metal and therefore are probably not possibilities for the group 13 elements.

VI. Comparison to Transition-Metal Compounds

The majority of the known trivalent transition-metal compounds are similar to either the five-coordinate neutral compounds (compounds **1**−**50**) or the octahedral cationic compounds (**86**−**103**) in structure. In contrast to group 13 compounds, the five-coordinate transition-metal derivatives are square pyramidal.[99] The lack of evidence for a trigonal bypyramidal geometry may be attributed to the predominant use of Salen ligands with short backbone connections. In octahedral transition-metal complexes the ligand can coordinate through equatorial[100] or three equatorial and one axial site (called the β-cis configuration).[101] For the group 13 elements the ligand is only equatorial.

The bonding in higher-coordinate group 13 compounds appears to be electrostatic in nature. Transition metals, in contrast, bond more selectively due to the presence of d orbitals. For example, the metal−chloride bond in SalenFeCl cannot be cleaved by the addition of water or other bases,[102] as found for SalenAlCl in the formation of $[\text{SalenAl(base)}_2]^+\text{Cl}^-$. This may be attributed to a relatively weak bond between the group 13 element and the group occupying the fifth apical coordination site. The bonding is more appropriately described as electrostatic, and the reactivity of these groups in polar solvents supports this notion. In some cases, however, the transition-metal bond is susceptible to cleavage, as in $[\text{SalenCr(H}_2\text{O)}_2]^+\text{Cl}^-$.[103] Thus, electronic effects and electron count must be taken into consideration for predicting or explaining the reactivity of transition-metal compounds supported by the Salen ligands.

VII. Related Derivatives

It is interesting to compare the types of complexes that can be formed by the closely related SalanH$_4$ ligands (Figure 24a) in combination with group 13 reagents.[104] The SalanH$_4$ ligands are derived from the SalenH$_2$ ligands by reduction of the imine bond. The naming of the Salan ligands is, by design, associated with that of the Salen ligands. For example, the salen ligand having three methylenes in its backbone is called “SalpenH$_2$”. The analogous Salan derivative is called “SalpanH$_4$. The only difference between these two ligands is the hybridization of the N−C bond; sp^2 in Salen and sp^3, and thus more flexible, in the SalanH$_4$ ligands. The contrasts in these two ligands is striking. While it appears that there is an unlimited number of neutral and cationic monometallics available for the Salen ligands, only one related neutral Salan compound is known. The potentially five-coordinate SalpanH$_2$AlMe (Figure 24b) may have the same structure as the neutral salen complexes, although this has yet to be determined crystallographically.[23] Bimetallic derivatives of the Salen ligands have the expected structures where each side of the ligand acts as a bidentate chelate onto a tetrahedral metal. The Salan complexes are more complicated with two types of group 13 metals in a dimeric arrangement, two that are terminal and two that are chelated and five-coordinate (the molecular structure of [SalomphanAl{Al(^{i}Bu)$_2$}]$_2$ is shown in Figure 25). These bimetallics have one more chelating site (and a disposable proton for alkane eliminations) for an additional MR$_2$ unit and the formation of unique metal-rich trimetallics.[75] A comprehensive series of trimetallics are known for both aluminum[105] and gallium (one example, SalomphanAl(AlEt$_2$)$_2$, is shown in Figure 26).[106] Upon the basis of the disposition of the ligand backbone, these compounds can be in either a cis (as shown in Figure 26) or a trans geometry. If trimetallics are ever to be known for the Salen ligands they will have to be formed by C−H

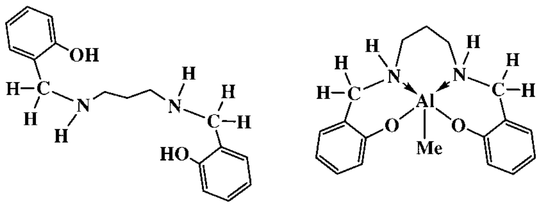


Figure 24. Representation of the SalpanH$_4$ ligand (a) and SalpanH$_2$AlMe (b).

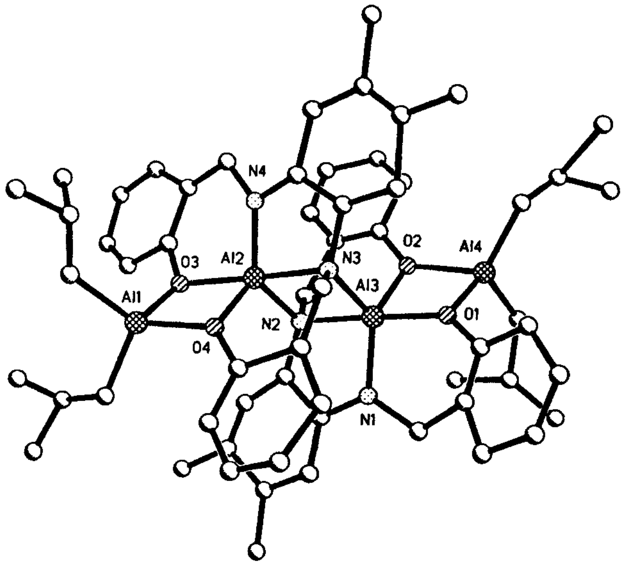


Figure 25. Molecular structure of [SalomphanAl{Al(^{i}Bu)$_2$}]$_2$.

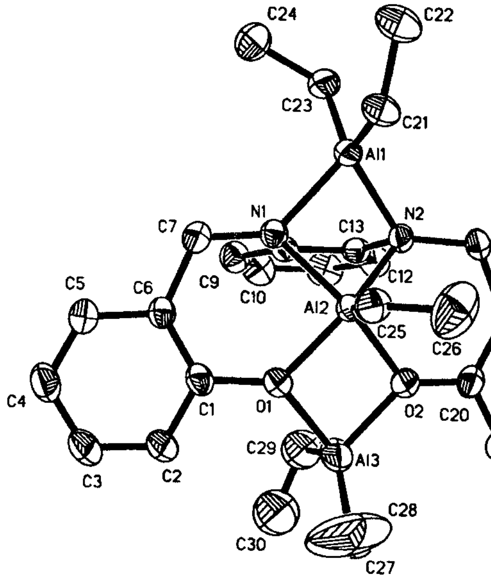


Figure 26. Molecular structure of SalophanAl(AlEt$_2$)$_2$.

activation[107] or will require several Lewis acid–base contacts.

VIII. Summary

In a previous review it was predicted that "the reactivity of five-coordinate complexes would certainly be different than that of the four-coordinate derivatives".[108] Structurally and spectroscopically, there is very little difference in the higher-coordinate compounds when compared to the four-coordinate derivatives. However, the prediction was remarkably accurate, if not a bit understated, for the reactivity of these compounds. There appears to be a tremendous potential in catalysis and synthesis for the five-coordinate derivatives, far more possibilities than exist for the lower-coordinate derivatives. Furthermore, the higher-coordinate derivatives are rarely air or moisture sensitive and, thus, may be handled under a wider range of conditions. Although reactions such as oxirane and lactide polymerizations are fairly well-known now with five- and six-coordinate aluminum compounds, the potential of these compounds has only begun to be developed. It is easy to imagine that these types of compounds will see wider use than the related transition-metal compounds.

IX. Acknowledgments

Financial support for the portions of this review completed in my laboratory was provided by the National Science Foundation (9625376). None of this work would have appeared were it not for the enthusiastic and original contributions of Drew Rutherford as a graduate student (currently teaching at Moorehead College, Moorhead, MN) and the postdoctoral research of Dr. Pingrong Wei (postdoctoral fellow at the University of Calgary) and Dr. Miguel-Munoz-Hernandez (now Assistant Professor in the Chemistry Department at Quernavaca University, Mexico).

X. References

(1) Schiff, H. *Ann. Suppl.* **1864**, *3*, 343.
(2) Dubsky, J. V.; Sokol, A. *Collect. Czech. Chem. Commun.* **1931**, *3*, 548.
(3) Calligaris, M.; Randaccio, L. *Comprehensive Coordination Chemistry*; Pergamon Press: London, 1987; Vol. 2, Chapter 20.
(4) Holm, R. H.; Everett, G. W.; Chakrovoty, A. *Prog. Inorg. Chem.* **1966**, *7*, 83. Yamada, S. *Coord. Chem. Rev.* **1966**, *1*, 415.
(5) Jacobsen, E. N. In *Catalytic Asymmetric Synthesis*; Ojima, I., Ed.; VCH: New York, 1993; Chapter 4. Jacbonsen, E. N. In *Comprehensive Organometallic Chemistry II*, Abel. E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: New York, 1995; Vol. 12, Chapter 11.
(6) Serrano, J.-L.; Oriol, L. *Adv. Mater.* **1995**, *7*, 365.
(7) van Bommel, K. J. C.; Verboom, W.; Kooijman, H.; Spek, A. L.; Reinhoudt, D. N. *Inorg. Chem.* **1998**, *37*, 4197.
(8) Louie, A. Y.; Meade, T. J. *Proc. Natl. Acad. Sci.* **1998**, *95*, 6663. Takeuchi, T.; Bottcher, A.; Quezada, C. M.; Meade, T. J. Gray, H. B. *Bioorg. Med. Chem.* **1999**, *7*, 815.
(9) Canali, L.; Sherrington, D. C. *Chem. Soc. Rev.* **1999**, *28*, 85. Jacobsen, E. N. *Acc. Chem. Res.* **2000**, *33*, 421.
(10) Hall, D.; Moore, F. H. *Proc. Chem. Soc.* **1960**, 256. O'Conner, M. J.; West, B. O. *Aust. J. Chem.* **1967**, *20*, 2077. Singer, A. L.; Atwood, D. A. *Inorg. Chim. Acta.* **1998**, *277*, 157. Sano, T.; Nishio, Y.; Hamada, Y.; Takahashi, H.; Usuki, T.; Shibata, K. *J. Mater. Chem.* **1999**, *10*, 157.
(11) Ball, S. C.; Cragg-Hine, I.; Davididson, M. G.; Davies, R. P.; Lopez-Solera, M. I.; Raithby, P. R.; Reed, D.; Snaith, R.; Vogl, E. M. *J. Chem. Soc., Chem. Commun.* **1995**, 2147.
(12) Dzugan, S. J.; Goedken, V. L. *Inorg. Chem.* **1986**, *25*, 2858.
(13) Atwood, D. A.; Hill, M. S.; Jegier, J. A.; Rutherford, D. *Organometallics* **1997**, *16*, 2659.
(14) Leung, W.-H.; Chan, E. Y. Y.; Chow, E. K. F.; Williams, I. D.; Peng, S.-M. *J. Chem. Soc., Dalton Trans.* **1996**, 1229.
(15) Atwood, D. A.; Jegier, J. A.; Rutherford, D. *Inorg. Chem.* **1996**, *35*, 63.
(16) Hill, M. S.; Atwood, D. A. *Eur. J. Inorg. Chem.* **1998**, 67.
(17) Atwood, D. A.; Jegier, J. A.; Rutherford, D. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 2093.
(18) Hill, M. S.; Atwood, D. A. *Main Group Chem.* **1998**, *2*, 191.
(19) Shen, Y.-Z.; Pan, Y.; Wang, L.-Y.; Dong, G.; Jin, X.-P.; Huang, X.-Y.; Hu, Hongwen, *J. Organomet. Chem.* **1999**, *590*, 242.
(20) Rutherford, D.; Atwood, D. A. *Organometallics* **1996**, *15*, 4417.
(21) Sigman, M. S.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1998**, *120*, 5315.
(22) Under photolytic conditions (TPP)InEt (TPP = tetraphenylporphyrin) becomes zwitterionic, (TPP)$^-$ In$^+$: Hoshino, M.; Yamaji, M.; Hama, Y. *Chem. Phys. Lett.* **1986**, *125*, 369.
(23) Atwood, D. A.; Jegier, J. A.; Martin, K. J.; Rutherford, D. *Organometallics* **1995**, *14*, 1453
(24) Jones, A. C.; Cole-Hamilton, D. J.; Holliday, A. K.; Ahmad, M. M. *J. Chem. Soc., Dalton Trans.* **1983**, 1047.
(25) Niewmeyer, M.; Goodwin, T. J.; Risbud, S. H.; Power, P. P. *Chem. Mater.* **1996**, *8*, 2745.
(26) Bradley, D. C.; Chudzynska, H.; Faktor, M. C.; Frigo, D. M.; Hursthouse, M. B.; Hussain, B.; Smith, L. M. *Polyhedron* **1988**, 1289.
(27) Arif, A. M.; Benac, B. L.; Cowley, A. H.; Jones, R. A.; Kidd, K. B.; Nunn, C. M. *New J. Chem.* **1988**, *12*, 553.
(28) Atwood, D. A.; Cowley, A. H.; Jones, R. A.; Atwood, J. L.; Bott, S. G. *J. Coord. Chem.* **1992**, *26*, 293.
(29) Hillwig, R.; Harms, K.; Dehnicke, K. *J. Organomet. Chem.* **1995**, *501*, 327.
(30) Benn, R.; Rufinska, A.; Lemkuhl, H.; Janssen, E.; Kruger, C. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 779. Benn, R.; Rufinska, A. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 861.
(31) Munoz-Hernandez, M.-A.; Keizer, T. S.; Wei, P.; Atwood, D. A. *Organometallics*, submitted for publication.
(32) Addison, A. W.; Rao, T. N.; Reedjik, J.; van Rijn, J.; Verschoor, G. C. *J. Chem. Soc., Dalton Trans.* **1984**, 1349.
(33) Guilard, R.; Lecomte, C.; Kadish, K. M. *Struct. Bonding* **1987**, *64*, 205.
(34) Bradley, D. C.; Chudzynska, H.; Faktor, M. M.; Frigo, D. M.; Hursthouse, M. B.; Hussain, B.; Smith, L. M. *Polyhedron* **1988**, *7*, 1289.
(35) Shearer, H. M. M.; Twiss, J.; Wade, K. *J. Organomet. Chem.* **1980**, *184*, 309.
(36) Keizer, T.; Munoz-Hernandez, M. A.; Atwood, D. A. To be submitted.
(37) This compound has the shortest Al–N distance out of a remarkable 17 structurally characterized compounds: Bradley, D. C.; Harding, I. S.; Maia, I. A.; Motevalli, M. *J. Chem. Soc., Dalton Trans.* **1997**, 2969.
(38) Kim, Y.; Kim, J. H.; Park, J. E.; Song, H., Park, J. T. *J. Organomet. Chem.* **1997**, *545–546*, 99.
(39) Schnitter, C.; Waezsada, S. D.; Roesky, H. W.; Teichert, M.; Uson, I.; Perisini, E. *Organometallics* **1997**, *16*, 1197.
(40) Shulz, S.; Voigt, A.; Roesky, H. W.; Haming, L.; Herbst-Irmer, R. *Organometallics* **1996**, *15*, 5252.

(41) Another example is $(^t\text{Bu})_2$GaOH(thf): Power, M. B.; Cleaver, W. M.; Apblett, A. W.; Barron, A. R.; Ziller, J. W. *Polyhedron* **1992**, *11*, 477.

(42) Gurian, P. L.; Cheatham, L. K.; Ziller, J. W.; Barron, A. R. *J. Chem. Soc., Dalton Trans.* **1991**, 1449.

(43) Elmali, A.; Elerman, Y.; Svoboda, I.; Fuess, H.; Griesar, K.; Haase, W. *Z. Naturforsch.* **1993**, *48b*, 313. Ashmawy, F. M.; Ujaimi, A. R.; McAuliffe, C. A.; Parish, R. V.; Pritchard, R. G. *Inorg. Chim. Acta* **1991**, *187*, 155. Lewis, J.; Mabbs, F. E.; Richards, A. *J. Chem. Soc. A* **1967**, 1014.

(44) Le Borgne, A.; Vincens, V.; Jouglard, M.; Spassky, N. *Makromol. Chem. Macromol. Symp.* **1993**, *73*, 37.

(45) Munoz-Hernandez, M. A.; Keizer, T. S.; Parkin, S.; Zhang, Y.; Atwood, D. A. *J. Chem. Cryst.* **2000**, in press.

(46) Ovitt, T. M.; Coates, G. W. *J. Am. Chem. Soc.* **1999**, *121*, 4072.

(47) Radano, C. P.; Baker, G. L.; Smith, M. R., III *J. Am. Chem. Soc.* **2000**, *122*, 1552.

(48) Apblett, A. W.; Warren, A. C.; Barron, A. R. *Can. J. Chem.* **1992**, *70*, 771.

(49) Chandrasekhar, V.; Murugavel, R.; Voigt, A.; Teichert, M.; Uson, I.; Roesky, H. Schmidt, H.-G.; Noltemeyer, M. *Organometallics* **1996**, *15*, 918.

(50) For an overview of metallasiloxanes see: Murugavel, R.; Chandrasekhar, V.; Roesky, H. W. *Acc. Chem. Res.* **1996**, *29*, 183.

(51) Apblett, A. W.; Warren, A. C.; Barron, A. R. *Can. J. Chem.* **1992**, *70*, 771.

(52) Apblett, A. W.; Barron, A. R. *J. Crystallogr. Spectrosc. Res.* **1993**, *23*, 529.

(53) Veith, M.; Jarczyk, M.; Huch, V. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 117.

(54) Bissinger, P.; Paul, M.; Riede, J.; Schmidbaur, H. *Chem. Ber.* **1993**, *126*, 2579.

(55) First described in: Atwood, D. A.; Jegier, J. A.; Rutherford, D. *J. Am. Chem. Soc.* **1995**, *117*, 6779.

(56) For a short overview of aluminum cation chemistry, see: Atwood, D. A. *Main Group Chem. News* **1998**, *5*, 30.

(57) For a complete review of cationic group 13, see: Atwood, D. A. *Coord. Chem. Rev.* **1998**, *176*, 407.

(58) Munoz-Hernandez, M.-A.; Wei, P.; Atwood, D. A. *J. Am. Chem. Soc.* submitted.

(59) Davidson, M. G.; Lambert, C.; Lopez-Solera, I.; Raithby, P. R.; Snaith, R. *Inorg. Chem.* **1995**, *34*, 3765.

(60) Duxbury, J. P.; Cawley, A.; Thornton-Pett, M.; Wantz, Laurent; Warne, J. N. D.; Greatrex, R.; Brown, D.; Kee, T. P. *Tetrahedron Lett.* **1999**, *40*, 4403.

(61) Munoz-Hernandez, M.-A.; Yearwood, B.; Wei, P.; Atwood, D. A. *J. Chem. Crystallogr.* **2000**, in press.

(62) Jegier, J. A.; Munoz-Hernandez, M.-A.; Atwood, D. A. *J. Chem. Soc., Dalton Trans.* **1999**, 2583.

(63) Munoz-Hernandez, M.-A.; Sannigrahi, B.; Atwood, D. A. *J. Am. Chem. Soc.* **1999**, *121*, 6747.

(64) Thomas, C. L. *Anhydrous Aluminum Chloride in Organic Chemistry*; Reinhold: New York, 1945; p 725.

(65) Liu, S.; Munoz-Hernandez, M.-A.; Atwood, D. A. *J. Organomet. Chem.* **2000**, *596*, 109.

(66) Wei, P.; Atwood, D. A. *Inorg. Chem.* **1997**, *36*, 4060.

(67) Wei, P.; Keizer, T.; Atwood, D. A. *Inorg. Chem.* **1999**, *38*, 3914.

(68) Wei, P.; Atwood, D. A. *Inorg. Chem.* **1998**, *37*, 4934.

(69) Atwood, D. A.; Jegier, J. A.; Remington, M. P.; Rutherford, D. *Aust. J. Chem.* **1996**, *49*, 1333.

(70) Wei, P.; Atwood, D. A. *J. Organomet. Chem.* **1998**, *563*, 87.

(71) Montero, M. L.; Uson, I.; Roesky, H. W. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2103. Montero, M. L.; Voigt, A.; Teichert, M.; Uson, I.; Roesky, H. W. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2504.

(72) Unless condensation unites two of the siloxy units: Veith, M.; Jarczyk, M.; Huch, V. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 117. Veith, M.; Jarczyk, M.; Huch, V. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 105.

(73) Mason, M. R.; Mashuta, M. S.; Richardson, J. F. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 239. Yang, Y.; Walawalkar, M. G.; Pinkas, J.; Roesky, H. W.; Schmidt, H.-G. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 96. Walawalkar, M. G.; Murugavel, R.; Roesky, H. W.; Uson, I.; Kraetzner, R. *Inorg. Chem.* **1998**, *37*, 473.

(74) Chong, K. S.; Rettig, S. J.; Storr, A.; Trotter, J. *Can. J. Chem.* **1977**, *55*, 2540.

(75) Hill, M. S.; Wei, P.; Atwood, D. A. *Polyhedron* **1998**, *17*, 811.

(76) Van Aelstyn, M.; Keizer, T. S.; Klopotek, D. L.; Liu, S.; Munoz-Hernandez, M.-A.; Wei, P. Atwood, D. A. *Organometallics*, **2000**, *19*, 1796.

(77) *Inorganic Chemistry, Principles of Structure and Reactivity*, 4th ed.; Huheey, J. E., Keiter, E. A., Keiter, R. L., Eds.; HarperCollins, New York, 1993; p 114.

(78) Atwood, D. A.; Cowley, A. H.; Jones, R. A. *J. Organomet. Chem.* **1992**, *430*, C29.

(79) Atwood, D. A.; Cowley, A. H.; Jones, R. A.; Atwood, J. L.; Bott, S. G. *J. Coord. Chem.* **1992**, *26*, 293.

(80) Beachley, O. T., Jr.; Kirss, R. U.; Bianchini, R. J.; Royster, T. L. *Organometallics* **1987**, *6*, 724.

(81) Atwood, D. A.; Rutherford, D. *Comm. Inorg. Chem.* **1996**, *19*, 25.

(82) Chaney, J. D.; Goss, C. R.; Folting, K.; Santarsiero, B. D.; Hollingsworth, M. D. *J. Am. Chem. Soc.* **1996**, *118*, 9432.

(83) Jegier, J. A.; Atwood, D. A. *Abstr. Pap. Am. Chem. Soc.* **1996**, *212*, 403-INOR (Part 1 Aug 25, 1996).

(84) Jegier, J. A.; Rutherford, D.; Atwood, D. A. *Abstr. Pap. Am. Chem. Soc.* **1996**, *211*, 311-INOR (Part 1 Mar 24, 1996).

(85) Vincens, V.; Le Borgne, A.; Spassky, N. *Makromol. Chem. Rapid Commun.* **1989**, *10*, 623. Le Borgne, A.; Vincens, V.; Jouglard, M.; Spassky, N. *Makromol. Chem. Macromol. Symp.* **1993**, *73*, 37.

(86) Aida, T.; Inoue, S. *Acc. Chem. Res.* **1996**, *29*, 39.

(87) Aida, T.; Inoue, S. *Acc. Chem. Res.* **1996**, *29*, 39.

(88) Ooi, T.; Miura, T.; Maruoka, K. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 2347; Ooi, T.; Itagaki, Y.; Miura, T.; Maruoka, K. *Tetrahedron Lett.* **1999**, *40*, 2137.

(89) Osamura, Y.; Terada, K.; Kobayashi, Y.; Okazaki, R.; Ishiyama, Y. *J. Mol. Struct.* **1999**, *461*−*462*, 399.

(90) Berberich, H.; Roesky, P. W. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 1569; Ooi, T.; Miura, T.; Takaya, K.; Maruoka, K. *Tetrahedron Lett.* **1999**, *40*, 7695.

(91) Santelli, M.; Pons, J.-M. *Lewis Acids and Selectivity in Organic Synthesis*; CRC Press: New York, 1996; Chapter 1.

(92) Saito, S.; Shiozawa, M.; Ito, M.; Yamamoto, H. *J. Am. Chem. Soc.* **1998**, *120*, 813. Nelson, S. G.; Peelen, T. J.; Wan, Z. *Tetrahedron Lett.* **1999**, *40*, 6541.

(93) Santelli, M.; Pons, J.-M. *Lewis Acids and Selectivity in Organic Synthesis*, CRC Press: New York, 1996; Chapter 6.

(94) Yoon, T. P.; Dong, V. M.; MacMillan, D. W. C. *J. Am. Chem. Soc.* **1999**, *121*, 9726.

(95) Foley, S. R.; Yap, G. P. A.; Richeson, D. S. *Organometallics* **1999**, *18*, 4700.

(96) Atwood, D. A. Patent pending.

(97) Ovitt, T. M.; Coates, G. W. *J. Am. Chem. Soc.* **1999**, *121*, 4072. Radano, C. P.; Baker, G. L.; Smith, M. R., III *J. Am. Chem. Soc.* **2000**, *122*, 1552.

(98) Cameron, P. A.; Gibson, V. C.; Irvine, D. J. *Angew. Chem., Int. Ed.* **2000**, *39*, 2141.

(99) For a recent example see: Das, D.; Cheng, C. P. *J. Chem. Soc., Dalton Trans.* **2000**, 1081.

(100) Wang, X.; Pennington, W. T.; Ankers, D. L.; Fanning, J. C. *Polyhedron* **1992**, *17*, 2253.

(101) Gatehouse, B. M.; Reichert, B. E.; West, B. O. *Acta Crystallogr.* **1976**, *B32*, 30.

(102) Pecorano, V. L.; Butler, W. M. *Acta Crystallogr.* **1986**, *C42*, 1151.

(103) Coggon, P.; McPhail, A. T.; Mabbs, F. E.; Richards, A.; Thornley, A. S. *J. Chem. Soc.* **1970**, 3296.

(104) Main group salan chemistry is described in Atwood, D. A. *Coord. Chem. Rev.* **1997**, *165*, 267.

(105) Atwood, D. A.; Rutherford, D. *Organometallics* **1995**, *14*, 3988.

(106) Atwood, D. A.; Rutherford, D. *Organometallics* **1995**, *14*, 2880.

(107) Wei, P.; Atwood, D. A. *J. Chem. Soc., Chem. Commun.* **1997**, 1427.

(108) Oliver, J. P.; Kumar, R. *Polyhedron* **1990**, *9*, 409.

CR990008V