Comments on Inorganic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455155

The Trimetallic Structural Motif in Group 13 Chemistry

David A. Atwood[a]; Drew Rutherford[a]
[a] Center for Main Group Chemistry, Department of Chemistry, North Dakota State University, Fargo, North Dakota

To cite this Article Atwood, David A. and Rutherford, Drew(1996) 'The Trimetallic Structural Motif in Group 13 Chemistry', Comments on Inorganic Chemistry, 19: 1, 25 — 45
To link to this Article: DOI: 10.1080/02603599608032726
URL: http://dx.doi.org/10.1080/02603599608032726

The Trimetallic Structural Motif in Group 13 Chemistry

DAVID A. ATWOOD and DREW RUTHERFORD
Center for Main Group Chemistry,
Department of Chemistry,
North Dakota State University,
Fargo, North Dakota 58105

Received April 26, 1996

In the context of this Comment, a trimetallic complex will be defined as one in which three group 13 metals are contained in one complex by either one or two multidentate ligands. This motif has been observed sporadically in the literature throughout the years. Up until the present work, however, this unique structural arrangement has not been the focus of a systematic study. This Comment will comprise a discussion of such complexes, focusing on those employing the Salan class of ligands.

Members of the Salan class of tetradentate ($-N_2O_2$) ligand, N,N′-bis(*o*-hydroxybenzyl)-1,2-diaminoethane ($SaleanH_4$), N,N′-bis(*o*-hydroxybenzyl)-1,3-diaminopropane ($SalpanH_4$), N,N′-bis(*o*-hydroxybenzyl)-1,2-diaminobenzene ($SalophanH_4$), N,N′-bis(*o*-hydroxybenzyl)-1,2-diamino(4,5-dimethyl)benzene ($SalomphanH_4$), form unique, monomeric trimetallic complexes when combined with three equivalents of MR_3 (where M = Al, Ga; R = Me, Et, ^{t}Bu). The aluminum complexes form cis ligand complexes with Salpan, Salophan and Salomphan and trans complexes when Salean is employed. However, when the Salean ligand is used with $^t Bu_3Al$, a sterically congested cis complex results. By way of contrast, the gallium derivatives adopt trans geometries in every case. A general feature of these compounds is the presence of a rigid solution state geometry as evidenced by the ^{1}H NMR. The presence of a shielding interaction between the protons on the alkyl group 13 reagent and the aryl amine backbones of the Salophan and Salomphan ligands will be discussed.

Key Words: *trimetallic, aluminum, gallium, x-ray structure*

Comments Inorg. Chem.
1996, Vol. 19, No. 1, pp. 25–45
Reprints available directly from the publisher
Photocopying permitted by license only

INTRODUCTION

Tetradentate Schiff base molecules, known generally as $SalenH_2$ (Fig. 1a), have had a long and continuing history with the transition metal elements.[1] To a lesser extent, main group element complexes with these ligands have also been prepared. For instance, there have been reports of Salen complexes with zinc,[2] aluminum alkyls[3] and alkoxides,[4] and gallium alkyls.[5] More recently, these ligands have been used to prepare a new class of aluminum cations which demonstrate catalytic activity for the oligomerization of oxiranes.[6]

The reduced form of the Salen ligand (Fig. 1b) should also be useful in the formation of unique main group element complexes. These are the $SalanH_4$ class of ligands (N,N′-bis(*o*-hydroxybenzyl)-1,2-diamino alkyl or aryl).[7] They not only offer greater flexibility than the Schiff base analogs, but also possess two additional sites capable of sigma bonding. For example, the first monoligated aluminum anions were prepared using this class of ligand.[8] Moreover, these ligands have been used to support a series of transition metal complexes which undergo unusual reactivity with molecular oxygen.[9]

The most systematically explored compounds employing the Salan ligands (Fig. 2) are the trimetallic group 13 derivatives[10] which are the subject of this Comment. They provide a unique opportunity to explore the trimetallic motif in group 13 chemistry. Trimetallic complexes have been reported sporadically throughout the literature since the mid 1970's. The pioneering work in this area involved the synthesis and structural characterization of the complex, $HAl[(EtN(CH_2)_2NEt)AlH_2]_2$ (Fig. 3(a)).[11] In recent years another diamine complex, $MeAl[(HN(CH_2)_2NH)AlMe_2]_2$ (Fig. 3(b)),[12] and a series of diol derivatives, one example

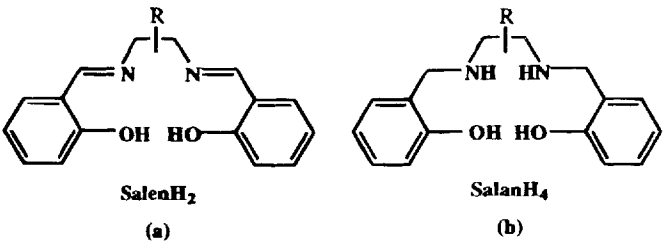


FIGURE 1 The Salen (a) and Salan (b) classes of ligands.

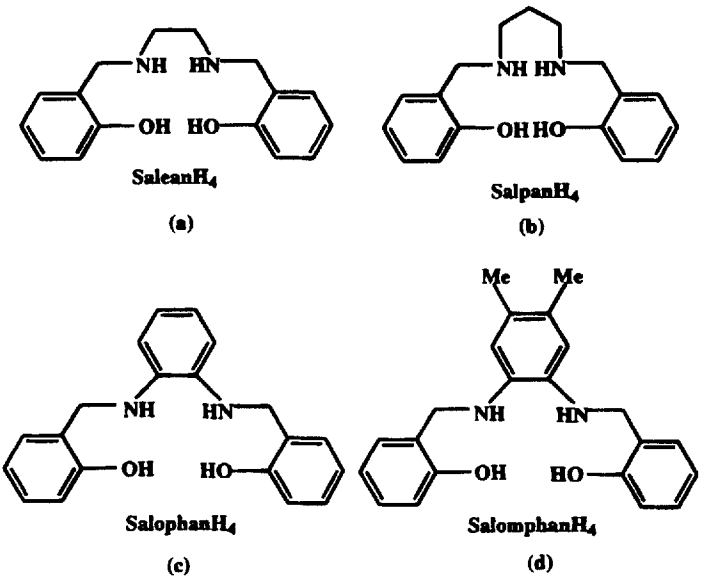


FIGURE 2 General depiction of the $SalanH_4$ ligands described in this Comment.

of which is the bis-hydroxymethylbenzene complex, $AlMe[(C_6H_4)CH_2O)_2AlMe_2)]_2$ (Fig. 3(c)),[13] have been prepared. Furthermore, this geometry need not employ traditional ligands. This is exemplified in the structure of $ClAl[(Ph_2B_2O_3)AlCl_2]_2$ (Fig. 3(d)).[14]

We were intrigued by the appearance of this trimetallic type of structure and surprised at how few such complexes had been reported. This Comment summarizes our findings with regard to the unique properties of this type of complex.

GENERAL SYNTHESES

Aluminum. The aluminum compounds were prepared by the addition of three equivalents of aluminum trialkyl to the $SalanH_4$ ligand followed by reflux in toluene (Eq. (1)). High yields (>90%) of the trimetallics can be isolated following removal of the solvent. They are moderately air sensitive, decomposing in air on standing after several hours (Fig. 4).

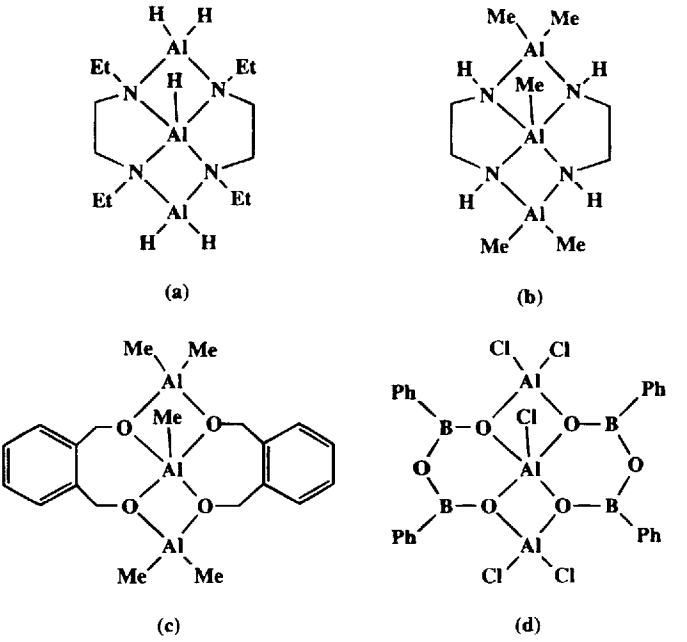


FIGURE 3 Structurally characterized examples of previously reported trimetallic aluminum complexes.

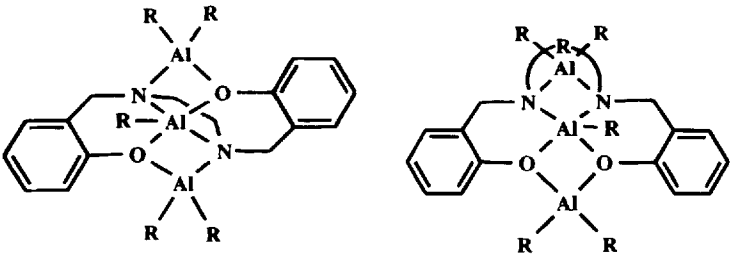


FIGURE 4 The Salan complexes of aluminum adopt both trans and cis geometries.

$$\text{SalanH}_4 + 3\text{AlR}_3 \xrightarrow[(R=Mc,Et,^{i}Bu)]{\text{Tol, } -4\text{RH}} \text{SalanAlR(AlR}_2)_2 \qquad (1)$$

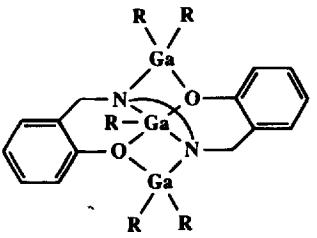
Gallium. Compared to aluminum much less chemistry has been reported for gallium. This is primarily due to the relatively lower abundance of gallium. It has an abundance of 0.015 g/kg in the earth's crust compared to 82 g/kg for aluminum.[15] However, the two elements are actually very similar to one another. Thus, it was of interest to see what differences may exist between them in conjunction to the Salan ligands.

The gallium derivatives were prepared by the exothermic reaction of the respective SalanH_4 ligand with trialkyl gallium in a 1:3 stoichiometry in a manner similar to the procedure used for the aluminum complexes (Eq. (2)). Likewise, the gallium complexes were also stable in air for a few hours. The products were isolated in yields of ≥92% (Fig. 5).

$$\text{SalanH}_4 + 3\text{GaR}_3 \xrightarrow[(R=Me,Et)]{\text{Tol, } -4\text{RH}} \text{SalanGaR(GaR}_2)_2 \qquad (2)$$

SPECTROSCOPIC TRENDS

Rigid Solution State Geometries. For each compound the ^{1}H NMR data revealed a complex pattern of coupling indicative of a rigid solution state geometry. A hallmark of this behavior is the presence of two doublets which can be assigned to the PhCH_2 groups. In this interpretation, each of the methylene groups are equivalent, while the protons within the



Salan = Salean, R = Me, Et
Salpan, Me, Et
Salophan, Me, Et
Salomphan, Me, Et

FIGURE 5 The Salan complexes of gallium adopt trans geometries.

methylene group are inequivalent as an AB spin system, giving rise to the two doublets.

The alkyl backbones of the complexes also demonstrate a complex pattern of coupling. Examples are shown in Figs. 6A and 6B for SaleanAlMe($AlMe_2$)$_2$ and SalpanAlMe($AlMe_2$)$_2$, respectively. In Fig. 6A the N–CH_2 resonances result in two doublets centered at δ 2.51 and 2.81 ppm. In Fig. 6B the propyl resonances were manifested as multiplets at δ 1.15 and 2.15 ppm for the $NCH_2C\underline{H}_2$ group and as multiplets at δ 2.59 and 2.94 ppm for the $NC\underline{H}_2CH_2$ groups.

In the absence of sterically encumbered groups on Al or Ga the Salean ligand always adopts a trans geometry. This allows the methylene groups to adopt an energetically more favored staggered geometry. In the cis conformation these groups will be eclipsed. The chief difference between the cis and trans geometries lies in the disposition of the $AlMe_2$ groups. In the trans geometry these groups give rise to two ^{1}H NMR resonances, indicating the symmetrical bridging of a nitrogen and oxygen atom by each aluminum. In the cis geometry, however, these groups are manifested as four distinct resonances. There are two for the $AlMe_2$ bridging the oxygens and two for the bridging group on the nitrogens. There are also two resonances in the ^{27}Al NMR spectrum of these compounds. One corresponds to the central five-coordinate Al which is assigned to the resonances in the range δ 50–77 ppm and the other to the peripheral four-coordinate Al atoms assigned to the resonances in the range δ 147–220 ppm. The ^{1}H NMR spectrum for SalomphanAlEt($AlEt_2$)$_2$ is shown in Fig. 7.

SalenAl^{i}Bu(Al^iBu_2)$_2$ is an exception to the general trend of trans structures for the Salean ligand. The spectroscopic data indicated that the ligand adopted a cis geometry. There were five resonances which could be attributed to the ^{i}Bu groups, indicating that all of the ^{i}Bu groups are inequivalent. Its formation may be attributed to the presence of the relatively more sterically demanding ^{i}Bu groups (compared to Me and Et). In the cis conformation one AlR_2 unit bridges the two oxygens, one bridges the two nitrogens, and one is five-coordinate in the center of the ligand. This gives rise to five sets of Al-R resonances in the ^{1}H NMR.

Like the aluminum compounds, the gallium derivatives also maintain a rigid solution state geometry. However, for the gallium complexes, the disposition of the alkyl amine backbone was determined to be trans by the ^{1}H NMR data. In this configuration the gallium-alkyl

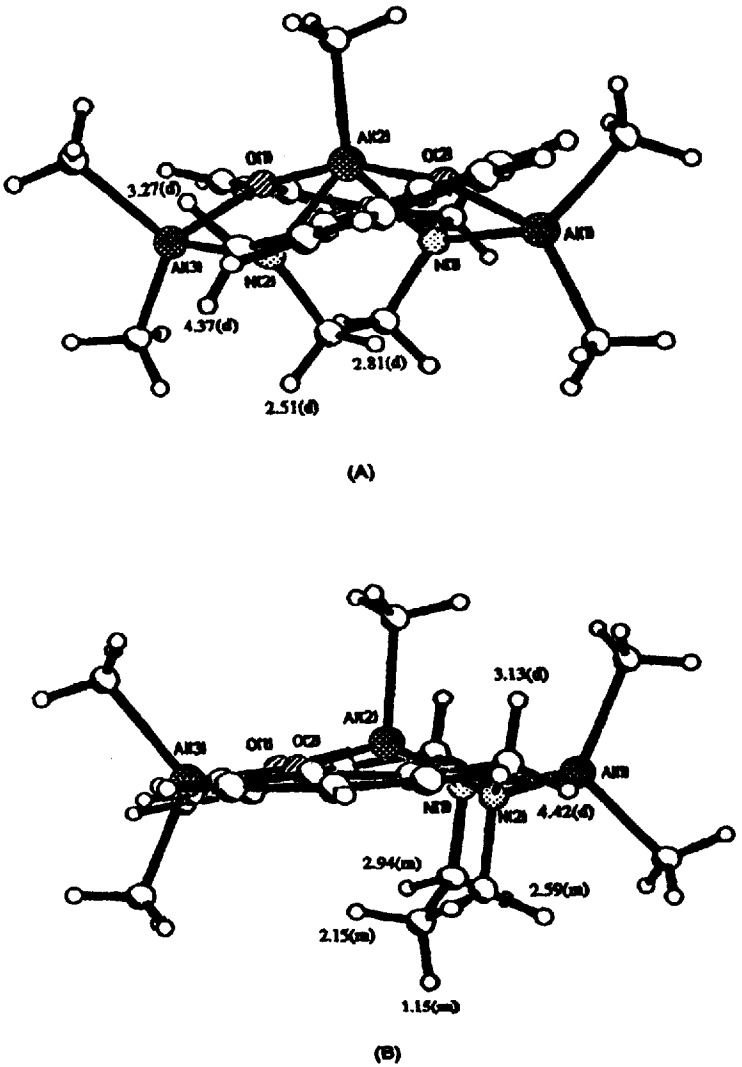


FIGURE 6 Side views and selected ^{1}H NMR assignments for SaleanAlMe($AlMe_2$)$_2$ and SalpanAlMe($AlMe_2$)$_2$.

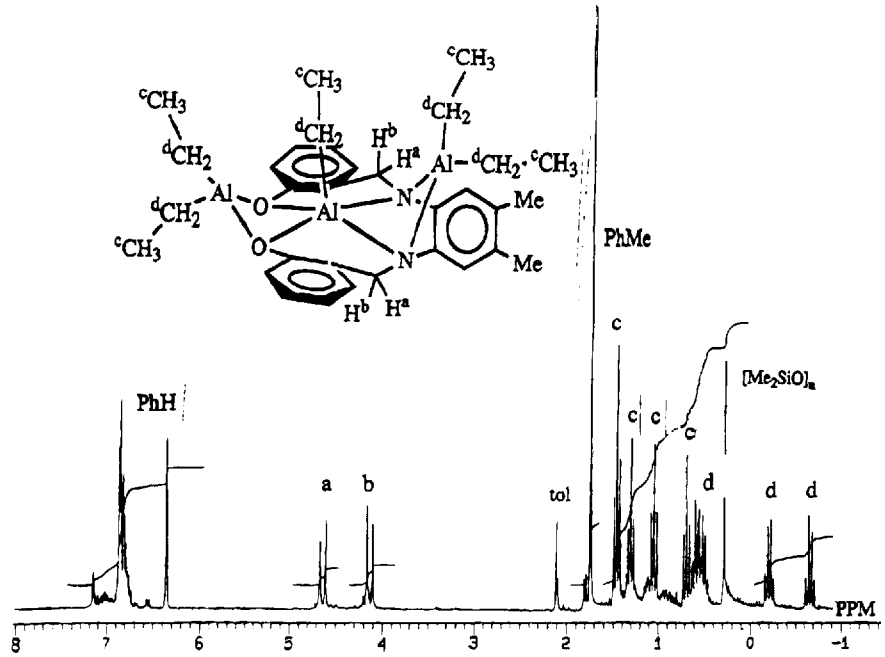


FIGURE 7 ^{1}H NMR spectrum of SalomphanAlEt($AlEt_2$)$_2$ with chemical shift assignments.

groups were manifested as a series of three singlets (for GaMe) and three pairs of multiplets (for Ga-Et) in the region δ 0.6 to – 0.4 ppm. A representative ^{1}H NMR spectrum for the trans geometry is shown in Fig. 8 for SalpanGaMe$(GaMe_2)_2$. A rationale for the difference in structural types can be derived from the X-ray structural data (see below).

We were interested to see if the SalanMR$(MR_2)_2$ (M = Al, Ga; R = Me, Et) molecules would undergo exchange of either the metal-alkyl units or the individual alkyl groups in solution. In order to test this, three types of reactions were examined. In the first, equimolar amounts of SalpanGaMe$(GaMe_2)_2$ and SalpanAlMe$(AlMe_2)_2$ were mixed together in toluene and then stirred at 25°C for 8 h (Eq. (3)). Analysis by ^{1}H NMR of the solid remaining after solvent removal indicated that each of the reagents were unchanged from the mixing. The second and third reactions were directed at the possibility of exchange of the alkyl groups between Ga atoms and were conducted in situ in 5 mm NMR tubes. Thus, the trimetallic derivatives SalpanGaMe$(GaMe_2)_2$ and SalpanGaEt$(GaEt_2)_2$ were mixed in C_6D_6 at 25°C and stirred for two hours (Eq. (4)).

$$\begin{aligned}&\text{SalpanGaMe}(GaMe_2)_2\\&+\text{SalpanAlMe}(AlMe_2)_2 \xrightarrow[\text{Tol}]{25^\circ\text{C}} \text{No Reaction}\end{aligned} \tag{3}$$

$$\begin{aligned}&\text{SalpanGaMe}(GaMe_2)_2\\&+\text{SalpanGaEt}(GaEt_2)_2 \xrightarrow[C_6D_6]{25^\circ\text{C}} \text{No Reaction}\end{aligned} \tag{4}$$

$$\text{SalpanGaMe}(GaMe_2)_2 + GaEt_3 \xrightarrow[C_6D_6]{25^\circ\text{C}} \text{No Reaction} \tag{5}$$

Similarly, the GaMe complex was mixed with a fifty-fold excess of $GaEt_3$ and stirred for two hours. The NMR spectra of these mixtures were comprised of well-defined resonances which could be attributed to unchanged starting materials (Eq. (5)). These experiments served to indicate that compounds of this type are non-fluxional and non-dissociative at 25°C in aryl solvents.

Although such rigid solution state geometries are uncommon for the heavier main group elements, a similar solution state geometry was found for the trimetallic diol derivatives, $[R(O)_2]_2AlMe(AlMe_2)_2$.[13] The

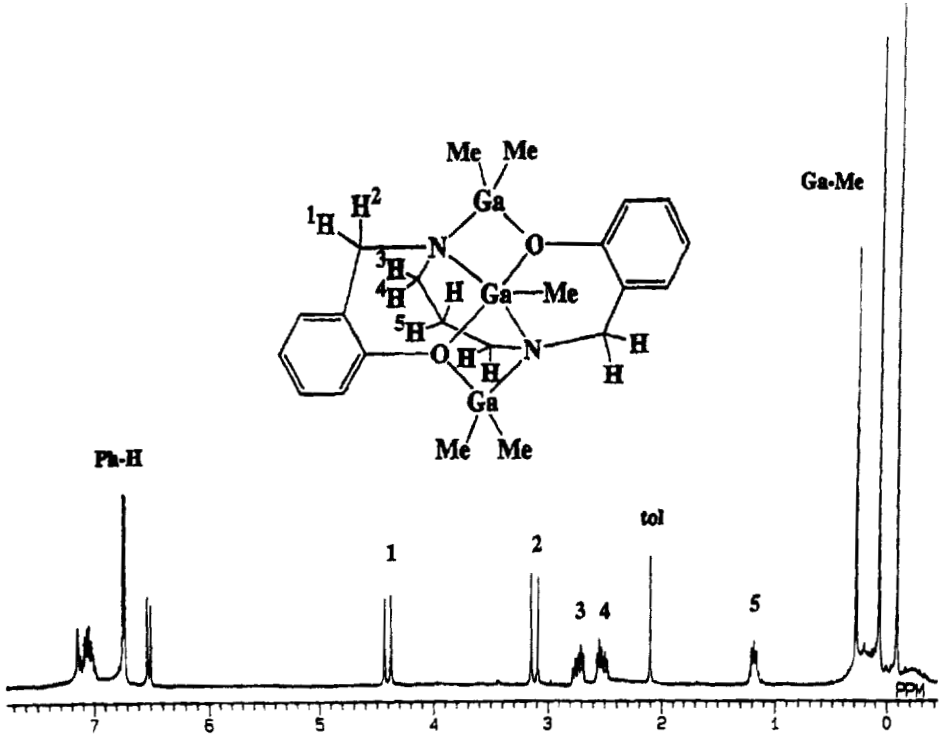


FIGURE 8 ^{1}H NMR spectrum of SalpanGaMe($GaMe_2$)$_2$ with chemical shift assignments.

methylene protons in these systems also appear as a set of two doublets. When two ligands are used to form this type of trimetallic complex, they exercise a symmetric influence on the Al-Me groups. Thus, they appear as two singlets, one set for the terminal $AlMe_2$ groups and one set for the central AlMe group. In the Salan systems the ligand is asymmetric with respect to the three aluminum locations. Thus, these resonances appear as either three singlets (for the trans conformation) or five singlets (for the cis conformation).

Ring Current Effects. Interestingly, the complexes possessing an aryl amine backbone demonstrate two resonances that are shifted further upfield to that demonstrated for complexes possessing an alkyl amine backbone. This can be attributed to a ring current effect between the aryl group and the terminal alkyl group 13 moiety. 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.[16] 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.[17] Similarly, the differences between the two methyls of the terminal $GaMe_2$ groups for SalophanGaMe$(GaMe_2)_2$ and SalomphanGaMe$(GaMe_2)_2$ are $\Delta\delta$ 0.85 and 0.78 ppm, respectively (Table III). The closest contact between the hydrogens of this methyl group and the centroid of the aryl ring is in the range 2.82–3.19 Å. Due to the trans orientation of the ligand, only one set of resonances are observed for each molecule. However, the distances differ slightly in the solid state. When the ligand is in the cis conformation, there are two inequivalent sets of terminal M-Me resonances (as shown in Table III for SalophanAlMe$(AlMe_2)_2$). This contact is maximized when the proton is centered above the aryl group. Thus, the angle that the C–H bond makes with the plane of the aryl group is 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 are oblique and consequently the shift is not as pronounced. A view accentuating these two angles is shown in Fig. 9 for SalophanGaMe$(GaMe_2)_2$. By comparison, the angles for Salophan-AlMe$(AlMe_2)_2$ more closely approach 90° and the shift differential is correspondingly larger ($\Delta\delta$ 1.00 ppm) (Table III).

TABLE I

Selected NMR data (ppm) for the aluminum compounds.

	^1H				^{27}Al ($w_{1/2}$)	
Compound	$PhCH_2$	NCH_2	NCH_2CH_2	$AlCH_3$	Al(central)	$AlMe_2$
Salean$AlMe(AlMe_2)_2$	3.27	2.51	–	−0.66 to	55	185
	4.37	2.81		−0.28	(6770)	(9374)
Salean$AlEt(AlEt_2)_2$	3.42	2.52	–	0.21 to	69	162
	4.37	2.81		1.72	(5200)	(5400)
Salean$Al^iBu(Al^iBu_2)_2$	3.55	2.52	–	0.17 to	65	180
	4.44	2.98		2.45	(8200)	(30000)
Salpan$AlMe(AlMe_2)_2$	3.13	2.59	1.15	−0.41 to	85	185
	4.42	2.94	2.15	−0.10	(3126)	(9374)
Salpan$AlEt(AlEt_2)_2$	3.27	2.65	~1.15	0.13 to	77	175
	4.50	2.95	2.18	1.56	(3120)	(14560)
Salpan$Al^iBu(Al^iBu_2)_2$	3.38	2.75	~1.15	0.21 to	50	160
	4.57	3.02	~2.15	2.46	(7200)	(25000)
Salophan$AlMe(AlMe_2)_2$	3.89	–	–	−1.22 to	66	182
	4.70			−0.11	(3645)	(16143)
Salophan$AlEt(AlEt_2)_2$	4.04	–	–	−0.73 to	71	159
	4.60			1.48	(5200)	(15700)
Salophan$Al^iBu(Al^iBu_2)_2$	4.16	–	–	−0.89 to	55	190
	4.69			2.31	(7100)	(35000)
Salomphan$AlMe(AlMe_2)_2$	4.00	–	–	−1.25 to	60	147
	4.53			−0.10	(5208)	(2083)
Salomphan$AlEt(AlEt_2)_2$	4.13	–	–	−0.66 to	67	157
	4.63			1.46	(6760)	(15600)
Salomphan$Al^iBu(Al^iBu_2)_2$	4.23	–	–	−0.94 to	55	220
	4.71			2.38	(6500)	(32000)

TABLE II

Selected ^1H NMR data for the gallium compounds.

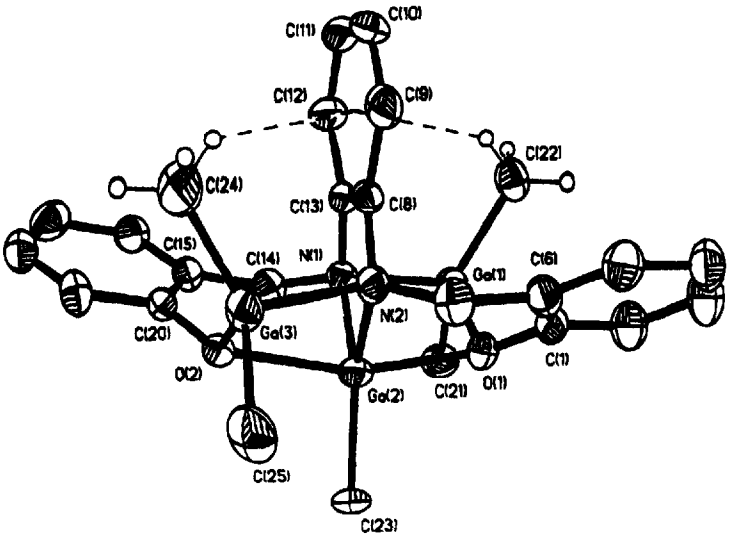
	^1H			
Compound	GaR	NCH_2CH_2	NCH_2	$PhCH_2$
SaleanGaMe$(GaMe_2)_2$	– 0.25, 0.03, 0.20	–	2.40, 2.92	3.33, 4.46
SaleanGaEt$(GaEt_2)_2$	– 0.22– 0.99 1.16 –1.23	–	2.47, 2.96	3.51, 4.58
SalpanGaMe$(GaMe_2)_2$	– 0.10, 0.07, 0.29	1.18	2.53, 2.72	3.12, 4.40
SalpanGaEt$(GaEt_2)_2$	– 0.47– 0.88 1.20 –1.48	0.95 –1.07	2.61, 2.78	3.31, 4.53
SalophanGaMe$(GaMe_2)_2$	– 0.72, 0.13, 0.53	–	–	3.94, 4.62
SalophanGaEt$(GaEt_2)_2$	– 0.19 – 0.10 0.40–1.50	–	–	4.13, 4.74
SalomphanGaMe$(GaMe_2)_2$	– 0.62, 0.16, 0.56	–	–	3.96, 4.64
SalomphanGaEt$(GaEt_2)_2$	– 0.16 – 0.02 0.43 –1.52	–	–	4.18, 4.76

TABLE III

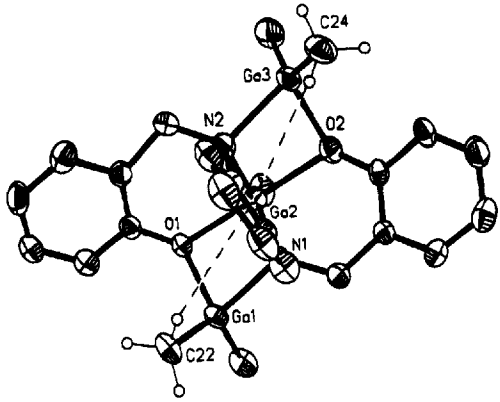
Comparison of chemical shifts resulting from the ring current effects of the salan ligands possessing an arylamine backbone.

Compound (Contact)	Shift (ppm)[a]	Distance (Å)	Angle-1 (deg)[b]	Angle-2[c]
SalophanAlMe($AlMe_2$)$_2$	0.80	2.97	90.8	64.5
(Al– CH_3···Ph)	1.00	3.03	92.5	97.7
SalophanAlEt($AlEt_2$)$_2$	0.80	no structure available		
(Al– CH_2···Ph)	1.23			
SalophanAl^{i}Bu(Al^{i}Bu$_2$)$_2$	0.95	no structure available		
(Al– CH_2···Ph)	1.41			
SalomphanAlEt($AlEt_2$)$_2$	0.74	no structure available		
(Al– CH_2···Ph)	1.19			
SalomphanAl^{i}Bu(Al^{i}Bu$_2$)$_2$	0.89	no structure available		
(Al– CH_2···Ph)	1.45			
SalophanGaMe($GaMe_2$)$_2$	0.85	2.82	72.6	82.1
(Ga – CH_3···Ph)		2.93	65.3	81.4
SalomphanGaMe($GaMe_2$)$_2$	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 shielded group from that of the unaffected group on the same metal.
[b]Vertical displacement from ring centroid (ideal = 90°). An example of this angle is given in Fig. 9a.
[c]Lateral displacement from ring centroid (ideal = 90°). An example of this angle is given in Fig. 9b.



(a)



(b)

FIGURE 9 Views accentuating the vertical (a) and lateral (b) angles formed by the methyl hydrogen and the plane of the aryl ring.

STRUCTURAL CHARACTERIZATION

Aluminum. An X-ray crystallographic study of several of the aluminum derivatives was undertaken in order to correlate the proposed solution state structures with the solid state. Representative structures are shown in Figs. 10–13. In the structure of SaleanAlMe$(AlMe_2)_2$, the Salean ligand is coordinated in a tetradentate fashion to a central AlMe unit which is in a distorted trigonal-bipyramidal geometry (Fig. 10). In this geometry, the oxygen atoms are located at the axial positions and the nitrogens and methyl carbon in equatorial positions. All of the bond angles are distorted from ideal. However, the most significant deviations occur for the N–Al–C angles. This may be explained by the fact that the ligand is distorting towards a square-pyramidal geometry wherein the oxygen and nitrogens form the basal plane. Through one oxygen and one nitrogen atom the ligand also acts as a bidentate chelate for the two peripheral $AlMe_2$ groups which adopt distorted tetrahedral geometries. The ethylene group of the ligand and the central Al-Me are oriented trans to one

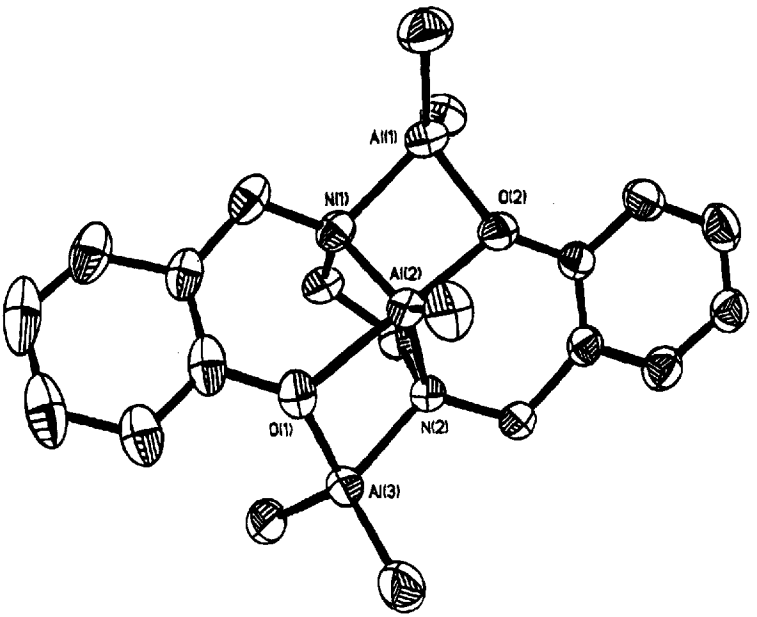


FIGURE 10 Molecular structure and atom numbering scheme for SaleanAlMe$(AlMe_2)_2$.

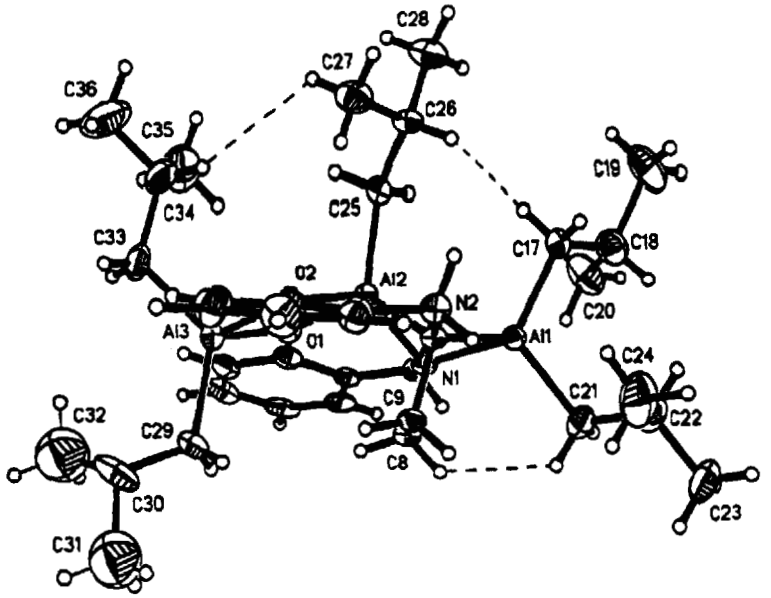


FIGURE 11 Molecular structure and atom numbering scheme for SaleanAliBu(AliBu$_2$)$_2$.

another to reduce steric interactions. In keeping with the electronegativity difference between oxygen and nitrogen, the Al–O bond distances for these atoms are somewhat shorter than the Al–N distances. However, for Al(2) the opposite trend is observed. The oxygen atoms are occupying the axial positions of the trigonal bipyramid.

As was stated earlier you can usually count on obtaining a trans structure with the Salean ligand. However, this trend breaks down when exceptionally bulky alkyl groups are employed on aluminum. One example, Salean$Al^iBu(Al^iBu_2)_2$, is shown in Fig. 11. The dotted lines show the points of closest intramolecular contact. These are on the order of 2.8 Å. Moreover, the hydrogen atoms on C8 and C9 are clearly in an energetically unfavorable eclipsed geometry. Another example of a cis conformation occurs in the SaleanH_2Sn complex.[18] However, the relatively larger size of the tin atom leads to a wider N–N separation which, in turn, removes the possibility of eclipsing for the methylene groups.

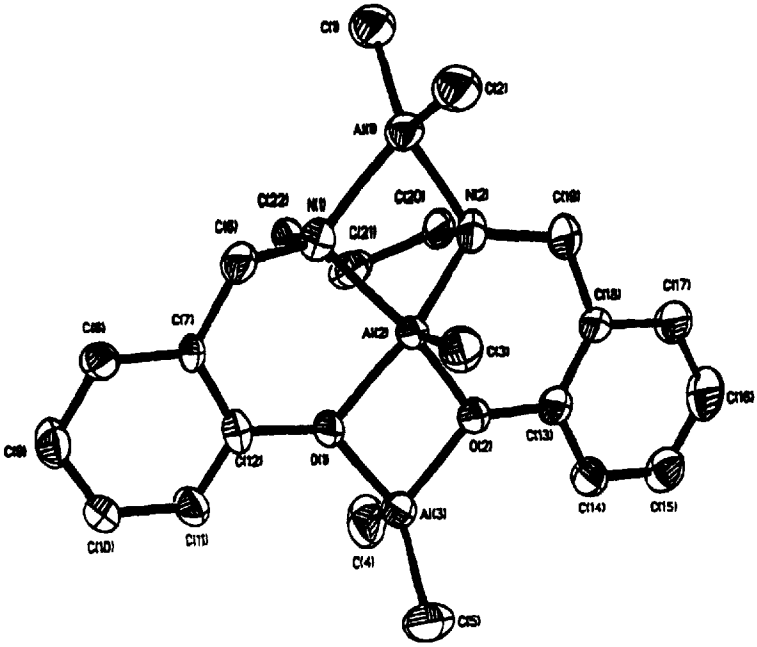


FIGURE 12 Molecular structure and atom numbering scheme for SalpanAlMe($AlMe_2$)$_2$.

In the structure of SalpanAlMe($AlMe_2$)$_2$ the tendency for the central aluminum to adopt a square-pyramidal geometry is realized (Fig. 12). The ligand now occupies the basal plane while the methyl group the apical position. This is the type of structure that is observed, in general, for all of the other aluminum complexes.

Some structures similar to that seen above have been observed for the bidentate alkyl amine complexes, $HAl[(EtN(CH_2)_2NEt)AlH_2]_2$ and $MeAl[(HN(CH_2)_2NH)AlMe_2]_2$. It is interesting to note that in the tridentate open-chain amine complexes, $[(MeAl)_2C_8H_{20}N_6](AlMe_2)_2$[19] and $[(MeAl)_2C_{12}H_{28}N_6](AlMe_2)_2$,[20] the central five-coordinate Al atoms also adopt trigonal-bipyramidal geometries.

Gallium. Despite the relatively small size difference between aluminum and gallium (0.62 and 0.69 Å for five-coordinate atoms, respectively), the gallium complexes form just one type of structure with the Salan ligands. In each structure the ligand adopts a trans orientation with respect to the location of the nitrogen and oxygen atoms. In this confor-

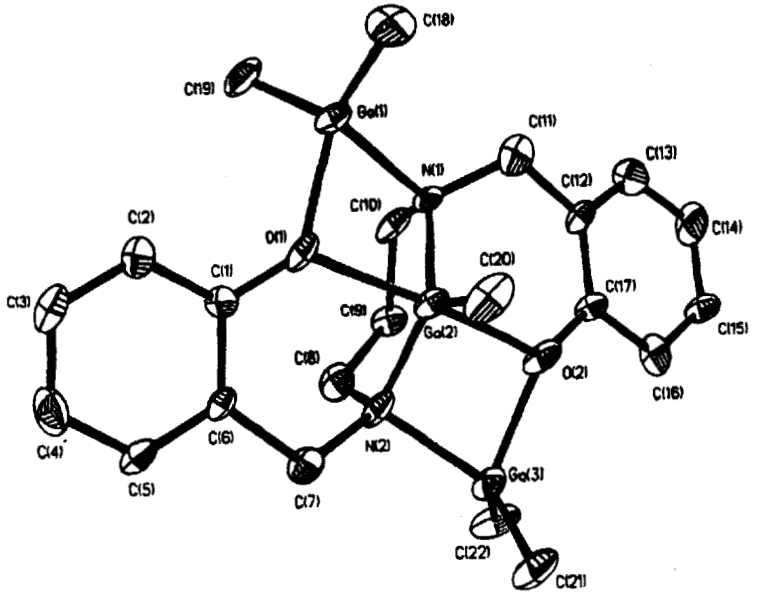


FIGURE 13 Molecular structure and atom numbering scheme for SalpanGaMe-$(GaMe_2)_2$.

mation each of the GaR_2 units bridge both a nitrogen and oxygen atom. This corresponds to that seen in the structure of SaleanAlMe$(AlMe_2)_2$. Two arguments may be used to reconcile the difference in bonding between Al and Ga. Although five-coordinate Ga(III) and Al(III) have very similar ionic radii, Ga is still 0.07 Å larger. If the ligand is such that there is very little energy difference between the tbp and sp geometries this difference in size may be enough to cause the transition to tbp geometry.

However, there may also be a tendency for Al and Ga to adopt different geometries. For instance, in SalpanAlMe$(AlMe_2)_2$ the N and O atoms form a square plane (maximum deviation = 0.031 Å for O(1)) above which the aluminum is located at a distance of 0.61 Å. The geometry is then distorted square pyramidal. In contrast, the geometry for the central gallium in SalpanGaMe$(GaMe_2)_2$ is best described as a distorted trigonal bipyramid with O(1) and O(2) occupying the axial positions and N(1), N(2) and C(3) occupying the equatorial sites (Fig. 13). For the central Ga atom, this leads to average Ga–N bonds (1.93 Å) that are shorter than the

Ga–O bonds (2.08 Å). By comparison, the central Al atom contains average Al–N and Al–O bond distances that are 2.004 Å and 1.934 Å, respectively.

CONCLUSION

We have demonstrated that there is an interesting range of complexes that are accessible in reactions involving MR_3 and the SalanH_4 class of ligands. In general, the ligands adopt a cis orientation when bound to aluminum and a trans orientation when bound to gallium. However, trimetallic complexes employing the SaleanH_4 ligand (with the ethyl amine backbone) generally adopt a trans geometry in the absence of steric effects.

The trimetallic derivatives of general formula Salan$MR(MR_2)_2$ offer evidence for solution state rigidity. The solution state geometry of these molecules was shown by X-ray crystallography to be the same as that of the solid state. Additionally, no exchange occurs upon mixing various trimetallic derivatives.

The trimetallic aluminum and gallium complexes formed using either SalophanH_4 or SalomphanH_4 demonstrate unusual chemical shifts due to ring current effects. The largest shift was observed to be δ 1.00 ppm at a distance of 2.9 Å.

FUTURE DIRECTIONS

Trimetallic complexes of aluminum have been prepared with a number of chelating ligands. These include diaminoethanes,[11,12] aryl and alkyl diols,[13] and the Salan ligands.[10] These have as a common feature the use of nitrogen and oxygen binding sites and the formation of predominantly five-membered chelate rings upon complexation. Aluminum has been the most extensively examined of the group 13 elements. With regards to the SalanH_4 ligands gallium also readily forms trimetallic derivatives. Thus far, no such complexes incorporating indium have been prepared.

Other derivatives featuring this structural morphology should be accessible in conjunction to aluminum and gallium. For instance, organic molecules such as aromatic and alkyl diols, diamines and diphosphines should be of utility in this context.

Acknowledgments

Gratitude is expressed to the National Science Foundation (NSF-OSR-9452892) and the donors of the Petroleum Research Fund (Grant 30057-G3), administered by the American Chemical Society, for support. The receipt of an NSF-CAREER award is also gratefully acknowledged (1996–2000).

References

1. (a) R. H. Holm, G. W. Everett, Jr. and A. Chakravorty, Progress in Inorganic Chemistry, **7**, 83 (1966); (b) M. D. Hobday and T. D. Smith, Coord. Chem. Rev. **9**, 311 (1972).
2. (a) D. Hall and F. H. Moore, Proc. Chem. Soc. 256 (1960); (b) M. J. O'Connor and B. O. West, Aust. J. Chem. **20**, 2077 (1967).
3. S. J. Dzugan and V. L. Goedken, Inorg. Chem. **25**, 2858 (1986).
4. P. L. Gurian, L. K. Cheatham, J. W. Ziller and A. R. Barron, J. Chem. Soc. Dalton Trans. 1449 (1991).
5. K. S. Chong, S. J. Rettig, A. Storr and J. Trotter, Can. J. Chem. **55**, 2540 (1977).
6. (a) D. A. Atwood, J. A. Jegier and D. Rutherford, J. Am. Chem. Soc. **117**, 6779 (1995); (b) D. A. Atwood, J. A. Jegier and D. Rutherford, Inorg. Chem. **35**, 63 (1996).
7. D. A. Atwood, J. Benson, J. A. Jegier, N. F. Lindholm, K. J. Martin and D. Rutherford, Main Group Chem. **1**, 99 (1995).
8. D. A. Atwood and D. Rutherford, Inorg. Chem. **34**, 4008 (1995).
9. (a) S. F. Gheller, T. W. Hambley, M. R. Snow, K. S. Murray and A. G. Wedd, Aust. J. Chem. **7**, 911 (1984); (b) A. Bottcher, H. Elias, E.-G. Jager, H. Langfelderova, M. Mazur, L. Muller, H. Paulus, P. Pelikan, M. Rudolph and M. Valko, Inorg. Chem. **32**, 4131 (1993); (c) D. A. Atwood, J. A. Jegier, N. F. Lindholm, K. J. Martin and D. Rutherford, J. Coord. Chem. **38**, 305 (1996).
10. (a) D. A. Atwood, J. A. Jegier, K. J. Martin and D. Rutherford, Organometallics **14**, 1453 (1995); (b) D. A. Atwood and D. Rutherford, Organometallics **14**, 2880 (1995); (c) D. A. Atwood and D. Rutherford, Organometallics **14**, 3988 (1995).
11. G. Perego, G. Del Piero, M. Corbellini and M. Bruzzone, J. Organomet. Chem. **136**, 301 (1977).
12. Z. Jiang, L. V. Interrante, D. Kwon, F. S. Tham and R. Kullnig, Inorg. Chem. **30**, 995 (1991).
13. (a) S. Pasynkiewicz and W. Ziemkowska, J. Organomet. Chem. **423**, 1 (1992); (b) S. Pasynkiewicz and W. Ziemkowska, J. Organomet. Chem. **437**, 99 (1992); (c) W. Ziemkowska, S. Pasynkiewicz and E. Kalbarczyk, J. Organomet. Chem. **465**, 93 (1994).
14. R. Koster, K. Angermund, J. Serwatowski and A. Sporzynski, Chem. Ber. **119**, 1301 (1986).
15. J. P. Riley and R. Chester, *Introduction to Marine Chemistry* (Academic, New York, 1971).
16. J. S. Waugh and R. W. Fessenden, J. Am. Chem. Soc. **79**, 846 (1957).
17. C. E. Keller and R. Petitt, R. J. Am. Chem. Soc. **88**, 604 (1966).
18. D. A. Atwood, J. A. Jegier, K. J. Martin and D. Rutherford, J. Organomet. Chem. **503**, C4 (1995).
19. G. H. Robinson and S. A. Sangokoya, J. Am. Chem. Soc. **109**, 6852 (1987).
20. G. H. Robinson, F. Moise, W. T. Pennington and S. A. Sangokoya, Polyhedron **8**, 127 (1989).