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Chloro (aryloxy/alkoxy) gallium compounds: synthesis and structures of $(2,4,6\text{-}Me_3C_6H_2O)_2GaCl{\cdot}tBuNH_2$, $(2,6\text{-}(tBu)_2\text{-}4\text{-}(Me)C_6H_2O)GaCl_2{\cdot}OEt_2$ and $[tBuNH_3]^+$ $[(Cl_3Ga)_2O\text{-}2,4,6\text{-}Me_3C_6H_2]^-$[†]

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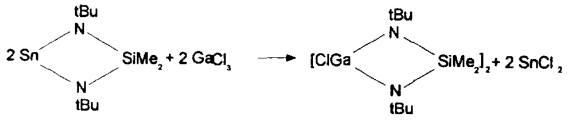
Summary – Reaction of $[ClGa(tBuN)_2SiMe_2]_2$ **1** with 2,4,6-trimethylphenol (1:2 stoichiometry) affords $(2,4,6\text{-}Me_3C_6H_2O)_2GaCl \cdot tBuNH_2$ **2**. This main product is accompanied by a crystalline side product which has the composition $tBuNH_3^+$ $\{2,4,6\text{-}Me\text{-}C_6H_2O\}(GaCl_3)_2^-$ **6** as found from X-ray structure analysis. A similar reaction of **1** with *t*-butanol affords a crystalline product **3** formulated as $(tBuO)_2GaCl$. When 2,6-dimethyl benzenethiol is used, the compound $Ga(S\text{-}2,6\text{-}Me_2C_6H_3)_3 \cdot tBuNH_2$ **4** is isolated. The reaction of gallium trichloride with $2,6\text{-}(tBu)_2\text{-}4\text{-}Me\text{-}C_6H_2OLi \cdot OEt_2$ in toluene led to $\{2,6\text{-}(tBu)_2\text{-}4\text{-}Me\text{-}C_6H_2O\}GaCl_2 \cdot OEt_2$ **5**. The identity of **2**, **5** and **6** were confirmed by X-ray structure determination; **5** is the first structurally characterized dichloro(aryloxy)gallane and **2** exists as a H-bonded dimer in the solid state. Compound **6** contains an alcoholate anion $R\text{-}O^-$, the oxygen atom of which is in a trigonal planar environment of two gallium and one carbon atom.

gallium / chlorogallium compound / aryloxy gallane

We have been interested in partially substituted chlorogallium compounds with bulky alkoxy/aryloxy substituents because these are useful precursors for synthesizing new Ga-Ga-bonded species or Ga(I) derivatives. They also serve as good substrates that can lead to novel galloxane compounds of the type $[(2,4,6\text{-}(tBu)_3C_6H_2)Ga(Mn(CO)_5]_2O$ reported recently by Cowley *et al* [1]. An attractive possibility is to use the compound $[ClGa(NtBu)_2SiMe_2]_2$ **1** which we reported recently (eq 1) [2]. In view of the potential synthetic utility of tnese gallium compounds we are keen to develop more straightforward routes to stable aryloxy compounds of gallium. The results of our investigations on the reaction of **1** with phenols/alcohols, and the synthesis of $\{2,6\text{-}(tBu)_2\text{-}4\text{-}Me\text{-}C_6H_2O\}GaCl_2$ as an etherate are reported here. The X-ray structures of $\{2,4,6\text{-}Me_3C_6H_2O\}GaCl \cdot tBuNH_2$ **2**, $\{2,6\text{-}(tBu)_2\text{-}4\text{-}Me\text{-}C_6H_2O\}GaCl_2 \cdot OEt_2$ **5** and $tBuNH_3{}^+\{2,4,6\text{-}Me\text{-}C_6H_2O\}(GaCl_3)_2^-$ **6** thus obtained are also described. Compound **5** is the first chloro aryloxy gallane to be structurally characterized.



(1)

1

Results and Discussion

Synthesis

The reaction of **1** with two molar equivalents of 2,4,6-trimethylphenol was performed in order to see if pure $(2,4,6\text{-}Me_3C_6H_2O)_2GaCl$ could be synthesized by this route (eq 2)

$$0.5\ \mathbf{1} + 2\ 2,4,6\text{-}Me_3C_6H_2OH \not\rightarrow (2,4,6\text{-}Me_3C_6H_2O)_2GaCl + Me_2Si(NHtBu)_2 \qquad (2)$$

Surprisingly the reaction did not proceed in the expected manner. Instead the *t*-butylamine adduct $(2,4,6\text{-}Me_3C_6H_2O)_2GaCl \cdot tBuNH_2$ **2** was obtained (eq 3).

$$\mathbf{1} + 4\ 2,4,6\text{-}Me_3C_6H_2OH \longrightarrow 2\ \underbrace{(2,4,6\text{-}Me_3C_6H_2O)_2GaCl \cdot tBuNH_2}_{\mathbf{2}} + [tBuNSiMe_2]_2 \qquad (3)$$

The silylamine $Me_2Si(HNtBu)_2$ was not detected in the reaction mixture (^1H NMR). By contrast, in

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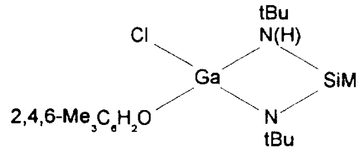
[†] This paper is dedicated to Prof Raymond Calas

* Correspondence and reprints

the reactions of both t-butanol and phenyl dimethyl carbinol with **1** the product mixtures showed the expected amount of $Me_2Si(HNtBu)_2$ (^1H NMR). In the case of t-butanol a crystalline solid **3** formulated as $(tBuO)_2GaCl$ on the basis of elemental analysis was isolated.

For the reactions of both t-butanol and 2,4,6-$Me_3C_6H_2OH$, the first step is most likely the formation of **A**. Such a species is similar to $Cl_2Ga\{HN(tBu)SiMe_2N(tBu)\}$ [3] and (Me)ClGa-$\{(OtBu)SiMe_2(NtBu)\}$ [4], which have been reported previously. A possible explanation for the differences in the final products may arise from the different donor characteristics of t-butanol and 2,4,6-trimethylphenol, the latter being more acidic. Thus in the case of 2,4,6-trimethylphenol, when the second molecule of phenol reacts, gallium may prefer to hold on to the NHtBu end leading to protonation at this site and thus resulting in formation of the adduct **2**.



(A)

In the case of the 1:2 reaction of **1** with 2,6-dimethylbenzenethiol, the adduct $(2,6\text{-}Me_2C_6H_3S)_3Ga \cdot tBuNH_2$ **4** is isolated in good yields. At the present, it is not clear as to how the third molecule of the benzenethiol enters, but such an occurrence has also been observed for tin [5]. Under similar experimental conditions, t-butylthiol, triphenyl carbinol and 2,6-di(t-butyl)-4-methylphenol did not react with **1**.

An interesting feature of the t-butoxy compound **3** is that a solid that analyzed as $[(tBuO)GaO]_n$ was obtained upon sublimation. However since this was not the theme of the present work we did not attempt to characterize it further.

The compound $[2,6\text{-}(tBu)_2\text{-}4\text{-}Me\text{-}C_6H_2O]GaCl_2 \cdot OEt_2$ **5**, a synthetically attractive precursor, can be readily obtained as a crystalline solid from hexane containing traces of diethyl ether following equation (4). In the absence of ether an oily material is normally obtained, possibly because of slow exchange/elimination of coordinated ether. Such a process has been suggested recently for $[2,4,6\text{-}(iPr)_3C_6H_2]GaCl_2 \cdot THF$ [6].

$$2,6(tBu)_2\text{-}4\text{-}Me\text{-}C_6H_2OLi + GaCl_3 + OEt_2 \longrightarrow LiCl + \underset{\mathbf{5}}{2,6(tBu)_2\text{-}4\text{-}Me\text{-}C_6H_2O\text{-}GaCl_2 \cdot OEt_2} \quad (4)$$

Formation of $[tBuNH_3]^+[(Cl_3Ga)_2O\text{-}2,4,6\text{-}Me_3C_6H_2]^-$ **6** as a side product in reaction (2) is unique but not totally unpredictable because the gallium product formed in the reaction of $(Et_2N)_2SiMe_2$ with gallium trichloride (1:1), $[Cl_2Ga(NEt_2)_2SiMe_2]^+ [(Cl_3Ga)_2NEt_2]^-$, has a similar anion [7].

Structural aspects

Figures 1-3 show the molecular structures of the compounds **2**, **5** and **6** respectively. Selected bond distances and bond angles are presented in tables I-III.

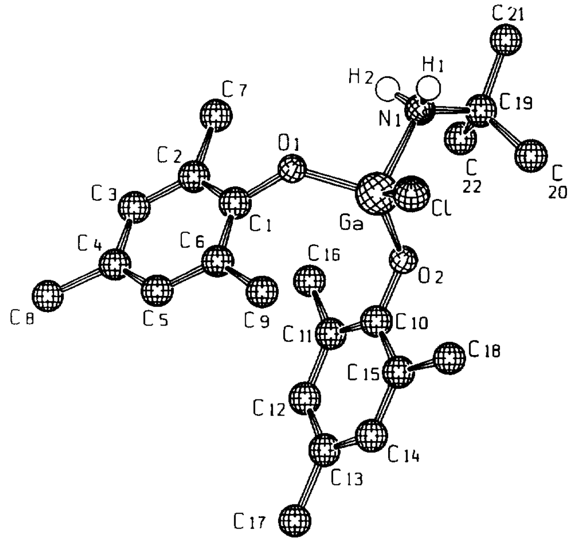


Fig 1. Molecular structure of **2**.

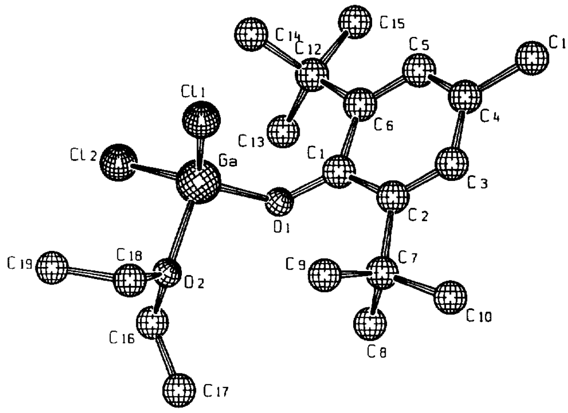


Fig 2. Molecular structure of **5**.

Molecule **2** crystallizes in a triclinic lattice. The two molecules within the cell are aggregated around a center of symmetry through loose H(2)...Cl (2.99 Å) and H(1')...O(1) (2.30 Å) hydrogen bonds. Only one of the phenoxide oxygens [O(1)] participates in the H-bonding; the corresponding Ga-O distance is slightly longer than that with no H-bonding. The dimeric unit arising from these interactions is illustrated in figure 4. A cage of 12 atoms is formed (2 Ga, 2 N, 2 O, 2 Cl, 4 H), which has a drum shape. In the crystal structure of **5** no intermolecular contacts other than of the van der Waals type can be detected. The molecule again has C_1 symmetry and the gallium atom is coordinated as a distorted tetrahedron. Finally, the crystal structure of **6** is made up of two units : the *tert*-butyl ammonium cation and a phenolate, the oxygen atom of which is

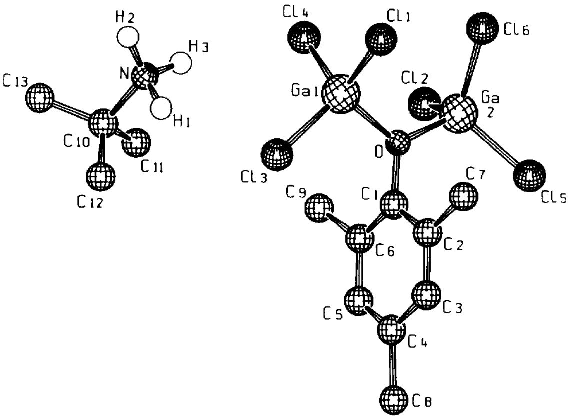


Fig 3. Molecular structure of **6**.

Table I. Selected bond lengths (Å) and bond angles (°) in **2**.

Ga-O(1)	1.808 (2)	Ga-O(2)	1.790 (3)
O(1)-C(1)	1.379 (4)	Ga-N(1)	1.998 (3)
O(2)-C(10)	1.372 (4)	Ga-Cl	2.175 (2)
N(1)-C(19)	1.511 (5)		
O(2)-Ga-O(1)	120.1 (1)	N(1)-Ga-Cl	101.8 (1)
O(2)-Ga-N(1)	106.5 (1)	C(1)-O(1)-Ga	130.8 (2)
O(1)-Ga-N(1)	100.5 (1)	C(10)-O(2)-Ga	128.4 (2)
O(2)-Ga-Cl	118.5 (1)	O(1)-C(1)-C(6)	121.3 (3)
O(1)-Ga-Cl	106.5 (9)	O(1)-C(1)-C(2)	117.7 (3)
O(2)-C(10)-C(11)	119.5 (3)	C(20)-C(19)-N(1)	107.6 (4)
O(2)-C(10)-C(15)	119.7 (3)	N(1)-C(19)-C(22)	107.6 (3)
C(19)-N(1)-Ga	122.9 (2)	N(1)-C(19)-C(21)	108.4 (3)

Table II. Selected bond lengths (Å) and bond angles (°) in **5**.

Ga-O(1)	1.795 (3)	O(2)-C(16)	1.459 (7)
Ga-O(2)	1.972 (3)	O(2)-C(18)	1.483 (7)
Ga-Cl(1)	2.133 (2)	O(1)-C(1)	1.380 (5)
Ga-Cl(2)	2.143 (2)		
O(1)-Ga-O(2)	103.3 (2)	O(1)-Ga-Cl(1)	115.5 (1)
O(2)-Ga-Cl(1)	104.7 (1)	O(1)-Ga-Cl(2)	115.0 (1)
O(2)-Ga-Cl(2)	97.9 (1)	Cl(1)-Ga-Cl(2)	116.95 (9)
C(1)-O(1)-Ga	128.1 (3)	C(16)-O(2)-C(18)	117.0 (4)
C(16)-O(2)-Ga	115.4 (4)	C(18)-O(2)-Ga	122.5 (3)
O(1)-C(1)-C(2)	119.1 (4)	O(1)-C(1)-C(6)	119.7 (4)

Table III. Selected bond lengths (Å) and bond angles (°) in **6**.

Ga(1)-O	1.912 (6)	Ga(2)-O	1.916 (6)
Ga(1)-Cl(3)	2.143 (4)	Ga(2)-Cl(2)	2.131 (4)
Ga(1)-Cl(1)	2.143 (4)	Ga(2)-Cl(6)	2.139 (4)
Ga(1)-Cl(4)	2.145 (3)	N-C(10)	1.537 (13)
Ga(2)-Cl(5)	2.143 (3)	O-C(1)	1.421 (11)
O-Ga(1)-Cl(3)	106.4 (2)	Cl(1)-Ga(1)-Cl(4)	109.6 (1)
O-Ga(1)-Cl(1)	111.2 (2)	O-Ga(2)-Cl(2)	110.6 (2)
Cl(3)-Ga(1)-Cl(1)	110.9 (2)	O-Ga(2)-Cl(6)	103.7 (2)
O-Ga(1)-Cl(4)	105.3 (2)	Cl(2)-Ga(2)-Cl(6)	111.7 (2)
Cl(3)-Ga(1)-Cl(4)	113.4 (1)	O-Ga(2)-Cl(5)	107.4 (2)
Cl(2)-Ga(2)-Cl(5)	111.3 (2)	Cl(6)-Ga(2)-Cl(5)	111.7 (2)
C(1)-O-Ga(1)	118.9 (5)	C(1)-O-Ga(2)	116.0 (5)
Ga(1)-O-Ga(2)	125.0 (3)	C(6)-C(1)-O	119.1 (9)
C(2)-C(1)-O	118.8 (8)		

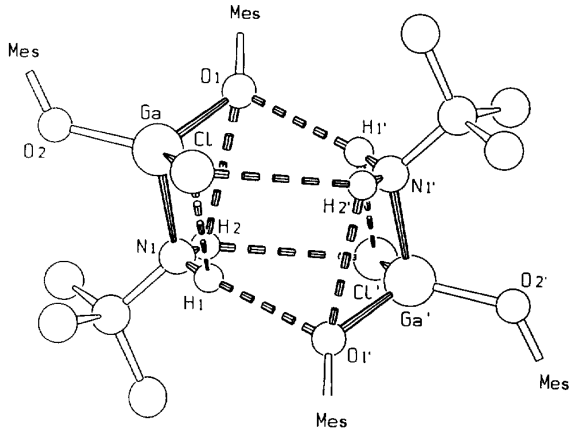


Fig 4. H-bonding scheme in **2**.

coordinating to two gallium trichloride molecules. There are weak hydrogen chloride interactions in the crystal. The oxygen atom in the anion is the center of a trigonal planar coordination site (sum of the angles around O = 359.0°) and the O-C distance is only 1.42(1) Å since two sp^2-hybridized atoms are linked together.

Although the Ga-N distance (1.997 Å) in **2** is short, it is not too far from the corresponding Ga-N distances in $Me_2Ga(OCH_2CH_2NH_2)$ (mean = 2.064 Å), [8] **1** (mean = 2.027 Å), [2] and $[(Me)ClGa\text{-}NHSiMe_3]_2$ (2.012 Å) [9]. The Ga-Cl distances in **2**, **5** and **6** are normal and comparable with those in the literature [2, 7]. As expected, the Ga-O distance to the aryloxide is significantly longer in **6** when compared to **2** and **5**. In fact the Ga-O distances in **2** (mean = 1.798 Å) and **5** (1.795 Å) are shorter than in $Me_2Ga(OCH_2CH_2NH_2)$ (1.917 Å) and Roesky's cage $(Mes_2Ga_6O_4(OH)_4$ (1.88 Å) [10], but are very close to the oxo-bridged galloxane $[Mes^*GaMn(CO)_5]_2O$ (**B**) (1.786 Å) [1].

The Ga-O(ether) distance in **5** (1.972 Å) is shorter than that in the analogous $[2,4,6\text{-}(i\text{Pr})_3C_6H_2]GaCl_2 \cdot THF$ (**C**) (2.01 Å) [6] or $[Me_2Ga\text{-}O\text{-}C_6H_4\text{-}o\text{-}CHO]$ (**D**) (2.12 Å) [11]. This may arise because in **C** gallium is connected to the less electronegative carbon and in **D** gallium is pentacoordinated. There does not appear any important steric effect on the Ga-O-C bond angle in **2** when compared to **5**. However, the Ga-O-Ga angle in **6** (125.0°) is significantly lower than that found in Cowley's compound **B** (150.2°). The difference is related to the coordination number at oxygen, which is three coordinated in **6** and two coordinated in **B**.

There is a dependence between the electron-acceptor property of the GaX_3 unit in D-GaX_3 (D = donor, X = substituent) and the sum of the angles of GaX_3 when different donors coordinate to gallium. The sum of the corresponding angles is 345.0° in **2** (N-donor), 347.4° in **5** (O-donor) and 333.9 and 334.7° in **6** (O^--donor). In the last example, the sum is approaching the sum of tetrahedral angles (328°), while in the former

Table IV. Crystallographic data for **2, 5** and **6**.

mol formula	$C_{22}H_{33}ClGaNO_2$ **2**	$C_{19}H_{33}Cl_2GaO_2$ **5**	$C_{13}H_{23}Cl_6Ga_2NO$ **6**
fw	448.69	434.07	561.46
Crystal dimensions (mm)	0.3×0.4×0.4	0.2×0.1×0.4	0.1×0.2×0.3
Crystal color	coloress	coloress	coloress
Crystal system	triclinic	monoclinic	monoclinic
Space group	P-1	$C2/c$	$P2_1/c$
a, Å	9.084 (9)	31.11 (2)	8.584 (6)
b, Å	10.779 (9)	9.782 (5)	14.109 (11)
c, Å	13.705 (11)	15.305 (8)	19.021 (14)
α (°)	68.90 (3)	90	90
β (°)	86.88 (4)	105.33 (4)	96.332 (12)
γ (°)	69.78 (2)	90	90
V, (Å^3)	1 171 (2)	4 491 (4)	2 290 (3)
Z	2	8	4
d, g cm^{-3}	1.272	1.284	1.629
No of independent data points	3 055	2 879	1 381
No of data with $I > 2\sigma(I)$	2 690	2 194	1 257
No of parameters	255	220	151
μ, mm^{-1}	1.304	1.471	3.055
$R(I > 2\sigma(I) : R_1$	0.032	0.0412	0.0424
wR_2	0.0886	0.1267	0.1085

cases the values found are nearer to a trigonal planar arrangement suggesting a less effective bonding of the donor.

Experimental section

All operations were carried out under an atmosphere of dry nitrogen using a modified Stock vacuum apparatus and Schlenk techniques. ^{1}H and ^{13}C NMR spectra were obtained on a Bruker WP 200 (200 MHz) instrument; chemical shifts as values were measured relative to Me_4Si. Elemental analyses were performed by Beller, Mikroanalytisches Labor, Göttingen, Germany.

Gallium trichloride was either procured from Aldrich or prepared [12], and was sublimed prior to use. Solvents were purified according to standard procedures [13].

The X-ray crystallographic studies were done by using Weissenberg camera (Stoe, Darmstadt, Germany) as well as a Siemens automatic four circle diffractometer type AED 2. Details of the experimental procedures have been described previously [14]. While mounting **5** inside the capillary, a minute amount of diethyl ether was inserted first *via* a glass fiber.

The details of data collection and structure determinations are summarized in table IV. The final atomic positional parameters as well as the isotropic B values calculated from U_{ij} values have been deposited in a data base [15].

Chloro-bis(2,4,6-trimethylphenoxy)gallium tert-*butylamide* $(2,4,6\text{-}Me_3C_6H_2O)_2GaCl \cdot tBuNH_2$ **2**

To a solution of 1,3-di-*tert*-butyl-2,2-dimethyl-4-chloro-1,3,2,4-diazasilagalletidine (0.65 g, 1.06 mmol) [2] in toluene (25 cm^3) a solution of sublimed 2,4,6-trimethylphenol (0.58 g, 4.25 mmol) in toluene (25 cm^3) was added dropwise at 20°C over a period of 15 min. The mixture was stirred for 24 h and all the volatiles were removed *in vacuo*. Upon dissolution in toluene (5 cm^3) with slight warming and cooling to 20°C, the residue afforded crystals of **2** after 24 h. Yield : 0.60 g (63%), mp 147°C [found C, 57.7; H, 7.5, calc for $C_{22}H_{33}ClGaNO_2$: C, 58.8; H, 7.4].

IR ($CHCl_3$) : 3 291 (s), 3 239 (w), 3 002 (s), 2 973 (s), 2 914 (s), 2 854 (s), 1 565 (s), 1 477 (vs), 1 377 (s), 1 306 (s), 1 232 (vs), 1 151 (vs), 856 (s), 823 (s), 808 (vs).

^{1}H NMR [C_6D_6 + C_6H_6] : 0.80 (s, 9H, C(CH_3)$_3$), 2.20 (s, 6H, p-CH_3), 2.30 (s, 12H, o-CH_3), 2.75 (br, s, 2H, NH_2), 6.60, 6.80 (s), each, 4H, H(Ar)).

Occasionally peaks at 2.17 (s, p-CH_3) and 2.33 (s, o-CH_3) were also observed in the ^{1}H NMR.

^{13}C NMR [C_6D_6 + C_6H_6] : 17.68 (s, C(CH_3)$_3$), 20.21 (s, p-CH_3), 28.70 (s, o-CH_3), 53.30 (s, C(CH_3)$_3$).

Tris [(2,6-dimethylphenyl)thio]gallium tert-*butylamine adduct* $(2,6\text{-}Me_2C_6H_3S)_3Ga \cdot tBuNH_2$ **3**

The same procedure as for **2** was followed using **1** (0.18 g, 0.29 mmol) and 2,6-dimethylbenzenethiol (0.16 g, 1.18 mmol) in toluene (5 + 5 cm^3). After removal of toluene *in vacuo*, the residue was dissolved in warm hexane. Crystals of **3** appeared after 24 h. Yield : 0.18 g (85% based on the thiol), mp 138°C. [Found : C, 60.82; H, 7.31. Calc for $C_{28}H_{38}GaNS_3$: C, 60.38; H, 6.86].

^{1}H NMR (C_6D_6) : 0.76 (s, 9H, C(CH_3)$_3$), 1.36 (s, 2H, NH_2), 2.55 (s, 18H, o-CH_3), 6.70-7.00 (m, 6H, H(Ar)).

^{13}C NMR : 23.46 (s, o-CH_3), 28.89 (s, C(CH_3)$_3$), 52.52 (s, CMe$_3$), 125.87, 126.98, 133.92, 142.71 (all C(Ar)).

Reaction of tert-*butanol with* **1**

The same procedure as for **2** was followed using **1** (0.51 g, 0.85 mmol), t-butanol (0.25 g, 3.40 mmol) and benzene (15 cm^3). The reaction mixture exhibited peaks in ^{1}H NMR at 1.18 and 0.17 ppm, corresponding to $Me_2Si(NH\text{-}tBu)_2$, in addition to several peaks at **ca** 1.40 ppm (see below). Upon removal of the solvent *in vacuo* and recrystallizing the residue from n-pentane a crystalline solid **4a** was obtained. Yield : 0.30 g (71%), mp 115-118°C. [Found : C, 36.26; H, 6.84, calc for $C_8H_{18}ClGaO_2$: C, 38.20; H, 7.16].

^{1}H NMR (C_6D_6) : 1.40, 1.41, 1.42 and 1.43 (all the equal intensity, O-C(CH_3)$_3$).

^{13}C NMR (C_6D_6) : 31.32, 33.05, 33.07, O-C(CH_3)$_3$), 72.75 (O-CMe$_3$), 80.11, 80.30 (very weak, O-CMe$_3$ (?)).

The crystals obtained were not suitable for X-ray structure determination.

When **4a** was heated **in vacuo** (0.01 mm/60°C) the resulting sublimate showed an analysis corresponding to [(tBuO)Ga(O)]$_n$. [Found : C, 30.45; H, 5.92; calc for $C_4H_9GaO_2$: C, 30.24; H, 5.67]. No further characterization was attempted.

Other reactions of 1

Reaction of **1** with 2,2-dimethylpropane-1,3-diol under similar conditions led to an insoluble solid. Triphenyl carbinol and 2,6-(tBu)$_2$-4-Me-C_6H_2OH did not react. The 1:2 reaction of **1** with tBuSH failed but proceeded with excess tBuSH (^{1}H NMR). No attempt was made to isolate the products. The reaction with PhMe$_2$COH showed a large number of methyl peaks in the ^{1}H NMR along with Me$_2$Si(NH-tBu)$_2$.

*2,6-Di-*tert*-butyl-4-(methylphenoxy) dichlorogallium etherate, (2,6-(*t*Bu)$_2$-4-Me-C_6H_2O)GaCl$_2$ · OEt$_2$* **5**

To a solution of gallium trichloride (1.88 g, 10.68 mmol) in toluene (10 cm^3), a solution of the lithium salt of 2,6-di-*tert*-butyl-4-methylphenol [15] in toluene (15 cm^3) was added dropwise with constant stirring over a period of 30 min. The mixture was stirred further overnight and filtered twice to remove insoluble materials. Removal of the solvent afforded an oil; addition of hexane (15 cm^3), filtration, concentration (to 5 cm^3) and then preservation at 0°C gave a crystalline solid. This was redissolved in hexane/ether mixture (1:1, 20 cm^3) and divided into two equal portions (A + B). From (A) most of the ether was removed (down to 5 cm^3). Voluminous crystals of **5** (0.80 g) formed after the solution was kept at 5°C for 24 h. These were used for the X-ray structure determination.

Most of the ether was also removed from portion (B) and a seed crystal from (A) was added. Within 3 h, the second modification of **1** was obtained as nice rectangular blocks (0.80 g). The solid-state structure of this compound could not be determined due to instability on exposure to X-rays [monoclinic : $a = 10.35$, $b = 20.02$, $c = 10.80$ Å, $\beta = 97.92°$, $V = 2\,217$ Å^3]. NMR spectra and other details of the crystals from (A) and (B) were identical.

5 : yield (total) : 1.60 g (35%), mp 95-100°C [Found : C, 51.50; H, 7.75, calc for $C_{19}H_{33}Cl_2GaO_2$: C, 52.56; H, 7.66. Found (after removal of ether) : C, 49.76; H, 7.75, calc for $C_{15}H_{23}Cl_2GaO$: C, 50.00; H, 6.39].

^{1}H NMR (C_6D_6) : 0.78 (t, 6H, CH$_2$CH_3), 1.62 (s, 18H, C(CH_3)$_3$), 2.28 (s, 3H, p-CH_3), 3.63 (q, 4H, OCH_2), 7.00-7.20 (br, 2H, H(Ar)).

^{13}C NMR (C_6D_6) : 12.74 (s, CH$_2$$CH_3$), 20.86 (s, p-CH$_3$), 31.51 (s, C(CH$_3$)$_3$), 34.78 (s, CMe$_3$), 68.73 (s, OCH$_2$), 126.21, 126.56, 140.15 (all C(Ar)).

tert-*Butyl ammonium (μ-2,4,6-trimethylphenoxy)-bis(trichlorogallium), [*t*BuNH$_3$]$^+$[(2,4,6-Me$_3$C$_6$H$_2$O)(GaCl$_3$)$_2$]$^-$* **6**

The procedure described for the formation of **2** was followed but the starting compound **1** was not completely separated from GaCl$_3$ (see literature [2]). As documented above, compound **2** was obtained in 60% yield but some crystals were found within **2** which had a different crystal shape. One of these crystals was exposed to X-ray radiation and showed a diffraction pattern different from **2**. A crystal structure determination revealed the crystals to have compositon of **6**.

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References

1 Cowley AH, Decken A, Olazabal CA, Norman NC, *Inorg Chem* (1994) 33, 3435

2 Veith M, Swamy KCK, Huch V, *Phosphor Sulfur and Silicon* (in press)

3 Veith M, Belo A, *Z Naturforsch B* (1988) 42, 325

4 Veith M, Pöhlmann J, *Z Naturforsch B* (1988) 43, 505

5 Reaction of nBuSnOOH with dithiodicyclohexyl phosphinic acid (1:1 stoichiometry) led only to nBuSn{S$_2$P(C$_6$H$_{11}$)$_2$}$_3$; part of the nBuSnOOH remained unreacted. KC K Swamy, RO Day, RR Holmes (unpublished results)

6 Petrie MA, Power PP, Dias RHV, Ruhlandt-Senge K, Waggoner KM, Wehmschulte R, *Organometallics* (1993) 12, 1909

7 Nutt WR, Blanton JS, Boccanfuso AM, Silks III LA, Garber AR, Odom JD, *Inorg Chem* (1991) 30, 4136

8 Chong KS, Rettig SJ, Storr A, Trotter J, *Can J Chem* (1979) 57, 586

9 Nutt WR, Stimson RE, Leopold MF, Rubin BH, *Inorg Chem* (1982) 21, 1909

10 Storre J, Belgardt T, Stalke D, Roesky HW, *Angew Chem Int Ed Engl* (1994) 33, 1244

11 Rettig SJ, Storr A, Trotter J, *Can J Chem* (1976) 54, 1278

12 Johnson WC, Huskew CA, *Inorg Synth* (1939) 1, 26

13 Perrin DD, Armarego WLF, Purification of Laboratory Chemicals, 3rd ed, Pergamon, Oxford, England, 1988

14 Veith M, Fischer J, Prout TR, Nötzel M, Hobein P, Huch V, *Inorg Chem* (1991) 30, 4130

15 Further data for X-ray structures of **2**, **5** and **6** have been deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD 401581 (**6**), 401582 (**5**), 401583 (**2**), the names of the authors, and the journal citation

16 Cetinkaya B, Gumrukiu I, Lappert MF, Atwood JL, Shakir R, *J Am Chem Soc* (1980) 102, 2086