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Salan complexes of the group 12, 13 and 14 elements

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Contents

Abstract

Although derived from the well-known and heavily utilized SalenH_2 ligands, the SalanH_4 ligands (*N*,*N*′-bis(*o*-hydroxybenzyl)-*o*-diaminoalkyl (or aryl)) have not been historically developed with regards to the main group elements. This situation has been drastically changed over the past four years, with the report of new complexes of the SalanH_4 ligands incorporating the group 12, 13 and 14 elements. This review will outline the various types of complexes

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that are currently available as well as provide guidance for future studies. Complexes having a metal-to-ligand stoichiometry of 1:1, 2:1 and 3:1 are known. The 1:1 complexes are of two types. They include the group 12 and 14 elements SalanH$_2$M (where M = Zn and Sn), and the group 13 elements, SalanH$_2$MR (where M = Al; R = Me). The structures of the zinc compounds are characterized by the incorporation of significant numbers of hydrogen bonded solvent. The second type are the unique anions of formula, [SalanAl(Li(THF)$_2$)]$_2$. The 2:1 complexes, SalanHMR(MR$_2$) (where M = Al and R = Me, NMe$_2$) can adopt one of two isomeric (*cis* or *trans*) forms. The heating of concentrated samples of some of these leads to the formation of the dimeric condensation products, [SalanMR(MR$_2$)]$_2$. The 3:1 complexes, SalanMR(MR$_2$)$_2$ (where M = Al, Ga; R = Me, Et, ^{i}Bu) can also adopt either a *cis* or a *trans* geometry. The spectroscopic characterization of the trimetallics shows them to be non-fluxional in solution. Moreover, those that incorporate either Salophan or Salomphan exhibit anisotropic ring current effects. © 1997 Elsevier Science S.A.

1. Introduction

As derivatives of the ubiquitous SalenH$_2$ ligands [1], the SalanH$_4$ ligands are relatively easy to prepare and can be isolated in high yields (Scheme 1) [2]. They possess four sites (two NH and two OH) that may be used in either covalent or coordinate covalent bonding to one or several metals. The properties of the ligand may be manipulated by changing the alkyl or aryl group, R, making up the "backbone" of the diamine, or by changing the groups, R′ and R″ (Scheme 1). A listing of the better known members of this ligand class is shown in Fig. 1.

A trivial nomenclature for these ligands is based upon the traditional naming of the SalenH$_2$ ligands. SalanH$_4$ is the root name. The most simple abbreviation for the group connecting the diamine is then inserted between the "l" and the second "a". For example, the ethyl derivative is known as SaleanH$_4$, the propyl as SalpanH$_4$, and so on for those containing alkyl groups. Note that the corresponding SalenH$_2$ deriva-

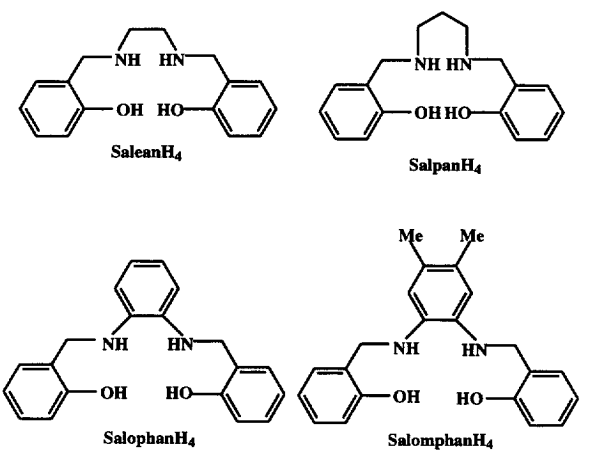
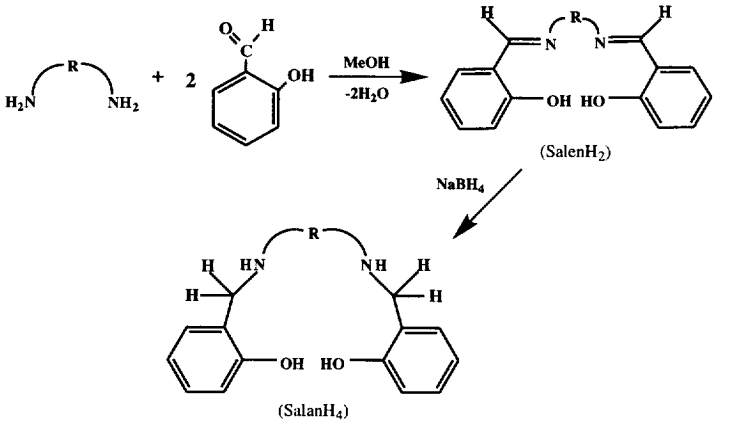


Fig. 1. Depiction of the specific SalanH$_4$ ligands described in this review.



Scheme 1. General synthesis of the $SalanH_4$ ligands.

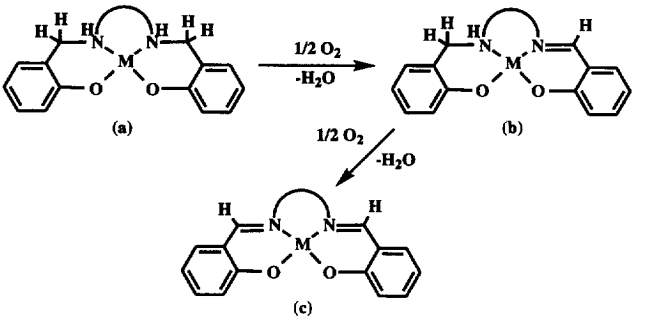
tives are known as $SalenH_2$ and $SalpenH_2$. The main point of confusion in this system of nomenclature arises from the fact that the general designation, $SalenH_2$, is also the specific name of the ethyl derivative. When an aryl backbone is utilized the name becomes $SalophanH_4$ for *o*-phenyl and $SalomphanH_4$ for *o*-(3,4-dimethyl)phenyl. The corresponding $SalenH_2$ ligands are called $SalophenH_2$ and $SalomphenH_2$. When the ligand has a substituent on the phenol ring, the abbreviation for the substituent is placed in parentheses. For example, the Salean(^{t}Bu)H_4 ligand is *N,N'*bis(2,4-di-*tert*-butyl-1-hydroxyphenylene) diaminoethane.

A growing number of transition metal complexes are known for these ligands [3]. These complexes might be expected to offer a unique insight into how the Salan ligands would coordinate to a main group element. However, most of them undergo spontaneous oxidation and form the metal–Salen complex when exposed to the air. In one exceptional instance, partially oxidized species, $[SalanHFeOMe]_2$, (Salan = Salophan and Salomphan) were isolated (Scheme 2b) [4]. Thus, the transition metals are of lessened utility in attempts to elucidate the binding of metals by the Salan ligands. The main group elements appear to offer the most promise for the isolation of stable compounds incorporating these ligands. This review will describe the various classes of main group complexes that have been reported using the Salan class of ligand.

2. Complexes having a metal–ligand stoichiometry of 1:1

2.1. Group 12 complexes, $SalanH_2M$ (M = Zn)

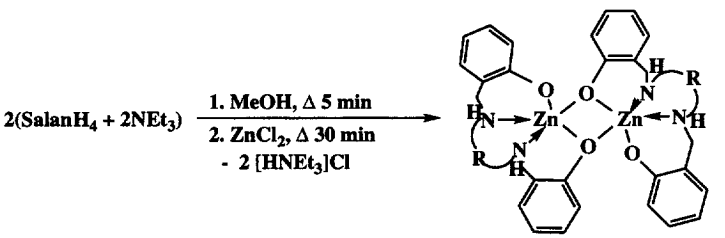
The first structurally characterized Salen complex of zinc was $SalenZn \cdot H_2O$ [5]. Following the determination of the bonding arrangement around the zinc atom in carbonic anhydrase (CA) the design of ligands able to enforce a coordination number of five became important. The $SalenZn \cdot H_2O$ complex, however, was never examined as to its relevance to CA or other zinc-containing enzymes [6]. This may be attributed



Scheme 2. Conversion of $SalanH_2$-transition metal complexes (a) to the partially (b) and fully (c) dehydrogenated complex.

to a combination of the inflexible planar coordination mode of the Salen ligands (the zinc atom in CA is in a distorted tetrahedral geometry) and the fact that Salen–main group complexes are generally insoluble in most common solvents (toluene, diethylether, hexane, for example). In efforts to provide a more flexible coordination geometry around zinc, the Salan ligands were explored in this context [2].

Deprotonation of the $SalanH_4$ ligands with excess NEt_3 in MeOH, followed by addition of anhydrous $ZnCl_2$, generally resulted in a clear solution with a small amount of white precipitate (Scheme 3). Storage at −30 °C for 6–12 h, followed by filtration, resulted in high yields of the zinc–ligand complexes, $[SaleanH_2Zn]_2$ (**1**), $[SalpanH_2Zn]_2$ (**2**), $[SalbanH_2Zn]_2$ (**3**), $[SalhanH_2Zn]_2$ (**4**), $[SalophanH_2Zn]_2$ (**5**) and $[SalomphanH_2Zn]_2$ (**6**).



Scheme 3. General synthesis of the zinc complexes (**1–6**).

Solution state studies were hindered by the relative insolubility of the zinc complexes. The solubility of complexes with alkyl backbones (compounds **1–4**) in MeOH fell in the range of 0.3–0.6 g L^{-1}. As a result, the proton NMR spectra at 25 °C generally displayed broad resonances. However, the aryl derivatives **5** and **6** were very soluble in DMF and were, thus, amenable to detailed NMR studies. In the ^1H NMR spectrum of the aryl derivatives in D_7-DMF at 25 °C, the phenyl-H resonances occur as a series of three broad resonances, and the methylene resonance as a broad singlet. Upon cooling, the broad resonances for the phenyl protons began showing more resolved coupling, reaching a maximum in resolution at −60 °C. At this temperature there were eight multiplets for the Ph–H protons, as well as two

doublets and two triplets for the methylene protons. For the Salomphan derivative there were two sharp singlets for the Ph–Me groups. This data is consistent with the maintenance of a dimeric species in solution. At ambient temperatures they are fluxional.

Crystal structures were determined for **2** and **5**. Each was crystallized from hydrous methanol. The Salophan derivative was also crystallized from DMF. Each structure contained varying amounts of solvent in the crystalline lattice. For **2** there were four MeOH and three H_2O molecules. Compound **5** contained two MeOH molecules and one H_2O in one structure and five DMF molecules in the other.

The solvent–dimer distances within these structures are somewhat short. There are two in **2**, between an H_2O and the phenyl ring (2.317 Å), and the methyl group of a MeOH and O(1) of the ligand (2.753 Å). The O(1) atoms of the Salophan derivatives are also the site of solvent contact with distances of 2.36 Å (MeOH) and 2.530 Å (DMF). These also occur through the methyl groups of the solvent. Considering that hydrogen bonding in these molecules is expected to occur through either the OH or NH atoms of the solvent molecules, the close contacts may be attributed to crystal packing forces. Additionally, the structural parameters for the zinc dimers do not deviate systematically as a result of these contacts. For instance, the shortest and longest Zn(1)–O(1) distances are found for the molecules of **2** (1.952(9) Å) and **5** (DMF) (1.977(8) Å) that do not contain the solvent contact. The structures of **2** and **5** (DMF) also contained two unique dimers in the unit cell. The solvent was shown to have no effect on the bond lengths and angles within each dimeric unit.

The individual molecules consist of centrosymmetric, oxygen-bridged zinc dimers. A representative example of the dimeric structure is shown in Fig. 2 (for $[SalophanH_2Zn]_2$). The zinc atoms are five-coordinate and adopt distorted trigonal bipyramidal geometries. In each case the equatorial positions are occupied by an oxygen and nitrogen atom from one ligand and a bridging oxygen atom from the second ligand. The N–Zn–O axial angles fall in the range of 166.1–177.2°. The range of Zn–O bond lengths with O(terminal) is 1.873–1.977 Å and with O(bridging), 1.945–2.123 Å. This compares closely to the bridging Zn–O distances found for the five-coordinate Zn in $[Zn(SALAMP)(NO_3)]_2$ (SALAMP = 2-[[2-pyridinyl-methyl-amino] methyl] phenol) (2.024 Å(ave)) [7] and SalenZn (1.94 Å) [5]. As expected, the Zn–N distances are somewhat longer than the Zn–O bond lengths, falling in the range, 2.128–2.204 Å.

Although there was no previous structural information for $SalanH_4$ complexes of zinc, their dimerization is in keeping with the results found for the related complex, bis(*N*-methylsalicylaldiminato)zinc [8]. However, the results contrast with that found for the structure of SalenZn, which is monomeric [5]. The structural difference between the Salen and Salan derivatives may be attributed to the increased flexibility of the $SalanH_4$ class of ligand.

2.2. *Group 13 complexes, $SalanH_2MR$ ($M = Al$; $R = Me$)*

The combination of a $SalenH_2$ ligand and group 13 reagent usually leads to products having a 1:1 metal ligand stoichiometry. The first of this type of complex

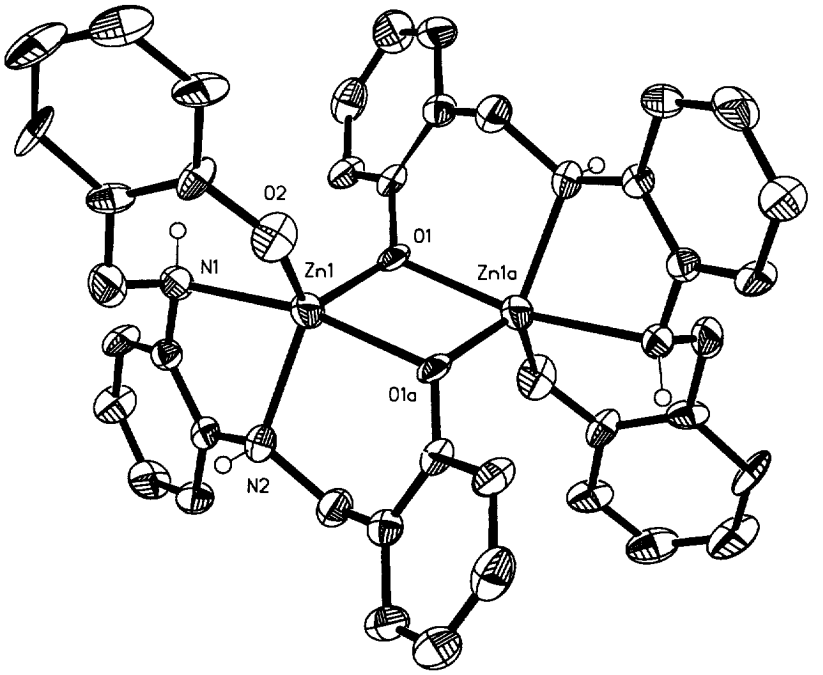
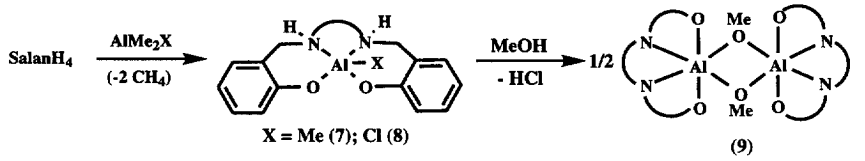


Fig. 2. Molecular structure of [SalophanH_2Zn]$_2$ (**5**).

to be reported and structurally characterized was SalpenAlEt [9]a. In this structure, the aluminum atom is in a square pyramidal geometry in which the N and O atoms form the basal plane. Other known compounds include aluminum alkyls [9], alkoxides [10] and cations [11].

Analogous Salan complexes have proven far more difficult to isolate. Indeed, there are only three reported example of such complexes, SalpanH_2AlMe (**7**) [12], SaleanH_2AlCl (**8**) and [SaleanH_2AlOMe]$_2$ (**9**) [4] despite attempts to prepare the complete series of Salan complexes. Compounds **7** and **8** were prepared by the exothermic reaction of $AlMe_2X$ (where X = Me, Cl) with the appropriate SalanH_4 ligand in a 1:1 stoichiometry (Scheme 4). In the synthesis of **8** the added precaution of pre-cooling the Me_2AlCl to -30 °C was taken to limit HCl elimination during the targeted alkane elimination. The crystal structure data for SalenAlEt demonstrated a square pyramidal geometry for the central aluminum atom. A similar monomeric structure was also proposed for **7** and **8**. Additionally, **7** displayed a broad ($W_{1/2}$ = 6249 Hz) ^{27}Al resonance at δ 15 ppm which corroborates the assignment of a monomeric five coordinate geometry for the aluminum atoms in **7** and **8**. Under refluxing conditions, these complexes apparently undergo partial alkane or HCl elimination to form a complex having the putative formula, [SalanHAl]$_2$.

The dissolution of **8** in MeOH resulted in the formation of a methoxide bridged dimeric compound (**9**). This was confirmed by an X-ray crystallographic study



Scheme 4. Synthesis of SalanH$_2$AlX derivatives (with X = Me, Cl).

(Fig. 3). In the structure the Al_2O_2 four-membered ring is planar with somewhat widened Al–O–Al′ angles (103.3(2)°) and correspondingly narrowed O–Al–O′ angles (76.7(2)°). The oxygen atoms display a planar three-coordinate geometry with O–Al bond lengths of 1.864(5) Å. The overall morphology of the structure is very similar to [AcenAlOMe]$_2$ (Acen = *N,N′*-ethylenebis(2-hydroxyphenylene-(methyl)imine) [12]b. In this derivative the O–Al distances are 1.90 Å (ave).

2.3. *Anionic group 13 complexes, [SalanAl(Li(thf)$_4$)]$_2$*

The vast majority of research dealing with aluminum has focused on neutral systems [13]. By comparison, anionic (aluminate) complexes have received somewhat less attention. Perhaps the most widely studied of the organometallic aluminates are

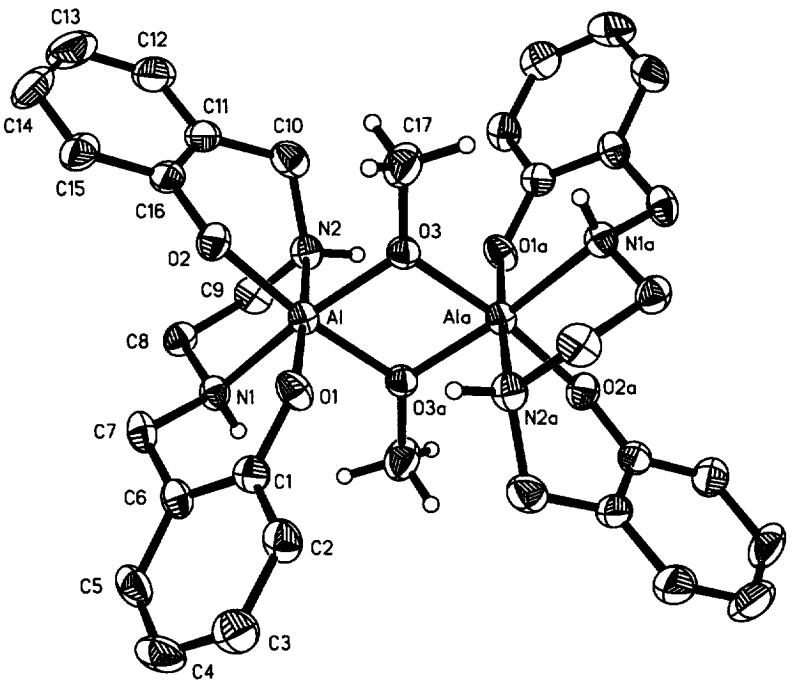
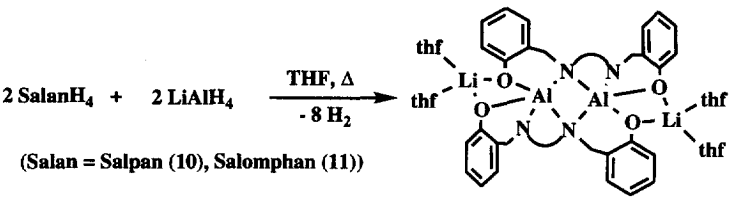


Fig. 3. Molecular structure of [SaleanAlOMe]$_2$ (**9**).

the aluminum alkoxide [14] complexes, although reports of other aluminates [15] have appeared in the literature. The anionic aluminum complexes discussed in this section were the first to be coordinated by a single ligand.

As an anion all four sigma bonding sites on the Salan ligand must by employed. This has been achieved by the reaction of $LiAlH_4$ with the appropriate $SalanH_4$ ligand in refluxing THF (Scheme 5) [16]. The spectroscopic characterization of **10** and **11** supported the maintenance of dimeric solution state species. In **10** there were four distinct $PhCH_2$ resonances while **11** exhibited two. This implied the possibility that **11** might be asymmetrical in solution. The ^{27}Al NMR chemical shifts for **10** and **11** (δ 50.10 ($W_{1/2}=2083$ MHz), 55.65 ($W_{1/2}=1562$ MHz)) were comparable to those found for the central five-coordinate aluminum atoms in the $SalanAlMe(AlMe_2)_2$ complexes (range, 55–85 ppm ($W_{1/2}=3645$–6770 MHz) see Section 4. This is in keeping with the supposition that geometrical, rather than electronic, factors determine ^{27}Al chemical shifts [17]. However, it is interesting to note that the peak widths for these anions were much narrower than for the neutral examples.



Scheme 5. The general synthesis of the dimeric Salan–aluminates.

The structural characterization of **10** and **11** confirmed that the compounds exist as dimers in the solid state. The molecular structure and atom numbering schemes for **10** and **11** are shown in Figs. 4 and 5, respectively. In each of the structures, the nitrogen atoms of the ligand act to bridge two central Al anions. The lithium cations are bridged by two oxygens from the same ligand and are coordinated to two THF molecules, forming a distorted tetrahedral geometry. The geometry of the central Al atoms in **10** is distorted trigonal bipyramidal. Using the atoms around Al(1) as an example, this is exemplified by an axial O(1)–Al(1)–N(2) angle of 166.4(5)° The equatorial positions would then be occupied by N(1), O(2) and N(4). The dimerization of **10** leads to the formation of a bent Al_2N_2 four-membered ring with the largest deviation from planarity being 0.141 Å. The two four-membered rings formed by the Al–O–Li–O atoms are planar (max. dev. 0.051 Å) and form dihedral angles of +50.0° (for Al(1)) and −53.2° (for Al(2)). It is interesting to note that the twist represented by these angles gives the structure helical chirality. This would also serve to explain the absence of a symmetry element.

Compound **11** possesses a center of inversion which makes the two $(SalomphanAl)Li(THF)_2$ units equivalent to one another. The coordination geometry of the Al atoms in this molecule is trigonal bipyramidal. Two nitrogens and an oxygen atom make up the equatorial coordination of the Al, while one oxygen and a nitrogen atom occupy the axial positions. The equatorial Al–N bonds (ave. 1.89 Å)

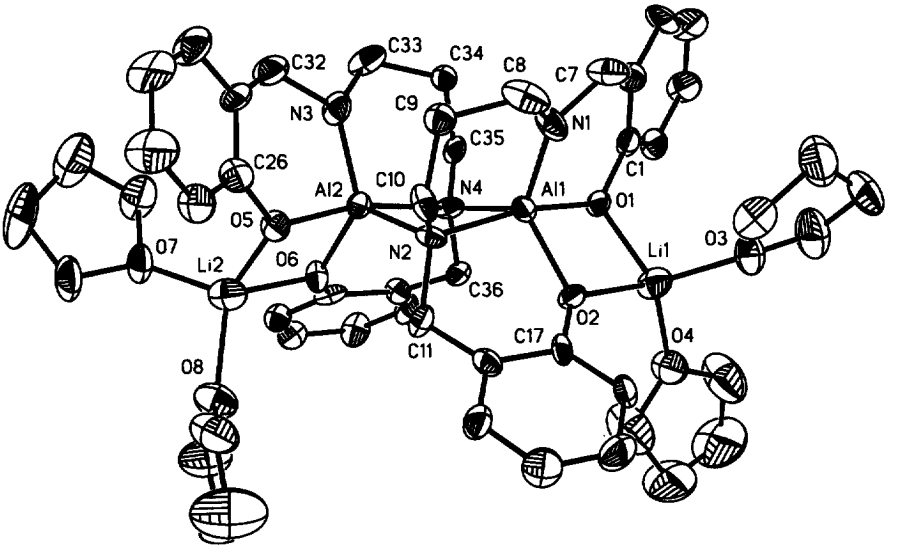


Fig. 4. Molecular structure of [SalpanAl(Li(thf)$_2$]$_2$ (**10**).

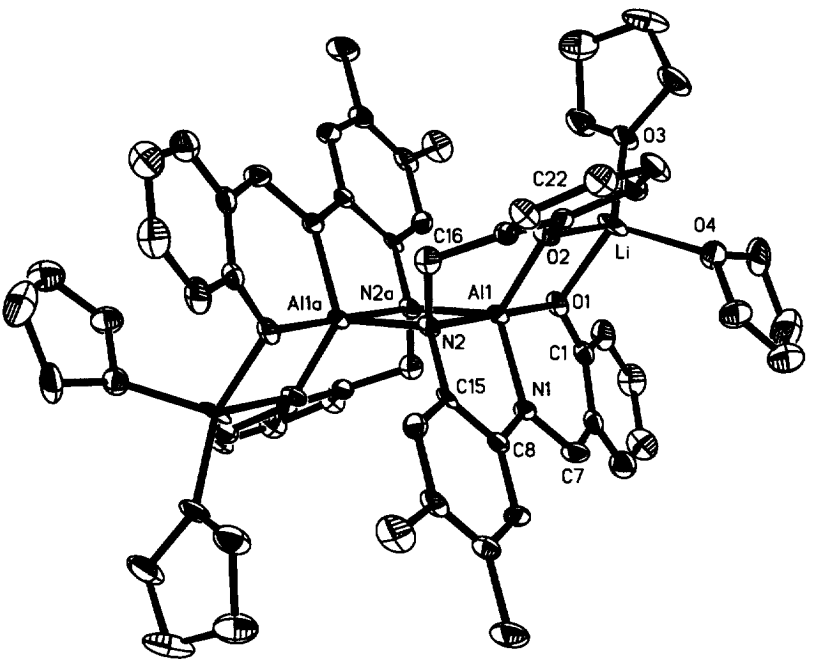


Fig. 5. Molecular structure of [SalomphanAl(Li(thf)$_2$)$_2$]$_2$ (**11**).

are somewhat shorter than the axial bonds (2.03 Å). The same trend holds for the oxygen bonds in equatorial (1.82 Å) and axial (1.85 Å) positions. Both the Al_2N_2 and AlO_2Li four-membered rings are planar (max. dev. 0.015 Å) and form a dihedral angle of 124.8°.

The primary difference between **10** and **11** lies in the type and disposition of the amine backbone. In **10** the propyl amine backbones are oriented *cis* in relation to the Al_2N_2 four-membered ring. In **11**, the phenylamine groups are oriented in a symmetrical, *trans*, configuration around the Al_2N_2 ring. This configuration also allows the center of symmetry that is found in the crystal structure of **11**.

2.4. Group 14 complexes, $SalanH_2M$ ($M = Sn$)

The Salen ligands have been used extensively in the preparation of unimolecular Sn(IV) [18,19] and to a lesser extent, Sn(II) complexes [18,20]. Based upon spectroscopic data, and in rare cases, X-ray analysis, these complexes have been demonstrated to adopt octahedral ($SalenSnR_2$) and square pyramidal (SalenSn) geometries. In each case the ligand occupies the equatorial coordination sites around the central tin atom. In attempts to explore how the binding of a Sn(II) center might change when the Salan ligands were employed, the complexes, $SaleanH_2Sn$ (**12**), $SalpanH_2Sn$ (**13**) and $SalophanH_2Sn$ (**14**) were examined [21].

They were prepared by the addition of $SnCl_2$ to a stirring solution of the $SalanH_4$ ligand and NEt_3 in MeOH. The solution was allowed to reflux for 35 min at which point it was filtered while hot to remove a small amount of insoluble material which had formed. After cooling to 25 °C the solution was stored at −30 °C for 15 h during which time the products appeared as pale yellow solids in moderate yield. Compounds **12** and **13** were soluble in a wide range of solvents including benzene, toluene, MeOH, DMSO and THF. Compound **14** proved to be completely insoluble in these and other solvents.

The ^1H NMR data for **12** and **13** exhibited broad resonances with no resolved coupling. Collection of the NMR data at −80 °C did not appreciably affect the spectra. There were two broad singlets which were attributed to the $PhCH_2$ groups and two broad singlets for the N–CH_2 groups. The ^{119}Sn NMR of **12** and **13** demonstrated broad singlets at −523.6 and −521.3 ppm. These values are similar

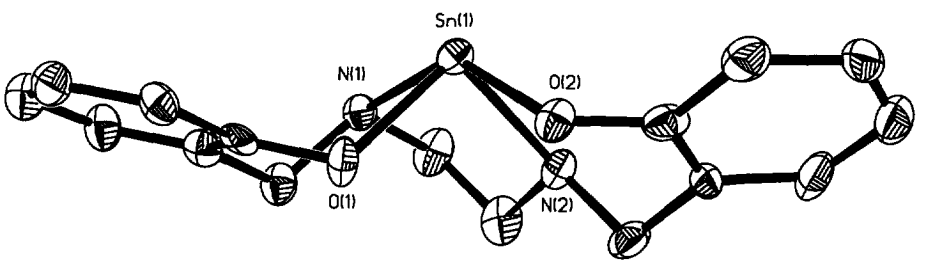
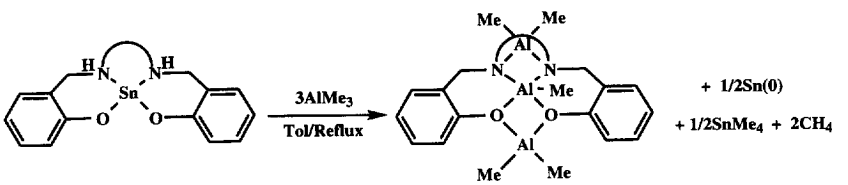


Fig. 6. A side view of the molecular structure of $SaleanH_2Sn$ (**12**).

to what has been observed for SalenSn (−564.04 ppm) and SalophenSn (−543.3 ppm) [19]. The mass spectral data for **12** and **13** corresponded to monomeric species in the gas phase. For **14**, however, the highest mass peak corresponded to a dimeric formulation. This would presumably give rise to a structure in which an oxygen of each ligand bridges the two Sn atoms. This would be the same type of structure seen for the zinc Salan complexes and for Sn(II) complexes such as $[Sn(Salop)]_2$ (Salop = *N*-(2-oxidophenyl)salicylideneiminato) [19].

The molecular structure and atom numbering scheme for **12** is shown in Fig. 6. The Sn atom adopts a square pyramidal geometry with the Salean ligand forming the basal plane and the Sn lone pair in the axial position. The Sn atom is displaced 1.08 Å from the N_2O_2 plane. There are significant variations in the Sn–O (Sn–O(1) 2.095(7) and Sn–O(2) 2.202(6) Å) and Sn–N (Sn–N(1) 2.535(9) and Sn–N(2) 2.369(8) Å) bond lengths. The longest of these distances (to O(2) and N(1)) also include the atoms forming the most obtuse bond angle (O(2)–Sn–N(1) 141.9(3)°). This is indicative of a trigonal bipyramidal distortion in the square pyramidal coordination geometry around Sn. In this configuration the O(2) and N(1) atoms occupy the axial positions and O(1), N(2) and the Sn lone pair of electrons occupy the equatorial sites. This structure may be compared to a related Sn(II) Schiff base complex, SalomphenSn(II) (Salomphen = *N*,*N*′-(4,5-dimethyl-1,2-phenylene)bis (salicylideneiminato)) [19]. In this structure the Sn atom is in a square-pyramidal geometry with equivalent Sn–O (2.137(8) Å) and Sn–N (2.376(10) Å) bonds and the Sn atom 1.126 Å above the N_2O_2 plane. The widest bond angle in this structure is 119.4(5)°.

The accessibility of Ge(II) and Sn(II) lone pairs of electrons has been well established [22]. One notable example is the reaction of tmtaaM(II) (M = Ge, Sn, tmtaa = dibenzotetramethyltetraaza [14]-annulene) with $Cr(CO)_5THF$ to yield the donor complexes tmtaaM→$Cr(CO)_5$ [23]. Reactions between **12–14** and $AlMe_3$ in a 1:1, 1:2 and 1:3 stoichiometry at 25 °C led to product mixtures that were difficult to characterize. However, when **13** and **14** (1.24 mmol) were each combined with 3 equivalents (3.72 mmol) of $AlMe_3$ in refluxing toluene, a clean transmetallation reaction occurred (Scheme 6). The main products of this reaction were the trimetallic complexes, SalpanAlMe$(AlMe_2)_2$ and SalophanAlMe$(AlMe_2)_2$. The by-products were Sn(0) and $SnMe_4$. The trimetallic derivatives can also be formed by the direct reaction of $AlMe_3$ with the Salan ligands in a 3:1 stoichiometry (see Section 4).

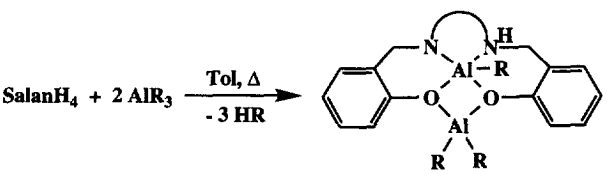


Scheme 6. Transmetallation of $SalanH_2Sn$ to yield trimetallic aluminum derivatives.

3. Complexes having a metal–ligand stoichiometry of 2:1

3.1. Group 13 complexes, SalanHMR(MR_2) (M = Al; R = Me) Et, iBu)

The first attempted synthesis of bimetallic complexes having the formula SalanHAlR(AlR_2) involved the addition of two equivalents of the aluminum reagent to the ligand followed by extended reflux in toluene (~8 h). After work-up and analysis, a mixture of products was observed. This was shown to include some of the trimetallic derivatives, SalanAlR(AlR_2)$_2$, and some other compound which appeared to be the targeted 2:1 product [24]. As was discovered later the reactions involving the Salophan and Salomphan ligands also contained a modest amount of the fully condensed compounds, [SalanAl(AlR_2)]$_2$. After systematically varying the reaction conditions, it was found that high yields of **15–23** could be obtained by refluxing the reaction mixture for not more than 10 min in toluene (Scheme 7). No bimetallic complexes of the Salpan ligand could be obtained with this procedure or any other modification.



Salan; R = Salean; Me (15), Et (16), ^{i}Bu (17)
= Salophan; Me (18), Et (19), ^{i}Bu (20)
= Salomphan; Me (21), Et (22), ^{i}Bu (23)

Scheme 7. General synthesis of the complexes of formula SalanHAlR(AlR_2).

For the aryl Salan ligands, the color change during the course of the reaction was intense. As the reaction progressed the initially colorless solution gradually became dark purple. This color change was also observed for the aromatic trimetallic complexes when they were exposed momentarily to the atmosphere. No analogous color change was observed for the Salean ligand.

Characterization by IR of the material remaining after removal of the volatiles showed the presence of a strong absorption in the NH region of the spectrum (3244–3291 cm^{-1}). A mass spectrum of the first bimetallic synthesized, SaleanHAlMe($AlMe_2$) (**15**), suggested a monomeric formulation as did its ^{27}Al-NMR spectrum, which showed an aluminum in a five-coordinate geometry and another tetravalent aluminum. The ^{1}H-NMR spectrum of the bimetallics revealed extensive coupling. As a representative example the ^{1}H-NMR spectrum of SaleanHAlMe($AlMe_2$) is given in Fig. 7. The proton assignments that are given were deduced by selective ^{1}H–^{1}H irradiation experiments with additional evidence gathered from COSY and HETCOR data.

Although no examples of SalanHAlR(AlR_2) have been structurally characterized, they might be similar in structure to a dimethylaluminum complex of

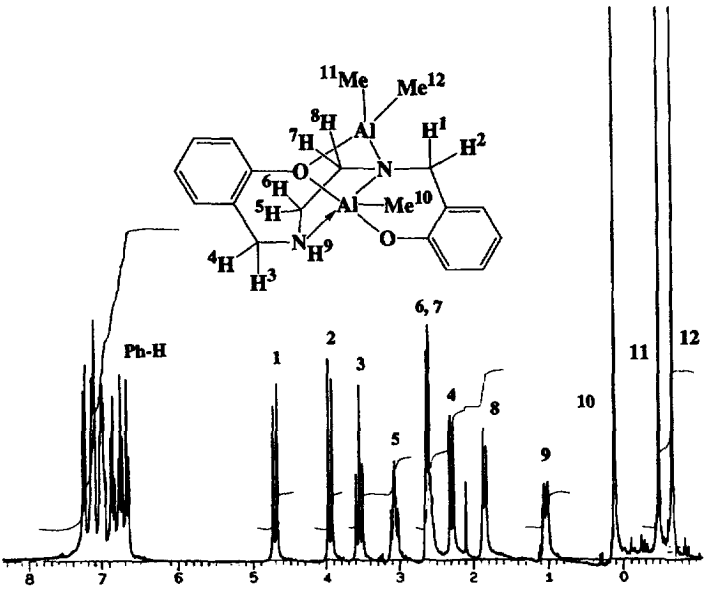


Fig. 7. ^{1}H NMR spectrum of SaleanHAlMe($AlMe_2$) (**15**).

N,N'-bis(3-aminopropyl)ethylenediamine (Fig. 8(a)) [25]. In this complex the central aluminum is in a five-coordinate trigonal-bipyramidal environment. The terminal $AlMe_2$ group is in a distorted tetrahedral geometry. It is clear, however, that the bimetallic Salan complexes differ from the type of bimetallic that has been observed for the Salen derivatives which take predominantly open structures (Fig. 8(b)) [26].

3.2. Thermal conversion of SalanHMR(MR_2) to [SalanM(MR_2)]$_2$ (M = Al; R = Me, ^{i}Bu)

Initial attempts to synthesize the bimetallic complex SalophanHAlMe($AlMe_2$) in refluxing toluene resulted in a mixture of products. One of the minor products

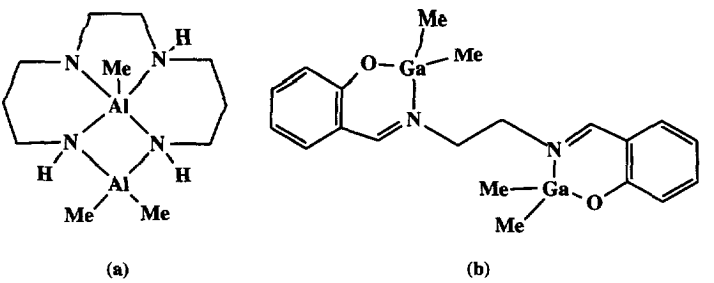
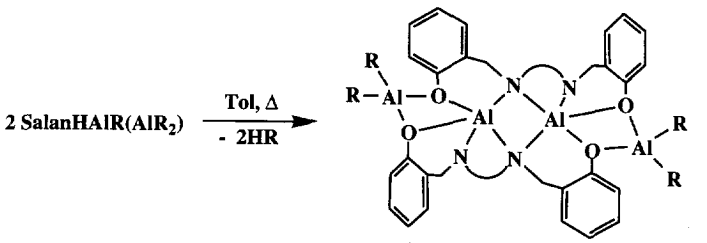


Fig. 8. Bimetallic aluminum (a) and gallium (b) complexes.

in this reaction had been identified as the fully condensed product $[SalophanAl(AlMe)_2]_2$. This product was presumed to arise from the thermolysis of an additional MeH molecule from $SalophanHAlMe(AlMe_2)$.

The first attempts to prepare these complexes involved reflux of the $SalanHAlR(AlR_2)$ complexes in a concentration of 0.04 g mL^{-1}. This led to a mixture of products which included starting material. The key to successfully converting $SalanHAlR(AlR_2)$ to $[Salan(AlR)_2]_2$ in high yields was the use of long reaction times and high concentrations. Ultimately, the reflux in toluene of the Me or ^{i}Bu derivatives of the Salophan or Salomphan ligands for a day or more, at a concentration of 0.075 to 0.25 g mL^{-1}, led to the formation of the condensation product, $[SalanAl(AlR_2)]_2$ (Scheme 8). Attempts to effect this transformation for the Salean derivatives were not successful. The NH protons on these complexes were apparently not acidic enough to undergo alkane elimination reactions. Even reflux in xylene for 48 h did not result in the desired product.



Salan; R = Salophan; Me (24), ^{i}Bu (25)
= Salomphan; Me (26), ^{i}Bu (27)

Scheme 8. General synthesis of the $[SalanAl(AlR_2)]_2$ derivatives.

The spectroscopic data for these complexes differed from that of the starting materials in two significant ways. First, there was no evidence for the NH group (by NMR and IR spectroscopic techniques) and second, the central Al no longer possessed an alkyl group. A representative ^{1}H-NMR spectrum for one of these, **27**, is shown in Fig. 9. There were resonances which were attributed to two separate benzylic methylene groups with diastereotopic protons (1–4), as was observed for the $SalanHAlR(AlR_2)$ bimetallics. This was the first evidence that the complex was dimeric and not a symmetrical monomer. Furthermore, there were two Ph–Me resonances also hinting at the asymmetric nature of the complex. The ^{i}Bu resonances were somewhat difficult to assign (5–7), but there were clearly at least two unique ^{i}Bu groups, and potentially four. For each of the $[SalanAl(AlR_2)]_2$ bimetallics, a dimeric complex was proposed due to the presence of four distinct $PhCH_2$ resonances.

The reactivity of the bimetallics was explored to elucidate the types of interconversion reactions that may be possible between the bimetallic and the trimetallic complexes. Three such reactions were explored: conversion of $SalanHAlR(AlR_2)$ to $SalanAlR(AlR_2)_2$ by the addition of one equivalent of trialkylaluminum, conversion of $[SalanAl(AlR_2)]_2$ to $SalanAlR(AlR_2)_2$ by the addition of two equivalents of

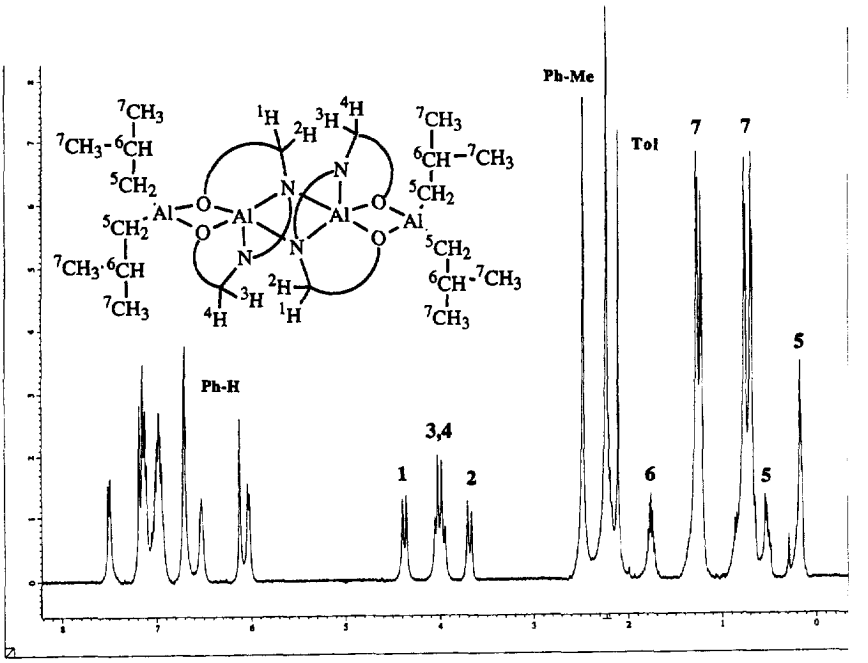


Fig. 9. ^{1}H NMR spectrum of [SalomphanAl(Al^{i}Bu$_2$)]$_2$ (**27**).

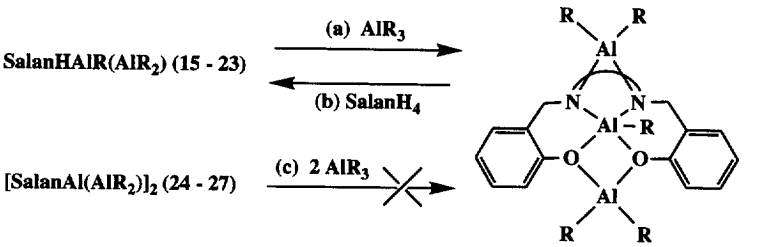
trialkylaluminum, and the conversion of SalanAlR(AlR$_2$)$_2$ to SalanHAlR(AlR$_2$) by addition of one equivalent of ligand to the trimetallic.

The addition of one equivalent of trimethylaluminum to the bimetallic complex, SaleanHAlMe(AlMe$_2$), produced the corresponding trimetallic compound, SaleanAlMe(AlMe$_2$)$_2$, in quantitative yield. A similar reaction using SalophanHAlMe(AlMe$_2$) produced the same result (Scheme 9a). This reaction can be reversed by the addition of one equivalent of SalanH$_4$ ligand into a solution of a trimetallic complex (Scheme 9b). The third reaction involved mixing [SalanAl(AlMe$_2$)]$_2$ with two equivalents of AlR$_3$ (Scheme 9c). In all cases the final product was identified as unreacted starting material. Thus, it appeared that a requirement for the conversion of these species was the presence of an available NH group.

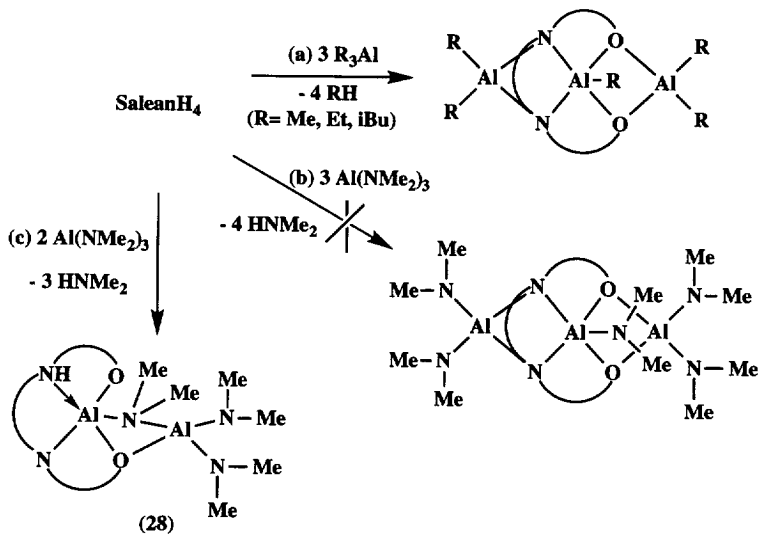
3.3. *A unique amido derivative, SaleanHAl(Al(NMe$_2$)$_3$)*

SaleanHAl(Al(NMe$_2$)$_3$) (**28**) was originally isolated from the reaction of SaleanH$_4$ with Al(NMe$_2$)$_3$ in a 1:3 ratio [27]. The targeted compound was that of formula SaleanAlNMe$_2$(AlNMe$_2$)$_2$ (Scheme 10b) which would be isomorphous to the trimetallic examples (See Section 4). In view of the distinctive ^{1}H NMR spectra for the trimetallics, it was apparent that such a complex had not formed.

Indeed, the trimetallic motif could not be achieved under these circumstances



Scheme 9. Attempts to convert the bimetallic to the trimetallic derivatives.



Scheme 10. The general syntheses relating to SaleanHAl(Al(NMe_2)$_3$).

using any of the four Salan ligands. Moreover, the synthesis of a 2:1 derivative was not straightforward. The use of 2 equivalents of Al(NMe_2)$_3$ in these reactions also led to mixtures of products. In only one case, using the $SaleanH_4$ ligand, was a reasonable yield of a 1:2 product (**28**) obtained (Scheme 10c). The presence of the NH group was supported by ^{1}H NMR and IR data.

A crystal structure revealed the bonding arrangement for **28** (Fig. 10). In the structure one aluminum atom is chelated by the ligand while the second is bound to an oxygen of the ligand and three NMe_2 groups (one in a bridging capacity between the two aluminum atoms). Although this is a unique bonding arrangement for the Salan ligands, it is similar to the alkyl aluminum analogs, SalanHAlR(AlR_2). In these complexes the terminal AlR_2 group bridges the two oxygen atoms of the ligand. In **28** one of these O–Al bonds has been replaced by a bridging NMe_2 group.

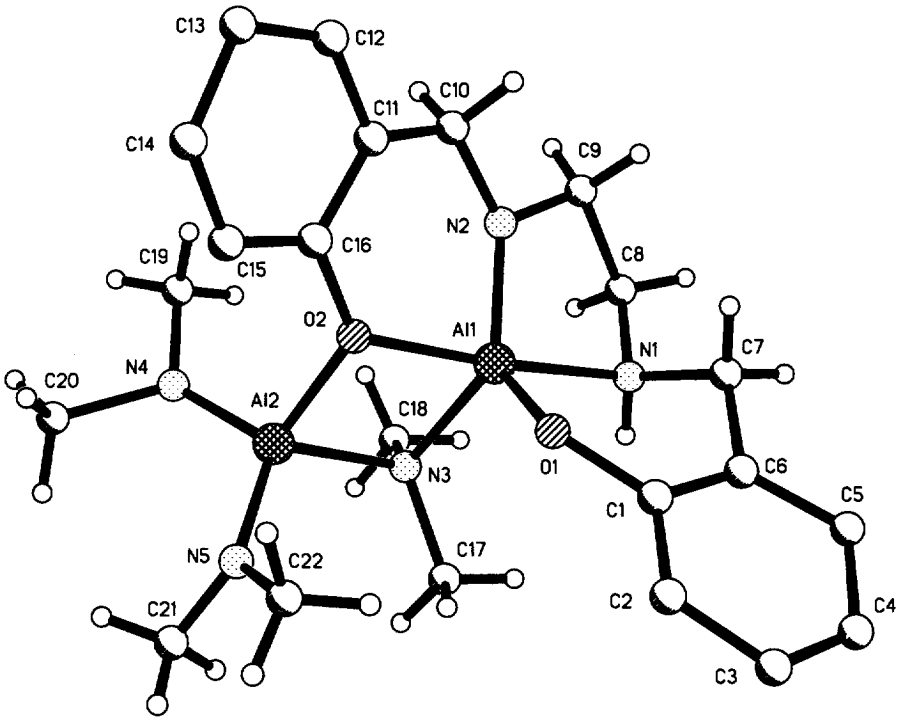


Fig. 10. Molecular structure of SaleanHAlNMe$_2$(Al(NMe$_2$)$_2$) (**28**).

4. Complexes having a metal:ligand stoichiometry of 3:1

4.1. Group 13 complexes, SalanMR(MR$_2$)$_2$ (M=Al, Ga; R=Me, Et, ^{i}Bu)

Trimetallic group 13 complexes have appeared sporadically in the literature over the past 20 years. In general these complexes have been made up of two bidentate ligands. These ligands chelate a central group 13 element and bridge two other group 13 fragments through the heteroatoms (Fig. 11(a)). Most of the reported examples are aluminum complexes of bidentate alcohols [28] and amines [29]. Symmetrical structures predominate for these complexes although one gallium example was not (Fig. 11(b)) [30].

The availability of the Salan ligands offered a unique opportunity to systematically study this unusual group 13 arrangement. These ligands are similar in appearance and have the basic requirements (four acidic protons) of the bidentate ligand systems. However, the Salan ligands may be viewed as two bidentate ligands that are tethered together with either an alkyl or aryl "backbone." This allows for the added feature of being able to vary this ligand backbone and manipulate the geometries of the resulting complexes.

The reaction of three equivalents of a trialkyl group 13 reagent with each of the

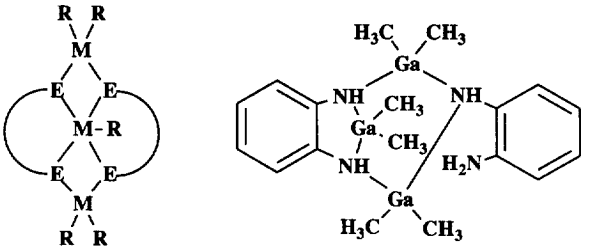


Fig. 11. General structural motif of trimetallic group 13 complexes (a) and an asymmetric gallium example (b).

SalanH$_4$ ligands suspended in toluene resulted in trimetallic compounds having the general formula, SalanMR(MR$_2$)$_2$ (Eq. (1)) [12,31]. This formulation was supported by the absence of –OH and –NH resonances in the infrared spectra combined with elemental analysis and mass spectral data. The ^{1}H-NMR data added further support for this formulation and revealed a complex pattern of coupling which could be interpreted in terms of a rigid solution state geometry.

As a representative example, the ^{1}H-NMR spectrum for SaleanAlMe(AlMe$_2$)$_2$ (**29**) is shown in Fig. 12. The benzylic hydrogens of the ligand (PhCH$_2$) become

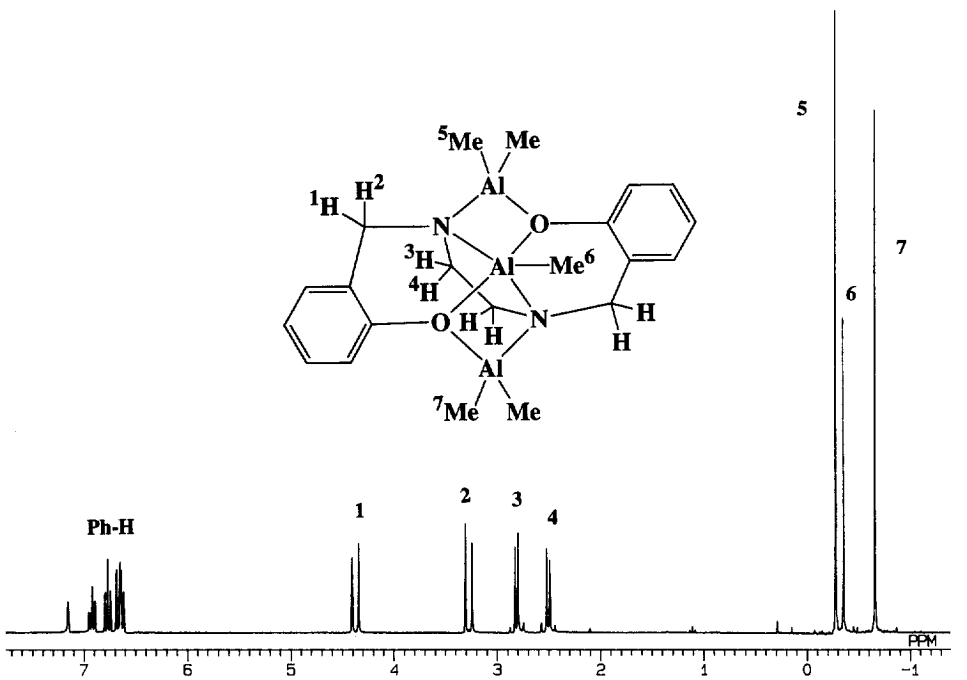


Fig. 12. ^{1}H NMR spectrum of SaleanAlMe(AlMe$_2$)$_2$ (**29**).

diastereotopic upon formation of the complex and appear as a set of two doublets (1 and 2) with coupling consistent with a geminal interaction ($J=17$ Hz). The observation of two doublets for the benzylic hydrogens is a hallmark behavior for the trimetallic structural motif and was shown to be present for all of the trimetallic aluminum complexes. The protons of the backbone (3 and 4) were similarly coupled.

$$\text{SalanH}_4 + 3\text{MR}_3 \xrightarrow{\text{Tol},-4\text{RH}} \text{SalanMR}(\text{MR}_2)_2 \quad (1)$$

(M = Al, Ga; R = Me, Et, ^{i}Bu)

The integration of the Al–Me region of the spectrum confirmed the presence of five aluminum methyls. The relative intensities of peaks 5, 6 and 7 having a ratio of 2:1:2 could be explained by assigning 5 and 7 to $AlMe_2$ units while 6 was the AlMe unit of the five-coordinate central aluminum as depicted in the structure above the spectrum. In this arrangement, each $AlMe_2$ unit bridged an oxygen and a nitrogen of the ligand. This gave the molecule C_2 symmetry, and each $AlMe_2$ unit became equivalent in the ^{1}H-NMR, but each of the geminal methyls were inequivalent (5 and 7). This arrangement where each $AlMe_2$ unit bridges a nitrogen and an oxygen is termed *trans* (Fig. 14(a)).

A similar product was obtained with the $SalpanH_4$ ligand (**32**). It also lacked the –OH and –NH infrared peaks of the ligand and elemental analysis and mass spectra confirmed that it was trimetallic. In the ^{1}H NMR (Fig. 13) the benzylic hydrogens appeared as a set of two doublets (1 and 2). The propyl backbone, however, was considerably more complex. The NCH_2 resonances appeared as two doublets of doublets (3 and 4). The NCH_2CH_2 resonances appeared as inequivalent multiplets (5 and 6).

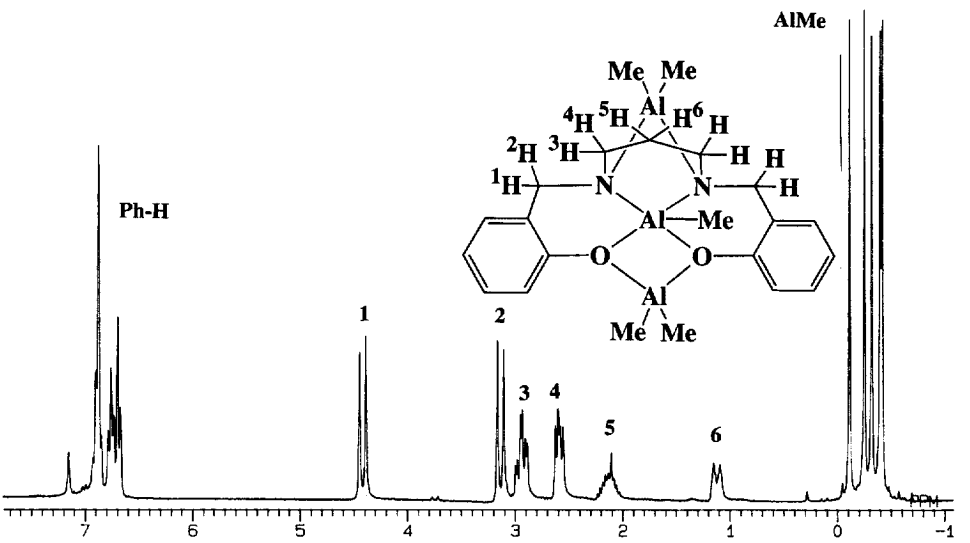


Fig. 13. ^{1}H NMR spectrum of $SalpanAlMe(AlMe_2)_2$ (**32**).

The difference between (**29**) and (**32**) is evident in the AlMe region of the ^{1}H-NMR spectrum. Instead of three resonances for the AlMe protons, as for **29**, **32** exhibits five resonances. Integration of the resonances showed that each singlet had three protons and corresponded to one methyl group. The explanation for this observation concerns the disposition of the ligand backbone. The two $AlMe_2$ units bridge two oxygens and two nitrogens, respectively. This bonding arrangement disrupts the C_2 symmetry present in SaleanAlMe$(AlMe_2)_2$ and leads to five inequivalent AlMe resonances. The structures where one $AlMe_2$ bridges both oxygens and the other $AlMe_2$ unit bridged the two nitrogens are designated *cis* (Fig. 13(b)).

The ^{27}Al-NMR spectra of the complexes showed the presence of two distinct types of aluminum atoms: one relatively sharp in the five-coordinate region of the spectra (50–85 ppm) and another relatively broad in the four-coordinate region of the spectra (147–220 ppm).

With ^{1}H-NMR being used as a tool to discriminate between *cis* and *trans* geometries, the series of trimetallic complexes of general formula SalanMR$(AlR_2)_2$ (where M = Al; R = Me, Et, ^{i}Bu; M = Ga; R = Me, Et) were synthesized from the combination of the four SalanH_4 ligands and the appropriate group 13 starting material. This represented the first deliberate and systematic synthesis of monomeric, trimetallic group 13 complexes. It demonstrated that a *trans* geometry is always adopted for the Salean ligand except in a complex incorporating the bulky ^{i}Bu group, Salean$Al^iBu(Al^iBu_2)_2$ (**31**) which adopts a *cis* conformation. In this conformation the methylene groups in the ethyl backbone are eclipsed. All of the other aluminum complexes adopt a *cis* conformation. In contrast, all of the known gallium derivatives adopt a *trans* geometry. This difference may be attributed to a tendency for gallium to adopt a trigonal bipyramidal coordination mode.

4.1.1. Solution state rigidity

The trimetallics were shown to adopt rigid solution state geometries. This behavior was manifested in the ubiquitous appearance of diastereotopic protons for positions that would be equivalent if the molecule was fluxional. They do not undergo averaging of the benzylic hydrogens through either bond-breaking or molecular motions. In all of the reported trimetallics the benzylic protons ($PhCH_2$) of the ligand became a set of two doublets upon complexation. In cases where the backbone was either ethyl or propyl (Salean or Salpan), the hydrogens of the alkyl tether were also manifested as a set of discrete multiplets consistent with diastereotopic behavior.

This phenomenon was also evident in the alkyl groups on the aluminum or gallium. In either the *cis* or *trans* geometries, the geminal alkyl groups on the tetradentate group 13 atom(s) were observed to be inequivalent in the ^{1}H-NMR spectra. If the molecules were fluxional in solution and the MR_2 unit was dissociating then reassociating this process would have led to a single time-averaged peak in the ^{1}H-NMR instead of the observed inequivalent resonances. This type of behavior, although rare, has been described before in group 13 complexes incorporating chiral alkoxides [32] and amine alcohols [33].

The relatively rigid solution state behavior of these complexes implied that exchange reactions might not occur. To address this point a series of four

exchange reactions were performed. In the first, equimolar amounts of SalpanGaMe$(GaMe_2)_2$ (**43**) and **30** were mixed together in toluene and then stirred at 25 °C for 8 h (Eq. (2)). Analysis by ^{1}H-NMR of the solid remaining after solvent removal indicated that each of the reagents were unchanged from the mixing. The remaining reactions were directed at the possibility of exchange of the alkyl groups between aluminum or gallium atoms and were conducted in situ in 5 mm NMR tubes.

$$\text{SalpanGaMe}(\text{GaMe}_2)_2 + \text{SalpanAlMe}(\text{AlMe}_2)_2 \xrightarrow[\text{Toluene}]{25^\circ\text{C}} \text{NR} \quad (2)$$

$$\text{SalpanGaMe}(\text{GaMe}_2)_2 + \text{SalpanGaEt}(\text{GaEt}_2)_2 \xrightarrow[C_6D_6]{25^\circ\text{C}} \text{NR} \quad (3)$$

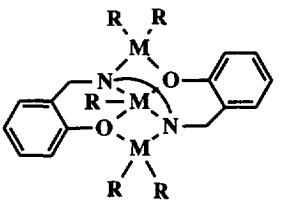
$$\textit{SalpanAlMe}(\textit{AlMe}_2)_2 + \textit{AlEt}_3 \xrightarrow[C_6D_6]{25^\circ\text{C}} \textit{NR} \quad (4)$$

$$\textit{SalpanGaMe}(\textit{GaMe}_2)_2 + \textit{GaEt}_3 \xrightarrow[C_6D_6]{25^\circ\text{C}} \textit{NR} \quad (5)$$

Thus, the trimetallic derivatives **43** and **44** were mixed in C_6D_6 at 25 °C and stirred for two hours (Eq. (3)). Similarly **30** was mixed with a fifty-fold excess of triethylaluminum (Eq. (4)) and **43** was mixed with a fifty-fold excess of triethylgallium and stirred for two hours (Eq. (5)). The ^{1}H-NMR spectra of these mixtures were comprised of well-defined resonances which could be attributed to unchanged starting materials. These experiments served to indicate that compounds of this type are non-fluxional and non-dissociative at 25 °C in aryl solvents.DUMMY Fig. 14

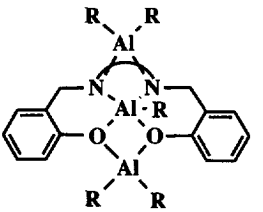
4.1.2. π-Anisotropic effects

After the entire series of trimetallic complexes had been synthesized, an interesting observation was made: the complexes possessing an aryl amine backbone had either



(a)

Salean, M = Al; R = Me (29), Et (30)
Ga; R = Me (41), Et (42)
Salpan; M = Ga; R = Me (43), Et (44)
Salophan; M = Ga; R = Me (45), Et (46)
Salomphan; M = Ga; R = Me (47), Et (48)



(b)

Salean; R = ^{i}Bu (31)
Salpan; R = Me (32), Et (33), ^{t}Bu (34)
Salophan; R = Me (35), Et (36), ^{t}Bu (37)
Salomphan; R = Me (38), Et (39), ^{t}Bu (40)

Fig. 14. The *cis* and *trans* coordination for the group 13 Salan complexes.

one or two resonances that were shifted farther upfield to that demonstrated for complexes possessing an alkyl amine backbone. Analysis of the ^{1}H-NMR data combined with the X-ray crystal structures indicated that this could be attributed to an anisotropic ring current effect between the aryl group of the backbone (Salophan and Salomphan) and the terminal alkyl group 13 moiety. This is shown for **45** in Figs. 15(a) and (b). It has been previously demonstrated that the relative shielding effect in these systems varies with the distance of the proton from the aryl group. An optimal value of H···aryl-centroid was calculated to be 2.25 Å [34]. At this distance, the chemical shift differential between the affected and unaffected protons ($\Delta\delta$) would be maximized. In an extreme example, the chemical shift difference between the geminal hydrogens of the homotropylium cation was shown to be 5.8 ppm [35]. Table 1 lists some values for the trimetallics. The closest contact between the hydrogens of these methyl groups and the centroid of the aryl ring was in the range of 2.82–3.19 Å. There are two such contacts for the molecules in a *cis* configuration and one for the *trans* configuration. This situation is shown in Figs. 15(a) and (b). The contact was maximized when the proton was centered above the aryl group. Thus, the angle that the C–H bond made with the plane of the aryl group was also important. The greatest shielding would then occur at angles of 90°, directly in line with the magnetic field produced by the aryl ring. For SalophanGaMe(GaMe$_2$)$_2$ and SalomphanGaMe(GaMe$_2$)$_2$, these angles were oblique and consequently the shift was not as pronounced. By comparison, the angles for SalophanAlMe(AlMe$_2$)$_2$ more closely approached 90° and the shift differential was correspondingly larger ($\Delta\delta$ 1.00 ppm).

4.1.3. The trans configuration

To better understand the solid-state structure of the trimetallic aluminum and gallium complexes, a number of X-ray crystallographic studies were undertaken. The structure of SaleanAlMe(AlMe$_2$)$_2$ (**29**) is shown in Fig. 16. In the structure, the Salean ligand is coordinated in a tetradentate fashion to the central AlMe unit (Al(2)), which is in a distorted trigonal-bipyramidal geometry. The ethylene backbone of the ligand is in a *trans* configuration. In keeping with the electronegativity difference between oxygen and nitrogen, the oxygen atoms were located in the axial positions and the nitrogens and the methyl carbon in equatorial positions. This led to longer Al–O bonds (1.982(3) Å and 1.959(3) Å) than Al–N bonds (average 1.931(2) Å) for the central aluminum (Al(2)). The opposite trend was observed for the two peripheral AlMe$_2$ units, with each bridging an oxygen and a nitrogen of the ligand. The aluminums were in a distorted tetrahedral geometry with the bonds to oxygen being significantly shorter (average 1.85 Å) than the bonds to nitrogen (average 1.95 Å).

The *trans* conformation was the only type of structure that was observed for gallium regardless of which Salan ligand was used. Structures have been determined for **41**, **42**, **43** and **45**. In each case the central gallium atom is in a trigonal bipyramidal geometry. Compound **43** is shown in Fig. 17 as an example. The apical positions are occupied by two oxygens (Ga–O 2.08(2) Å(ave)). The trigonal plane contains the two nitrogens (Ga–N 1.92(2) Å(ave)) and the α-carbon of the alkyl

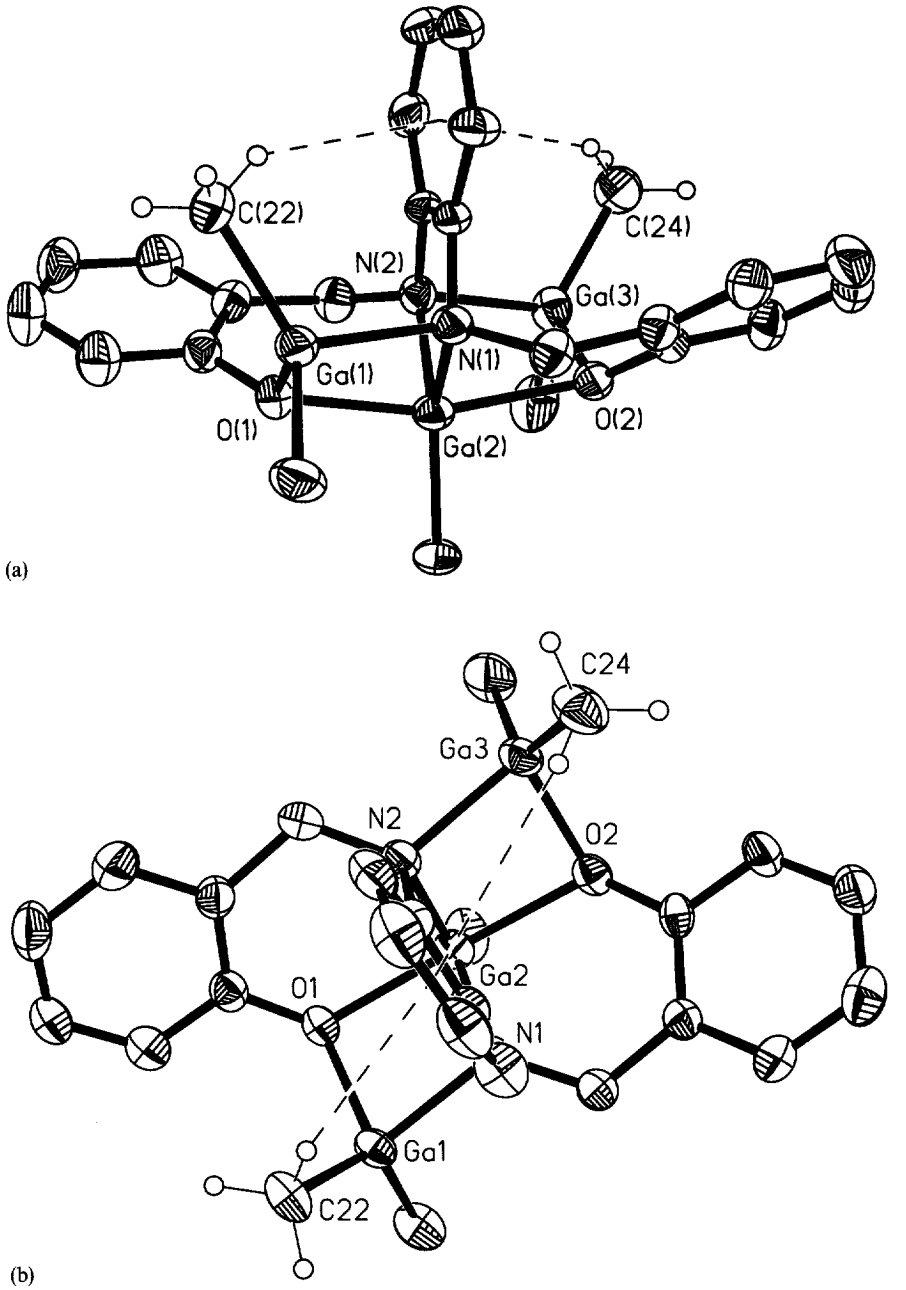


Fig. 15. Vertical (a) and lateral (b) angles for the ring current effect in **45**.

Table 1
Comparison of chemical shifts resulting from the ring current effects of the Salan ligands possessing an arylamine backbone

Compound (contact)	Shift (ppm)[a]	Distance (Å)	Angle-1 (deg)[b]	Angle-2 (deg)[c]
SalophanAlMe($AlMe_2$)$_2$ (**35**)	0.80	2.97	90.8	64.5
(Al–CH_3···Ph)	1.00	3.03	92.5	97.7
SalophanAlEt($AlEt_2$)$_2$ (**36**)	0.80	–No structure available–		
(Al–CH_2···Ph)	1.23			
SalomphanAlEt($AlEt_2$)$_2$ (**39**)	0.74	–No structure available–		
(Al–CH_2···Ph)	1.19			
SalophanAl*i*-Bu(Al*i*-Bu_2)$_2$ (**37**)	0.95	–No structure available–		
(Al–CH_2···Ph)	1.41			
SalomphanAl*i*-Bu(Al*i*-Bu_2)$_2$ (**40**)	0.89	–No structure available–		
(Al–CH_2···Ph)	1.45			
SalophanGaMe($GaMe_2$)$_2$ (**45**)	0.85	2.82	72.6	82.1
(Ga–CH_3···Ph)		2.93	65.3	81.4
SalomphanGaMe($GaMe_2$)$_2$ (**47**)	0.78	3.01	59.5	80.4
(Ga–CH_3···Ph)		3.19	55.1	79.6

[a] Defined by subtracting the chemical shift (ppm) of the deshielded group from that of the unaffected group on the same metal.
[b] Vertical displacement from ring centroid (ideal = 90°).
[c] Lateral displacement from ring centroid (ideal = 90°).

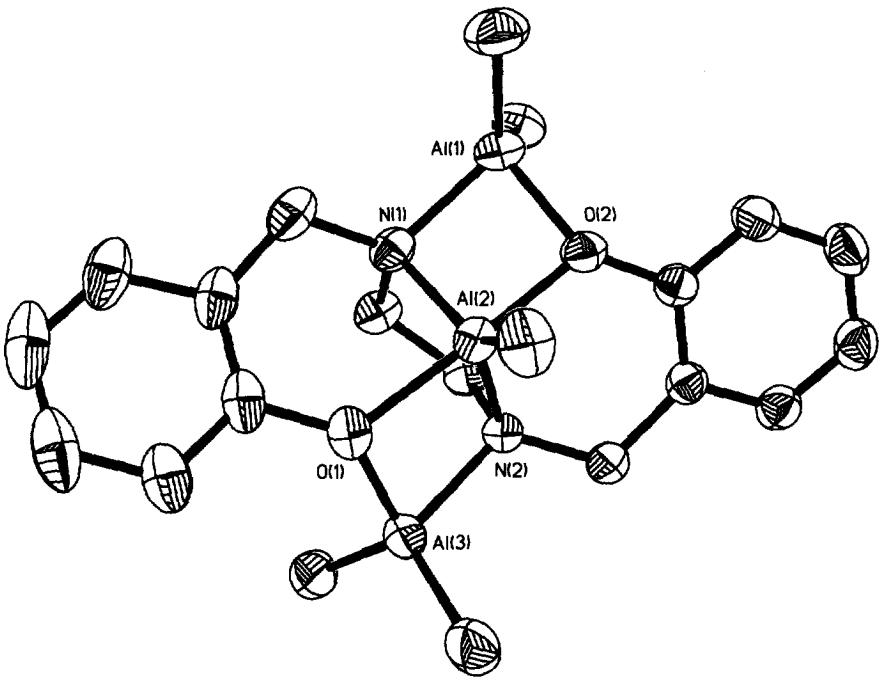


Fig. 16. Molecular structure of SaleanAlMe($AlMe_2$)$_2$ (**29**).

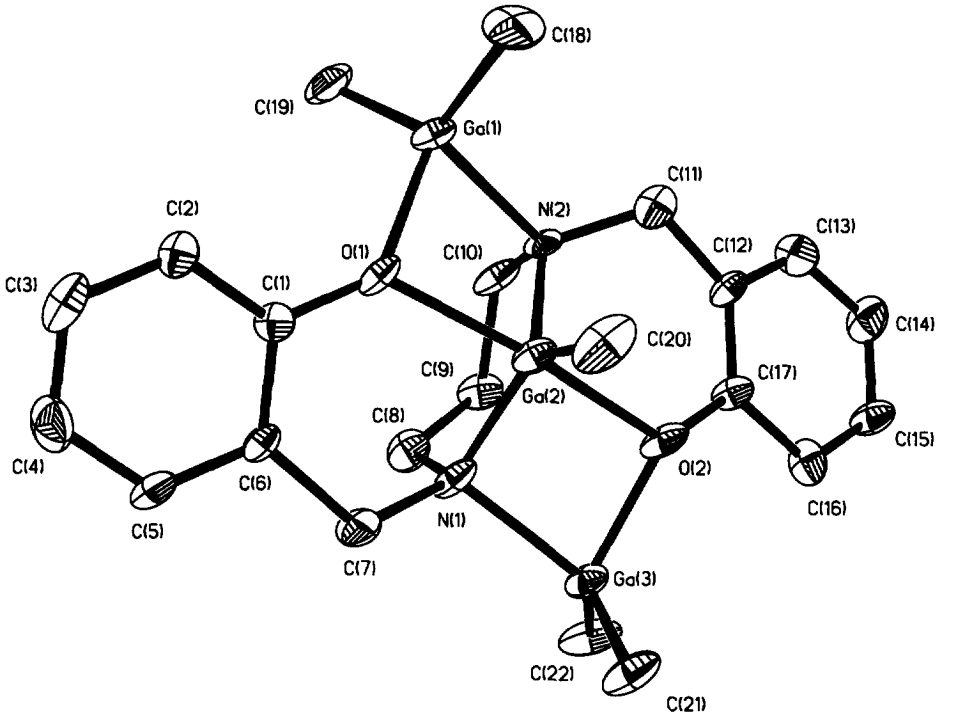


Fig. 17. Molecular structure of SalpanGaMe(GaMe$_2$)$_2$ (**43**).

group (Ga–C 1.948(18) Å). The greatest deviation from ideal values for the trigonal plane was found for the N1–Ga2–N2 angle (109.9(6)°). The O1–Ga2–O2 angle was 164.5(4)°.

4.1.4. The cis configuration

As an example of the *cis* configuration the structure of **32** is shown in Fig. 18. The central aluminum is in a five-coordinate square-pyramidal geometry. The basal plane of the square pyramid is formed by the oxygens and the nitrogens (maximum deviation = 0.031 Å for O(1) of the ligand) with the methyl carbon at the apical position. The aluminum is perched slightly above the plane at a distance of 0.61 Å. The square-pyramidal geometry of the central aluminum allowed for shorter bonds to oxygen than nitrogen. The average Al–O bond to Al(2) was 1.90(1) Å while the average Al–N bond was 1.97(1) Å. The four-coordinate aluminums adopted slightly distorted tetrahedral geometries. In the *cis* geometry, one aluminum bridges both oxygens of the ligand while the other peripheral aluminum bridges both nitrogens.

The structural characterization of other aluminum derivatives (**29**, **31**, **32**, **35** and **36**) demonstrated that the structural parameters for **32** were prototypical. For example, comparison of the bond lengths and angles of **32** and **35** revealed that the change from an alkyl backbone to an aryl backbone changed very little in the overall

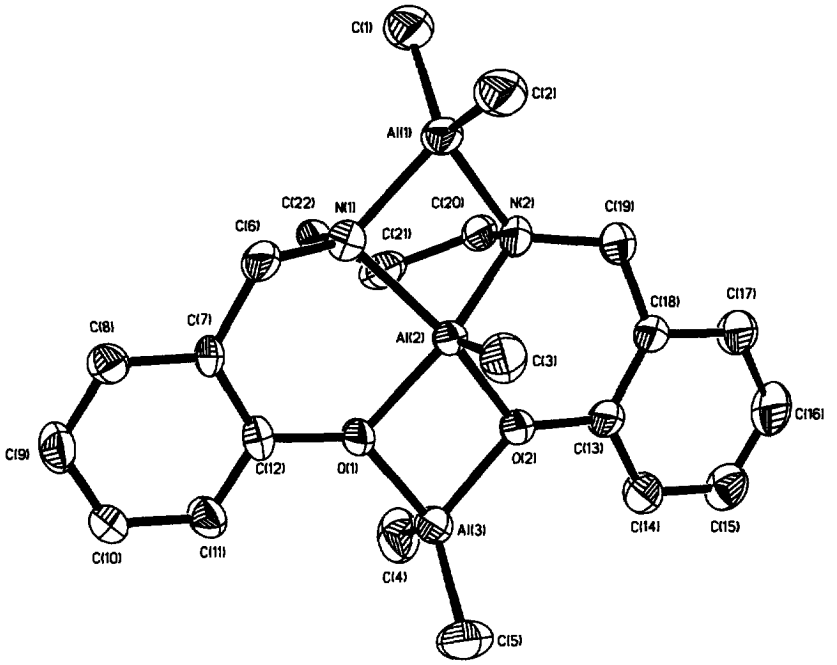


Fig. 18. Molecular structure of SalpanAlMe$(AlMe_2)_2$ (**32**).

geometry of the trimetallic complex. The only notable difference was that the central aluminum atom in **35** was perched farther out of the plane formed by the oxygens and nitrogens of the ligand (0.96 Å versus 0.61 Å).

Salean$Al^iBu(Al^iBu_2)_2$ (**31**) is an exception to the rule of Salean–group 13 complexes adopting a *trans* geometry. A side view of this structure is shown in Fig. 19. The hydrogens are shown with dotted lines indicating sites of closest contact. These ranged from 2.3 to 2.5 Å. For Al(2) the Al–N bonds (average 1.97 Å) were slightly longer than Al–O bonds (average 1.91 Å). The Al(2)–C length (1.964(7) Å) was not lengthened from any steric effects. In the *cis* configuration the hydrogens of the ethyl backbone are in nearly perfect alignment (maximum deviation 0.015 Å).

5. Conclusions

A general overview of the known main group–Salan complexes is shown in Scheme 11. The group 13 elements, in particular, aluminum have been most extensively explored. The widest range of metals are known for the monometallic Salan derivatives (Zn, Al and Sn). The Al and Sn complexes were shown to be monomeric. This paralleled the established chemistry of the Salen ligands. The zinc–Salan complexes were observed to form oxygen-bridged dimers. This represents a new capability for the Salan ligands when compared with the Salen ligands. The presence of an

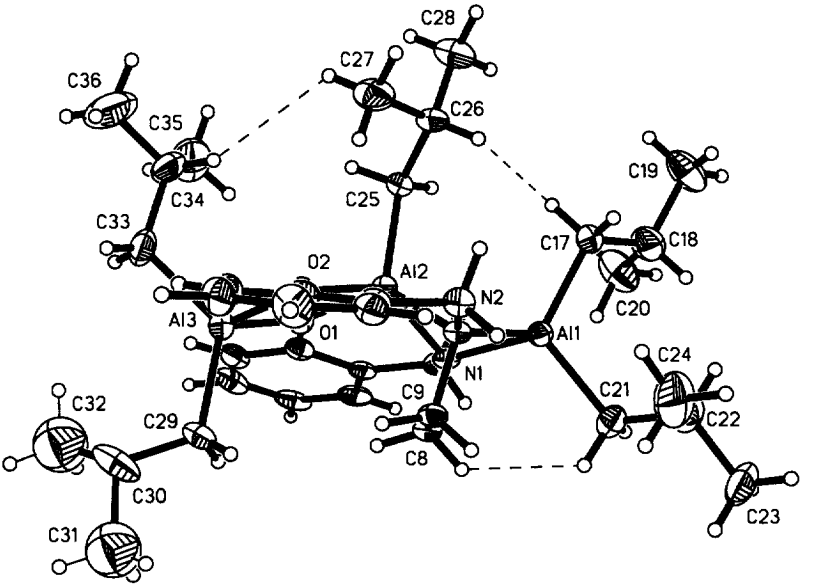
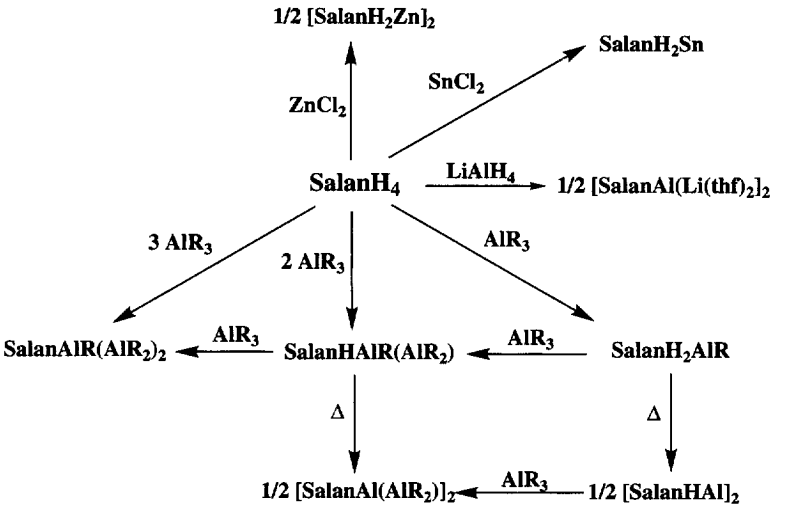


Fig. 19. Side view of the molecular structure of SaleanAl^{i}Bu(Al^{i}Bu$_2$)$_2$ (**31**).

amine (NH–CH$_2$) in place of the imine (N=CH) linkage provides the ligand with the necessary flexibility for dimerization. By utilizing all of the NH and OH sites, unique anionic nitrogen-bridged dimers, [SalanAl(Li(THF)$_2$)]$_2$ were obtained. When the Salan ligand is Salomphan a helically chiral molecule was obtained.

The NH functionalities were utilized to form unique bimetallic aluminum com-



Scheme 11. Preparation and interconversion of the Salan–aluminum complexes.

plexes. These were primarily of the form SalanHAlR(AlR_2). In one unusual case an amido derivative, SalpanH($AlNMe_2$)(Al(NMe_2)$_2$)), was isolated. The remaining NH group on the aluminum alkyl complexes containing an aryl backbone was acidic enough to undergo a further alkane elimination to form the nitrogen bridged dimers, [SalanAl(AlR_2)]$_2$. The morphology of these dimeric species was similar to that observed for the anions. This dimeric structural motif (either through bridging oxygens or nitrogens) represents one of the two that have proven common for the Salan ligands.

The predominant structural motif is that manifested in the trimetallic derivatives, SalanMR(MR_2)$_2$. These contained a centrally coordinated metal and two peripheral four-coordinate metals. Either a *cis* or *trans* isomer could be obtained depending on the nature of the ligand backbone and the metal. These trimetallics demonstrated two unique features. The most important with regards to reactivity was a rigid solution state geometry characterized by the presence of diastereotopic protons. They did not undergo exchange of either the alkyl groups or the metal-alkyl units in toluene. When the ligand contained an aryl backbone anisotropic shielding effects occur. Based upon correlations between solid and solution state data a maximum shielding effect was observed at lateral and vertical angles of 90° and distances of about 2.9 Å.

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References

[1] (a) J.V. Dubsky, A. Sokol, Collection Czech. Chem. Commun. 3 (1931) 548;(b) R.H. Holm, G.W. Everett, Jr., A. Chakravorty, Progress in Inorganic Chemistry 7 (1966) 83;(c) M.D. Hobday, T.D. Smith, Coord. Chem. Rev. 9 (1972) 311.

[2] D.A. Atwood, J. Benson, J.A. Jegier, N.F. Lindholm, K.J. Martin, R.J. Pitura, D. Rutherford, D. Main Group Chemistry 1 (1995) 99.

[3] (a) M. Schumann, A.v. Holtum, K.J. Wannowius, H. Elias, Inorg. Chem. 21 (1982) 606.;(b) R. Warmuth, H. Elias, Inorg. Chem. 30 (1991) 5027;(c) A. Bottcher, H. Elias, L. Muller, H. Paulus,

Angew. Chem. Int. Ed. Engl. 31 (1992) 623;(d) P. Baran, A. Bottchner, H. Elias, W. Haase, M. Huber, H. Fuess, H. Paulus, Z. Naturforsch. 47B (1992) 1681;(e) A. Bottcher, H. Elias, E.-G. Jager, H. Langfelderova, M. Mazur, L. Muller, H. Paulus, P. Pelikan, M. Rudolph, M. Valko, Inorg. Chem. 32 (1993) 4131;(f) P. Subramian, J.T. Spence, R. Ortega, J.H. Enemark, Inorg. Chem. 23 (1984) 2564;(g) S.F. Gheller, T.W. Hambley, M.R. Snow, K.S. Murray, A.G. Wedd, Aust. J. Chem. 37 (1984) 911;(h) L. Borer, L. Thalken, C. Ceccarelli, M. Glick, J.H. Zhang, W.M. Reiff, Inorg. Chem. 22 (1983) 1719.

[4] D.A. Atwood, J.A. Jegier, N.F. Lindholm, K.J. Martin, D. Rutherford, J. Coord. Chem. 38 (1996) 305.

[5] (a) M.J. O'Connor, B.O. West, Aust. J. Chem. 20 (1967) 2077;(b) D. Hall, F.H. Moore, Proc. Chem. Soc. (1960) 256.

[6] (a) P. Wooley, Nature 258 (1975) 677;(b) S.R. Brown, J. Huguet, N.J. Curtis, in: Metal Ions in Biologic Systems, H. Sigel (Ed.), Marcel Dekker, Inc., New York, 1983, ch. 2.

[7] G.E. Batley, D.P. Graddon, Aust. J. Chem. 20 (1967) 877.

[8] S.S. Tandon, S. Chander, L.K. Thompson, J.N. Bridson, V. McKee, Inorg. Chim. Acta. 219 (1994) 55.

[9] (a) S.J. Dzugan, V L. Goedken, Inorg. Chem. 25 (1986) 2858;(b) W.-H. Leung, E.Y.Y. Chan, E.K.F. Chow, I.D. Williams, S.-M. Peng, J. Chem. Soc. Dalton Trans. (1996) 1229.

[10] P.L. Gurian, L.K. Cheatham, J.W. Ziller, A.R. Barron, J. Chem. Soc. Dalton Trans. (1991) 1449.

[11] (a) D.A. Atwood, J.A. Jegier, D.J. Rutherford, J. Am. Chem. Soc. 117 (1995) 6779;(b) D.A. Atwood, J.A. Jegier, D. Rutherford, Inorg. Chem. 35 (1996) 63;(c) M.G. Davidson, C. Lambert, I. Lopez-Solera, P.R. Raithby, R. Snaith, Inorg. Chem. 34 (1995) 3765.

[12] D.A. Atwood, J.A. Jegier, K.J. Martin, D. Rutherford, Organometallics 14 (1995) 1453.

[13] (a) J.J. Eisch, in: Comprehensive Organometallic Chemistry, Vol. 1, G. Wilkinson, F.G.A. Stone, E.W. Abel (Eds.), Pergamon Press, Oxford, England, 1982, ch. 6;(b) Coordination Chemistry of Aluminum, G.H. Robinson (Ed.), VCH Publishers, Inc., New York, 1993. (c) Chemistry of Aluminum, Gallium, Indium and Thallium, A. J. Downs (Ed.), Chapman & Hall, New York, 1993.

[14] (a) M. Veith, W. Frand, F. Toliner, H. Lange, J. Organomet. Chem. 326 (1987) 315;(b) K.G. Caulton, L.G. Hubert-Pfalzgraf, Chem. Rev. 90 (1990) 969;(c) U.M. Tripathi, A. Singh, R.C. Mehrota, S.C. Goel, M.Y. Chiang, W.E. Buhro, J. Chem. Soc., Chem. Commun. (1992) 152;(d) T.Y. Her, C.-C. Chang, L.-K. Liu, Inorg. Chem. 31 (1992) 2291;(e) J. Sassmannshausen, R. Riedel, K.B. Pflanz, H.Z. Chmiel, Naturforsch. 48B (1993) 7;(f) J.A. Meese-Marktscheffel, R. Weimann, H. Schumann, J.W. Gilje, Inorg. Chem. 32 (1993) 5894;(g) J.A. Meese-Marktscheffel, R. Fukuchi, M. Kido, G. Tachibana, C.M. Jensen, J.W. Gilje, Chem. Mater. 5 (1993) 755;(h) J.A. Meese-Marktscheffel, R.E. Cramer, J.W. Gilje, Polyhedron 13 (1994) 1045.

[15] (a) J.L. Atwood, D.C. Hrncir, R.D. Priester, R.D. Rogers, Organometallics 2 (1983) 985;(b) W.J. Evans, T.J. Boyle, J.W. Ziller, Polyhedron 11 (1992) 1093;(c) G. Wilkinson, A.A. Danopoulos, B. Hussain-Bates, M.B. Hursthouse, J. Chem. Soc. Dalton Trans. (1990) 2753.

[16] D.A. Atwood, D. Rutherford 34 (1995) 4008.

[17] J.J. Delpuech, in: NMR of Newly Accessible Nuclei Vol 2, P. Laszlo (Ed.), Academic Press, Inc., New York, 1983, p. 153.

[18] (a) A. van den Bergen, R.J. Cozens, K.S. Murray, J. Chem. Soc. (A) (1970) 3060;(b) K. Kawakami, M. Miya-Uchi, T. Tanaka, J. Inorg. Nucl. Chem. 33 (1971) 3773;(c) W.D. Honnick, J.J. Zuckerman, Inorg. Chem. 18 (1979) 1437;(d) G.H. Havanur, V.K. Revankar, V.B. Mahale, Indian J. Chem. 27 (1988) 803;(e) K.K. Sarma, T.S. Basu Baul, E. Rivarola, R.P. Agrawal, Polyhedron 13 (1994) 2217.

[19] R.C. Mehrota, G. Srivastava, B.S. Saraswat, Rev. on Si, Ge, Sn, and Pb Cmpd. 6 (1982) 171.

[20] A.M. van den Bergen, J.D. Cashion, G.D. Fallon, B.O. West, Aust. J. Chem. 43 (1990) 1559.

[21] D.A. Atwood, J.A. Jegier, K.J. Martin, D. Rutherford, J. Organomet. Chem. 503 (1995) C4.

[22] (a) P. Jutzi, W. Steiner, E. Konig, G. Huttner, A. Frank, U. Schubert, Chem. Ber. 111 (1978) 606;(b) P. Jutzi, W. Steiner and K. Stroppel, Chem. Ber. 113 (1980) 3357.

[23] D.A. Atwood, V.O. Atwood, A.H. Cowley, H.R. Gobran, J.L. Atwood, Inorg. Chem. 32 (1993) 4671.

[24] D.A. Atwood, M.P. Remington, D. Rutherford, Organometallics 15 (1996) 4763.

[25] G.H. Robinson, S.A. Sangokoya, F. Moise, W.T. Pennington, Organometallics 7 (1988) 1887.

[26] K.S. Chong, S.J. Rettig, A. Storr, J. Trotter, Can. J. Chem. 55 (1977) 2540.

[27] D.A. Atwood, J.A. Jegier, M.P. Remington, D. Rutherford, Aust. J. Chem. 49 (1996) 1333.
[28] (a) S. Pasynkiewicz, J. Ziemkowska, J. Organomet. Chem. 423 (1992) 1;(b) J. Ziemkowska, S. Pasynkiewicz, E. Kalbarczyk, J. Organomet. Chem. 465 (1994) 93;(c) S. Pasynkiewicz, J. Ziemkowska, J. Organomet. Chem. 437 (1992) 99;(d) J. Ziemkowska, S. Pasynkiewicz, J. Organomet. Chem. 508 (1996) 243;(e) W. Uhl, R. Gerding, A. Vester, J. Organomet. Chem. 513 (1996) 163.
[29] G. Perego, G. Del Piero, M. Corbellini, M. Bruzzone, J. Organomet. Chem. 136 (1977) 301.
[30] R.L. Wells, H. Rahbarnoohi, P.B. Glaser, L.M. Liable-Sands, A.L. Rheingold, Organometallics 15 (1996) 3204.
[31] (a) D.A. Atwood, D. Rutherford, Organometallics 14 (1995) 2880;(b) D.A. Atwood, D. Rutherford, Organometallics 14 (1995) 3988;(c) D.A. Atwood, D. Rutherford, Comm. Inorg. Chem. (1996) to be published.
[32] M.L. Sierra, R. Kumar, V.S.J. de Mel, J.P. Oliver, Organometallics 11 (1992) 206.
[33] (a) M.L. Sierra, V.S.J. de Mel, J.P. Oliver, Organometallics 8 (1989) 2486;(b) D.A. Atwood, F.P. Gabbai, J. Lu, M.P. Remington, D. Rutherford, M.P. Sibi, Organometallics 15 (1996) 2308;(c) H. Schumann, S. Wernik, F. Girgsdies, R. Weimann, Main Group Met. Chem. 19 (1996) 331.
[34] J.S. Waugh, R.W. Fessenden, J. Am. Chem. Soc. 79 (1957) 846.
[35] C.E. Keller, R.J. Petitt, Am. Chem. Soc. 88 (1966) 604.