Formation and Reactivity of Five-Coordinate Gallium Supported by Salen Ligands

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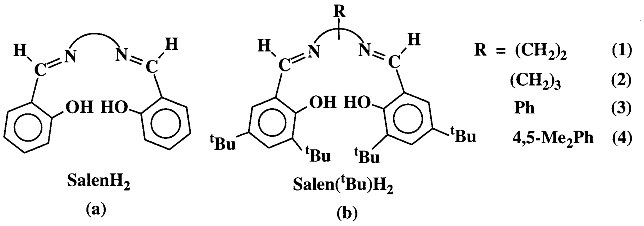
This work is an exploration into the synthesis and reactivity of five-coordinate gallium complexes of the ligands, Salen(*t*Bu)H_2 [*N,N'*-ethylenebis(3,5-di-*tert*-butylsalicylideneimine), (**1**)], Salpen(*t*Bu)H_2 [*N,N'*-propylenebis(3,5-di-*tert*-butylsalicylideneimine), (**2**)], Salophen(*t*Bu)H_2 [*N,N'*-phenylenebis(3,5-di-*tert*-butylsalicylideneimine), (**3**)], and Salomphen(*t*Bu)H_2 [*N,N'*-(4,5-dimethyl)phenylenebis(3,5-di-*tert*-butylsalicylideneimine), (**4**)]. Fully characterized examples include those of general formula LGaX, where L = **1**, X = Cl (**5**), Et (**6**); **3**, X = Cl (**7**), Et (**10**); **4**, X = Cl (**8**), Me (**9**) Et (**11**). X-ray structural data is presented for **6**, **7**, **9**, **10**, and **11**. The ability of these complexes to undergo either alkane or salt elimination reactions is described. In one reaction the unusual salt: $[\{\text{Salophen}(t\text{Bu})\text{Ga}(\text{MeOH})\}_2]^+\text{BPh}_4^-$ (**12**) is obtained.

Despite the fact that Salen ligand (Figure 1a) complexes of transition metals[1] have been known for over sixty years,[2] very little has been accomplished with regards to the main group elements. Until recently, monomeric group-13 derivatives of the form, SalenMX (where M = Al, Ga, In and X = halide or alkyl) were uncommon. The first example to be reported was SalpenAlEt.[3] Since that time more have appeared in the literature, including those of aluminum [Salen(*t*Bu)AlX; X = Me, Et, *i*Bu,[4] chloride[5]; SalcenAlEt[6]], indium [Salen(*t*Bu)InX; X = Me, Et, Cl, Br][7] and some aluminum alkoxides[8] and siloxides.[4] The solubilizing influence of the Salen(*t*Bu) ligand (Figure 1b) makes these compounds much more amenable to solution state studies than those of the underivatized Salen ligands (Figure 1a). They provide a unique opportunity to examine the formation and reactivity of the group-13 elements in a five-coordinate geometry. Depending on the nature of the ligand and the substituents on the group-13 element, either a square-pyramidal or trigonal bipyramidal geometry is observed. From these early studies it is clear that there are marked differences in reactivity of the elements in this geometry compared to the more traditional four-coordinate, tetrahedral geometry. The present work will add to this growing base of knowledge on five-coordinate group-13 elements with a description of the first gallium examples. These are of the form LGaX [where L = Salen(*t*Bu)].

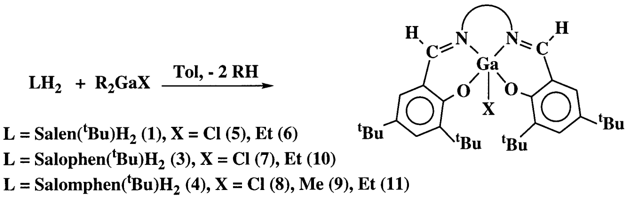
Results and Discussion

Combining one equivalent of Et_2GaCl with **1** or **2** leads to a mixture of predominantly LGaEt with some LGaCl. In the case of the derivatives obtained from **1**, these products (**5** and **6**) can be separated by fractional crystallization. Similar problems were observed in the formation of the analogous aluminum derivatives. In fact, ligands **1** and **2** most readily form open, bimetallic compounds of the sort $L(MR_2)_2$ (where M = Al, Ga and R = alkyl).[9] Use of the the ligands containing an aryl backbone, **3** and **4**, leads to high yields of the chloride derivatives, **7** and **8** without contamination from any LGaEt products. Likewise, the combination of these ligands with $GaEt_3$ leads to isolation of **10** and **11** in high yields.

Figure 1. General depiction of the Salen (a) and Salen(*t*Bu) (b) classes of ligands



Scheme 1. The general synthetic pathway for the preparation of **5**–**11**



Monomeric species are generally obtained in these types of reactions. For all of the compounds the *t*Bu resonances of the ligands are manifested as a pair of singlets in the region δ = 1.3–1.5. Dimeric derivatives normally show more complexity for these resonances. This is the case, for example with $\{\text{Salen}(t\text{Bu})\text{Al}\}_2\text{O}$.[8] Furthermore, the derivatives of **4** contain only one resonance for the Me–Ph group. The Ga–Et groups are observed as well-defined

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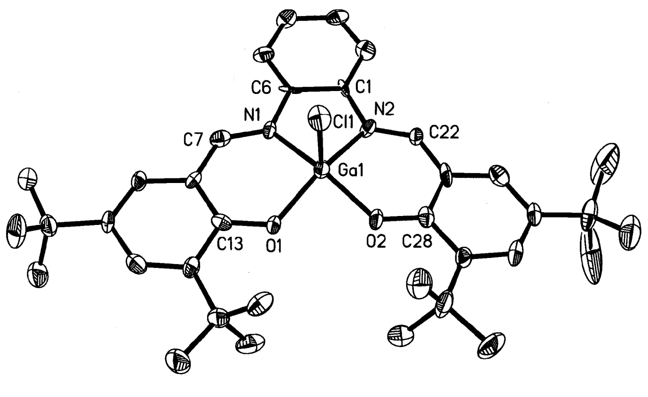
triplets and quartets. The aryl derivatives show greater deshielding of these groups with shifts in the range of $\delta = 0.2$ and 0.7. Compound **5** is marginally more shielded with values of $\delta = 0.26$ and 0.83.

The Me resonance of **9** occurs at $\delta = 0.59$. This can be compared to the same shift in the four-coordinate derivatives, $Me_3Ga{-}thf$ ($\delta = -0.3$)[10], $Me_3Ga{-}NH(i\text{Pr})_2$ ($\delta = 0.33$)[11], $Me_3Ga{-}PPh_3$ ($\delta = 0.17$)[12], and $(Me_3Ga)_2{-}$diphos ($\delta = 0.15$). From the limited amount of data that is available it would appear that the five-coordinate shifts occur at lower field than those observed for four-coordinate derivatives.

The five-coordinate environment around the gallium atoms was confirmed structurally for **6**, **7**, **9**, **10**, and **11**. The structure of **7** is the third reported for a group-13 halide bound by a Salen(*t*Bu) ligand (Figure 2).[7] The Ga atom is in a distorted square pyramidal geometry with the ligand occupying the basal plane at a $Ga{-}N_2O_2$ plane distance of 0.49 Å. The chloride occupies the apical site at a distance of 2.199(3) Å. A similar geometry is observed for the methyl derivative, **9** (Figure 3) which has a $Ga{-}N_2O_2$ plane distance of 0.63 Å. The Ga−O and Ga−N bond distances shorten by comparison to **7**. Compare, for instance, the Ga−O axial distances (ave = 1.87 Å for **7** and 1.90 Å for **9**). This is a result of the lessened inductive effect of the Me group when compared to Cl. The Ga−Me distance [1.939(5) Å] is fairly standard for four- and five-coordinate compounds.[9][10][11] For example this distance in $[Me_2GaNH(t\text{Bu})]_2$ and $Me_3Ga{-}NH_2(t\text{Bu})$ is 1.978(7) Å and 2.01(1) Å, respectively.[13] Compound **9** is actually dimeric in the solid state. The two monomeric units are held together by a relatively close Ga···H (from a Ph−Me group) contact of approximately 3.1 Å.

Figure 2. Molecular structure and atom numbering scheme for Salophen(*t*Bu)GaCl (**7**)



Compound (**6**) adopts a geometry that may best be described as distorted square pyramidal (Figure 4). It contains a fairly obtuse angle [O(2)−Ga(1)−N(1)] of 153.2(4)° that is indicative of a trigonal bipyramidal distortion. Compounds **10** and **11** are more ideally square-pyramidal as a result of the enforced planarity inherent to the aryl backbones of ligands **3** and **4** [a figure (Figure 5) is provided for **10** only]. The $Ga{-}N_2O_2$ plane distances for **6**, **10**, and **11** are close to one another with values of 0.67 Å, 0.63 Å, and 0.64 Å, respectively. The $Ga{-}CH_2$ distance does not vary substantially based upon the geometry of the gallium.

Figure 3. Molecular structure and atom numbering scheme for Salomphen(*t*Bu)GaMe (**9**)

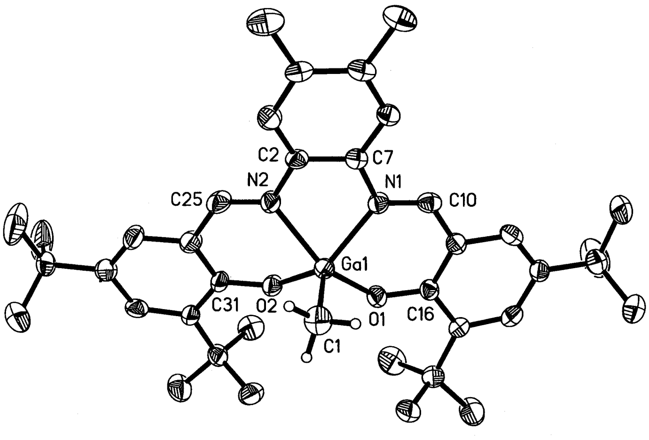


Figure 4. Molecular structure and atom numbering scheme for Salen(*t*Bu)GaEt (**6**)

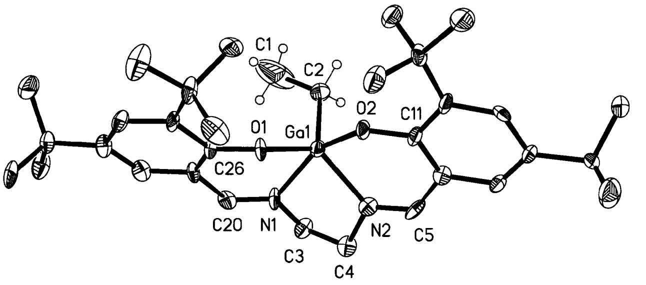
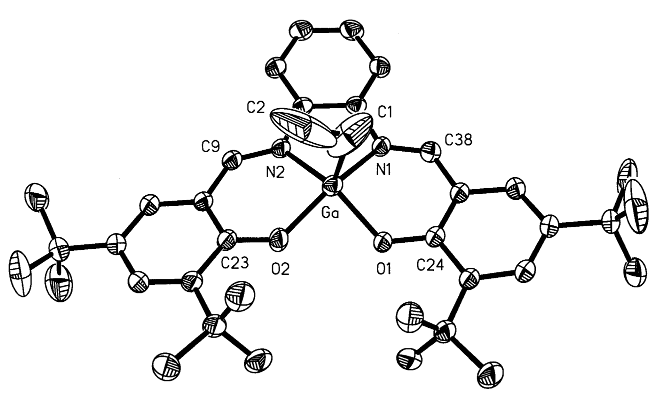
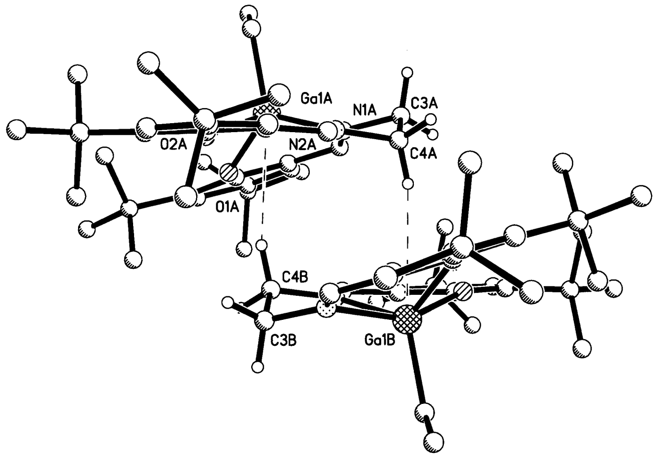


Figure 5. Molecular structure and atom numbering scheme of Salophen(*t*Bu)GaEt (**10**)



In a manner similar to compound **9**, one of the ethylene hydrogen atoms of **6** is close (3.15 Å) to the gallium atom of a second Salen(*t*Bu)GaEt unit (Figure 6). Dimerization through such close contacts is becoming commonplace in these types of structures.[7] They are also observed in square pyramidal indium derivatives. This may be an indication that a sixth coordination site may be available, at least to small nucleophiles, in these compounds.

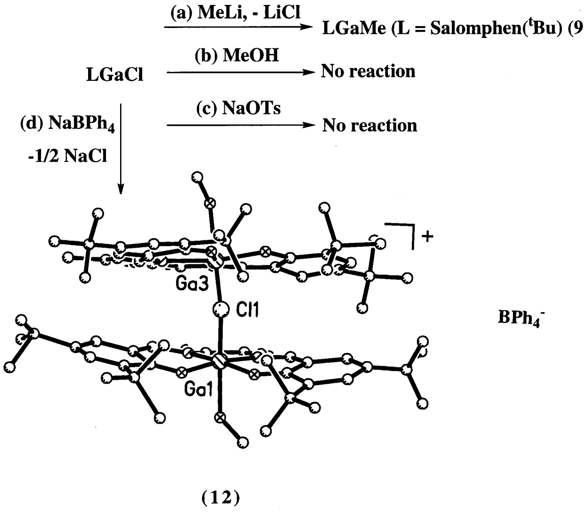
Figure 6. Dimerization of **6** through hydrogen contacts



Reactivity Studies

The gallium halide derivative **8** will undergo a salt elimination reaction with MeLi to form the methyl derivative, **9** [Scheme 2(a)]. The same type of product is obtained in the analogous reaction with indium.[7] However, the gallium halide complexes will not undergo halide displacement with Lewis bases such as MeOH [Scheme 2(b)]. This is in contrast to the same reaction for aluminum in which cationic complexes are formed (eg. [SalenAl(MeOH)$_2$]$^+$Cl$^-$).[14] Similarly, salt eliminations with the gallium halides and NaOTs (OTs = toluenesulfonic acid) do not occur [Scheme 2(c)] despite the fact that, for aluminum, a wide range of cations ([SalenAl(base)$_2$]$^+$OTs$^-$) can be accessed in this manner.[14] For these two reactions [Scheme 2(b) and (c)] gallium and indium behave identically.

Scheme 2. Reactions involving the five-coordinate halide derivatives



(12)

Cationic aluminum complexes can also be formed containing [BPh$_4$]$^-$ as the anion. While this reaction was not successful for indium, a new product can be isolated when using gallium. The product is the unusual salt comprised of a cation containing two gallium atoms and the BPh$_4$ counter-anion [Scheme 2(d)]. The ^{1}H-NMR data is complex and difficult to interpret. However, the results of a partial crystal structure determination and elemental analyses confirms the proposed formulation. Unfortunately, the structure is complicated by the presence of as many as five molecules of MeOH in the independent unit so the structure could not be satisfactorily refined.[15] It can be viewed as being an adduct between the cationic species, Salen(*t*Bu)Ga(MeOH)$_2$]$^+$ and a neutral Salen(*t*Bu)GaCl molecule. Within the limits of the quality of the structure, both of the Ga−Cl distances are the same (ca. 2.0 Å) and form a Ga−Cl−Ga′ angle of 149°. That species like **12** may, in fact, represent a new class of bimetallic compounds is evidenced by the Ti^{III} compound, [{(acacen)Ti(NO$_3$)}$_2$O] (acacen = *N,N′*-ethylenebisacetylacetoneiminato) which has been used to prepare a range of interesting oligomeric metal-chelate derivatives.[16] It will be interesting to see if compound **12** can be utilized similarly.

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Experimental Section

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) and are reported relative to SiMe$_4$ and 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}. The reagent 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde was prepared according to the literature.[17] − All of the X-ray data was collected on a Siemens SMART-CCD unit. A complete data set was collected (Θ = 55°) in each case although this number could be reduced to provide a better structure in the final stages of the structure determination. All of the hydrogen atoms were placed into calculated, idealized positions. The structures were solved with the Siemens SHELXTL-Plus suite of programs.

Reaction of Salen(tBu)H$_2$ and Et$_2$GaCl: To a stirred solution of Et$_2$GaCl, prepared in situ from triethylgallium (0.32 g, 2.03 mmol) and gallium trichloride (0.18 g, 1.02 mmol) in toluene (20 ml), was added Salen(*t*Bu)H$_2$ (1.50 g, 3.05 mmol). The resultant yellow solution was refluxed for a total of 14 h before removal of solvent in vacuo to yield a yellow solid. NMR analysis of this material indicated a single major product identified as Salen(*t*Bu)GaCl (ca. 60% by integration) and a number of minor products. Attempted fractional cystallisation from methanol solution yielded yellow crystals identified as Salen(*t*Bu)GaEt by single crystal X-ray analysis [0.10 g, 5.5% based on Salen(*t*Bu)H$_2$, m.p. 223 °C]. Attempts to isolate an analytically pure sample of Salen(*t*Bu)GaCl however were unsuccessful.

Table 1a. Crystal data for Salophen(tBu)GaCl (**7**)and Salomphen(tBu)GaMe (**9**)

	7	**9**
Formula	$C_{72}H_{92}Cl_2Ga_2N_4O_4$	$C_{39}H_{57}GaN_2O_4$
Formula weight	1287.84	687.59
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
a [Å]	10.8756(7)	15.6740(8)
b [Å]	17.029(1)	10.4407(6)
c [Å]	20.584(1)	23.784(1)
α [°]	107.241(1)	90
β [°]	90.021(1)	90.498(1)
γ [°]	107.550(1)	90
V [Å^3]	3454.5(4)	3892.0(4)
Z	2	4
D(calcd) [Mg/m^3]	1.238	1.173
Crystal size [mm^3]	$(0.40)^3$	$(0.5)^3$
Colour, habit	pale yellow cube	pale yellow cube
Temperature [K]	298	298
Abs coeff. [mm^{-1}]	0.906	0.745
θ range solution [°][a]	1.04−18.00	1.55−19.00
Collected refl.	8126	10104
Independent refl.	4643 (r_{int} = 0.0673)	3123 (r_{int} = 0.0559)
Obsd. with $I > 2\sigma(I)$	4606	3115
R_1	0.0591	0.0469
R_1 (all data)	0.0777	0.0558
Goodness of fit on F^2	1.214	1.232
Largest diff. peak and hole	0.358 and −0.341	0.365 and −0.309

[a] All of the data sets were collected to 55°. The range was narrowed during refinement to improve the structure solution.

Salen(tBu)GaCl (**5**): ^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.10 [s, 18 H, $C(CH_3)_3$], 1.40 [s, 18 H, $C(CH_3)_3$], 3.80−4.18 (m, ca. 4 H, CH_2CH_2), 6.72 (s, 2 H, Ar-*H*), 7.47 (s, 2 H, Ar-*H*), 8.50 (s, 2 H, Ar-C*H*).

Salen(tBu)GaEt (**6**): ^{1}H NMR (270 MHz, $CDCl_3$): δ = 0.26 (q, 2 H, CH_2Ga), 0.83 (t, 3 H, CH_2CH_3), 1.27 [s, 18 H, $C(CH_3)_3$], 1.50 [s, 18 H, $C(CH_3)_3$], 3.66−3.68 (m, 2 H, CH_2CH_2), 3.83−3.85 (m, 2 H, CH_2CH_2) 6.87 (s, 2 H, Ar-*H*), 7.40 (s, 2 H, Ar-C*H*), 8.27 (s, 2 H, Ar-*H*). − IR (KBr, cm^{-1}): ṽ = 2953 s, 2903 s, 2864 s, 1649 s, 1618 s, 1535 s, 1440 m, 1411 m, 1303 m, 1253 m, 1199 m, 1168 m, 1055 w, 979 w, 877 w, 831 w, 787 m, 742 m, 700 w, 667 w, 561 w, 462 w. − $C_{34}H_{51}GaN_2O_2$ (589.49): calcd. (found) C 69.30 (69.36), H 8.66 (8.37), N 4.76 (4.63).

Reaction of Salpen(tBu)H_2 and Et_2GaCl: An identical procedure to that described above, utilizing triethylgallium (0.319 g, 2.03 mmol), gallium trichloride (0.179 g, 1.02 mmol) and Salpen(tBu)H_2 (1.544 g, 3.05 mmol) in toluene solution (20 ml), provided a pale green solid upon removal of the solvent. This was demonstrated to be a complex mixture of products by ^{1}H NMR and proved insensitive to further purification by fractional crystallization in a variety of polar and non-polar solvents.

Synthesis of Salophen(tBu)GaCl (**7**): This compound was synthesized utilizing a similar procedure to that described above, employing triethylgallium (0.194 g, 1.23 mmol), gallium trichloride (0.109 g, 0.62 mmol) and Salophen(tBu)H_2 (1.00 g, 1.85 mmol) in toluene solution (20 ml). In vacuo removal of solvent afforded the title compound as a pale orange solid in stoichiometric yield which could be crystallized from methanol solution as pale orange crystals suitable for X-ray analysis (0.98 g, 82%) m.p. >260 °C. ^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.33 [s, 18 H, $C(CH_3)_3$], 1.58 [s, 18 H, $C(CH_3)_3$], 7.14 (s, 2 H, Ar-*H*), 7.40 (m, 2 H, Ar-*H*), 7.62 (s, 2 H, Ar-*H*), 7.72 (m, 2 H, Ar-*H*), 8.92 (s, 2 H, Ar-C*H*). − IR (KBr, cm^{-1}): ṽ = 2959 s, 2906 m, 2868 m, 1614 s, 1583 s, 1533 s, 1465 m, 1388 m, 1359 m, 1315 w, 1257 m, 1026 w, 835 w, 785 w, 744 m, 540 w. − $C_{72}H_{92}Cl_2Ga_2N_4O_4$ (1287.84): calcd. (found) C 67.16 (67.37), H 7.15 (6.95), N 4.35 (4.17).

Synthesis of Salomphen(tBu)GaCl (**8**): This compound was synthesized by a similar procedure to that outlined above employing triethylgallium (0.276 g, 1.76 mmol), gallium trichloride (0.158 g, 0.88 mmol) and Salomphen(tBu)H_2 (1.50 g, 2.64 mmol). In vacuo removal of the solvent produced an orange solid [containing ca.

Table 1b. Crystal data for Salen(tBu)GaEt (**6**), Salophen(tBu)GaEt (**10**), and Salomphen(tBu)GaEt (**11**)

	6	**10**	**11**
Formula	$C_{34}H_{51}GaN_2O_2$	$C_{38}H_{51}GaN_2O_2$	$C_{40}H_{56}GaN_2O_2$
Formula weight	589.49	637.53	666.84
Crystal system	monoclinic	triclinic	monoclinic
Space group	$P2_1/c$	$P\bar{1}$	$P2_1/c$
a [Å]	11.909(1)	9.9771(5)	14.4606(8)
b [Å]	15.593(1)	12.9593(7)	14.6625(8)
c [Å]	18.460(2)	14.7505(8)	19.124(1)
α [°]	90	85.868(1)	90
β [°]	103.340(2)	79.493(1)	106.443(1)
γ [°]	90	71.458(1)	90
V [Å^3]	3321.5(2)	1777.7(2)	3888.9(4)
Z	4	2	4
D(calcd.) [Mg/m^3]	1.179	1.191	1.139
Crystal size [mm^3]	$(0.50)^3$	$(0.4)^3$	$(0.50)^3$
Colour, habit		orange cube	
Temperature [K]	298	298	298
Abs coeff. [mm^{-1}]	0.858	0.807	0.740
θ range solution [°][a]	1.73−20.00	1.40−21.50	1.47−19.99
Collected refl.	9580	6432	11403
Independent refl.	3081 (r_{int} = 0.1732)	3999 (r_{int} = 0.0499)	3608 (r_{int} = 0.0358)
Obsd. with $I > 2\sigma(I)$	3081	3974	3588
R_1	0.1346	0.0493	0.0613
R_1 (all data)	0.1756	0.0527	0.0717
Goodness of fit on F^2	1.710	1.519	1.569
Largest diff. peak and hole	0.931 and −0.388	0.565 and −0.485	1.085 and −0.463

[a] All of the data sets were collected to 55°. The range was narrowed during refinement to improve the structure solution.

Table 2a. Selected bond lengths [Å] and angles [°] for **7** (one molecule only), and **9**

7		**9**	
Ga(1)−O(1)	1.862(6)	Ga(1)−O(1)	1.901(3)
Ga(1)−O(2)	1.881(6)	Ga(1)−O(2)	1.909(3)
Ga(1)−N(1)	2.045(7)	Ga(1)−N(1)	2.064(4)
Ga(1)−N(2)	2.016(7)	Ga(1)−N(2)	2.105(4)
Ga(1)−Cl	2.199(3)	Ga(1)−C(1)	1.939(5)
O(1)−C(13)	1.32(1)	O(1)−C(16)	1.326(5)
O(2)−C(28)	1.30(1)	O(2)−C(31)	1.322(5)
N(1)−C(7)	1.30(1)	N(1)−C(7)	1.404(6)
N(1)−C(6)	1.40(1)	N(1)−C(10)	1.295(6)
N(2)−C(22)	1.30(1)	N(2)−C(2)	1.397(6)
N(2)−C(1)	1.41(1)	N(2)−C(25)	1.270(6)
O(1)−Ga(1)−O(2)	87.4(3)	O(1)−Ga−O(2)	86.4(1)
O(1)−Ga(1)−N(1)	89.5(3)	O(1)−Ga−N(1)	88.5(2)
O(2)−Ga(1)−N(1)	153.8(3)	O(2)−Ga−N(1)	136.8(2)
O(1)−Ga(1)−N(2)	147.2(3)	O(1)−Ga−N(2)	148.8(2)
O(2)−Ga(1)−N(2)	90.1(3)	O(2)−Ga−N(2)	86.8(2)
N(1)−Ga(1)−N(2)	78.6(4)	N(1)−Ga−N(2)	76.0(2)
O(1)−Ga(1)−Cl(1)	109.3(2)	O(1)−Ga−C(1)	109.0(2)
O(2)−Ga(1)−Cl(1)	106.2(2)	O(2)−Ga−C(1)	111.4(2)
N(1)−Ga(1)−Cl(1)	99.4(2)	N(1)−Ga−C(1)	110.8(2)
N(2)−Ga(1)−Cl(1)	102.7(2)	N(2)−Ga−C(1)	101.8(2)

Table 2b. Selected bond lengths [pm] and angles [°] for **6**, **10**, and **11**

6		**10**		**11**	
Ga(1)−O(1)	1.900(8)	Ga(1)−O(1)	1.905(2)	Ga(1)−O(1)	1.913(4)
Ga(1)−O(2)	1.932(9)	Ga(1)−O(2)	1.907(3)	Ga(1)−O(2)	1.910(4)
Ga(1)−N(1)	2.09(1)	Ga(1)−N(1)	2.107(3)	Ga(1)−N(1)	2.091(5)
Ga(1)−N(2)	2.06(1)	Ga(1)−N(2)	2.072(3)	Ga(1)−N(2)	2.109(5)
Ga(1)−C(2)	1.95(1)	Ga(1)−C(1)	2.019(8)	Ga(1)−C(39)	1.970(9)
O(1)−C(26)	1.31(1)	O(1)−C(24)	1.324(4)	O(1)−C(15)	1.314(7)
O(2)−C(11)	1.32(1)	O(2)−C(23)	1.330(5)	O(2)−C(30)	1.310(7)
N(1)−C(3)	1.45(2)	N(1)−C(38)	1.294(5)	N(1)−C(9)	1.287(7)
N(1)−C(20)	1.27(2)	N(1)−C(3)	1.413(5)	N(1)−C(6)	1.433(7)
N(2)−C(4)	1.50(2)	N(2)−C(9)	1.305(5)	N(2)−C(24)	1.291(7)
N(2)−C(5)	1.29(2)	N(2)−C(8)	1.418(5)	N(2)−C(1)	1.418(7)
O(1)−Ga(1)−O(2)	86.6(4)	O(1)−Ga−O(2)	86.9(1)	O(1)−Ga(1)−O(2)	87.2(2)
O(1)−Ga(1)−N(1)	85.9(4)	O(1)−Ga−N(1)	85.7(1)	O(1)−Ga(1)−N(1)	87.3(2)
O(2)−Ga(1)−N(1)	153.2(4)	O(2)−Ga−N(1)	147.6(1)	O(2)−Ga(1)−N(1)	137.7(2)
O(1)−Ga(1)−N(2)	127.0(4)	O(1)−Ga−N(2)	137.2(1)	O(1)−Ga(1)−N(2)	146.3(2)
O(2)−Ga(1)−N(2)	86.8(4)	O(2)−Ga−N(2)	88.1(1)	O(2)−Ga(1)−N(2)	86.2(2)
N(1)−Ga(1)−N(2)	77.5(5)	N(1)−Ga−N(2)	76.4(1)	N(1)−Ga(1)−N(2)	75.9(2)
O(1)−Ga(1)−C(2)	116.3(5)	O(1)−Ga−C(1)	111.8(2)	O(1)−Ga(1)−C(39)	111.5(3)
O(2)−Ga(1)−C(2)	106.0(5)	O(2)−Ga−C(1)	113.3(3)	O(2)−Ga(1)−C(39)	112.4(3)
N(1)−Ga(1)−C(2)	100.4(6)	N(1)−Ga−C(1)	98.7(2)	N(1)−Ga(1)−C(39)	108.6(3)
N(2)−Ga(1)−C(2)	116.0(5)	N(2)−Ga−C(1)	109.1(2)	N(2)−Ga(1)−C(39)	101.6(3)

5% Salomphen(*t*Bu)GaEt by NMR] which was recrystallized from hexane/toluene solution at −30 °C to yield the title compound as an orange microcrystalline solid (1.35 g, 76%) m.p. >260 °C. − ^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.33 [s, 18 H, C(C*H*$_3$)$_3$], 1.58 [s, 18 H, C(C*H*$_3$)$_3$], 2.36 (s, 6 H, Ar-C*H*$_3$), 7.14 (s, 2 H, Ar-*H*), 7.49 (s, 2 H, Ar-*H*), 7.60 (s, 2 H, Ar-*H*), 8.87 (s, 2 H, Ar-C*H*). − IR (KBr, cm^{-1}): ṽ = 2960 s, 2908 m, 2868 m, 1616 s, 1591 s, 1550 s, 1465 m, 1435 m, 1388 m, 1359 m, 1249 m, 1176 s, 1134 w, 1024 w, 839 m, 785 m, 746 w, 653 w, 538 w, 505 w. − calcd. (found) C 67.94 (67.51), H 7.45 (7.63), N 4.17 (3.97).

Synthesis of Salomphen(tBu)GaMe (**9**): Salomphen(*t*Bu)GaCl (0.25 g, 0.37 mmol) was dissolved in diethyl ether (20 ml) and stirred at −78 °C. MeLi (0.27 ml, 1.4 M in diethyl ether, 0.37 mmol) was added producing a deep brown solution. This was allowed to warm to room temperature before evaporation of the solvent to produce a brown solid. Extraction in toluene (15 ml), followed by in vacuo removal of solvent produced a red-brown solid which was recrystallized from methanol in air to yield the title compound as a dihydrate as orange crystals suitable for single crystal X-ray analysis (0.15 g, 65%) m.p. >260 °C. − ^{1}H NMR (270 MHz, $CDCl_3$): δ = −0.59 (s, 3 H, Ga-C*H*$_3$), 1.3 [s, 18 H, C(C*H*$_3$)$_3$], 1.52 [s, 18 H, C(C*H*$_3$)$_3$], 2.36 (s, 6 H, Ph-C*H*$_3$), 3.48 (br. s, 4 H, H_2O), 7.04 (s, 2 H, Ar-*H*), 7.40 (s, 2 H, Ar-*H*), 7.48 (s, 2 H, Ar-*H*), 8.66 (s, 2 H, Ar-C*H*). − IR (KBr, cm^{-1}): ṽ = 2962 s, 2918 m, 2874 m, 1616 s, 1591 s, 1465 w, 1398 m, 1259 m, 1172 m, 1016 m, 808 m, 787 w, 705 w, 491 w. − $C_{39}H_{57}GaN_2O_4$ (687.59): calcd. (found) C 68.35 (68.48), H 8.03 (8.17), N 4.09 (4.67).

Synthesis of Salophen(tBu)GaEt (**10**): A solution of $GaEt_3$ (0.29 g, 1.85 mmol) in toluene (5 ml) was added at room temperature to a stirred solution of Salophen(*t*Bu)H_2 (1.0 g, 1.85 mmol) in toluene (15 ml). The initial golden yellow solution was stirred for 2 h at which point the solvent was removed to yield a pale brown solid. NMR analysis of this material indicated a mixture of products. The solid was redissolved in a further 20 ml of toluene and refluxed for 15 h producing an orange/brown solution. Removal of solvent and subsequent recrystallisation from a hexane/toluene solution yielded the title compound as ruby-red rectangular crystals suitable for X-ray analysis. (1.00 g, 81%). m.p >260 °C. − ^{1}H NMR (270 MHz, $CDCl_3$): δ = 0.23 (q, 2 H, C*H*$_2$Ga), 0.73 (t, 3 H, CH$_2$C*H*$_3$), 1.32 [s, 18 H, C(C*H*$_3$)$_3$], 1.54 [s, 18 H, C(C*H*$_3$)$_3$], 7.02 (d, 2 H, Ar-*H*), 7.34−7.36 (m, 2 H, Ar-*H*), 7.50 (d, 2 H, Ar-*H*), 7.61−7.64 (m, 2 H, Ar-*H*), 8,70 (s, 2 H, Ar-C*H*). − IR (KBr, cm^{-1}): ṽ = 2960 s, 2918 m, 2866 m, 1612 s, 1581 s, 1529 s, 1465 w, 1435 w, 1386 m, 1357 w, 1259 m, 1174 m, 1106 m, 1026 m, 866 w, 802 m, 748 m, 528 m. − $C_{38}H_{51}GaN_2O_2$ (637.53): calcd. (found) C 71.62 (71.31), 8.01 (7.75), N 4.40 (4.20).

Synthesis of Salomphen(tBu)GaEt (**11**): This compound was synthesized by an identical procedure as that outlined for Salophen(*t*Bu)GaEt from $GaEt_3$ (0.28 g, 1.76 mmol) and Salomphen(*t*Bu)H_2 (1.00 g, 1.76 mmol), recrystallisation from a hexane/toluene solution yielding the title compound as an orange rectangular crystals suitable for X-ray analysis. (1.06 g, 87%). m.p. >260 °C. − ^{1}H NMR (270 MHz, $CDCl_3$): δ = 0.19 (q, 2 H, C*H*$_2$Ga), 0.71 (t, 3 H, CH$_2$C*H*$_3$), 1.33 [s, 18 H, C(C*H*$_3$)$_3$], 1.54 [s, 18 H, C(CH_3)$_3$], 2.35 (s, 6 H, Ar-CH_3), 7.03 (d, 2 H, Ar-*H*), 7.40 (s, 2 H, Ar-*H*), 7.49 (s, 2 H, Ar-*H*), 8.67 (s, 2 H, Ar-C*H*). − IR (KBr, cm^{-1}): $\tilde{\nu}$ = 2962 s, 2910 m, 1618 s, 1593 m, 1548 m, 1410 w, 1261 m, 1174 m, 1089 m, 1018 m, 800 m, 534 w. − $C_{40}H_{56}GaN_2O_2$ (666.84): calcd. (found) C 72.21 (71.94), H 8.27 (8.25), N 4.21 (3.98).

Synthesis of {[Salomphen(tBu)Ga·MeOH]$_2$Cl}BPh$_4$ (**12**): Salomphen(*t*Bu)GaCl (0.30 g, 0.47 mmol) and sodium tetraphenylborate (0.16 g, 0.47 mmol) were stirred as a pale orange solution in methanol (15 ml) for 14 h. At this point the solution was reduced in volume to ca. 5 ml and allowed to crystallise by slow evaporation of the solvent. This produced the title compound as heavily solvated orange needles suitable for X-ray analysis. This material could be converted to a red unsolvated form by storage under vacuum for several hours (total yield, 0.41 g, 52%) m.p. 208−213 °C (dec). − ^{1}H NMR (270 MHz, $CDCl_3$): δ = 0.77−1.56 [complex multiplet, 72 H, C(CH_3)$_3$], 2.46−2.54 (m, 12 H, Ph-CH_3), 3.35 (s, 6 H, HO-CH_3), 6.43−7.60 (m, 32 H, Ar-*H*). − IR (KBr, cm^{-1}): $\tilde{\nu}$ = 2960 s, 2906 m, 2872 m, 1614 s, 1587 m, 1533 s, 1465 m, 1435 m, 1390 m, 1359 m, 1251 m, 1180 m, 1081 m, 806 w, 702 w, 613 w, 540 w, 503 w. − calcd. (found) C 72.62 (73.02), H 7.47 (7.36).

Attempted Reactions:

Salophen(tBu)GaCl and NaOTs (in Dichloromethane): Sodium *p*-toluenesulfonate (0.1 g, 0.51 mmol) was added as a solid to a stirred solution of Salophen(*t*Bu)GaCl (0.25 g, 0.39 mmol) in 15 ml of CH_2Cl_2, thf, or MeO H, dichloromethane (15 ml). The resultant suspension was stirred for 14 h before filtration and evaporation of the solvent to yield an orange solid. This was demonstrated to be unreacted Salophen(*t*Bu)GaCl by ^{1}H NMR.

Crystallographic data (excluding the structure factor tables) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication CCDC-100614. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB21EZ, UK [Fax: int. code +44 (0)1223/336-033; E-mail: deposit@chemcrys.cam.ac.uk].

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