

Reactions of gallium(III) chloride with $\text{Li}[\text{E}(\text{SiMe}_3)_3]$ ($\text{E} = \text{Si}$ or Ge): crystal structure of $(\text{R}_3\text{Ge})\text{ClGa}(\mu\text{-OEt})_2\text{GaCl}(\text{GeR}_3)$ ($\text{R} = \text{SiMe}_3$)

Frank Schwan, Siva P. Mallela and Russell A. Geanangel*

Department of Chemistry, University of Houston, Houston, Texas 77204-5641, USA

Reactions of $\text{Li}(\text{ER}_3)(\text{thf})_x$ ($\text{E} = \text{Si}$ or Ge , $\text{R} = \text{SiMe}_3$, $\text{thf} = \text{tetrahydrofuran}$) with gallium(III) chloride were carried out in diethyl ether with 1:1 and 2:1 stoichiometries. The 1:1 reactions gave products that decomposed upon recrystallization from pentane or drying *in vacuo*. The NMR spectra were consistent with a mixture of $\text{Li}[\text{R}_3\text{SiGaCl}_3](\text{thf})_4$ (major) and $\text{GaCl}_2(\text{SiR}_3)\cdot\text{thf}$ (minor) in the case of $\text{E} = \text{Si}$ and $\text{GaCl}_2(\text{GeR}_3)\cdot\text{thf}$ for $\text{E} = \text{Ge}$. The 2:1 $\text{E} = \text{Ge}$ reactions gave a mixture of two products exhibiting needle and plate crystal morphologies. The NMR spectra and a partial structure determination identified the former as $\text{Li}[\text{R}_3\text{GeGaCl}_3](\text{thf})_4$. A full structure determination of the latter showed it to be the diethoxy-bridged dimer, $(\text{R}_3\text{Ge})\text{ClGa}(\mu\text{-OEt})_2\text{GaCl}(\text{GeR}_3)$. The latter product is thought to result from cleavage of the ether solvent by either Ga_2Cl_6 or the intermediate gallium complex. Possible pathways are discussed.

Although organogallium compounds are plentiful, structurally characterized compounds with Ga–Si or Ga–Ge bonds are uncommon. The Cambridge Structure Database up to 15th October 1995 had only two structures with Ga–Si bonds and none with Ga–Ge bonds. An example of the former is **1**, a double chloride-bridged complex between $[\text{GaCl}[\text{Si}(\text{SiMe}_3)_3]]_2$ and solvated LiCl isolated from the reaction of 3 equivalents of $\text{Li}[\text{Si}(\text{SiMe}_3)_3](\text{thf})_3$ with gallium(III) chloride ($\text{thf} = \text{tetrahydrofuran}$).¹ One other example, $\text{Ga}[\text{Si}(\text{SiMe}_3)_3](\text{tmpip})_2$ (**2** ($\text{tmpip} = 2,2,6,6\text{-tetramethylpiperidine}$)), was prepared from equimolar quantities of $\text{GaCl}(\text{tmpip})_2$ and $\text{Li}[\text{Si}(\text{SiMe}_3)_3](\text{thf})_3$.² In both cases the structures show distortions due to the large steric demands of the $\text{Si}(\text{SiMe}_3)_3$ substituent. The Si–Ga–Si angle around four-co-ordinate Ga in **1** (138°) exceeds the expected tetrahedral value, while the Ga–Si bond lengths in both compounds [$2.439(5)$ and $2.468(1) \text{ \AA}^2$] are notably greater than the sum of the covalent radii of the atoms (2.37 \AA). Very recently, the structures of two silyl-digallane derivatives, $\text{Ga}_2[\text{Si}(\text{SiMe}_3)_3]_4$ and $\{[(\text{Me}_3\text{Si})_3\text{Si}]\text{ClGa-GaCl}[\text{Si}(\text{SiMe}_3)_3]\}_2$ (cage dimer of digallanes with bridging chlorides), have been published³ and in the same communication the new silylgallane, $\text{GaCl}_2[\text{Si}(\text{SiMe}_3)_3]\cdot\text{thf}$ was reported but not structurally characterized.

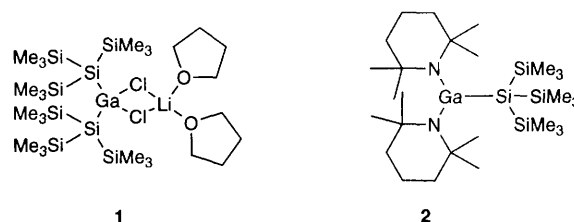
Our interest in the effects of $\text{E}(\text{SiMe}_3)_3$ ($\text{E} = \text{Si}$ or Ge) groups on the stabilities of Main Group compounds led us further to examine the reaction of gallium(III) chloride with the $\text{Li}[\text{E}(\text{SiMe}_3)_3]$ reagents. We report here the results of reactions in 1:1 and 2:1 stoichiometries.

Experimental

Except as noted, all manipulations were conducted using Schlenk techniques under argon dried with P_4O_{10} . Diethyl ether and tetrahydrofuran were distilled from LiAlH_4 under dry nitrogen, pentane and hexane from sodium just before use. The reagents $\text{Li}[\text{Ge}(\text{SiMe}_3)_3](\text{thf})_{2.5}$ and $\text{Li}[\text{Si}(\text{SiMe}_3)_3](\text{thf})_3$ were prepared according to literature methods⁴ using low halide (chloride) methyl lithium from Aldrich. Other starting materials were from Aldrich except Ga_2Cl_6 and GeCl_4 which were from Strem and used as received. The NMR spectra were recorded using a General Electric QE-300 instrument.

Reactions of gallium(III) chloride

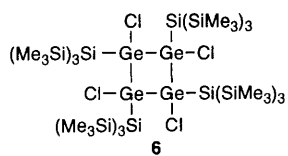
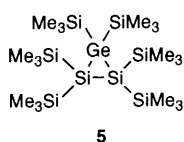
With $\text{Li}[\text{Si}(\text{SiMe}_3)_3](\text{thf})_3$ in 1:1 ratio. To a solution of Ga_2Cl_6 (1.77 g, 5.03 mmol) in ether (25 cm^3) at -78°C was



added dropwise a solution of $\text{Li}[\text{Si}(\text{SiMe}_3)_3](\text{thf})_3$ in ether. Stirring was continued as the reaction mixture warmed slowly to room temperature and then for 16 h. A fine white precipitate was filtered off over Celite, the solvent was removed under reduced pressure and replaced with pentane (75 cm^3). After stirring, the pentane suspension was filtered and the filtrate cooled to -45°C yielding white crystals (1.4 g). These were recrystallized from pentane at 0°C [$\text{NMR}(\text{C}_6\text{D}_6)$: ^1H , δ 0.38 (s, minor), 0.54 (s, SiMe_3), 1.34 (m, CH_2 , thf) and 3.56 (m, OCH_2 , thf); ^{13}C , δ 2.86, 25.3 (CH_2) and 68.7 (OCH_2)], but $(\text{Me}_3\text{Si})_3\text{Si-Si}(\text{SiMe}_3)_3$ [^1H , δ 0.39 (s)] was also present and repeated crystallization until the signals of it and the thf were absent caused decomposition of the product to an unidentified viscous oil that was insoluble in pentane and benzene. Decomposition also occurred when the crystals were dried *in vacuo*, probably owing to loss of thf .

With $\text{Li}[\text{Ge}(\text{SiMe}_3)_3](\text{thf})_{2.5}$ in 1:1 ratio. The reaction was carried out by a procedure similar to that used for the silyl reagent yielding an impure white solid (1.4 g). After one recrystallization from pentane, spectra showed the presence of a product [$\text{NMR}(\text{C}_6\text{D}_6)$: ^1H , δ 0.42 (s, SiMe_3), 1.17 (m, CH_2), and 3.64 (m, OCH_2); ^{13}C , δ 3.47, 25.0(CH_2) and 69.9(OCH_2)] in fair purity. After a second crystallization the thf resonances were absent, however the product decomposed to a viscous oil.

In 2:1 ratio. To $\text{Li}[\text{Ge}(\text{SiMe}_3)_3](\text{thf})_{2.5}$ (5.478 g, 11.4 mmol) in ether (150 cm^3) at -78°C was added dropwise a solution of Ga_2Cl_6 (1.006 g, 2.85 mmol) in ether (50 cm^3). The stirred mixture was warmed to room temperature over 24 h giving a pale yellow solution over a white solid. Solvent was removed *in vacuo*, pentane (100 cm^3) was added, the mixture stirred for 1 h and filtered over Celite. The yellow filtrate was concentrated to about 50 cm^3 and cooled to 0°C for 2 d giving white crystals (2.125 g). Inspection of the highly air-sensitive, clear, colourless crystals revealed two morphologies: plates (**3**) and needle crystals (**4**). The pronounced hygroscopic character of both



compounds precluded satisfactory elemental analyses. Redissolved, crystals of **3** gave (C_6D_6): 1H , δ 0.43 (s, SiMe₃), 1.17 (m, CH₃) and 3.64 (m, CH₂); ^{13}C , δ 3.83 (SiMe₃). The ^{13}C resonances of the C₂H₅ groups later found to be present in **3** were not observed. Candidate crystals of both types were selected for X-ray crystallography. X-Ray analysis of **4** could not be completed due to severe disorder in the structure but progressed sufficiently to identify the product with reasonable certainty as Li[(Me₃Si)₃GeGaCl₃](thf)₄. Redissolved crystals of **4** gave (C_6D_6): 1H , δ 0.56 (s, 27 H, SiMe₃), 1.43 (m, 16 H, CH₂), and 3.58 (m, 16 H, OCH₂); ^{13}C , δ 3.54 (SiMe₃), 25.5 (CH₂), and 68.4 (OCH₂).

Crystallography

A colourless block of compound **3** having approximate dimensions 0.20 × 0.25 × 0.40 mm was cut from a long tapering flat column and mounted in a random orientation on a Nicolet R3m/V automatic diffractometer. The sample was held in a stream of dry nitrogen gas at -60 °C, and the radiation used was Mo-K α (λ 0.710 73 Å) monochromatized by a highly ordered graphite crystal. Final cell constants, as well as other information pertinent to data collection and refinement, are listed in Table 1. The Laue symmetry was determined to be $\bar{1}$, and the space group was shown to be either *P1* or $P\bar{1}$. Intensities were measured using the ω -scan technique, with the scan rate depending on the count obtained in rapid pre-scans of each reflection. Two standard reflections were monitored after every 2 h or every 100 data collected, and these showed no significant change. During data reduction Lorentz-polarization corrections were applied, as well as a semiempirical absorption correction based on ψ scans of 10 reflections having χ values between 70 and 90°.⁵

Since the unitary structure factors displayed centric statistics, space group $P\bar{1}$ was chosen from the outset. The structure was solved by the SHELXTL direct methods program which revealed the positions of most of the atoms in the asymmetric unit, consisting of one-half molecule situated about an inversion centre. Remaining atoms were located in subsequent Fourier-difference syntheses. The usual sequence of isotropic and anisotropic refinement was followed, after which all hydrogens were entered in ideal calculated positions and constrained to riding motion, with a single variable isotropic thermal parameter for all of them. After all shift/e.s.d. ratios were less than 0.1, convergence was reached at the agreement factors listed in Table 1. No unusually high correlations were noted between any of the variables in the last cycle of full-matrix least-squares refinement on *F*, and the final difference density map showed a maximum peak of about 0.25 e Å⁻³. All calculations were made using SHELXTL PLUS.

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/216.

Results and Discussion

The steric demands of the Si(SiMe₃)₃ (hypersilyl) group appear to limit the number of such groups that can be accommodated on a central metal atom. Single substitutions of the groups are common but fewer instances of disubstitutions have been structurally characterized. Bis[tris(trimethylsilyl)silyl]-zinc,

Table 1 Data collection and processing parameters for compound **3**

Formula	C ₂₂ H ₆₄ Cl ₂ Ga ₂ Ge ₂ O ₂ Si ₆
<i>M</i>	884.92
Crystal symmetry	Triclinic
Space group	$P\bar{1}$
<i>a</i> /Å	9.264(1)
<i>b</i> /Å	9.496(2)
<i>c</i> /Å	14.506(2)
α /°	101.01(1)
β /°	92.84(1)
γ /°	116.41(1)
<i>U</i> /Å ³	1109
<i>Z</i>	1
<i>D_c</i> /g cm ⁻³	1.33
μ /cm ⁻¹	28.22
<i>F</i> (000)	456
No. reflections	2888
Independent reflections [<i>I</i> > 3 σ (<i>I</i>)	2353
No. variables	164
<i>R</i>	0.021
<i>R'</i>	0.021

$$R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, \quad R' = \frac{[\sum w^2(|F_o| - |F_c|)^2 / \sum |F_o|^2]^{\frac{1}{2}}}{\sigma(F)^2}, \quad w^{-1} = \sigma(F)^2.$$

-cadmium and -mercury derivatives are known and the zinc compound was shown to have the expected linear Si-Zn-Si skeleton,⁶ minimizing the steric interaction of the bulky silyls. The first disubstituted tin(II) compound was isolated in the form of a lithium chloride complex, [(Me₃Si)₃Si]₂Sn(μ -Cl)Li(thf)₃,⁷ and the parent stannylene, Sn[Si(SiMe₃)₃]₂, was recently reported to be a dimer in the solid state.⁸ In SnCl₂[E(SiMe₃)₃]₂ (E = Si⁹ or Ge¹⁰) the E-Sn-E angles exceed 140° indicative of severe steric crowding around Sn^{IV}. In the recently reported Pb[Si(SiMe₃)₃]₂ the Si-Pb-Si bond angle was 113.56°, consistent with a somewhat lessened steric strain between the hypersilyl groups when attached to the large lead atom.⁸ Two disubstituted boron compounds, BR[Si(SiMe₃)₃]₂ (R = OMe or NMe₂), have been reported, however neither was structurally characterized.¹¹

To our knowledge, efforts to surround gallium with more than two hypersilyl substituents have not, as yet, been fruitful. The only structurally characterized, disubstituted case known to us, the double chloride-bridged complex **1** between GaCl[Si(SiMe₃)₃]₂ and solvated LiCl, was prepared from 3 equivalents of Li[Si(SiMe₃)₃](thf)₃ with gallium(III) chloride¹ but no trisubstituted product was isolated. The fact that the product is an ionic complex with four-co-ordinate Ga complicates comparisons of its steric distortion but the Si-Ga-Si bond angle of 138° and the lengthened Si-Ga distances (2.439 Å) suggest appreciable crowding. Results of molecular mechanics calculations on the as yet unprepared tris[tris(trimethylsilyl)silyl]gallane were consistent with moderate strain in the heavy-atom skeleton. They predicted slightly shorter Ga-Si bonds (2.42 Å) than those in **1** and **2**, but average Si-Si angles were compressed to 103° indicative of moderate crowding around the Ga atom.

The fact that attempts to prepare the crowded, disubstituted germanium derivatives, Ge[Si(SiMe₃)₃]₂ and GeCl₂[Si(SiMe₃)₃]₂, gave instead unexpected cyclic products, **5**¹² and **6**,¹⁰ respectively, led us to investigate the reaction of gallium(III) chloride with Li[Si(SiMe₃)₃](thf)₃ and Li[Ge(SiMe₃)₃](thf)₂,⁵ anticipating that, due to similar steric crowding, cyclic gallium compounds might result.

1 : 1 Li[E(SiMe₃)₃](thf)_{3/2,5}-gallium(III) chloride reactions (E = Si or Ge)

Using diethyl ether as the solvent, reactions were initiated at low temperature, stirred to ambient, filtered, solvent stripped and the residue extracted into pentane. With E = Si a product

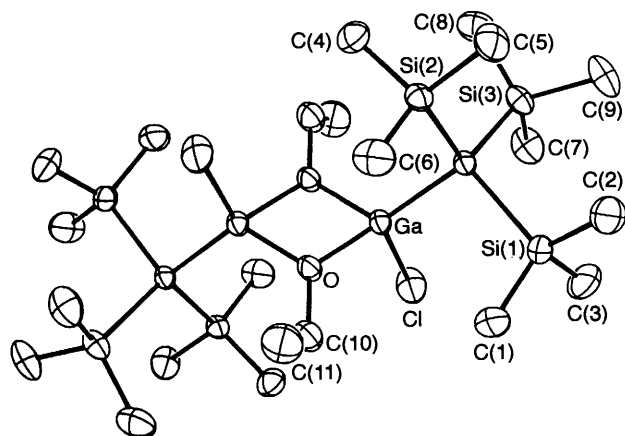


Fig. 1 View of compound 3 showing the atom numbering scheme. Thermal ellipsoids are 40% equiprobability envelopes with hydrogens omitted

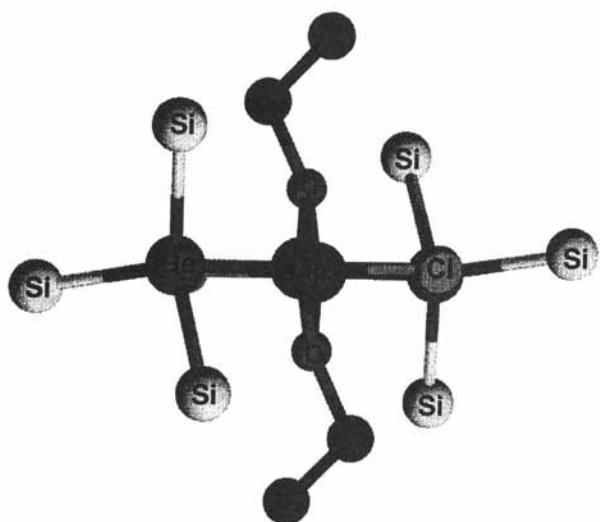
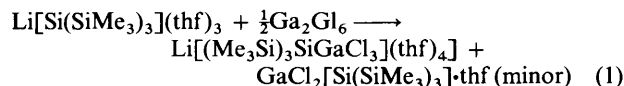


Fig. 2 View of the heavy-atom skeleton of compound 3 showing the planar Ga_2O_2 segment and the *trans* arrangement of the $\text{Ge}(\text{SiMe}_3)_3$ groups

was isolated but it decomposed upon recrystallization to an intractable oil. The similarity of its NMR spectra (^1H , δ 0.54, 1.34, 3.56; ^{13}C , δ 2.86, 25.3, 68.7) to those of the better characterized product of the 2:1 E = Ge reaction allowed us tentatively to identify the product as $\text{Li}[(\text{Me}_3\text{Si})_3\text{SiGaCl}_3](\text{thf})_4$ (see below). A small signal in the ^1H spectrum at δ 0.38 matches the SiMe_3 resonance reported for $\text{GaCl}_2[\text{Si}(\text{SiMe}_3)_3]\text{thf}$,³ a reasonable by-product for this reaction [equation (1)].



The product of the 1:1 E = Ge reaction also decomposed upon recrystallization. Its Me_3Si NMR signals before decomposition (^1H , δ 0.42; ^{13}C , δ 3.47) do not match the values of compound 4 (^1H , δ 0.56; ^{13}C , δ 3.54), the expected product. Since Me_3Si ^1H and ^{13}C signals move downfield consistently upon substituting $(\text{Me}_3\text{Si})\text{Ge}$ for $(\text{Me}_3\text{Si})\text{Si}$,* an estimate of the

* Comparison of the Me_3Si shifts of six structurally characterized compounds containing $(\text{Me}_3\text{Si})_3\text{E}$ (E = Si or Ge) groups showed an average downfield shift of 0.030 ± 0.007 ppm for ^1H and 0.52 ± 0.22 ppm for ^{13}C when E = Ge compared to Si.

Table 2 Selected bond lengths (Å) and angles (°) for compound 3

Ge–Ga	2.407(1)	Ge–Si(1)	2.394(1)
Ge–Si(2)	2.388(1)	Ge–Si(3)	2.390(2)
Ga–Cl	2.196(1)	Ga–O	1.927(3)
Ga...Ga'	2.985(1)	Si(1)–C(1)	1.871(5)
Si(1)–C(2)	1.872(4)	Si(1)–C(3)	1.862(5)
O–C(10)	1.450(6)		
Ga–Ge–Si(1)	103.7(1)	Ga–Ge–Si(2)	110.4(1)
Si(1)–Ge–Si(2)	110.9(1)	Ga–Ge–Si(3)	109.3(1)
Si(1)–Ge–Si(3)	108.6(1)	Si(2)–Ge–Si(3)	113.5(1)
Ge–Ga–Cl	117.0(1)	Ge–Ga–O	123.9(1)
Cl–Ga–O	102.7(1)	Ge–Ga–O'	121.4(1)
Cl–Ga–O'	106.2(1)	O–Ga–O'	78.5(1)
Ge–Si(1)–C(1)	110.9(1)	Ge–Si(1)–C(2)	110.2(2)
C(1)–Si(1)–C(2)	107.4(2)	Ge–Si(1)–C(3)	110.7(2)
C(1)–Si(1)–C(3)	107.9(2)	C(2)–Si(1)–C(3)	109.7(2)
Ga–O–C(10)	127.9(2)	Ga–O–Ga'	101.5(1)
C(10)–O–Ga'	123.8(2)	O–C(10)–C(11)	109.3(4)
Si(1)–Ge–Ga–Cl	–52.9	Ga'–O–Ga–Ge	120.3
Si(1)–Ge–Ga–O	76.8	Ga'–O–Ga–Cl	–104.3
Si(1)–Ge–Ga–O'	174.2	Ga'–O–Ga–O'	0.0
Si(2)–Ge–Ga–Cl	–171.7	C(11)–C(10)–O–Ga	127.1
Si(2)–Ge–Ga–O	–42.0	C(11)–C(10)–O–Ga'	–87.2
Si(2)–Ge–Ga–O'	55.4	C(10)–O–Ga'–O'	–153.0
Si(3)–Ge–Ga–Cl	62.7	Ge–Ga–O'–Ga'	–122.8
Si(3)–Ge–Ga–O	–167.5	Cl–Ga–O'–Ga'	100.0
Si(3)–Ge–Ga–O'	–70.1	C(10)–O–Ga–O'	151.4
Si(2)–Ge–Si(3)–C(9)	76.2	C(10)–O–Ga–Cl	47.1
C(10)–O–Ga–Ge	–88.3		

Me_3Si chemical shifts for $\text{GaCl}_2[\text{Ge}(\text{SiMe}_3)_3]\text{thf}$ was obtained by adding the incremental shifts to those of $\text{GaCl}_2[\text{Si}(\text{SiMe}_3)_3]\text{thf}$.³ The estimates, ^1H δ 0.41 ± 0.007 and ^{13}C δ 3.32 ± 0.22 , match those of the 1:1 E = Ge product well enough tentatively to assign that product as $\text{GaCl}_2[\text{Si}(\text{SiMe}_3)_3]\text{thf}$. The shifts of an authentic sample of that compound (^1H , δ 0.418, 1.182, 3.702; ^{13}C , δ 3.475, 26.21, 70.09), prepared subsequently by another route,¹³ appear to support the assignment. The fact that the 1:1 E = Si reaction gave the ionic complex $\text{Li}[(\text{Me}_3\text{Si})_3\text{SiGaCl}_3](\text{thf})_4$ along with a small amount of the molecular form [equation (1)] while the 1:1 E = Ge reactions gave only the molecular germylgallane, $\text{GaCl}_2[\text{Ge}(\text{SiMe}_3)_3]\text{thf}$, may be attributable to small differences in solvent polarity arising from the larger amount of thf introduced from the silyl reagent $\text{Li}[\text{Si}(\text{SiMe}_3)_3](\text{thf})_3$ than from the germyl reagent $\text{Li}[\text{Ge}(\text{SiMe}_3)_3](\text{thf})_{2.5}$.

2:1 $\text{Li}[\text{E}(\text{SiMe}_3)_3](\text{thf})_{3/2.5}$ –Gallium(III) chloride reactions (E = Si or Ge)

One exploratory 2:1 E = Si reaction was carried out but no Ga–Si compounds were isolated and it was decided to concentrate on the 2:1 E = Ge reaction where conditions were readily found that gave isolable Ga–Ge products. Evaporation of the ether 2:1 E = Ge reaction mixture, followed by extraction into and crystallization from pentane, gave both needle crystals and plates that could be physically separated. Some of the plates were collected for NMR analysis and a structure determination identified the product as the diethoxy-bridged, digallium compound 3, in which each gallium bears one chloride and one tris(trimethylsilyl)germyl group (Fig. 1).

Data collection parameters are given in Table 1. The coordination geometry around the four-co-ordinate Ga atoms is somewhat distorted with the Ge–Ga–Cl angle at 117° and the two Ge–Ga–O angles at 121.4 and 123.9° (Table 2), exceeding the expected tetrahedral angle, in part due to the crowding by the germyl group. The O–Ga–O angle is 78.5° , probably

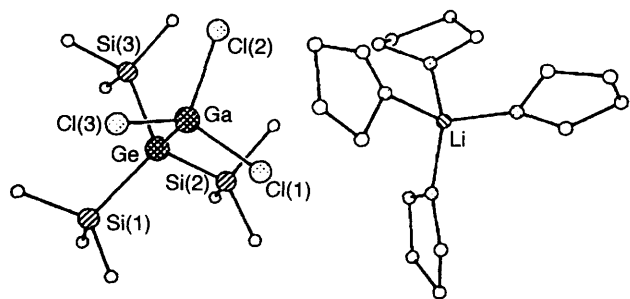


Fig. 3 View of the molecular geometry of compound **4** based on a structure determination ($R = 0.10$) that could not be completed due to extensive disorder

reflecting the structural restraints of the Ga–O–Ga bridge system. The Ga_2O_2 fragment is planar and the two Ge and two Cl atoms lie in a plane perpendicular to the Ga_2O_2 plane. (The Ge–Ga–Ga–Cl improper torsion angle is less than 0.5° .) The tris(trimethylsilyl)germyl groups are situated in *trans* positions with respect to the Ga_2O_2 ring. The Ga–Ge distance (2.407 Å) compares closely to the sum of the covalent radii of Ga (1.20 Å) and Ge (1.22 Å)¹⁴ and is actually less than that of the Ga–Si bonds in **1** and **2**. This, along with the minimum distortion of the heavy-atom skeleton (Fig. 2), and the closeness of the Si–Ge–Si angles to tetrahedral values indicate that the $\text{Ge}(\text{SiMe}_3)_3$ groups do not cause excessive crowding in **3**.

The structure of compound **3** resembles that of the recently reported $[\text{GaH}(\text{O}i\text{Bu})_2]_2$, a dimeric, di-*tert*-butoxygallane with bridging and terminal Bu'O groups, in which the terminal groups are also *trans* with respect to the Ga_2O_2 ring.¹⁵ {NMR spectra revealed the presence of both *cis* and *trans* isomers of $[\text{GaH}(\text{O}i\text{Bu})_2]_2$ in solution.} The O–Ga–O and Ga–O–Ga angles in the ring (79.4 and 100.6° , respectively) are nearly the same as those in **3** and the Ga–O distances average only 0.02 Å less. The corresponding bond lengths and angles in the related dimer $[\text{GaH}_2(\text{O}i\text{Bu})_2]_2$, that has bridging Bu'O groups, also have about the same values suggesting that the geometric parameters in such Ga_2O_2 rings may be fairly insensitive to the nature of the substituents.

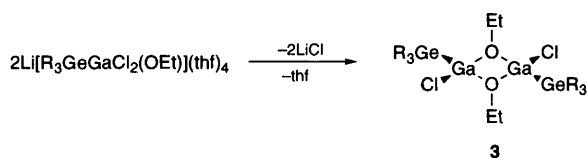
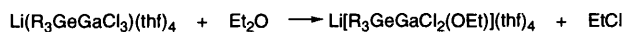
The NMR spectra of the second product (needle crystals) [^1H , δ 0.56 (s, 27 H), 1.43 (m, 16 H) (thf), 3.58 (m, 16 H, thf); ^{13}C , δ 3.54, 25.5, 68.4] are consistent with its being the monosubstituted trichlorogallate complex, $\text{Li}[(\text{Me}_3\text{Si})_3\text{GeGaCl}_3](\text{thf})_4$ **4**. An attempted structure determination on one of the needle crystals could not be completed due to massive disorder of the thf molecules in the cation along with rotational disorder of all three SiMe_3 groups. Although the identity of **4** was confirmed,[†] reliable structural parameters could not be obtained since the best R value was about 0.10. Fig. 3 shows the molecular geometry.

As noted above, the NMR spectra of the 1:1 (E = Si) reaction product (prior to its decomposition) closely resemble those of compound **4**, suggesting that it is probably the silyl analogue of **4**, $\text{Li}[(\text{Me}_3\text{Si})_3\text{SiGaCl}_3](\text{thf})_4$.[‡] Evidently the additional thf present in the 2:1 reactions stabilized the product enough that it could be crystallized.

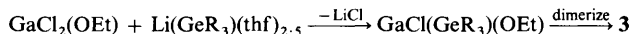
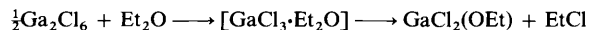
The question of how the dimer **3** originates in the 2:1

[†] Unit-cell parameters: space group $P\bar{1}$, triclinic; $a = 10.733(4)$, $b = 13.810(5)$, $c = 13.885(7)$ Å, $\alpha = 87.88(3)$, $\beta = 89.27(3)$, $\gamma = 86.53(3)$, $U = 2053$ Å³, molecular formula $\text{Li}^+\cdot\text{C}_9\text{H}_{27}\text{Si}_3\text{Cl}_3\text{GaGe}^-\cdot 4\text{C}_4\text{H}_8\text{O}$, $M = 763.71$, $Z = 2$, $D_c = 1.24$ g cm⁻³, $\mu = 16.8$ cm⁻¹, $T = -50$ °C.

[‡] The NMR shifts of the Me_3Si groups in the 1:1 E = Si product are 0.2 and 0.68 ppm (^1H and ^{13}C) toward higher field than those of **4**. These shifts are in the same direction and fall within difference ranges observed between $(\text{Me}_3\text{Si})_3\text{Si}$ and $(\text{Me}_3\text{Si})_3\text{Ge}$ groups in related compounds (see footnote to p. 4185).



Scheme 1 $R = \text{SiMe}_3$



Scheme 2 $R = \text{SiMe}_3$

reaction is not yet resolved. Since the silicon analogue of **3** was not observed in the 1:1 E = Si reactions, it may be that the additional thf in the 2:1 reactions, by stabilizing **4**, allows formation of **3** to occur through the intermediacy of **4**. Group 13 halides are known to cleave ethers¹⁶ so complex **4** might also react with the ether solvent as shown in Scheme 1 leading to $\text{Li}[(\text{Me}_3\text{Si})_3\text{GeGaCl}_2(\text{OEt})](\text{thf})_4$ which could dimerize with the elimination of 2 equivalents of LiCl giving **3**. It is also possible that Ga_2Cl_6 first cleaves the ether to give an ethoxy-intermediate that subsequently reacts with the germyl lithium to give **3** (Scheme 2). Support for the former path involving **4** as an intermediate comes from a study of the reaction of Al_2Cl_6 with $\text{Li}[\text{C}(\text{SiMe}_3)_3]$ in hexane–ether solvent.¹⁷ After hydrolysis, the reaction mixture gave $(\text{Me}_3\text{Si})_3\text{COEt}$ (54% yield) as the only product, demonstrating ether cleavage. Since $\text{Li}[\text{C}(\text{SiMe}_3)_3]$ is known to be stable in ether, the investigator implicated a complex between the reactants, perhaps $\text{Li}[(\text{Me}_3\text{Si})_3\text{AlCl}_3]$, a counterpart of **4**, as responsible for ether cleavage leading to the ethoxy group in the hydrolysed product. A similar result was found for reactions of BF_3 and $\text{Li}[\text{C}(\text{SiMe}_3)_3]$, neither of which cleaves ether separately. In this regard it is also notable that NMR spectra of **4** in C_6D_6 solution, prepared from crystals, are unchanged over several months. Over the same period a sample of **3** held in refrigerated solution decomposed to a mixture of as yet unidentified products.

No disubstituted product, analogous to Cowley's compound **1**, was detected in any 2:1 reaction mixture. It is not clear why the second substitution step did not take place.

Acknowledgements

The authors gratefully acknowledge the support of this investigation by the Robert A. Welch Foundation under Grant E-1105. We are also grateful to James Korp for carrying out the structure determinations and to the University of Saarbrücken for partial support of one of us (F. S.).

References

- 1 A. M. Arif, A. H. Cowley, T. M. Elkins and R. A. Jones, *J. Chem. Soc., Chem. Commun.*, 1986, 1776.
- 2 R. Frey, G. Linti and K. Polborn, *Chem. Ber.*, 1994, 101.
- 3 G. Linti and W. Köstler, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 550.
- 4 A. G. Brook, F. Abderaken and H. Söllradl, *J. Organomet. Chem.*, 1986, **299**, 9; G. Gutekunst and A. G. Brook, *J. Organomet. Chem.*, 1982, **225**, 1.
- 5 G. M. Sheldrick, SHELXTL PLUS, Nicolet Instruments, 1987.
- 6 J. Arnold, T. D. Tilley, A. L. Rheingold and S. Geib, *Inorg. Chem.*, 1987, **26**, 2106.
- 7 A. M. Arif, A. H. Cowley and T. M. Elkins, *J. Organomet. Chem.*, 1987, **325**, C11.
- 8 K. Klinkhammer and W. Schwarz, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1334.
- 9 S. P. Mallela and R. A. Geanangel, *Inorg. Chem.*, 1990, **29**, 3525.

- 10 S. P. Mallela and R. A. Geanangel, *Inorg. Chem.*, 1994, **33**, 1115.
- 11 W. Biffer and H. Nöth, *Z. Naturforsch., Teil B*, 1981, **36**, 1509.
- 12 A. Heine and D. Stalke, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 113.
- 13 S. P. Mallela and R. A. Geanangel, unpublished work.
- 14 J. Huheey, *Inorganic Chemistry*, 3rd edn., Harper and Row, New York, 1983, p. 258.
- 15 M. Vieth, S. Faber, H. Wolfanger and V. Huch, *Chem. Ber.*, 1996, **129**, 381.
- 16 See, for example, M. V. Bhatt and S. U. Kulkarni, *Synthesis*, 1983, 249.
- 17 C. L. Smith, *Organometallics*, 1995, **14**, 3098.

Received 31st May 1996; Paper 6/03790I