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Bimetallic mixed-metal complexes of the salen(^{t}Bu) ligands

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Abstract—The Salen(^{t}Bu) ligands, Salen(^{t}Bu), (N,N′-ethylenebis(3,5-di-*tert*-butylsalicylideneimine) and Salpen(^{t}Bu), (N,N′-propylenebis(3,5-di-*tert*-butylsalicylideneimine) can be combined with $GaEt_3$ to prepare the 'open' monometallic compounds, Salen(^{t}Bu)H($GaEt_2$) (**1**) and Salpen(^{t}Bu)($GaEt_2$) (**2**). These, in turn, can be converted to the bimetallic derivatives, Salen(^{t}Bu)($GaEt_2$)$_2$ (**3**) and Salpen(^{t}Bu)($GaEt_2$)$_2$ (**4**) by addition of $GaEt_3$. Alternatively, **3** and **4** can be made by the addition of two moles of $GaEt_3$ to the appropriate ligand. This was the method used to prepare Salben(^{t}Bu)($GaEt_2$)$_2$ (**5**) (Salben(^{t}Bu) = N,N′-butylenebis(3,5-di-*tert*-butylsalicylideneimine) and Salhen(^{t}Bu)($GaEt_2$)$_0$ (**6**) [Salhen(^{t}Bu) = N,N′-hexylenebis(3,5-di-*tert*-butylsalicylideneimine]. Compounds **1** and **2** can be utilized to form the unique mixed-metal derivatives L($GaEt_2$)(MR_2) (where L = Salen(^{t}Bu), M : R = Al, Me (**7**); Al, Et (**9**); and L = Salpen(^{t}Bu), M : R = Al, Me (**8**); Al, Et (**10**). At ambient temperatures in non-polar solvents, **7**–**12** do not undergo exchange of either the alkyl or MR_2 groups. All of the compounds were characterized by Mp, analyses, ^{1}H NMR, IR and, in the case of **1** and **3**–**6**, by X-ray crystallography.

Keywords: Group 13; salen(^{t}Bu); bimetallic.

The Salen [1] class of ligands has been used extensively to support transition metal bonding schemes [2] and to a much lesser extent those of the main group elements. Some Group 13 examples include those incorporating aluminum [3] and gallium [4] alkyls, aluminum alkoxides [5] and aluminum cations [6]. The dominant structural motif for these complexes is one in which one metal is coordinated by all of the heteroatoms of the ligand in a planar arrangement [Fig. 1(a)]. In fact, many of the applications associated with these ligands rely upon this arrangement and the predominance of the chelate effect. For the main group elements there has historically been only one exception to this coordination mode. This is the bimetallic complex, Salpen($GaMe_2$)$_2$, which was formed using an excess of $GaMe_3$ in a heated, sealed tube reaction [4]. Unfortunately, these relatively harsh reaction conditions have given the false impression that extreme measures must be taken in order to prevent the Salen ligand from forming the monometallic chelate.

The Salen ligands have been shown to support bimetallic formulations for an alkyl borane [7] and a number of borates having the arrangement shown in Fig. 1(b) [8]. However, this is not surprising considering that boron generally does not go beyond a coordination number of four (a monomeric, fully chelated derivative would be five-coordinate). What we have recently discovered, however, is that the heavier congeners of the Group 13 elements, and in particular gallium, readily form open structures with the Salen ligands. Not only does this imply that monometallic [Fig. 1(c)] and bimetallic [Fig. 1(b)] open structures are accessible but that mixed metal derivatives may also readily be formed [Fig. 1(d)].

The potential isolation of dialkyl Group 13 derivatives having an open structure was implied in the proposed mechanism of formation of some of the first Salen-Al derivatives [3] as well as some tmtaa derivatives [9]. In this mechanism 1 equiv. of alkane is eliminated as the slow first step, followed by ring closure and elimination of a second equivalent of alkane. Under the conditions that were employed,

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† Dedicated to Prof. D. C. Bradley on the occasion of his 73rd birthday.

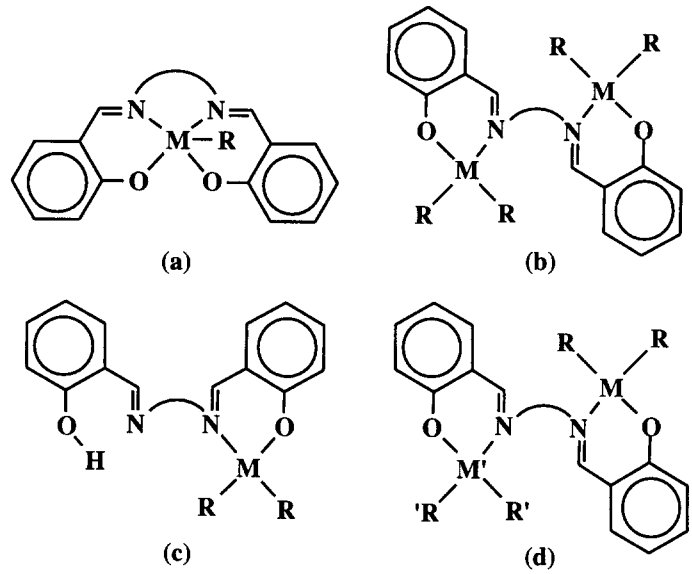
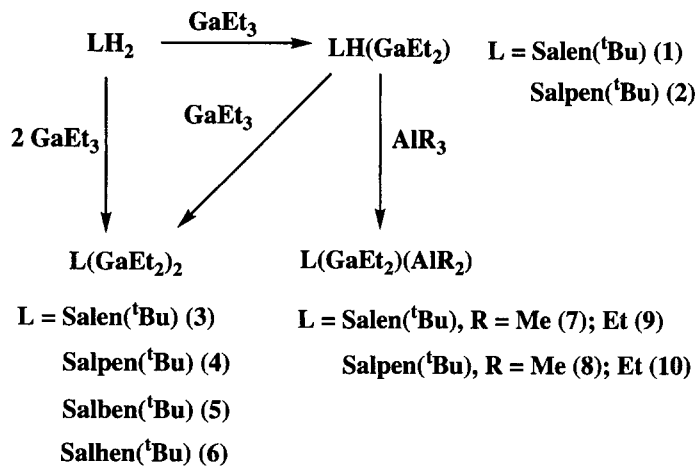


Fig. 1. General depiction of the structures that the Salen ligands adopt with the Group 13 elements.



Scheme 1. Reactions leading to the formation of **1**–**10**.

however, the Salen intermediates were not able to be isolated.

One considerable limitation in using the Salen ligands lies in the fact that they are generally insoluble when bound in a neutral complex. Occasionally, this problem can be tempered somewhat by use of the Acen ligand [Figure 2(b)]. In order to avoid solubility problems altogether we have begun investigating derivatives that feature pendant alkyl groups. One such Salen derivative is Salen('Bu)H_2 [10] which possesses tertiary butyl groups at two positions on each of the phenol rings. The present work will explore the isolation and subsequent reactions of open Salen('Bu)–gallium combinations.

RESULTS AND DISCUSSION

Synthesis and Characterization

The monometallic compounds, **1** and **2**, are prepared in high yield by the addition of $GaEt_3$ to the ligand at 25°C. They can be refluxed in toluene for up to 4 h with effecting ring closure. Under these conditions the same reaction with either aluminum [11] or indium [12] reagents leads to ring closure and formation of the five-coordinate monometallic derivatives. Thus, the R_2Ga^- unit appears to be remarkably stable in relation to the aluminum and indium derivatives. The aqueous stability of Me_2Ga^+ serves as an

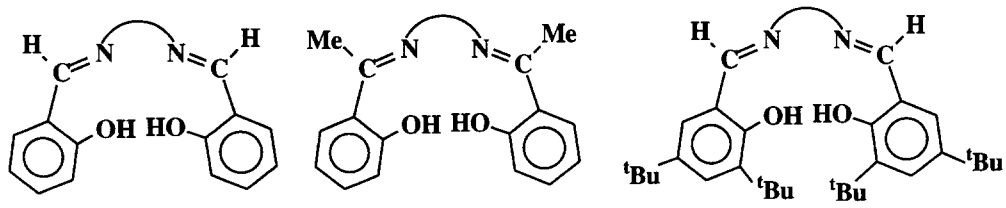


Fig. 2. General depiction of the Salen (a), Acen (b) and Salen('Bu) (c) ligands.

example of this fact [13]. The ^{1}H NMR data for **1** and **2** are consistent with an asymmetric structure in solution (Table 1). Specifically, there are two resonances for the imine (N=C*H*) groups. Addition of another mole of Et_3Ga to **1** and **2** leads to formation of the symmetric bimetallic derivatives, **3** and **4**. Alternatively, **3** and **4** (as well as **5** and **6**) can be formed by the addition of 2 moles of $GaEt_3$ to one of the ligands. Based upon the ^{1}H NMR data, these compounds are symmetric in solution. The Ga-Et resonances for **1–6** are fairly consistent and are similar to the shifts reported for other compounds containing the GaEt group such as the monometallic derivatives, LGaEt [L = Salen('Bu), Salophen('Bu) and Salomphen('Bu)] [14].

Formation of **1** or **2**, *in situ*, followed by addition of AlR_3, affords the mixed-metal derivatives, **7–10**. They are readily characterized by their distinctive ^{1}H NMR data in which there are two sets of resonances that can be ascribed to each of the MR_2 groups. The ethyls on each metal are equivalent as was seen in the homobimetallic complexes, **3–6**. There are two imine peaks (2H, total) that integrate with each set of the Ga-ethyl groups (CH_2CH_3, 6 H) in a 1 : 3 ratio. In contrast, the imine is observed as a sharp singlet for **3–6**. The CH : Me integration of 1 : 3 would also be observed if the solution consisted of a mixture of the respective bimetallic derivatives, $L(GaEt_2)_2$ and $L(AlR_2)_2$. However, in an equilibrium mixture these two species would be present with the mixed-metal as well and the ^{1}H NMR spectra would be correspondingly more complex. Thus, at ambient temperatures there is no evidence for either metal or alkyl exchange in solution **7–10**. A similar observation (that of a 'rigid' solution state geometry) has been made for Group 13 derivatives of the reduced Salen ligand, Salan [15].

Structural Characterization

A summary of data collection parameters and selected bond lengths and angles for compounds **1** and **3–6** are listed in Tables 2 and 3. In all of the structures (Figs 3–7) the gallium atoms are coordinated by the ligand and the two alkyl groups in a distorted Td geometry. Deviation from ideal angles are seen in a narrowed N—Ga—O angle and consequently widened C—Ga—C angles. According to Bent's Rule bonds to more electronegative atoms contain more *p* character [16]. Thus, the angles that the Salen ligands make are close to what would be observed in a tetraligated complex containing two heteroatoms and two alkyl functionalities. In $Me_2AlOAr(NH_2^tBu)$ [Ar = 2,6-('Bu)$_2$Ph], for instance, the O—Al—N angle is 99.2 (2)° while the C—Al—C angle is 115.9 (4)° [17]. This partially accounts for the stability of the MR_2 unit in these ligands. The Ga—O [av. = 1.92 (2) Å] and Ga—N [2.07 (3) Å] bond distances in the five-coordinate 'closed' structure of Salen('Bu)GaEt [14] the distances in **1**, and **3–6** are longer than [av. Ga—O = 1.87 (2); Ga—N = 2.02 (1) Å]. This is in keeping with the trend for larger bond lengths with increasing coordination numbers.

In bimetallic Salen borate derivatives [$L(BOR_2)_2$ (R = Me, Et)] highly ordered secondary structures are found in the packing diagrams of the compounds where L = Salben('Bu), Salpten('Bu) and Salhen('Bu). However, in **4–6** the length of the ligand backbone does not affect the packing diagrams of the compounds in any systematic way. Moreover, there are no significant deviations in the bond lengths and angles that can be correlated to the length of the ligand backbone.

EXPERIMENTAL

General considerations

All manipulations were conducted using Schlenk techniques in conjunction to an inert atmosphere glove box. All solvents were rigorously dried prior to use. NMR data were obtained on JEOL-GSX-400 and -270 instruments at 270.17 (^{1}H) MHz in $CDCl_3$ unless otherwise indicated. Chemical shifts are reported relative to $SiMe_4$ and are in ppm. Elemental analyses were obtained on a Perkin–Elmer 2400 Analyzer. Infrared data were recorded as KBr pellets on a Matheson Instruments 2020 Galaxy Series spectrometer and are reported in cm^{-1}. Both the infrared and elemental analyses for the compounds are listed in the supporting information. The reagent, 3,5-di-

Table 1. Selected ^{1}H NMR data for compounds **1**–**10**[a]

Compound	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
GaR_2	0.38 (m)	0.36 (m)	0.43 (m)	0.41 (m)	0.41 (m)	0.39 (m)	0.42 (m)	0.38 (m)	0.45 (m)	0.42 (m)
	1.06 (t)	1.05 (t)	1.09 (t)	1.08 (t)	1.04 (t)	1.05 (t)	1.10 (t)	1.07 (t)	1.04 (m)	1.07 (m)
AlR_2							−0.70 (s)	−0.74 (s)	−0.08 (s)	−0.08 (s)
									1.04 (m)	1.07 (m)
Ph-^{t}*Bu*	1.21 (s), 1.26 (s)	1.26 (s), 1.31 (s)	1.23 (s)	1.28 (s)	1.26 (s)	1.24 (s)	1.22 (s), 1.24 (s)	1.27 (s), 1.29 (s)	1.23 (s), 1.24 (s)	1.30 (s), 1.32 (s)
	1.38 (s), 1.45 (s)	1.40 (s), 1.46 (s)	1.40 (s)	1.43 (s)	1.40 (s)	1.41 (s)	1.39 (s), 1.40 (s)	1.41 (s), 1.42 (s)	1.40 (s), 1.41 (s)	1.44 (s), 1.45 (s)
N=C*H*	8.05 (s), 8.37 (s)	8.05 (s), 8.39 (s)	8.00 (s)	8.04 (s)	8.00 (s)	8.01 (s)	7.97 (s), 8.05 (s)	8.02 (s), 8.11 (s)	7.99 (s), 8.08 (s)	8.06 (s), 8.16 (s)

[a] Samples were run in $CDCl_3$ at 270 MHz.

tert-butyl-2-hydroxybenzaldehyde was prepared according to the literature [18].

Details of the crystal data and a summary of data collection parameters for the complexes are given in Table 3. Data were collected on a Siemens CCD diffractometer using graphite monochromated Mo-K_α (0.71073 Å) radiation. All calculations were performed on a PC using the Siemens software package, SHELXTL-Plus.

Synthesis of salen(^{t}Bu)HGaEt$_2$ (**1**)

A solution of $GaEt_3$ (0.32 g, 2.03 mmol) in toluene (5 cm^3) was added to a stirred solution of Salen(^{t}Bu)H$_2$ (1.00 g, 2.03 mmol) in toluene (5 cm^3) at room temperature. The initial pale yellow solution became pale green upon stirring for 5 h. Removal of the solvent *in vacuo* yielded a green solid which was recrystallized at 25°C from methanol to yield the title compound as pale green needles (0.98 g, 77%). M.p. 99–100°C. A similar procedure performed with an additional 4 h reflux yielded an identical product in similar yield. ^{1}H NMR: 3.81–3.84 (br.s, 4H, CH_2H_2), 6.80 (d, 1H, Ph-*H*), 7.05 (d, 1H, Ph-*H*), 7.36–7.40 (m, 2H, Ph-*H*).

Synthesis of salpen(^{t}Bu)HGaEt$_2$ (**2**)

This compound was synthesized by an identical procedure to that outlined above from Salpen(^{t}Bu)H$_2$ (1.00 g, 1.98 mmol) and $GaEt_3$ (0.31 g, 1.98 mmol), *in vacuo* removal of the solvent yielded the title compound as pale green solid in stoichiometric yield. M.p. 52–56°C. ^{1}H NMR: 2.06–2.12 (m, 2H, $CH_2CH_2CH_2$), 3.51–3.70 (m, 4H, $CH_2CH_2CH_2$), 6.85 (d, 1H, Ph-*H*), 7.08 (d, 1H, Ph-*H*), 7.39–7.45 (m, 2H, Ph-*H*).

Synthesis of salen(^{t}Bu)(GaEt$_2$)$_2$ (**3**)

A solution of triethyl gallium (0.64 g, 4.06 mmol) in toluene (5 cm^3) was added at room temperature to a stirred solution of Salen(^{t}Bu)H$_2$ (1.00 g, 2.03 mmol) in toluene (20 cm^3). The resulting yellow solution was stirred for 24 h at which point removal of solvent resulted in a yellow solid which was recrystallized from toluene at −30°C to yield the title compound as a pale green crystalline solid (1.44 g, 95%). M.p. 109–111°C. Subsequent recrystallisation of a small portion realized crystals suitable for X-ray analysis. ^{1}H NMR: 3.70 (s, 4H, CH_2CH_2), 6.79 (d, 2H, Ph-*H*), 7.44 (d, 2H, Ph-*H*).

Synthesis of salpen(^{t}Bu)(GaEt$_2$)$_2$ (**4**)

This compound was synthesized via similar method to that above from triethylgallium (0.31 g, 1.98 mmol) and Salpen(^{t}Bu)H$_2$, (0.50 g, 0.99 mmol), recrystallisation from hexane at −30°C yielding the title

Table 2. Selected bond distances (Å) and angles (°) for compounds **1, 3, 4, 5** and **6**

Salen('Bu)HGaEt$_2$ (**1**)

Ga(1)—N(1)	2.03 (1)	Ga(1)—O(1)	1.871 (8)
Ga(1)—C(1)	1.97 (2)	Ga(1)—C(3)	1.89 (2)

N(1)—Ga(1)—O(1)	92.3 (4)	O(1)—Ga(1)—C(3)	109.3 (7)
O(1)—Ga(1)—C(1)	110.5 (5)	C(3)—Ga(1)—C(1)	123.4 (8)
C(3)—Ga(1)—N(1)	107.7 (6)	C(1)—Ga(1)—N(1)	109.1 (6)

Salen('Bu)(GaEt$_2$)$_2$ (**3**) (one molecule only)

Ga(1)—O(1)	1.874 (5)	Ga(1)—C(35)	1.98 (1)
Ga(1)—C(33)	1.99 (1)	Ga(1)—N(1)	2.010 (6)
Ga(2)—O(2)	1.868 (5)	Ga(2)—C(37)	1.93 (1)
Ga(2)—C(39)	1.956 (9)	Ga(2)—N(2)	2.030 (6)

O(1)—Ga(1)—C(35)	107.8 (3)	O(1)—Ga(1)—C(33)	109.2 (3)
C(35)—Ga(1)—C(33)	124.1 (5)	O(1)—Ga(1)—N(1)	92.4 (2)
C(35)—Ga(1)—N(1)	111.8 (4)	C(33)—Ga(1)—N(1)	106.9 (4)
O(2)—Ga(2)—C(37)	107.0 (3)	O(2)—Ga(2)—C(39)	110.1 (3)
C(37)—Ga(2)—C(39)	127.3 (5)	O(2)—Ga(2)—N(2)	91.1 (2)
C(37)—Ga(2)—N(2)	105.2 (4)	C(39)—Ga(2)—N(2)	110.4 (4)

Salpen('Bu)(GaEt$_2$)$_2$ (**4**)

Ga(1)—O(1)	1.863 (6)	Ga(1)—C(40)	1.95 (1)
Ga(1)—C(38)	1.95 (1)	Ga(1)—N(1)	2.024 (6)
Ga(2)—O(2)	1.858 (6)	Ga(2)—C(34)	1.95 (1)
Ga(2)—C(36)	1.99 (1)	Ga(2)—N(2)	2.028 (6)

O(1)—Ga(1)—C(40)	104.7 (4)	O(1)—Ga(1)—C(38)	110.3 (4)
C(40)—Ga(1)—C(38)	126.4 (5)	O(1)—Ga(1)—N(1)	92.5 (2)
C(40)—Ga(1)—N(1)	110.0 (4)	C(38)—Ga(1)—N(1)	107.6 (4)
O(2)—Ga(2)—C(34)	107.0 (3)	O(2)—Ga(2)—C(36)	109.8 (4)
C(34)—Ga(2)—C(36)	125.7 (6)	O(2)—Ga(2)—N(2)	91.9 (3)
C(34)—Ga(2)—N(2)	109.6 (5)	C(36)—Ga(2)—N(2)	107.4 (4)

Salben('Bu)(GaEt$_2$)$_2$ (**5**) (one molecule only)

Ga(1)—O(1)	1.88 (1)	Ga(1)—C(37)	1.95 (2)
Ga(1)—C(35)	1.96 (2)	Ga(1)—N(1)	2.02 (1)
Ga(2)—O(2)	1.88 (1)	Ga(2)—C(39)	1.99 (4)
Ga(2)—C(41)	2.05(4)	Ga(2)—N(2)	2.03 (1)

O(1)—Ga(1)—C(37)	107.3 (7)	O(1)—Ga(1)—C(35)	110.2 (6)
C(37)—Ga(1)—C(35)	125.8 (8)	O(1)—Ga(1)—N(1)	90.9 (6)
C(37)—Ga(1)—N(1)	110.3 (8)	C(35)—Ga(1)—N(1)	106.7 (6)
O(2)—Ga(2)—C(39)	105 (1)	O(2)—Ga(2)—C(41)	108 (1)
C(39)—Ga(2)—C(41)	134 (2)	O(2)—Ga(2)—N(2)	91.0 (6)
C(39)—Ga(2)—N(2)	108 (1)	C(41)—Ga(2)—N(2)	102 (1)

Salhen('Bu)(GaEt$_2$)$_2$ (**6**)

Ga(1)—O(1)	1.886 (4)	Ga(1)—C(19)	1.949 (7)
Ga(1)—C(21)	1.956 (7)	Ga(1)—N(1)	2.013 (5)

O(1)—Ga(1)—C(19)	108.0 (3)	O(1)—Ga(1)—C(21)	109.9 (3)
C(19)—Ga(1)—C(21)	124.6 (3)	O(1)—Ga(1)—N(1)	91.5 (2)
C(19)—Ga(1)—N(1)	109.0 (3)	C(21)—Ga(1)—N(1)	108.8 (3)

compound as a pale green crystals suitable for X-ray analysis (0.61 g, 81%). M.p. 104–106°C. ^{1}H NMR: 2.08–2.16 (m, 2H, $CH_2CH_2CH_2$), 3.53–3.56 (m, 4H, CH_2-N), 6.86 (d, 2H, Ph–*H*), 7.48 (d, 2H, Ph–*H*), 8.04 (s, 2H, Ph-C*H*).

*Synthesis of salben('*Bu)(GaEt$_2$)$_2$ (**5**)

This compound was synthesized *via* similar method to that above from triethylgallium (0.42 g, 2.65 mmol) and Salben('Bu)H$_2$, (0.69 g, 1.33 mmol), recrys-

Table 3. Data collection and processing parameters for compounds **1**, **3**–**6**

Complex	**1**	**3**	**4**	**5**	**6**
Formula	$C_{36}H_{57}GaN_2O_3$	$C_{60}H_{99}Ga_3N_3O_3$	$C_{41}H_{68}Ga_2N_2O_2$	$C_{863}H_{105}Ga_3N_3O_3$	$C_{29}H_{45}GaNO$
Formula weight	619.56	1119.58	760.41	1161.66	493.38
Crystal size (mm)	$0.60 \times 0.50 \times 0.50$	$(0.40)^3$	$0.50 \times 0.40 \times 0.40$	$(0.40)^3$	$(0.40)^3$
Crystal system	Orthorhombic	Triclinic	Triclinic	Triclinic	Monoclinic
Space group	$Pna2_1$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$C2/c$
a (Å)	10.7206 (6)	10.9678 (6)	12.1087 (9)	9.7232 (6)	15.080 (1)
b (Å)	16.3322 (9)	15.5929 (9)	12.8082 (9)	14.5796 (9)	16.917 (1)
c (Å)	21.109 (1)	19.893 (1)	16.042 (1)	24.978 (2)	23.208 (1)
α (°)	90	78.107 (1)	111.073 (1)	106.664 (1)	90
β (°)	90	76.264 (1)	90.862 (2)	94.251 (1)	100.586 (2)
γ (°)	90	89.602 (1)	106.834 (1)	94.286 (1)	90
V (Å^3)	3695.9 (4)	3230.6 (3)	2202.2 (3)	3365.7 (4)	5819.9 (7)
Z	4	2	2	2	8
F(000)	1336	1194	812	1242	2120
D(calcd) (g cm^{-3})	1.113	1.151	1.147	1.146	1.126
μ (mm^{-1})	0.774	1.282	1.255	1.233	0.964
θ_{range} (°)	1.58–20.00	1.08–19.00	1.37–20.00	0.86–17.00	1.79–19.99
Refl. (collected)	10732	8944	6596	7053	8413
Refl. (independent)	3008 [$F \geqslant 4\sigma(F)$]	5128 [$F \geqslant 4\sigma(F)$]	3963 [$F \geqslant 4\sigma(F)$]	3829 [$F \geqslant 4\sigma(F)$]	2702 [$F \geqslant 4\sigma(F)$]
No. of variables,	369	622	424	650	289
$R1$ (%)*[a]	8.28	6.37	7.23	9.70	5.71
R (all data) (%)	8.90	7.07	8.21	12.22	8.09

[a]* $R = (\Sigma||F_o| - |F_c||)/\Sigma|F_o|$.

tallisation from toluene at −30°C yielded the title compound as pale yellow crystals suitable for X-ray analysis (0.76 g, 75%). M.p. 129–131°C. ^{1}H NMR: 1.73 (m, 4H, CH_2CH_2), 3.51 (m, 4H, CH_2-N), 6.84 (d, 2H, Ph-*H*), 7.42 (d, 2H, Ph-*H*), 8.00 (s, 2H, Ph-C*H*).

Synthesis of salhen(^{t}Bu)($GaEt_2$)$_2$ (**6**)

This compound was synthesized via similar method to that above from triethylgallium (0.51 g, 3.20 mmol) and Salhen(^{t}Bu)H_2, (0.88 g, 1.60 mmol), recrystallisation from toluene at −30°C yielding the title compound as pale yellow crystals suitable for X-ray analysis (0.95 g, 74%). M.p. 109–110°C. ^{1}H NMR: 1.70 (m, 4H, CH_2CH_2), 3.47 (m, 4H, CH_2-N), 6.85 (d, 2H, Ph-*H*), 7.43 (d, 2H, Ph-*H*).

Synthesis of salen(^{t}Bu)($GaEt_2$)($AlMe_2$) (**7**)

A solution of triethylgallium (0.32 g, 2.03 mmol) in toluene (5 cm^3) was added at room temperature to a

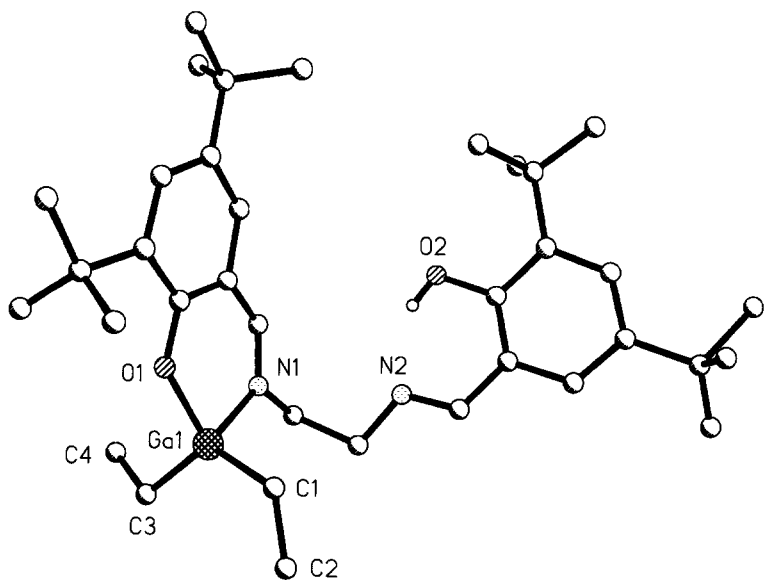


Fig. 3. Molecular structure and atom numbering scheme for Salen(^{t}Bu)H($GaEt_2$) (**1**).

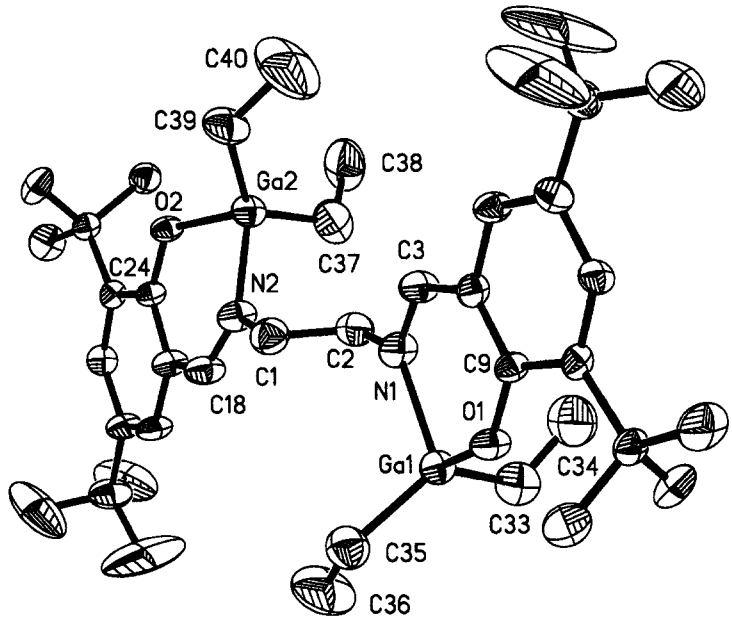


Fig. 4. Molecular structure and atom numbering scheme for Salen('Bu)$(GaEt_2)_2$ (**3**).

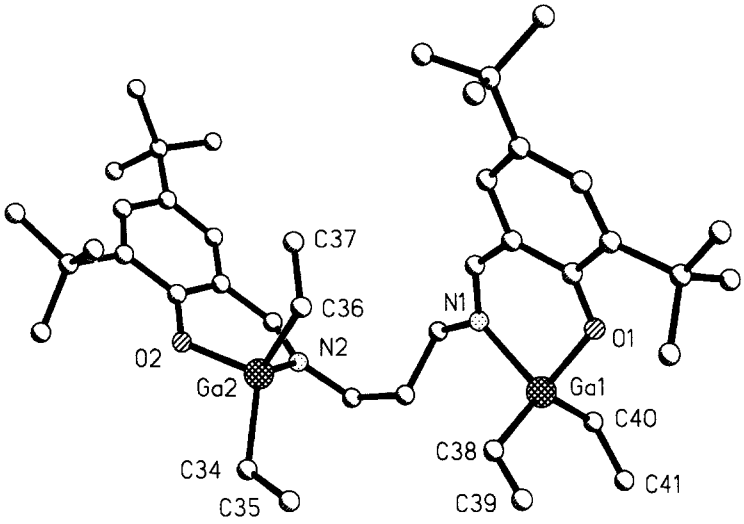


Fig. 5. Molecular structure and atom numbering scheme for Salpen('Bu)$(GaEt_2)_2$ (**4**).

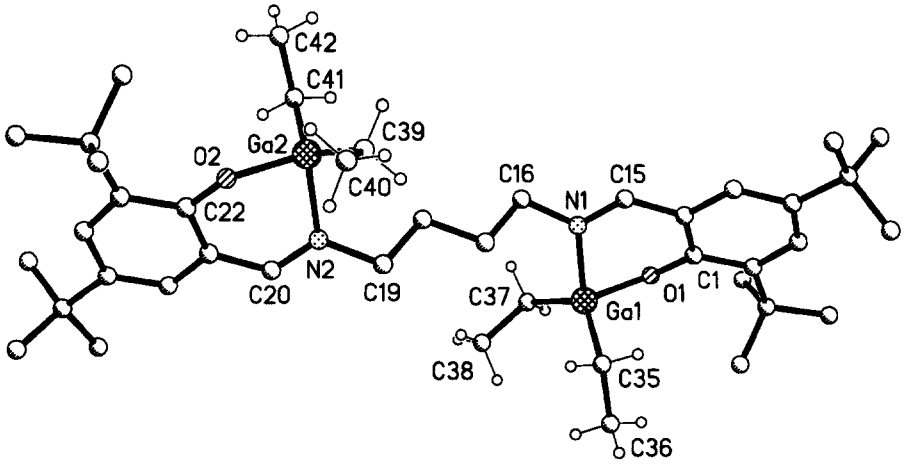


Fig. 6. Molecular structure and atom numbering scheme for Salben('Bu)$(GaEt_2)_2$ (**5**).

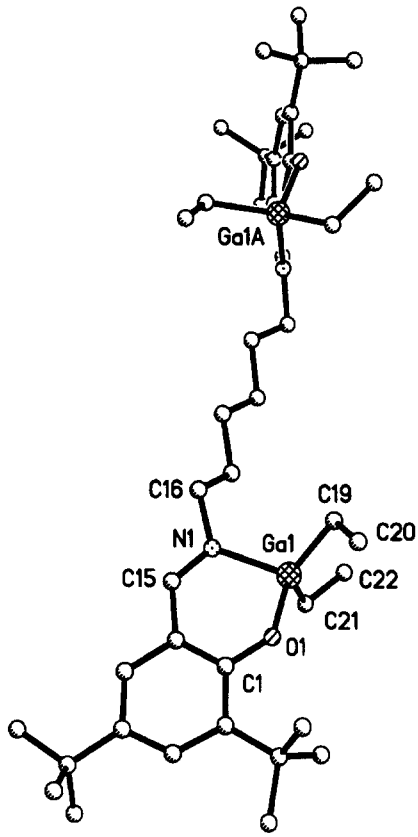


Fig. 7. Molecular structure and atom numbering scheme for Salhen('Bu)($GaEt_2$)$_2$ (**6**).

stirred solution of Salen('Bu)H_2 (1.00 g, 2.03 mmol) in toluene (15 cm^3). The resulting pale yellow solution was stirred for 15 min at which point a solution of trimethyl aluminum (0.147 g, 2.03 mmol) in toluene (5 cm^3) was added. After stirring for 2 h the solvent was removed under reduced pressure to yield a yellow solid which was crystallised as rectangular pale green blocks from toluene at −30°C (0.98 g, 72%). M.p. 108–110°C. ^{1}H NMR: 3.71–3.97 (m, 4H, CH_2-N), 6.76 (m, 1H, Ph-H), 6.90 76 (m, 1H, Ph-H), 7.43 (d, 1H, Ph-H), 7.52 (d, 1H, PhH), 7.97 (s, 1H, PhCH).

Synthesis of salpen('Bu)($GaEt_2$)($AlMe_2$) (**8**)

This compound was synthesized via a similar procedure to that outlined above employing triethyl gallium (0.31 g, 1.98 mmol), Salpen('Bu)H_2 (1.00 g, 1.98 mmol) and trimethylaluminum (0.142 g, 1.98 mmol), and recovered in stoichiometric yield by removal of solvent under reduced pressure. M.p. 84–86°C. ^{1}H NMR: 2.08–2.24 (m, 2H, $CH_2CH_2CH_2$) 3.56–3.65 (m, 4H, CH_2-N), 6.85 (m, 1H, Ph-H), 6.99 (m, 1H, Ph-H), 7.47 (d, 1H, Ph-H), 7.54 (d, 1H, PhH).

Synthesis of salen('Bu)($GaEt_2$)($AlEt_2$) (**9**)

This compound was synthesized with a similar procedure to that outlined above employing triethyl gallium (0.24 g, 1.52 mmol), Salen('Bu)H_2 (0.75 g, 1.52 mmol) and triethylaluminum (0.17 g, 1.52 mmol), and recovered in stoichiometric yield by removal of solvent under reduced pressure. M.p. 138–141°C (dec). ^{1}H NMR: 3.71–3.82 (m, 4H, CH_2-N), 6.76 (m, 1H, Ph-H), 6.88 (m, 1H, Ph-H), 7.44 (d, 1H, Ph-H), 7.50 (d, 1H, PhH).

Synthesis of salpen('Bu)($GaEt_2$)($AlEt_2$) (**10**)

This compound was synthesized with a similar procedure to that outlined above employing triethyl gallium (0.24 g, 1.52 mmol), Salpen('Bu)H_2 (0.77 g, 1.52 mmol) and triethylaluminum (0.17 g, 1.52 mmol), and recovered in stoichiometric yield by removal of solvent under reduced pressure. M.p. 93–94°C. ^{1}H NMR: 2.10–2.22 (m, 2H, $CH_2CH_2CH_2$), 3.57–3.62 (m, 4H, CH_2-N), 6.88 (m, 1H, Ph-H), 7.00 (m, 1H, Ph-H), 7.49 (d, 1H, Ph-H), 7.57 (d, 1H, Ph-H).

CONCLUSION

A wide range of bimetallic and mixed-metal group 13 compounds are accessible when using the Salen('Bu) ligands. Their formation relies on the fact that the chelated $GaEt_2$ fragment is remarkably stable. For example, it does not undergo intramolecular alkane elimination with the phenol portion of the ligand, nor does it react with MeOH under ambient conditions. Furthermore, the mixed-metal derivatives do not undergo scrambling of either the -R or -MR_2 groups.

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