380 *Organometallics* **2002,** *21,* 380−388

Cyclosiloxanes Containing a Gallium Atom as Ring Member from the Reaction of *tert*-Butoxygallane with Di- and Trisiloxanediols

Michael Veith,* Heidi Vogelgesang, and Volker Huch

Institut für Anorganische Chemie, Universität des Saarlandes, Postfach 15 11 50, 66041 Saarbrücken, Germany

Received June 21, 2001

tert-Butoxygallane, $[tBuOGaH_2]_2$, reacts with tetraphenyl-1,3-disiloxanediol, $HO(Ph_2)Si{-}O{-}Si(Ph_2)OH$, with hydrogen elimination to form the bicyclic compound $[(OSiPh_2OSiPh_2O)[Ga(H)]_2(OtBu)_2]$ (**1**). The skeleton of molecule **1** consists of a four-membered Ga_2O_2 ring to which a five-membered O−Si−O−Si−O bridge is connected through Ga−O bonds. While the gallium atoms each have a hydrogen atom as further substituent, the oxygen atoms of the four-membered ring have *tert*-butyl substituents and the silicon atoms each bear two phenyl groups. When the reactant ratio is changed to $[tBuOGaH_2]_2$:1,3-disiloxanediol = 1:2, two new products are formed in almost equal amounts: $[(OSiPh_2OSiPh_2OSiPh_2O)GaH]_2$ (**2**) and $[(OSiPh_2OSiPh_2OSiPh_2O)GaOtBu]_2$ (**3**). Both compounds are centrosymmetric, forming either a central Ga_2O_2 ring to which two eight-membered GaO_4Si_3 rings are fused with two common GaO edges (**2**) or a central Ga_2O_2 ring, the gallium corners serving as spiro centers for again eight-membered GaO_4Si_3 rings (**3**). In comparison to **1**, molecules **2** and **3** contain Si−O chains with one further SiO unit and have lost either *tert*-butyl alcohol (**2**) or hydrogen (**3**) with respect to **1**. Compound **2** can also be obtained when, instead of tetraphenyl-1,3-disiloxanediol, hexaphenyl-1,5-trisiloxanediol ($HO(Ph_2)SiOSiPh_2OSi(Ph_2)OH$) is reacted with *tert*-butoxygalane. The central Ga_2O_2 rings in molecules **2** and **3** originate from Lewis acid and base interactions but are of different stability. In **2**, the ring is formed by oxygen atoms bearing a silicon substituent and therefore should have reduced basicity: consequently, **2** can be split (into halves) by simple reaction with triethylamine, the nitrogen atom serving as a donor to gallium. The product of this reaction is an eight-membered Si_3O_4Ga ring with hydrogen and triethylamine as ligands at gallium and two phenyl groups on each of the silicon atoms and has the formula $[(OPh_2SiOSiPh_2OSiPh_2O)GaH(NEt_3)]$ (**4**). Further change of the stoichiometry between *tert*-butoxygallane and the 1,5-trisiloxanediol in favor of the silicon compound again has a consequence for the reaction products. Using NEt_3 as crystallization promotor gave $[(OSiPh_2OSiPh_2OSiPh_2O)_2Ga{\cdot}HNEt_3]$ (**5**). In this compound a spiro-connected gallium atom is a member of two GaO_4Si_3 rings. The triethylamine group is coordinating a proton which forms a bridge between an oxygen atom of the rings and nitrogen. Compound **5** can also be obtained from **2** using a dilute solution of water in THF. Compounds **1**−**5** have been fully characterized by ^1H, ^{13}C, ^{29}Si NMR and IRspectroscopy and have been the subject of single-crystal X-ray diffraction studies.

Introduction

The *tert*-butoxyalane $(tBuOAlH_2)_2$ can be used very elegantly for the direct synthesis of polycyclic alumosiloxanes such as $[OSiPh_2OSiPh_2O]_4[AlOH]_4$ by treatment with diphenylsilanediol.[1] In this complex reaction, besides the formation of *tert*-butyl alcohol and hydrogen, a condensation of diphenylsilanediol forming tetraphenyl-1,3-disiloxanediol is observed. We have also shown in an alternative experiment that the hydride ligands on aluminum are more reactive toward silanols than the *tert*-butoxy groups.[1] Alumosiloxanes of the type described above may be considered as silaaluminates wrapped up in an organic matrix (phenyl groups) and may serve as metalloorganic counterparts of metal alumosilicates.[2] As a matter of fact, the hydroxy groups on the aluminum atoms in $[OSiPh_2OSiPh_2O]_4[AlOH]_4$ can be deprotonated to form to lithium salts such as $[OSiPh_2OSiPh_2O]_4[AlO]_4Li_4{\cdot}4OEt_2$.[3]

Meanwhile, alumosiloxanes and their metal derivatives have been largely explored and have been included in a compilation by Sullivan and King;[4] in addition, other metal derivatives of siloxanes have been reviewed by Edelmann et al. and Jurkschat and Beckmann.[5] A very recent paper of Gun'ko et al. reported the isolation and structural characterization of a molecular alumo-

---

(1) Veith, M.; Jarczyk, M.; Huch, V. *Angew. Chem.* **1997**, *109*, 140; *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 177.

(2) Montero, M. L.; Voigt, A.; Teichert, M.; Uson, I.; Roesky, H. W. *Angew. Chem.* **1995**, *107*, 2761; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2504.

(3) Veith, M.; Jarczyk, M.; Huch, V. *Angew. Chem.* **1998**, *110*, 109; *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 105.

(4) King, L.; Sullivan, A. C. *Coord. Chem. Rev.* **1999**, *189*, 19.

10.1021/om010544p CCC: $22.00

silicate, $[PyH][\{(Ph_2Si)_3O_4\}Al]$,[6] which is remarkably similar to one of our products (see below for compound **5**).

The incorporation of gallium instead of aluminum into siloxanes has attracted less attention, although reports on this subject appeared almost 40 years ago. Trimethylgallium is known to react with trimethylsilanol to form the dimeric dimethylgallium trimethylsiloxane $[Me_2GaOSiMe_3]_2$.[7] Gallium trichloride reacts with sodium trimethylsilanolate to give dimeric tris(trimethylsiloxy)gallium,[8] from which siloxygallates of the type $M[Ga(OSiR_3)_4]$ have been obtained[9] (see also a review of this early work[10]). Only recently have cage and polycyclic compounds with silicon, oxygen, and gallium and their X-ray structures been reported by Feher and co-workers (compounds derived from silesquioxanes),[11] by Roesky and co-workers (drum-shaped structures),[12] and by Murugavel and his group (polycyclic lithium gallosiloxanes).[13]

We have been interested in exploring whether the reactivity pattern observed for the reaction of $[tBuOAlH_2]_2$ with $Ph_2Si(OH)_2$ (see above) could be transposed to $[tBuOGaH_2]_2$.[14] In preliminary experiments we found that *tert*-butoxygallane and $Ph_2Si(OH)_2$ reacted differently, giving only a mixture of polymeric products, which could not be isolated. We therefore replaced $Ph_2Si(OH)_2$ by its higher condensation products $(HO)Ph_2SiOSiPh_2(OH)$ and $(HO)Ph_2SiOSiPh_2OSiPh_2(OH)$ in order to simplify the reaction with respect to the condensation of $Ph_2Si(OH)_2$. This change resulted in the formation of discrete and isolable products.

Syntheses of Phenyl-Substituted Gallacyclosiloxanes

When *tert*-butoxygallane, $(tBuOGaH_2)_2$,[14] was allowed to react with 1 equiv of tetraphenyl-1,3-disiloxanediol[15] in diethyl ether at room temperature, almost spontaneous evolution of hydrogen gas was observed. After separation from some precipitated oligomers, compound **1** could be isolated by simple crystallization from the solution (Scheme 1, *1:1* reaction).

The yield of **1** was 63%, but may be higher when using more dilute solutions. The ^1H NMR spectrum of **1** contains one signal for the *tert*-butyl groups, a broad resonance for a hydride connected to gallium, and the hydrogen atoms of the phenyl group. The presence of Ga−H bonds also could be deduced from the infrared spectrum, which showed $\nu(Ga-H)$ at 2021 cm^{-1}. The ^{13}C NMR spectrum is consistent with the data obtained from the ^1H NMR spectrum. The chemical shift of silicon in the ^{29}Si NMR spectrum is found at −45.7 ppm in the region typical for cyclic siloxanes.[16]

A change in the molar ratio of *tert*-butoxygallane and tetraphenyl-1,3-disiloxanediol to 1:2 had a dramatic effect on the products (Scheme 1, *1:2* reaction).

The two compounds **2** (36%) and **3** (25%) were obtained in almost equal amounts and could be separated easily, on the basis of their different solubilities in diethyl ether, the hydride compound **2** precipitating from the reaction mixture while **3** remains in solution. Both compounds form colorless crystals, soluble either in toluene or in diethyl ether (**3**). The ^{29}Si NMR spectra of **2** and **3** each have two resonances (in a 2:1 ratio), indicating a lengthening of the −O−Si−O−Si−O− chain by a further Si−O unit. While the ^1H NMR spectrum of **3** displays a signal for the *tert*-butyl group along with resonances due to the hydrogen atoms of the phenyl groups, the ^1H NMR spectrum of **2** shows a resonance of low intensity at 4.9 ppm consistent with a hydrogen atom bonded to gallium. The ^{13}C NMR spectra parallel the findings of the ^1H NMR spectra. The attribution of the signal at 4.9 ppm in the ^1H NMR spectrum of **2** to Ga−H could be confirmed by an absorption at 2015 cm^{-1} ($\nu_s(Ga-H)$) in the infrared spectrum.

The lengthening of the siloxane chain by one Si−O unit in the products prompted us to replace $(HO)SiPh_2OSiPh_2(OH)$ by $(HO)SiPh_2OSiPh_2OSiPh_2(OH)$ in the 1:2 equation of Scheme 1 and to repeat the reaction with *tert*-butoxygallane using the 1,5-trisiloxanediol. This had an effect neither on the products nor on their yields relative to $(tBuOGaH_2)_2$. The spectral data obtained of the reaction mixtures after 30 min of stirring were almost identical with those obtained from the reaction with the 1,3-disiloxanediol.

In retrospect, these results are not astonishing, as "ring expansion reactions" of metallasiloxanes have been described in various reports by Sullivan and co-workers[17−19] and by others.[20,21] The expansion reactions are believed to occur because siloxane rings with few members are more strained than the larger rings. Thus, cyclotrisiloxanes have strain energies of 16−21 kJ/mol, while cyclotetrasiloxanes and larger cyclosiloxanes have almost no strain energy.[17,22]

The mechanisms of these reactions are not fully understood. There can be expansion reactions of free silanols[23] or of coordinated siloxanes, and the Lewis acidity of metal atoms may play a role. Cyclic diphenylsiloxanes containing Ti(IV) as a ring member of

---

(5) (a) Lorenz, V.; Fischer, A.; Giessmann, S.; Gilje, J. W.; Gun'ko, Y.; Jacob, K.; Edelmann, F. T. *Coord. Chem. Rev.* **2000**, *206−207*, 321. (b) Beckmann, J.; Jurkschat, K. *Coord. Chem. Rev.* **2001**, *267−300*, 267.

(6) Gun'ko, Y. K.; Reilly, R.; Kessler, V. G. *New J. Chem.* **2001**, *25*, 528.

(7) Schmidbaur, H.; Schindler, F. *Chem. Ber.* **1966**, *99*, 2178.

(8) Schmidbaur, H. *Chem. Ber.* **1963**, *96*, 2696.

(9) Schmidbaur, H.; Schmidt, M. *Angew. Chem.* **1962**, *74*, 589.

(10) Schmidbaur, H. *Angew. Chem.* **1965**, *77*, 206; *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 201.

(11) Feher, F. J.; Budzichowski, T. A.; Ziller, J. W. *Inorg. Chem.* **1997**, *36*, 4082.

(12) Voigt, A.; Murugavel, R.; Parisini, E.; Roesky, H. W. *Angew. Chem.* **1996**, *108*, 823; *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 5,

(13) Murugavel, R.; Walawalkar, M. G.; Prabusankar, G.; Davis, P. *Organometallics* **2001**, *20*, 2639.

(14) Veith, M.; Faber, S.; Wolfanger, H.; Huch, V. *Chem. Ber.* **1996**, *129*, 381.

(15) Behbehani, H.; Brisdon, B. J.; Mahon, M. F.; Molloy, K. C. *J. Organomet. Chem.* **1993**, *463*, 41.

(16) O'Dowd, A. T.; Spalding, T. R.; Ferguson, G.; Gallagher, J. F.; Reed, D. *J. Chem. Soc., Chem. Commun.* **1993**, 1816.

(17) Hossain, M. A.; Hursthouse, M. B.; Mazid, M. A.; Sullivan, A. C. *J. Chem. Soc., Chem. Commun.* **1988**, 1305.

(18) Motevalli, M.; Shah, D.; Shah, S. A. A.; Sullivan, A. C. *J. Chem. Soc., Chem. Commun.* **1994**, 2427.

(19) Lazell, M.; Motevalli, M.; Shah, S. A. A.; Simon, C. K. S.; Sullivan, A. C. *J. Chem. Soc., Dalton Trans.* **1996**, 1449.

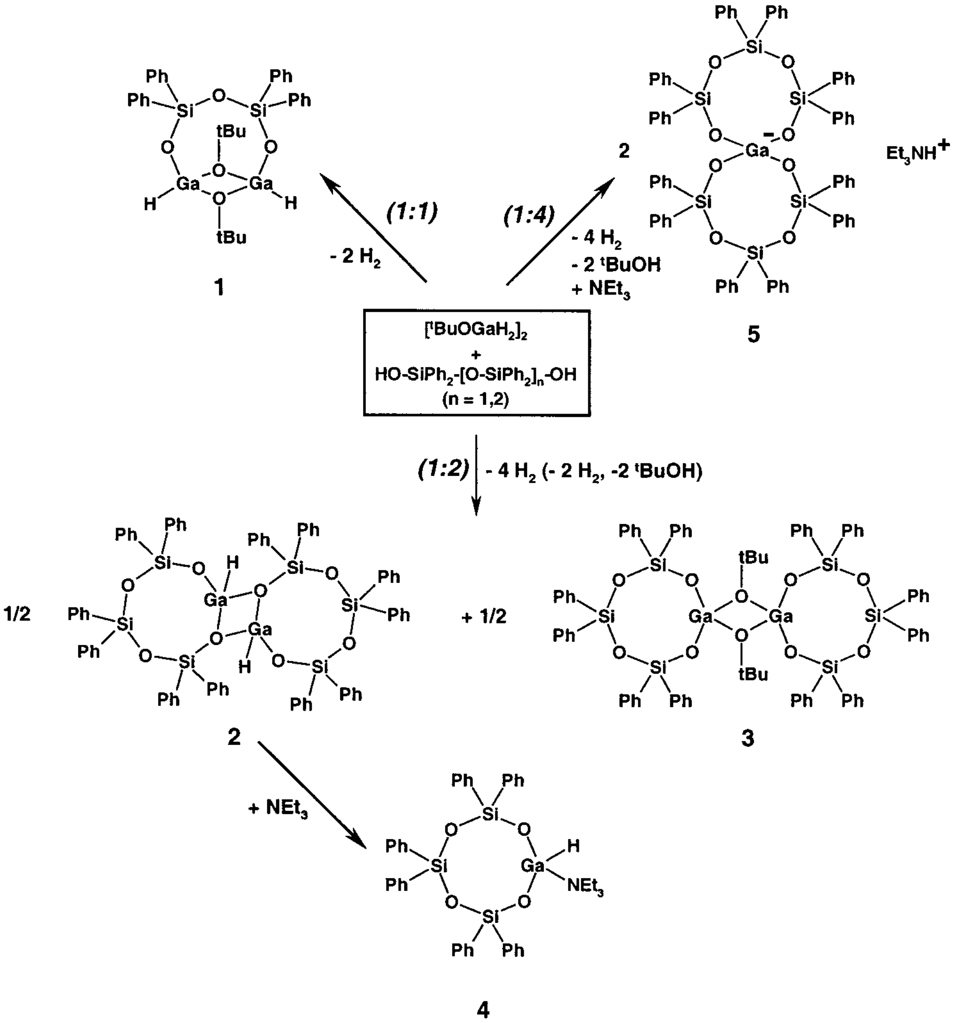
(20) Murugavel, R.; Voigt, A.; Walawalkar, M. G.; Roesky, H. W. *Chem. Rev.* **1996**, *96*, 2205.

(21) Murugavel, R.; Shete, V. S.; Baheti, K.; Davis, P. *J. Organomet. Chem.* **2001**, *625*, 195.

(22) Hossain, M. A.; Hursthouse, M. B.; Ibrahim, A.; Mazid, M.; Sullivan, A. C. *J. Chem. Soc., Dalton Trans.* **1989**, 2347.

(23) Rubinsztajn, S.; Cypryk, M.; Chojnowsky, J. *J. Organomet. Chem.* **1989**, *367*, 27.

Scheme 1



different ring sizes ($TiO(OSiPh_2)_n$ with $n = 2-4$) can be obtained from precursors with almost identical Si−O chain lengths, displaying slightly different basicities at the terminal oxygen atoms ($HOPh_2SiOSiPh_2OH$, $LiOPh_2SiOSiPh_2OLi$, $NaOPh_2SiOSiPh_2ONa$), or from $Ph_2Si(OH)_2$.[17,19,20,22]

Compound **2** instantaneously reacted with triethylamine to form the adduct **4**. As can be seen from the structural analysis (see below), this Lewis acid/base reaction can be used to split the dimeric **2** into halves (Scheme 1). The molecule **4** can be isolated by crystallization from diethyl ether in almost quantitative yield.

In the ^1H NMR spectrum of **4** the ethyl resonances of the amine, the Ga−H signal at 4.86 ppm and the signals of the phenyl groups are easily discernible. Similar to that of **2**, the ^{29}Si NMR spectrum of **4** contains two resonances in a 1:2 ratio. The $\nu_s(Ga-H)$ band in the infrared spectrum is found at 1914 cm^{-1}, which is a considerable shift to lower wavenumbers (**2**, 2015 cm^{-1}). Hence, the Ga−H bond energy is decreased in the NEt_3 adduct compared to the original dimer. This is in accord with a weak O−Ga acid/base interaction in **2**, which must be correlated to strong Si−O bonding inducing a reduced Lewis basicity at the oxygen atoms linked to gallium (see also structure determinations).

A further increase of the 1,5-trisiloxanediol/*tert*-butoxygallane molar ratio, as shown in Scheme 1, led to the complete substitution of the ligands at gallium, and the tetrasiloxygallate **5** is formed. It can be isolated as the triethylamine adduct and has the composition $[(OSiPh_2OSiPh_2OSiPh_2O)_2Ga]^-{\cdot}HNEt_3^+$ (Scheme 1, *1:4* reaction). Compound **5** may also be obtained in an alternative way starting with compound **2** and using water as reactant (eq 1). We were able to separate

$$\underset{\mathbf{2}}{[(OSiPh_2OSiPh_2OSiPh_2O)GaH]_2} + 2\,H_2O + NEt_3 \rightarrow 2\,H_2 + \underset{\mathbf{5}}{[(OSiPh_2OSiPh_2OSiPh_2O)_2Ga]^-{\cdot}HNEt_3^+} + \text{other products} \quad (1)$$

crystals of **5** from the reaction mixture in moderate yield (40%) but did not identify the other reaction products, which should contain $Ga(OH)_x$ or GaO entities.

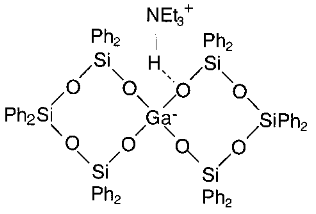
Compound **5** was characterized in THF solution by its ^1H, ^{13}C, and ^{29}Si NMR spectra. The two resonances in the ^{29}Si NMR spectrum as well as the few lines in the ^{13}C NMR spectrum indicate an overall point symmetry of S_4 or D_2 for the molecule in solution rather than C_s point symmetry, as would have been the case for an alternative description of **5** with the proton situated on one of the oxygen atoms coordinated to gallium, as may be seen from formulas **5a** and **5b**.

Of course, the observed higher symmetry of **5** in solution could also arise from equilibria between dif-

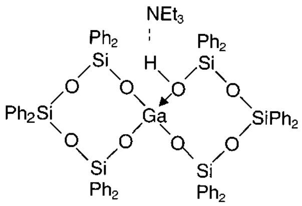
Table 1. Crystal Data, Data Collection and Refinement Parameters for 1−5

	1	2	3	4	5
empirical formula	$C_{32}H_{40}Ga_2O_5Si_2$	$C_{72}H_{62}Ga_2O_8Si_6 \cdot C_7H_8$	$C_{80}H_{78}Ga_2O_{10}Si_6 \cdot C_7H_8$	$C_{42}H_{46}GaNO_4Si_3$	$C_{78}H_{76}GaNO_8Si_6 \cdot 0.5C_4H_8O$
fw	700.26	1455.33	1599.59	782.79	1429.76
cryst size, mm; color	0.5 × 0.4 × 0.4; colorless	0.3 × 0.2 × 0.2; colorless	0.6 × 0.3 × 0.4; colorless	0.6 × 0.5 × 0.3; colorless	0.6 × 0.5 × 0.3; colorless
cryst syst, space group	monoclinic, $P2_1/n$	triclinic, $P\bar{1}$	triclinic, $P\bar{1}$	triclinic, $P\bar{1}$	monoclinic, $P2/c$
temp, K	293	293	293	293	293
unit cell dimens					
a, Å	9.891(2)	10.040(2)	10.184(2)	9.332(2)	27.764(6)
b, Å	17.099(3)	12.070(2)	13.513(3)	11.009(2)	13.641(3)
c, Å	21.162(4)	16.070(3)	17.014(3)	21.428(4)	21.844(4)
α, deg	90	76.28(3)	67.46(3)	85.14(3)	90
β, deg	98.94(3)	76.04(3)	74.13(3)	78.91(3)	92.38(3)
γ, deg	90	89.01(3)	80.54(3)	68.84(3)	90
V, Å^3; Z	3535.6(12); 4	1834.3(6); 1	2075.4(7); 1	2014.4(7); 2	8266(3); 4
calcd density, g/cm^3	1.316	1.317	1.280	1.291	1.148
abs coeff, mm^{-1} (Mo Kα)	1.626	0.887	0.791	0.813	0.470
2θ range for data collection, deg	2.28−24.02	1.93−23.95	2.45−24.05	1.94−22.50	1.89−24.06
no. of rflns collected	17 347	11 625	13 059	5250	49 309
no. of indep rflns	5220	5377	6060	5250	12 759
no. of obsd rflns	3862	4178	5249	4126	8343
abs cor	empirical				
refinement method	full-matrix least squares on F^2				
no. of params refined	384	434	454	468	938
goodness of fit	1.148	0.932	0.898	1.399	1.023
final R indices (obsd data): R1, wR2	0.0443, 0.1360	0.0313, 0.0690	0.0449, 0.1347	0.0647, 0.1664	0.0554, 0.1794
R indices (all data): R1, wR2	0.0619, 0.1447	0.0452, 0.0730	0.0511, 0.1420	0.0878, 0.1858	0.0872, 0.1954
largest diff peak and hole, e/Å^3	0.405, −0.390	0.330, −0.205	0.965, −0.607	1.772, −0.496	1.045, −0.407

ferent OH positions in **5b**, which would be rapid with respect to the NMR time scale. In the IR spectrum of **5**



5a



5b

a broad band of low intensity at 2710 cm^{-1} can be distinguished, which could arise from a proton coordinated to two basic centers (free Et_3NH^+ has an absorption at 3150 cm^{-1}, while $[Et_3N\cdots H\cdots py]^+$ absorbs around 2570 cm^{-1}).[24] As can be deduced from single-crystal X-ray diffraction (see below), in the crystal **5** seems to adopt a bonding which is better described as **5b**. This is in contrast to the recently characterized aluminum derivate $[PyH]^+[\{(Ph_2Si)_3O_4\}_2Al]^-$, which even in the crystal forms an ion pair with Al in an almost perfect tetrahedral O_4 environment.[6]

Crystal Structures of the Molecules 1−5

X-ray structure determinations of compounds **1**−**5** have been performed, and the most relevant data are assembled in Table 1. All compounds crystallize as distinct molecules in crystal structures with intermolecular van der Waals forces between the molecular units.

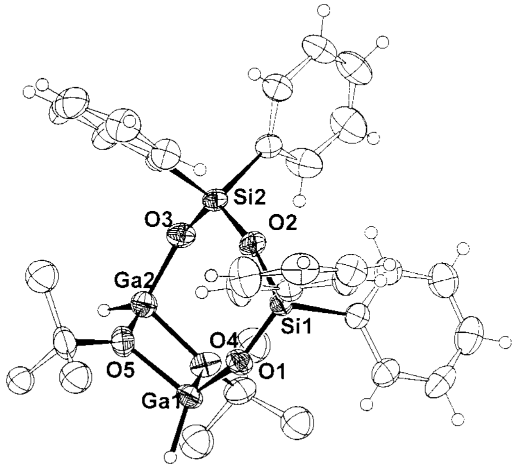


Figure 1. Structure of gallasiloxane **1**, $(OSiPhOSiPh_2O)[Ga(H)]_2(OtBu)_2$, from X-ray analysis, with 30% probability (also in Figures 2−5) thermal ellipsoids. The unlabeled atoms are either carbon or hydrogen. The hydrogen atoms at the *tert*-butyl groups are not shown.

Compound **1** may be described as a heterobicyclo[5.1.1]nonane, the two gallium atoms serving as connecting corners (see also Figure 1), a structural principle already established in other metallasiloxanes.[25] The point symmetry of the molecule is almost C_2, the pseudo 2-fold axis running through O(2) and the center of the basal Ga_2O_2 ring. This four-membered ring is nearly planar (sum of the angles 359.5°), with small angles at the gallium atoms (80.5°) and larger ones at the oxygen atoms (99.3°) (for bond distances and angles see Table 2). The mean Ga−O bond length (1.919(5) Å) within the four-membered ring is longer compared to the Ga−O(1,3) bond lengths (1.788(3) Å) as expected, because the coordination numbers at O(1) and O(3) are smaller

---

(24) Borah, B.; Wood, J. L. *J. Mol. Struct.* **1974**, *22*, 237.

(25) Mazzah, A.; Haoudi-Mazzah, A.; Noltemeyer, M.; Roesky, H. W. *Z. Anorg. Allg. Chem.* **1991**, *604*, 93.

Table 2. Selected Bond Lengths and Distances (Å) and Bond Angles (deg) for 1−3

	Compound **1**		
Ga(1)···Ga(2)	2.9250(8)	Ga(2)−H	1.44(5)
Ga(1)−O(1)	1.790(3)	Si(1)−O(1)	1.609(3)
Ga(1)−O(4)	1.912(3)	Si(1)−O(2)	1.620(3)
Ga(1)−O(5)	1.929(3)	Si(2)−O(2)	1.626(3)
Ga(2)−O(3)	1.787(3)	Si(2)−O(3)	1.611(3)
Ga(2)−O(4)	1.921(3)	O(4)−C(25)	1.461(6)
Ga(2)−O(5)	1.915(3)	O(5)−C(29)	1.462(6)
Ga(1)−H	1.43(5)	Si−C$_{\text{av}}$	1.873(5)
O(1)−Ga(1)−O(4)	108.8(1)	O(1)−Si(1)−O(2)	112.9(2)
O(1)−Ga(1)−O(5)	105.2(2)	O(3)−Si(2)−O(2)	113.2(2)
O(4)−Ga(1)−O(5)	80.4(1)	Si(1)−O(1)−Ga(1)	141.2(2)
O(3)−Ga(2)−O(4)	105.3(1)	Si(2)−O(3)−Ga(2)	141.1(2)
O(3)−Ga(2)−O(5)	108.8(2)	Si(1)−O(2)−Si(2)	162.0(2)
O(5)−Ga(2)−O(4)	80.5(1)	Ga(1)−O(4)−Ga(2)	99.5(2)
O(1)−Ga(1)−Ga(2)	109.1(1)	C(25)−O(4)−Ga(1)	129.2(3)
O(3)−Ga(2)−Ga(1)	109.09 (9)	C(25)−O(4)−Ga(2)	128.5(3)
		Ga(2)−O(5)−Ga(1)	99.1(2)
		C(29)−O(5)−Ga(1)	128.3(3)
		C(29)−O(5)−Ga(2)	129.9(3)
		O−Si−C$_{\text{av}}$	108.2(2)
		C−Si−C$_{\text{av}}$	110.9(2)
	Compound **2**		
Ga(1)···Ga(1)#1	2.9108(9)	Si(1)−O(1)	1.612(2)
Ga(1)−O(1)	1.799(2)	Si(1)−O(2)	1.640(2)
Ga(1)−O(4)	1.919(2)	Si(2)−O(2)	1.623(2)
Ga(1)−O(4)#1	1.934(2)	Si(2)−O(3)	1.627(2)
Ga(1)−H	1.38(6)	Si(3)−O(3)	1.621(2)
Si−C$_{\text{av}}$	1.858(3)	Si(3)−O(4)	1.657(2)
O(1)−Ga(1)−O(4)	104.37(8)	O(3)−Si(3)−O(4)	107.81(9)
O(1)−Ga(1)−O(4)#1	104.20(8)	Si(1)−O(1)−Ga(1)	132.0(1)
O(4)−Ga(1)−O(4)#1	81.86(7)	Si(2)−O(2)−Si(1)	149.8(1)
O(1)−Ga(1)−Ga(1)#1	109.06(7)	Si(3)−O(3)−Si(2)	165.6(1)
O(1)−Si(1)−O(2)	110.01(9)	Ga(1)−O(4)−Ga(1)#1	98.14(7)
O(2)−Si(2)−O(3)	110.46(9)	Si(3)−O(4)−Ga(1)	131.7(1)
		Si(3)−O(4)−Ga(1)#1	129.2(1)
		O−Si−C$_{\text{av}}$	108.9(1)
		C−Si−C$_{\text{av}}$	111.9(1)
	Compound **3**		
Ga(1)···Ga(1)#1	2.892(1)	Si(2)−O(2)	1.640(3)
Ga(1)−O(1)	1.782(2)	Si(2)−O(3)	1.617(3)
Ga(1)−O(4)	1.795(2)	Si(3)−O(3)	1.633(3)
Ga(1)−O(5)	1.904(3)	Si(3)−O(4)	1.625(3)
Ga(1)−O(5)#1	1.894(2)	O(5)−C(37)	1.476(4)
Si(1)−O(1)	1.615(2)	Si−C$_{\text{av}}$	1.869(4)
Si(1)−O(2)	1.640(3)		
O(1)−Ga(1)−O(4)	116.7(1)	O(3)−Si(2)−O(2)	111.1(1)
O(1)−Ga(1)−O(5)	115.9(1)	O(4)−Si(3)−O(3)	109.5(1)
O(1)−Ga(1)−O(5)#1	110.1(1)	Si(1)−O(1)−Ga(1)	146.5(2)
O(4)−Ga(1)−O(5)	112.7(1)	Si(2)−O(2)−Si(1)	144.5(2)
O(4)−Ga(1)−O(5)#1	115.4(1)	Si(2)−O(3)−Si(3)	168.6(2)
O(5)#1−Ga(1)−O(5)	80.8(1)	Si(3)−O(4)−Ga(1)	129.1(2)
O(1)−Ga(1)−Ga(1)#1	120.86(8)	Ga(1)#1−O(5)−Ga(1)	99.2(1)
O(4)−Ga(1)−Ga(1)#1	122.37(8)	C(37)−O(5)−Ga(1)#1	128.7(2)
O(1)−Si(1)−O(2)	111.2(1)	C(37)−O(5)−Ga(1)	128.4(2)
		O−Si−C$_{\text{av}}$	108.8(2)
		C−Si−C$_{\text{av}}$	110.8(2)

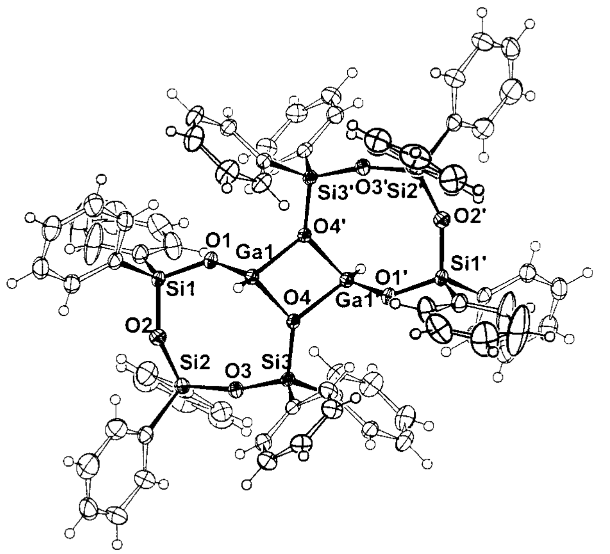


Figure 2. Structure of gallasiloxane **2**, [(OSiPh$_2$OSiPh$_2$OSiPh$_2$O)GaH]$_2$, from X-ray analysis (compare also caption of Figure 1).

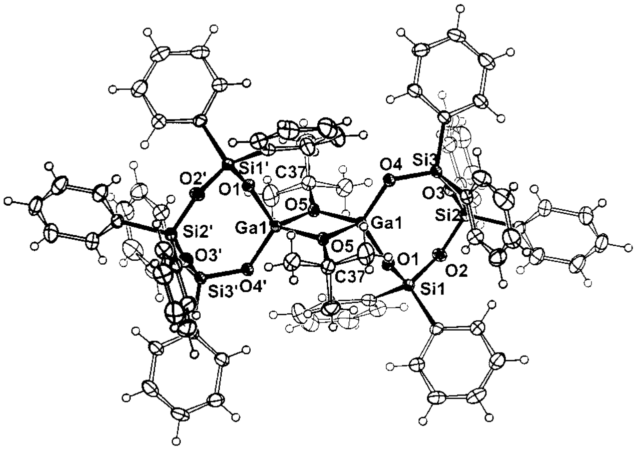


Figure 3. Structure of gallasiloxane **3**, [(OSiPh$_2$OSiPh$_2$OSiPh$_2$O)GaOtBu]$_2$, from X-ray analysis (see also caption of Figure 1).

(λ^2-O) than at O(4) and O(5) (λ^3-O). The five-membered disiloxane bridge composed of O(1−3) and Si(1,2) is not planar, with dihedral angles of O(3)−Si(2)−O(2)−Si(1) = 2.78° and O(1)−Si(1)−O(2)−Si(3) = −28.6°. The strain within the Si_2O_3 bridge may be derived from O−Si−O angles of 113.1(2)° (mean values) and Si−O−Si angles of 141.2(2)° (O(1) and O(3)) and 162.0(2)° (for O(2)). The hydrogen−gallium bond lengths in **1** (mean 1.43(5) Å) are shorter than in $(tBuOGaH_2)_2$ (1.60(5) Å) or in $[(tBuO)_2GaH]_2$ (1.53(7) Å).[14] Although these bond lengths should be discussed with caution because of the X-ray method, they nevertheless correlate well with the IR frequencies of the Ga−H bonds: **1**, 2021 cm^{-1}; $(tBuOGaH_2)_2$, 1906 cm^{-1}; $[(tBuO)_2GaH]_2$, 1949 cm^{-1} (see also below).

The two tricyclic compounds **2** and **3**, which result from the same reaction, crystallize in a triclinic crystal system, and both have centrosymmetric crystal symmetry. Although both are derived from trisiloxanes and have central Ga_2O_2 rings, which originate from Lewis acid/base interactions between gallium and oxygen, they are nevertheless distinctly different (Figures 2 and 3). In **2**, two eight-membered Si_3O_4Ga rings are fused to the central Ga_2O_2 ring, whereas in **3** the two eight-membered rings are spirocyclically connected through both gallium atoms and gallium−alkoxy bridges. The electron deficiency at the gallium atoms is compensated in different ways: in **2** the hydride function at gallium is in a terminal position, forcing the weakly basic oxygen O(4) of the siloxane ring to bond. On the other hand, the *tert*-butoxy ligand at gallium in **3** is basic enough to form the observed double bridge, the entire Si_3O_4Ga rings being engaged in no further donor/acceptor bonding. The central Ga_2O_2 ring in **2** displays bond lengths (1.919(2) and 1.934(2) Å) which are distinctly longer

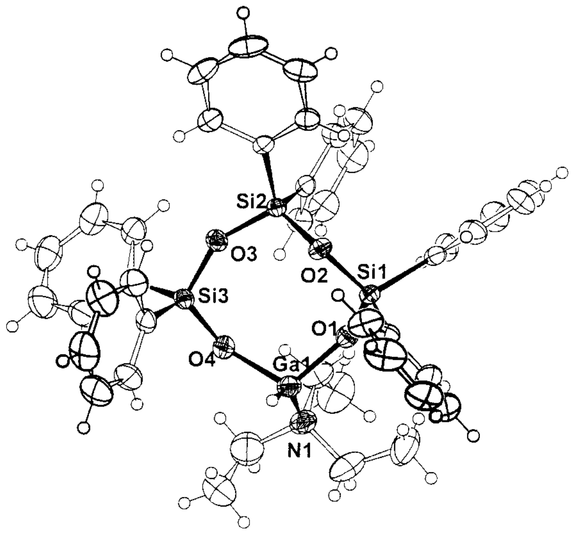


Figure 4. Structure of gallasiloxane **4**, $(OSiPh_2OSiPh_2OSiPh_2O)Ga(H)NEt_3$, from X-ray analysis (see also caption of Figure 1).

than those found in the four-membered Ga_2O_2 ring of **3** (1.904(3) and 1.894(2) Å), in accord with a less efficient Lewis acid/base interaction in molecule **2** (Table 2). As the electron donation to gallium in **2** is not very effective, the Ga−H bonding should be strong: Interestingly, a Ga−H bond length of 1.38(6) Å was found in the crystal together with a high ν(Ga−H) wavenumber of 2015 cm^{-1} in the IR spectrum. The Ga−H bond length in **2** is comparable to that found in **1** and seems to be at the lower end of Ga−H distances, which typically range from 1.36 to 1.86 Å.[26,27]

The gallium−oxygen bonds not involved in Lewis acid/base interactions in **2** (1.799(2) Å) and **3** (1.782(2), 1.795(2) Å) are comparable with respect to their bond lengths. This is also true for the $GaSi_3O_4$ eight-membered rings in **2** and **3**, which despite the fact of different bonding interactions have similar Si−O bond lengths and angles at the silicon and oxygen atoms (**2**, Si 107.8−110.5°, O 129.2−165.6°; **3**, Si 109.5−111.2°, O 129.1−168.6°) (see also Table 2). In comparison to **1**, which has eight-membered $Si_2Ga_2O_4$ rings, the deviation of bond angles at the silicon atoms from 109.5° is less important. In both compounds the rings are severely twisted, the central ring connections playing an important part in the configurations of the rings (see also further on).

In Figure 4, the structure of **4**, the triethylamine adduct of **2**, is depicted. The molecular structure (see also Table 3) consists of an eight-membered Si_3GaO_4 ring with phenyl substituents on the silicon atoms and a hydride and triethylamine ligand on the gallium atom. The molecule has no crystal symmetry, the $GaSi_3O_4$ ring displaying an almost coplanar conformation in the Ga−O(4)−Si(3)−O(3)−Si(2) section, while it is twisted in the other part of the ring. The Ga(1)−N(1) bond length of 2.054(6) Å is comparatively short,[28] indicating strong bonding and an important compensation of the electron deficiency at the gallium atom. The Ga−O bond lengths of 1.809(5) Å (mean value) are longer than the corresponding Ga−λ^2O bond lengths in **1**−**3** (see above), as the electrophilicity of the gallium atom is reduced by nitrogen bonding. Unfortunately, the location of the hydrogen atom at gallium could not be determined from difference Fourier synthesis, but the wavenumber of the Ga−H vibration (ν_s 1914 cm^{-1}) indicates a considerable reduction of bonding strength compared to **1** and **2**. The mean Si−O bond length in the ring is found to be 1.612(4) Å, with O−Si−O angles ranging from 110 to 114.3° (see Table 3). Again, these values are similar to those observed in the dimer **2**. The less strained situation in **4**, compared to **2**, may be deduced from the angles at the oxygen atoms, which range from 133.6(2) to 148.6(3) Å and have fewer deviations from one another (difference between extremes 15°) than in **2**, where a maximum difference of 36° is found.

Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) for 4 and 5

	Compound **4**		
Ga(1)−O(1)	1.798(4)	Si(2)−O(2)	1.613(4)
Ga(1)−O(4)	1.820(4)	Si(2)−O(3)	1.617(4)
Ga(1)−N(1)	2.054(6)	Si(3)−O(3)	1.621(4)
Si(1)−O(1)	1.603(4)	Si(3)−O(4)	1.585(4)
Si(1)−O(2)	1.633(4)	Si−C_{av}	1.860(6)
O(1)−Ga(1)−O(4)	108.2(2)	Si(1)−O(1)−Ga(1)	133.6(2)
O(1)−Ga(1)−N(1)	101.3(2)	Si(2)−O(2)−Si(1)	137.4(2)
O(4)−Ga(1)−N(1)	100.4(2)	Si(2)−O(3)−Si(3)	148.6(3)
O(1)−Si(1)−O(2)	110.3(2)	Si(3)−O(4)−Ga(1)	143.1(3)
O(2)−Si(2)−O(3)	110.0(2)	O−Si−C_{av}	108.9(2)
O(4)−Si(3)−O(3)	114.3(2)	C−Si−C_{av}	109.4(3)
	Compound **5**		
Ga(1)−O(1)	1.821(3)	Si(3)−O(3)	1.647(3)
Ga(1)−O(4)	1.801(3)	Si(3)−O(4)	1.601(3)
Ga(1)−O(5)	1.818(3)	Si(4)−O(5)	1.589(3)
Ga(1)−O(8)	1.860(3)	Si(4)−O(6)	1.652(3)
Si(1)−O(1)	1.601(3)	Si(5)−O(6)	1.630(3)
Si(1)−O(2)	1.639(4)	Si(5)−O(7)	1.617(3)
Si(2)−O(2)	1.623(3)	Si(6)−O(7)	1.622(3)
Si(2)−O(3)	1.615(3)	Si(6)−O(8)	1.609(3)
		Si−C_{av}	1.866(5)
O(4)−Ga(1)−O(1)	112.2(2)	O(8)−Si(6)−O(7)	112.3(2)
O(5)−Ga(1)−O(1)	109.6(2)	Si(1)−O(1)−Ga(1)	138.4(2)
O(1)−Ga(1)−O(8)	105.6(1)	Si(2)−O(2)−Si(1)	143.3(2)
O(4)−Ga(1)−O(5)	109.6(2)	Si(2)−O(3)−Si(3)	145.8(2)
O(4)−Ga(1)−O(8)	109.2(2)	Si(3)−O(4)−Ga(1)	147.2(2)
O(5)−Ga(1)−O(8)	110.8(1)	Si(4)−O(5)−Ga(1)	146.6(2)
O(1)−Si(1)−O(2)	112.4(2)	Si(5)−O(6)−Si(4)	132.7(2)
O(3)−Si(2)−O(2)	111.2(2)	Si(5)−O(7)−Si(6)	160.3(2)
O(4)−Si(3)−O(3)	112.3(2)	Si(6)−O(8)−Ga(1)	129.9(2)
O(5)−Si(4)−O(6)	112.5(2)	O−Si−C_{av}	108.5(2)
		C−Si−C_{av}	110.5(2)

Compound **5** is the only molecule in the series in which all former ligands of $[tBuOGaH_2]_2$ have been substituted: the gallium atom is spirocyclically connecting two Si_3O_4Ga rings and has a distorted-tetrahedral coordination from oxygen atoms (compare Figure 5 and Table 3). The crystal contains, besides the spirocyclic compound, a NEt_3 molecule in close proximity to the two rings of the spiro system and two THF molecules which serve as space-fillers in the crystal structure. The structure of the spiro system can also be described as a Ga^{3+} ion chelated by $(Ph_2Si)_3O_4{}^{2-}$ and $(Ph_2Si)_3O_3(OH)^-$ anions. As may be deduced from inspection of Figure 5, the NEt_3 base forms a hydrogen bridge (N···O found: 2.95(9) Å) to the oxygen atom

---

(26) Atwood, J. L.; Bott, S. G.; Elms, F. M.; Jones, C.; Raston, C. L. *Inorg. Chem.* **1991**, *30*, 3793.

(27) Lorberth, J.; Dorn, R.; Massa, W.; Wocadlo, S. *Z. Naturforsch.* **1993**, *B48*, 224.

(28) (a) Onyiriuka, E. C.; Rettig, St. J.; Storr, A.; Trotter, J. *Can. J. Chem.* **1987**, *65*, 782. (b) Kopp, M. R.; Neumüller, B. *Z. Anorg. Allg. Chem.* **1999**, *625*, 1413.

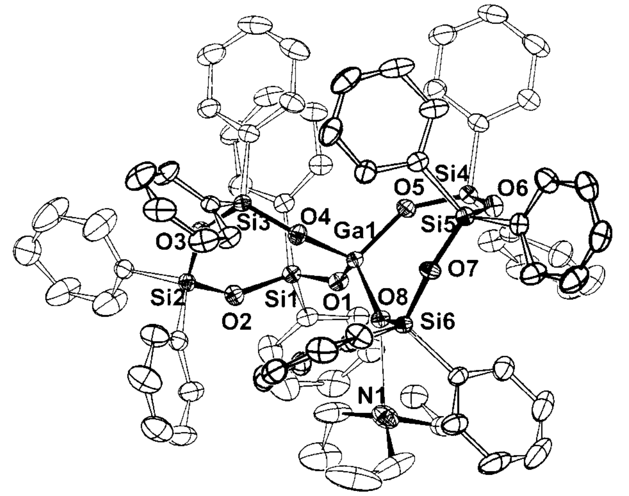


Figure 5. Structure of gallasiloxane **5**, $(OSiPh_2OSiPh_2OSiPh_2O)_2Ga{\cdot}HNEt_3$, from X-ray analysis. The hydrogen atoms at the carbon atoms have been omitted for clarity (see also caption of Figure 1).

O(8) which may be classified as long compared to other O−H···N bridges.[1,29] In the infrared spectrum of crystalline **5**, no absorption bands can be detected between 3050 and 3400 cm^{-1}, which suggests a shift of the hydrogen atom from oxygen to nitrogen. In contrast to the recently reported[6] $[(Ph_2Si)_3O_4]_2Al$ anion, the four corresponding gallium−oxygen bonds are found not to be equal; the three bonds Ga−O(1,4,5) have bond lengths of 1.801(3)−1.821(3) Å, and the fourth (Ga(1)−O(8)) is distinctly longer (1.862(3) Å). At least in the crystal this seems to be an indication of the hydrogen being closer to oxygen O(8) than to nitrogen N(1); otherwise, the Ga−O(8) bond lengthening is difficult to understand. For Ga−O(H)−Ga bonding the reported values are between 1.92 and 1.99 Å.[30−33] For Ga−O(H)−Si arrangements as in **5** we therefore expect values of 1.89 Å for Ga−O(H), taking into account the bond lengths found in Al−O(H)−Si systems.[1]

The two eight-membered $GaSi_3O_4$ rings in **5** both adopt twist conformations, with O−Si−O angles of 110.1−112.5° and Si−O−Si(Ga) angles of 129.5−160.3° in the second ring (compare also Table 3). The deviation from mean values is more pronounced in the second ring, which is again consistent with our model, the O(8) atom being part of a hydroxo group and therefore inducing an asymmetry in this ring.

Besides the molecular descriptions of structures **1**−**5**, there also is an alternative way of representation and discussion of the structures that may be used which is familiar to solid state chemistry and which is shown in Figure 6. Here we represent the coordination polyhedra around gallium and silicon, neglecting in a first approximation the nature of the ligand (O, C, or H) and replacing the organic groups by symbols. From these representations several conclusions are obvious: the comparatively high strain in compound **1**, the different fusions of the ring systems in **2** and **3**, the structural transformation from **3** to **4**, and the asymmetry in **5** caused by the NEt_3 interaction. In all molecules the gallium atoms are placed in tetrahedral sites which are slightly larger than those of the silicon but are compatible with the structures.

Another general conclusion is depicted in Figure 7, which is a plot of the Ga−H distances found in the X-ray experiments (and which have of course large standard deviations) against ν(Ga−H) values obtained from infrared spectra. We recognize a good correlation of the data, which is not unexpected, as force constants and bond lengths are mutually dependent. The plot may also be used to approximately estimate bond distances as in **4**, where the location of the hydrogen on gallium was not possible due to the unsatisfactory crystal quality. For 1914 cm^{-1} in **4** we should expect Ga−H bond lengths of about 1.58 Å.

Experimental Section

All compounds have been synthesized using Schlenk techniques under a nitrogen atmosphere excluding oxygen and water. Gallium(III) chloride was purchased from Aldrich; $[tBuOGaH_2]_2$,[14] $(HO)Ph_2SiOSiPh_2(OH)$,[15] and $(HO)Ph_2Si{-}O{-}SiPh_2{-}OSiPh_2(OH)$[15] were prepared as described before. Elemental analyses were obtained on a LECO CHN-900 analyzer, whereas IR spectra were recorded on a Bio-Rad FTS 165 apparatus. NMR spectra were recorded on a Bruker AC 200 F (^1H, 200.1 MHz, ^{13}C, 50.3 MHz) and a Bruker AC 200P (^{29}Si, 39.7 MHz) with TMS as internal and external reference, respectively. The X-ray diffraction data for **4** were collected on a Siemens AED 2 diffractometer using Mo Kα radiation, while those of **1**−**3** and **5** were obtained using a STOE IPDS Image Plate System, again with Mo Kα radiation ($\lambda = 0.710\ 69$ Å). The structures have been solved with the aid of SHELXS-97 and SHELXL-97[34,35] and have been plotted using Diamond.[36] The hydrogen atoms bonded to carbon (phenyl, methyl) were calculated in geometrically idealized positions with C−H distances of 0.93 Å (phenyl) and 0.97 Å (methyl). The hydrogen atoms bonded to gallium were found from difference Fourier analyses, with the exception of structure **4**. In **1** some *tert*-butyl groups are disordered around the C−O axes, and split atom positions (50%) were used. Compound **2** crystallizes with a toluene molecule which occupies an inversion center: therefore, the methyl group of this molecule is split; the same holds for compound **3**, in which the methyl group could not be located. The crystal structure of **5** contains two THF molecules on 2-fold axes which are randomly distributed between these two places (50%) as well as one phenyl group and the ethyl groups of NEt_3, which show statistical disorder.

$[HGaO^tBu]_2(Ph_2SiO)_2O$ (1). To 0.602 g (2.08 mmol) of $[GaH_2O^tBu]_2$ in 20 mL of diethyl ether at room temperature was added a solution of 0.861 g (2.08 mmol) of $(Ph_2SiOH)_2O$ in 20 mL of diethyl ether with stirring. Immediate evolution of hydrogen took place, and after a while a colorless precipitate formed. After 1 h the solid precipitate was separated by filtration and the solution was concentrated until crystals formed. Yield: 0.92 g (63%) of $[HGaO^tBu]_2(Ph_2SiO)_2O$ (**1**). ^1H

---

(29) Huheey, J.; Keiter, E.; Keiter, R. *Anorganische Chemie*, 2nd ed.; Walter de Gruyter: Berlin, New York, 1995. This book is a German translation and expansion of: Huheey, J. E. *Inorganic Chemistry, Principles of Structure and Reactivity*; Harper and Row: New York, 1983.

(30) Linti, G.; Köstler, W. *Chem. Eur. J.* **1998**, *4*, 942.

(31) Rendle, D. F.; Storr, A.; Trotter, J. *Can. J. Chem.* **1975**, *53*, 2944.

(32) Storre, J.; Klemp, A.; Roesky, H. W.; Schmidt, H. G.; Noltemeyer, M.; Fleischer, R.; Stalke, D. *J. Am. Chem. Soc.* **1996**, *118*, 1380.

(33) Schnitter, C.; Roesky, H. W.; Albers, T.; Schmidt, H. G.; Röpken, C.; Parisini, E.; Sheldrick, G. M. *Chem. Eur. J.* **1997**, *3*, 1783.

(34) Sheldrick, G. M. SHELXS-86 Program for Crystal Structure Solution; University of Göttingen, Göttingen, Germany, 1986.

(35) Sheldrick G. M. SHELXL-97 Program for Crystal Structure Refinement; University of Göttingen, Göttingen, Germany, 1997.

(36) Brandenburg, K. Diamond 2.1, Copyright Crystal Impact GbR, Germany.

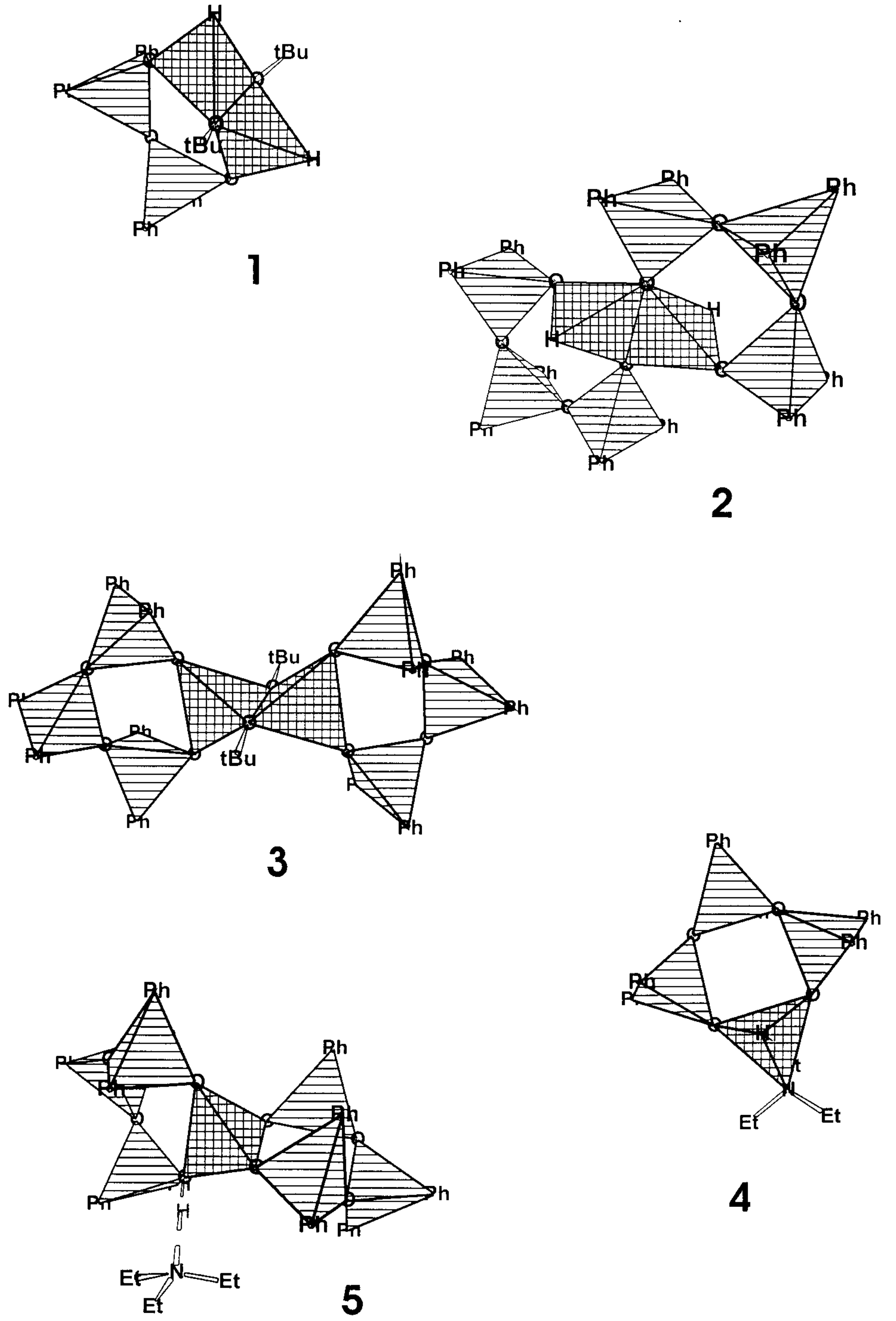


Figure 6. Structures of molecules **1**−**5** using tetrahedra around silicon (simple hatching) or gallium (double hatching). The corners of these tetrahedra are occupied by O (oxygen), Ph (phenyl), H (hydrogen), or NEt_3 (triethylamine).

NMR: δ 1.13 (s, 18 H, C−(C*H*$_3$)$_3$); 5.35 (broad s, 2H, Ga−*H*); 7.20 (m, 12 H, *m*-, *p-H* phenyl); 7.63 (m, 8H, *o-H* phenyl). ^{13}C NMR: δ 31.60 (s, 6 C, C(*C*H$_3$)$_3$); 77.18 (s, 2 C, *C*(CH$_3$)$_3$); 127.8 (s, 8 C, *m-C* phenyl); 129.5 (s, 4 C, *p-C* phenyl); 135.0 (s, 8 C, *o-C* phenyl); 139.6 (s, 4 C, Si−*C* phenyl); ^{29}Si NMR: δ −45.7. IR: ν 2021 cm^{-1} (Ga−H). Anal. Calcd for $C_{32}H_{40}Ga_2O_5Si_2$ (700.29): C, 54.88; H, 5.76. Found: C, 54.46; H, 5.71.

Synthesis of [GaH(Ph$_2$SiO)$_3$O]$_2$ (2) and [Ga(OtBu)(Ph$_2$SiO)$_3$O]$_2$ (3). To 0.582 g (2.01 mmol) of [GaH$_2$O^{t}Bu]$_2$ in 50 mL of diethyl ether at room temperature was added a solution of 1.660 g (4.04 mmol) of (Ph$_2$SiOH)$_2$O in 50 mL of diethyl ether with stirring. After 15 min of steady hydrogen evolution a precipitate was formed. The suspension was stirred for another 12 h and the solid residue separated from the solution by filtration. The colorless solid was analyzed as **2** and was recrystallized from a 50 °C warm toluene solution for X-ray purposes. The remaining solution was concentrated under reduced pressure until a voluminous residue formed. The residue was redissolved in a 1:1 mixture of toluene and diethyl ether, from which crystals of **3** were obtained.

Data for **2** are as follows. Yield: 0.98 g (36%). ^{1}H NMR (THF): δ 2.13 (s, 3H, C$_6$H$_5$−C*H*$_3$), 4.9 (broad, 2 H, Ga−*H*), 7.15 (m, 41 H, *m*-, *p-H* phenyl, toluene), 7.6 (m, 24 H, *o-H* phenyl); ^{13}C NMR (THF): δ 21.3 (s, 1 C, C$_6$H$_5$−*C*H$_3$), 125.6 (s, 1 C, toluene), 127.7 (s, 16 C, *m-C* phenyl), 127.8 (s, 8C, *m-C* phenyl), 128.5 (s, 2 C, toluene), 129.3 (s, 2 C, toluene), 129.4 (s, 8C *p-C* phenyl), 129.8 (s, 4C, *p-C* phenyl), 134.7 (s, 24 C, *o-C* phenyl), 136.9 (s, 4 C, Si−*C* phenyl), 137.7 (s, 1 C, toluene), 138.8 (s, 8 C, Si−*C* phenyl); ^{29}Si NMR: δ −45.7 (s, 4 Si), −43.9 (s, 2 Si). IR: ν 2015 cm^{-1} (Ga−H). Anal. Calcd for $C_{79}H_{70}Ga_2O_8Si_6$

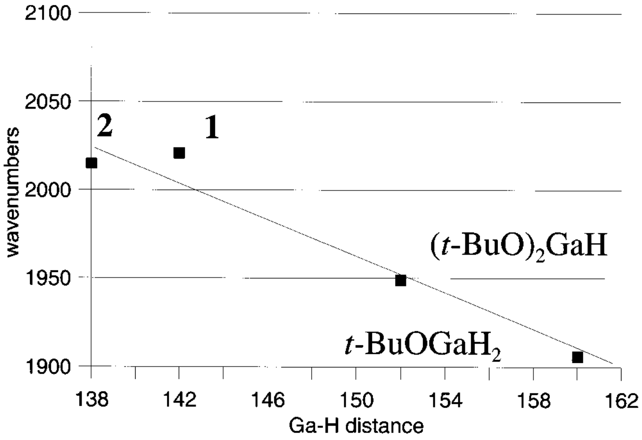


Figure 7. Correlation of Ga−H (100 × Å) distances and ν(Ga−H) (cm^{-1}) in compounds **1** and **2** compared to t-BuOGaH$_2$ and (tBuO)$_2$GaH.[14]

(1455.38; **2**·(toluene)): C, 65.20; H, 4.85. Found: C, 64.89; H, 4.79.

Data for **3** are as follows. Yield: 0.75 g (25%) ^{1}H NMR (dioxane): δ 1.14 (s, 18 H, C−(C*H$_3$*)$_3$), 2.13 (s, 3H, C_6H_5−C*H$_3$*), 7.1 (m, 41 H, *m*-, *p-H* phenyl, toluene), 7.55 (m, 24 H, *o-H* phenyl). ^{13}C NMR (dioxane): δ 21.3 (s, 1 C, C_6H_5−*C*H$_3$), 31.6 ppm (s, 6 C, C(*C*H$_3$)$_3$), 78.3 (s, 2 C, *C*(CH$_3$)$_3$), 125.6 (s, 1 C, toluene), 128.1 (s, 16 C, *m-C* phenyl), 128.5 (s, 2 C, toluene), 128.8 (s, 8 C, *m-C* phenyl), 129.3 (s, 2 C, toluene), 129.9 (s, 8 C, *p-C* phenyl), 130.2 (s, 4 C, *p-C* phenyl), 134.8 (s, 8 C, *o-C* phenyl), 135.0 (s, 16 C, *o-C* phenyl), 136.2 (s, 4 C, Si−*C*), 137.5 (s, 8 C, Si−*C*), 137.7 (s, 1 C, toluene). ^{29}Si NMR: δ −46.1 (s, 2 Si), −42.2 (s, 4 Si). Anal. Calcd for $C_{87}H_{86}Ga_2O_{10}Si_6$ (1599.59; **3**·(toluene)): C, 65.33; H, 5.41. Found: C, 65.02; H, 5.51.

The same products in comparable yields formed when $(Ph_2SiOH)_2O$ was replaced by $(Ph_2SiOH)_2(OSiPh_2O)$ (4.04 mmol), which was verified explicitly for **2**.

GaH(Ph$_2$SiO)$_3$O·NEt$_3$ (4). A 0.480 g (0.35 mmol) amount of **2** was dissolved in 10 mL of THF, and 10 mL of triethylamine was added. The solvent and the large excess of NEt$_3$ were removed after 2 h at reduced pressure (10^{-2} atm). The oily, voluminous residue was redissolved in diethyl ether, from which, after concentration, colorless crystals of **4** formed. Yield: 0.39 g (71%). ^{1}H NMR (dioxane): δ 0.9 (broad, 9 H, N−(CH$_2$C*H$_3$*)$_3$), 2.6 (broad, 6 H, N−(C*H$_2$*CH$_3$)$_3$), 4.85 (broad, 1 H, Ga−*H*), 7.17 (m, 18 H, *m*-, *p-H* phenyl), 7.6 (m, 12 H, *o-H* phenyl). ^{13}C NMR (dioxane): δ 9.26 (s, 3 C, N−(CH$_2$*C*H$_3$)$_3$), 47.41 (s, 3 C, N−(*C*H$_2$CH$_3$)$_3$), 127.8 (s, 8 C, *m-C* phenyl), 127.9 (s, 4 C, *m-C* phenyl), 129.4 (s, 4 C, *p-C* phenyl), 129.9 (s, 2 C, *p-C* phenyl), 134.7 (s, 8 C, *o-C* phenyl), 134.8 (s, 4 C, *o-C* phenyl), 137.0 (s, 2 C, Si−*C*), 139.2 (s, 4 C, Si−*C*). ^{29}Si NMR: δ −45.8 (s, 1 Si), −43.9 (s, 2 Si). IR: ν 1914 cm^{-1} (Ga−H). Anal. Calcd for $C_{42}H_{46}GaNO_4Si_3$ (782.82): C, 64.44; H, 5.92; N, 1.79. Found: C, 64.94; H, 5.87; N, 1.79.

Ga[(Ph$_2$SiO)$_3$O][(Ph$_2$SiO)$_3$OH]·NEt$_3$ (5). (a) To a solution of 0.168 g (0.58 mmol) of $[GaH_2O^tBu]_2$ in 10 mL of diethyl ether was added a solution of 1.42 g (2.32 mmol) of $HO(Ph_2SiO)_3OH$ in 10 mL of diethyl ether dropwise with stirring. Hydrogen evolution as well as precipitation of a colorless solid was observed. After 12 h of stirring 5 mL of triethylamine in 10 mL of THF was added, which dissolved the entire precipitate. When the solution was concentrated, colorless crystals of **5** were obtained. Yield: 0.95 g (59%).

(b) To a solution of 0.552 g (0.40 mmol) of **2** in 10 mL of THF was added 2.0 mL (0.81 mmol) of a THF/water mixture (from 0.146 g of H_2O in 20 mL of THF) dropwise and stirred overnight. Five milliliters of triethylamine was finally used, and the solution was concentrated to obtain colorless crystals of **5**. Yield: 0.46 g (75%).

^{1}H NMR (THF): δ 0.41 (t, 9 H, N−(CH$_2$C*H$_3$*)$_3$), 2.09 (q, 6H, N−(C*H$_2$*CH$_3$)$_3$), 7.1 (m, 36 H, *m*-, *p-H* phenyl), 7.59 (m, 24 H, *o-H* phenyl). ^{13}C NMR (THF): δ 8.50 (s, 3 C N−(CH$_2$*C*H$_3$), 45.9 (s, 3 C, N−(*C*H$_2$CH$_3$)$_3$), 127.4 (s, 16 C, *m-C* phenyl), 127.6 (s, 8 C, *m-C* phenyl), 128.9 (s, 8 C, *p-C* phenyl), 129.5 (s, 4 C, *p-C* phenyl), 134.9 (s, 8 C, *o-C* phenyl), 135.3 (s, 16 C, *o-C* phenyl), 137.2 (s, 4 C, Si−*C*), 139.3 (s, 8 C, Si−*C*). ^{29}Si NMR: δ −45.6 (s, 2 Si), −43.8 (s, 4 Si). IR: ν 2710 cm^{-1} (Et$_3$N···H···O−). Anal. Calcd for $C_{86}H_{92}GaNO_{10}Si_6$ (1537.89; **5**·2THF): C, 67.16; H, 6.03; N, 0.81. Found: C, 66.82; H, 6.18; N, 0.91.

Acknowledgment. We thank the DFG for supporting this work in the framework of the Schwerpunkt “Spezifische Phänomene in der Silicium-Chemie” and the Fonds der Chemischen Industrie for financial support.

Supporting Information Available: Further details of the crystal structure determination, including tables of bond lengths, bond angles, and anisotropic and isotropic displacement parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

OM010544P