# New Organogallium Peroxides

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*Dedicated to Professor Hubert Schmidbaur on the occasion of his 75th birthday*

Treatment of $(Me_3C)_2Ga\text{-}CH(SiMe_3)_2$ (**1**) with oxygen gave the oxidation of both quaternary carbon atoms of the *tert*-butyl groups, while the bis(trimethylsilyl)methyl substituent was not affected. One *tert*-butyl group was transferred to an alkoxide which in the dimeric formula unit of the product **2** occupies the bridging position between both gallium atoms. The second one afforded a terminally arranged *tert*-butylperoxo ligand by the insertion of a complete oxygen molecule into the respective Ga–C bond. Another organogallium peroxide (**5**) was obtained by the reaction of $Li(OEt_2)[H_3GaCH(SiMe_3)_2]$ (**3**) with $H\text{-}O\text{-}O\text{-}CMe_2OMe$ (**4**). Two hydrido ligands of the trihydridogallanate were replaced by peroxo groups, while the third Ga–H bond gave a hydroxide (Ga–OH) by insertion of a single oxygen atom. The product, $Li[Ga(OH)(OOCMe_2OMe)_2R]$ [**5**, $R = CH(SiMe_3)_2$], forms a singular dimeric formula unit with a complicated oligocyclic structure in which all peroxo groups are in bridging positions between lithium and gallium atoms.

*Key words:* Organoelement Compounds, Gallium, Peroxides, Heterocycles

## Introduction

Organoaluminium, -gallium or -indium peroxides show a fascinating coordination chemistry similar to isoelectronic hydroxylamido [1] or hydrazido compounds [2] which may be referred to the singular arrangement of two adjacent donor atoms. However, these peroxides are only transient species in many cases, because they have strongly reducing E–C bonds in close proximity to oxidizing peroxo groups. Hence, until recently only very few clearly identified and characterized compounds of that type were reported in the literature. Tri(*tert*-butyl)gallium and -indium gave the corresponding dimeric dialkylelement peroxides by the insertion of dioxygen molecules into E–C bonds [3]. A similar compound was postulated to be formed by the reaction of trimethylgallium with oxygen [4]. These compounds proved to be dangerously explosive in neat, solvent-free form when we repeated their syntheses in our laboratories. Hence, they must be handled with great care. Nevertheless, they were applied successfully in some secondary oxygen transfer reactions [3, 4]. We isolated a digallium peroxide in trace quantities when a cycloaddition product of the alkylgallium(I) compound $Ga\text{-}C(SiMe_3)_3$ came advertently in contact with oxygen [5]. It had an unprecedented molecular structure with two alkylgallium groups terminally attached to a central peroxo group. Motivated by this observation we started systematic investigations into the synthesis of persistent organoaluminium, -gallium or -indium peroxides. Our strategy comprised the application of bis(trimethylsilyl)methyl compounds because their E–C bonds proved to be rather insensitive towards an attack of oxygen in previous experiments. Three methods for the introduction of peroxo ligands were applied: (i) Insertion of dioxygen molecules into In–C bonds [6], (ii) reactions of corresponding element hydrides with the dihydrogen peroxide-DABCO adduct by hydrogen release [7, 8], and (iii) reactions of the same starting compounds with *tert*-butyl hydrogen peroxide [9, 10]. One of the most intriguing structures had three dianionic peroxo ligands bridged by three $Ga\text{-}CH(SiMe_3)_2$ groups [7]. In another case we were able to isolate a compound which had an intact Ga–H bond despite two peroxo ligands attached to the same gallium atom [9]. The latter compound is expectedly very reactive and unstable with respect to the insertion of an oxygen atom into the Ga–H

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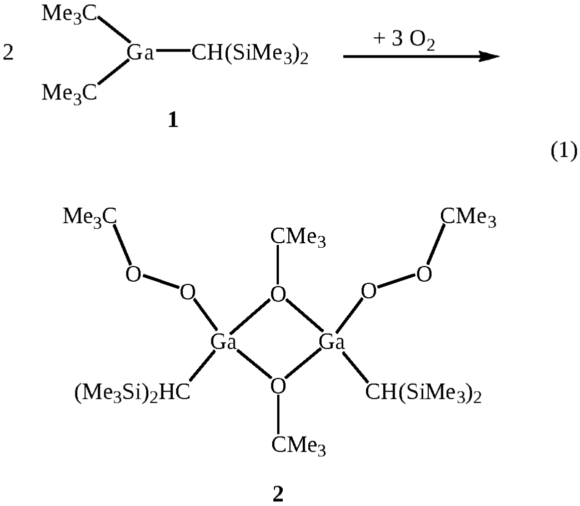
bond. In other cases relatively slow decomposition allows the handling of these organoelement peroxides in solution at room temperature for some hours. The syntheses and structures of two further organogallium peroxides are reported in this article. Those compounds may find application as facile oxygen transfer reagents (oxenoids according to Boche [11]).

## Results and Discussion

### *Reaction of $(Me_3C)_2Ga$-$CH(SiMe_3)_2$ with oxygen*

The starting compound $(Me_3C)_2Ga$-$CH(SiMe_3)_2$ (**1**) was obtained by the treatment of Cl-$Ga(CMe_3)_2$ with $LiCH(SiMe_3)_2$ in accordance with the synthesis of the corresponding aluminum derivative [12]. Bubbling of oxygen through a cooled solution (−78 °C) in *n*-hexane gave complete consumption of **1** in a few seconds (Eq. 1). A colorless solid precipitated which completely dissolved upon warming to −15 °C. Concentration of the solution at this temperature and cooling to −30 °C afforded colorless crystals of the organogallium peroxide **2** in 86 % yield. The $^1H$ NMR spectrum showed singlets of two chemically different *tert*-butyl groups and the resonances of a bis(trimethylsilyl)methyl substituent in the molar ratio of 1 : 1 : 1. The resonance of the Ga-CH hydrogen atoms ($\delta$ = −0.42) is shifted to a higher field compared to that of the starting compound **1** ($\delta$ = 0.36) which is indicative of an enhancement of the coordination number at the gallium atoms from three to four [13]. Hydrolysis of **2** with dilute $HNO_3$, treatment with iodide and titration of the resulting iodine with thiosulfate verified the occurrence of one peroxo group per gallium atom. The results of the crystal structure determination (Fig. 1) are in accordance with the experimental observations. The Ga–C bond to the bis(trimethylsilyl)methyl substituent was not affected by the reaction with oxygen. One $CMe_3$ group was transferred to an alkoxide by the insertion of a single oxygen atom into the Ga–C bond. Two alkoxy groups bridge both gallium atoms of the dimeric formula unit. Insertion of complete dioxygen molecules afforded peroxo groups, Ga-O-O-$CMe_3$, which occupy terminal positions at both gallium atoms. The peroxo ligands are on the same side of the central $Ga_2O_2$ heterocycle, which deviates only slightly from planarity (maximum deviation of an atom 2.9 pm). The molecular symmetry approaches the point group $C_{2v}$. The O–O bond lengths (146 pm on average) are in the normal range of peroxo compounds such as hydrogen peroxide [14] or the organoelement alkylperoxides described earlier [3, 6, 9, 10]. Longer distances were expectedly observed for dianionic peroxo ligands which bridge two gallium atoms [7, 8]. The Ga–O distances of the Ga–O–Ga bridges are longer (193 pm) than the terminal Ga–O bonds including the peroxo oxygen atoms (182 pm). In contrast to hydrogen peroxide (*gauche* conformation) the Ga–O–O–C torsion angles in **2** are at about 170° and verify an almost coplanar arrangement of these four atoms. A similar conforma-



(1)

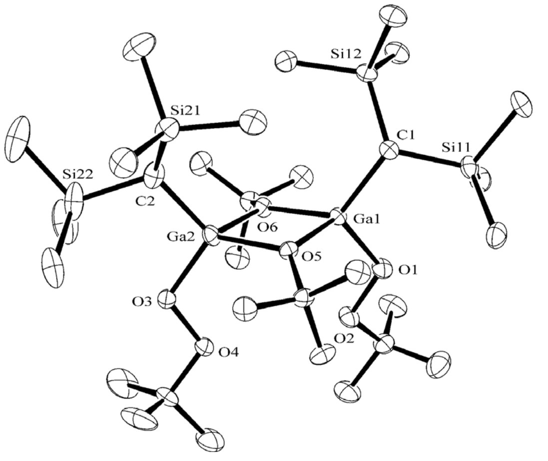
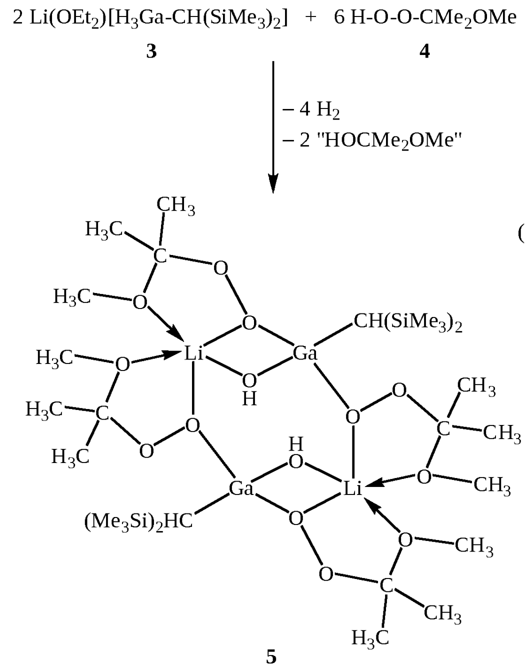


Fig. 1. Molecular structure of **2**. The ellipsoids are drawn at the 40 % probability level; hydrogen atoms are omitted. Selected bond lengths (pm) and angles (deg): Ga1–O1 182.7(2), Ga1–O5 193.9(2), Ga1–O6 191.6(2), Ga2–O3 180.4(3) (main component), Ga2–O5 191.6(2), Ga2–O6 193.3(2), O1–O2 146.8(3), O3–O4 146.1(5); Ga1–O1–O2 112.7(2), Ga2–O3–O4 109.8(3), O1–O2–C 106.0(2), O3–O4–C 106.9(4), Ga1–O1–O2–C 167.0(2), Ga2–O3–O4–C 172.7(4).

tion was observed for other organogallium peroxides. It may be favored by a minimization of steric interactions between the bulky substituents.

### *Reaction of* $Li(OEt_2)[H_3Ga\text{-}CH(SiMe_3)_2]$ *(**3**) with* $H\text{-}O\text{-}O\text{-}CMe_2OMe$ *(**4**)*

Treatment of lithium gallanates $Li[GaR_xH_{4-x}]$ with *tert*-butyl hydrogenperoxide represents a facile method for the generation of organogallium peroxides by hydrogen release [9]. However, in most cases these peroxides are thermally relatively unstable and decompose slowly at room temperature in solution or in the solid state. We hoped to enhance their stability by application of the slightly modified starting peroxide $H\text{-}O\text{-}O\text{-}CMe_2OMe$ (**4**) which should be able to coordinate the lithium counterion in a chelating manner. Reaction of the trihydrido compound $Li(OEt_2)[H_3Ga\text{-}CH(SiMe_3)_2]$ (**3**) with three equivalents of **4** proceeded at low temperature (Eq. 2). Hydrogen was released which was identified by absorption with a palladium wire and subsequent formation of molybdenum blue [15]. Colorless crystals of the product **5** were isolated in 86 % yield upon cooling of the concentrated reaction mixture to –30 °C. The $^1H$ NMR spectrum showed the expected resonances for the methoxy, $CMe_2$ and bis(trimethylsilyl)methyl groups in a molar ratio of 2 : 2 : 1. The $\alpha$-hydrogen atom ($GaCHSi_2$) of the organoelement substituent gave a resonance at $\delta = -0.78$, which is indicative of a coordination number of four at the gallium atoms in gallanates bearing negative charges [13]. Crystal structure determination (Fig. 2) revealed an interesting dimeric structure possessing a relatively complicated heptacyclic framework. Two hydrogen atoms of the trihydridogallium starting compound were replaced by peroxo ligands, the third one gave a hydroxo group by insertion of an oxygen atom. Hence, each gallium atom is coordinated by two peroxo groups, a hydroxo ligand and an intact alkyl substituent. All negatively charged $\alpha$-oxygen atoms of the peroxo ligands are in bridging positions between gallium and lithium atoms. The latter are further coordinated in a chelating manner by both methoxy groups of the respective peroxides. The coordination sphere of the lithium atoms (coordination number five) is completed by an interaction to a hydroxo group. The Li–O distances are in the range 194.0 to 237.0 pm. The longest one is to the peroxo oxygen atom O21. The distorted coordination sphere with one relatively long Li–O distance resembles that of other lithium or mixed lithium-gallium peroxides [9]. The O–O bond lengths (147.8 pm on average) correspond to standard values.



(2)

**5**

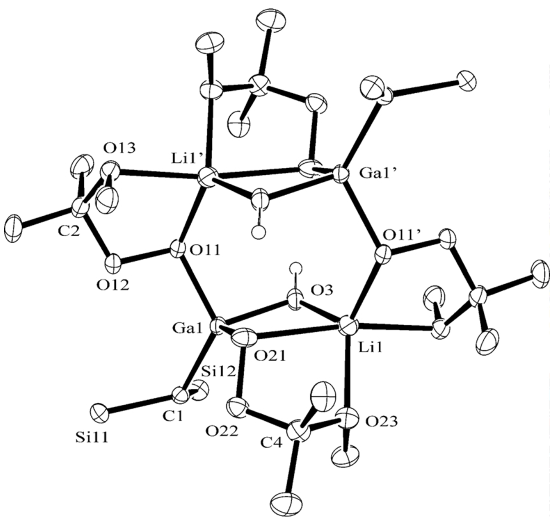


Fig. 2. Molecular structure of **5**. The ellipsoids are drawn at the 40 % probability level; hydrogen atoms with the exception of O-H are omitted. Selected bond lengths (pm) and angles (deg): Ga1–O11 189.1(1), Ga1–O21 190.5(1), Ga1–O3 186.0(1), Li1–O11′ 194.0(3), Li1–O21 237.0(3), Li1–O13′ 214.9(3), Li1–O23 204.3(3), Li1–O3 195.5(3), O11–O12 148.0(2), O21–O22 147.6(2); Ga1–O11–O12 103.42(8), Ga1–O21–O22 106.83(8), O11–O12–C2 108.3(1), O21–O22–C4 108.1(1), Ga1–O11–Li1′ 121.1(1); Li1′, O11′ and O13′ generated by $-x+1$, $-y+1$, $-z+1$.

Both peroxo compounds **2** and **5** are surprisingly stable in the solid state and in pentane solutions and can be handled at room temperature for several days without significant decomposition. They represent the most stable organoaluminum, -gallium and -indium peroxides obtained in our group so far.

## Experimental Section

All procedures were carried out under purified argon in dried solvents (*n*-pentane, cyclopentane and *n*-hexane over $LiAlH_4$). Cl-Ga$(CMe_3)_2$ [16], $LiCH(SiMe_3)_2$ [17], Li$(OEt_2)$[$H_3$Ga-CH$(SiMe_3)_2$] (**3**) [7] and H-O-O-$CMe_2$OMe (**4**) [18] were obtained according to literature procedures.

### *Synthesis of* $(Me_3C)_2$*Ga-CH*$(SiMe_3)_2$ *(**1**)*

A solution of Cl-Ga$(CMe_3)_2$ (1.54 g, 7.03 mmol) in 50 mL of *n*-hexane was added to a cooled (0 °C) suspension of $LiCH(SiMe_3)_2$ (1.16 g, 6.99 mmol) in 150 mL of the same solvent. The mixture was heated under reflux for 3 h and stirred at r. t. for 1 d. After filtration the solvent was removed *in vacuo*. The remaining colorless, highly viscous liquid was purified by vacuum distillation (45 °C, $10^{-3}$ Torr). Yield: 2.13 g (89 %). – IR (paraffin; CsBr plates): $\nu$ = 1306 w, 1248 m $\delta(CH_3)$; 1152 m, 1080 s $\nu$(CC); 1027 m $\delta(CHSi_2)$; 953 w, 843 vs, 773 m, 756 m $\rho(CH_3Si)$; 723 vs (paraffin); 679 w $\nu_{as}$(SiC); 615 m $\nu_s$(SiC); 571 vw, 442 $cm^{-1}$ w $\nu$(GaC). – $^1$H NMR (400 MHz, $C_6D_6$): $\delta$ = 1.22 and 1.15 (each, s, 9H, $CMe_3$), 0.36 (s, 1H, GaCH), 0.13 (s, 18H, $SiMe_3$). – $^{13}$C NMR (100 MHz, $C_6D_6$): $\delta$ = 30.3 and 30.2 (C*Me*$_3$), 29.2 and 28.6 (*C*Me$_3$), 12.0 ($GaCSi_2$), 3.9 ($SiMe_3$). – $^{29}$Si NMR (79.5 MHz, $C_6D_6$): $\delta$ = −3.5. – MS (EI, 20 eV, 20 °C): *m/z* (%) = 285 (100), 287 (77) [M−*t*Bu]$^+$, 327 (2), 329 (2) [M−$CH_3$]$^+$.

### *Reaction of* $(Me_3C)_2$*Ga-CH*$(SiMe_3)_2$ *with oxygen; synthesis of **2***

Dry oxygen was bubbled through a cooled (−78 °C) solution of $(Me_3C)_2$Ga-CH$(SiMe_3)_2$ (0.50 g, 1.5 mmol) in 50 mL of *n*-hexane for 15 s. A white solid precipitated. The suspension was slowly (10 min) warmed to about −15 °C until a clear solution was obtained. Colorless crystals of compound **2** were isolated after concentration and cooling of the solution to −30 °C. Yield: 0.49 g (86 %); the peroxide content was determined by reaction with iodide in dilute $HNO_3$ and titration of the resulting iodine with thiosulfate [19], which gave 90 % of the calculated value. M. p. (under argon, sealed capillary): 132 °C (dec.). – IR (paraffin; CsBr plates): $\nu$ = 1302 w, 1248 vs $\delta(CH_3)$; 1198 s, 1171 s $\nu$(CC); 1011 s $\delta(CHSi_2)$; 968 s $\nu$(OO?); 935 w, 866 s, 845 vs, 781 m, 758 m $\rho(CH_3Si)$; 723 m (paraffin); 677 m $\nu_{as}$(SiC); 615 m $\nu_s$(SiC); 559 w, 500 m, 465 $cm^{-1}$ m $\nu$(GaC), $\nu$(GaO). – $^1$H NMR (400 MHz, [$D_8$]toluene, 240 K): $\delta$ = 1.62 (s, 9H, $Ga_2OCMe_3$), 1.40 (s, 9H, $OOCMe_3$), 0.42 (s, 18H, $SiMe_3$), −0.42 (s, 1H, GaCH). – $^{13}$C NMR (100 MHz, [$D_8$]toluene, 240 K): $\delta$ = 78.6 (OO*C*Me$_3$), 78.2 ($Ga_2OCMe_3$), 31.7 ($Ga_2$OC*Me*$_3$), 26.9 (OOC*Me*$_3$), 4.4 ($SiMe_3$), 3.6 (GaC). – $^{29}$Si NMR (79.5 MHz, [$D_8$]toluene, 240 K): $\delta$ = 0.5.

Table 1. Crystal data, data collection, and structure refinement.

| | 2 | 5 |
|---|---|---|
| *Crystal data* | | |
| Empirical formula | $C_{30}H_{74}Ga_2O_6Si_4$ | $C_{30}H_{76}Ga_2Li_2O_{14}Si_4$ |
| $M_r$ | 782.69 | 926.59 |
| Crystal system | monoclinic | triclinic |
| Space group [21] | $P2_1/c$ (no. 14) | $P\bar{1}$ (no. 2) |
| *a*, pm | 2391.3(2) | 907.71(6) |
| *b*, pm | 964.09(9) | 1141.04(7) |
| *c*, pm | 1900.7(2) | 1336.71(8) |
| $\alpha$, deg | 90 | 109.772(1) |
| $\beta$, deg | 99.399(2) | 99.292(1) |
| $\gamma$, deg | 90 | 104.608(1) |
| $V$, × $10^{-30}$ m$^3$ | 4322.9(7) | 1213.6(1) |
| $\rho_{calc}$, g cm$^{-3}$ | 1.20 | 1.27 |
| $Z$ | 4 | 1 |
| $F(000)$, e | 1680 | 492 |
| $\mu(MoK_\alpha)$, mm$^{-1}$ | 1.4 | 1.3 |
| *Data collection* | | |
| $T$, K | 153(2) | 153(2) |
| Unique reflections | 13249 | 7205 |
| Reflections $I \geq 2\,\sigma(I)$ | 9160 | 6189 |
| *Refinement* | | |
| Refined parameters | 454 | 250 |
| Final $R$ values | | |
| $R1\ [I \geq 2\,\sigma(I)]^a$ | 0.065 | 0.034 |
| $wR2^b$ (all data) | 0.125 | 0.087 |
| $\rho_{fin}$ (max/min), e Å$^{-3}$ | 0.83/−0.65 | 0.87/−0.28 |

$^a$ $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $^b$ $wR2 = [\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma w(F_o{}^2)^2]^{1/2}$.

### *Reaction of Li[*$H_3$*Ga-CH*$(SiMe_3)_2$*](*$OEt_2$*) with H-O-O-*$CMe_2$*OMe; synthesis of **5***

A cooled (−78 °C) solution of Li$(OEt_2)$[$H_3$Ga-CH$(SiMe_3)_2$] (**3**, 0.63 g, 2.0 mmol) in 20 mL of cyclopentane was added slowly to a cooled (−78 °C) solution of H-O-O-$CMe_2$OMe (**4**, 0.64 g, 6.0 mmol) in 10 mL of cyclopentane. The mixture was warmed to 10 °C and concentrated. Cooling to −30 °C afforded colorless crystals of the product **5**. Yield: 0.80 g (86 %); the peroxide content was determined by reaction with iodide in dilute $HNO_3$ and titration of the resulting iodine with thiosulfate [19], which gave 92 % of the calculated value. M. p. (under argon, sealed capillary): 86 °C (dec.). – IR (paraffin; CsBr plates): $\nu$ = 1302 w, 1242 vs $\delta(CH_3)$; 1205 vs, 1184 sh, 1155 vs, 1043 vs $\nu$(CC), $\nu$(CO); 1016 s $\delta(CHSi_2)$; 951 s $\nu$(OO?); 870 sh, 843 vs, 787 m, 756 s, 739 m $\rho(CH_3Si)$; 677 m $\nu_{as}$(SiC); 648 m, 613 m $\nu_s$(SiC); 571 m, 528 w, 505 m, 462 $cm^{-1}$ m

$\nu$(GaC), $\nu$(GaO), $\nu$(LiO). – $^1$H NMR (400 MHz, [D$_8$]THF, 220 K): $\delta$ = 3.30 (s, 6H, OMe), 1.35 (s, 12H, CMe$_2$), 0.10 (s, 18H, SiMe$_3$), −0.78 (s, 1H, GaCH); OH not detected. – $^{13}$C NMR (100 MHz, [D$_8$]THF, 220 K): $\delta$ = 105.8 (OOC), 50.8 (OMe), 22.6 (CMe$_2$), 3.8 (SiMe$_3$), −0.6 (GaC). – $^{29}$Si NMR (79.5 MHz, [D$_8$]THF, 220 K): $\delta$ = 0.3. – $^7$Li NMR (155.5 MHz, [D$_8$]THF, 220 K): $\delta$ = 0.6.

### *Crystal structure determinations*

Single crystals were obtained upon cooling of the reaction mixtures as described above. Data collections were performed on a Bruker Smart Apex diffractometer. The structures were solved by Direct Methods and refined by full-matrix least-squares calculations based on $F^2$ [20]. The hydrogen atoms of methyl groups were calculated on ideal positions and refined by the riding model. Crystal data, data collection parameters and details of the structure refinement are given in Table 1. One *tert*-butylperoxo group of compound **2** (O3, O4) was disordered and was refined on split-positions (0.65 : 0.35). The molecules of compound **5** reside on crystallographic centers of symmetry.

CCDC 743158 (**2**) and 743159 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request /cif.

### *Acknowledgement*

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