Angewandte Chemie

Peroxides

DOI: 10.1002/anie.200704739

Strongly Oxidizing and Reducing Functions Combined in a Single Compound: An Alkyl Gallium Peroxide Possessing a Nine-Membered $(GaR)_3(O_2)_3$ Heterocycle**

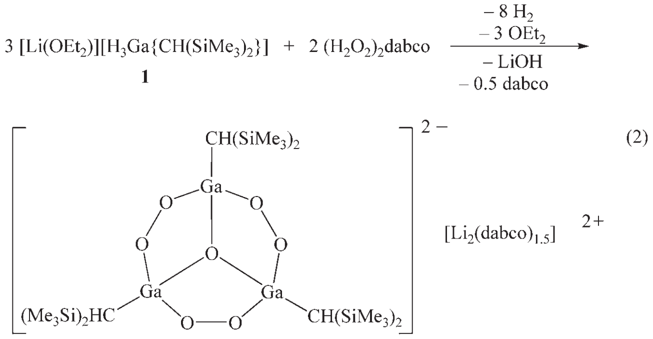
Werner Uhl and Mohammad Reza Halvagar*

Peroxides are well-known and highly interesting intermediates in chemical and biological processes. Many derivatives have been isolated in a molecular state and, like bis(trimethylsilyl) peroxide, have found broad synthetic application. However, in organometallic chemistry their extremely high reactivity often prevents their isolation and thorough characterization. This is particularly true for the organoelement compounds of the heavier Group 13 elements aluminum to indium, because the relatively strong reducing power of the E−C bond is opposed to the oxidizing power of the peroxo group. The rare examples of such organoelement peroxides were obtained by the insertion of dioxygen molecules into the E−C bonds of tri(*tert*-butyl)gallium or -indium but explode in the solid state upon application of mechanical stress.[1] A digallium peroxide with two alkyl gallium groups terminally attached to a bridging peroxo ligand was isolated in trace quantities.[2] It resulted from the accidental exposure of an organogallium compound to air. Usually, the treatment of such alkyl element compounds with oxygen or suitable peroxo derivatives gives the complete oxidation of all E−C bonds in the molecules. In only a few cases were intact peroxo groups detected in the oxidation products.[3] The synthesis and structural characterization of organoelement peroxides of Group 13 elements could allow access to a highly interesting new research area. The high functionality of the peroxo group and the large coordinative variability of these elements may result in the formation of unprecedented structural motifs. Furthermore, these compounds may find important applications as powerful oxygen-transfer reagents.

Treatment of alkyl gallium hydrides with hydrogen peroxide and elimination of elemental hydrogen seemed to be a promising method for the generation of such alkyl gallium peroxides. Former investigations in our group revealed that Ga−C bonds in bis(trimethylsilyl)methyl derivatives are relatively inert towards the attack of oxygen. However, hydrides of the type R_2GaH with $R = CH(SiMe_3)_2$ or the corresponding gallanates were not accessible before. We have now obtained such a compound by the treatment of $LiGaH_4$ with one equivalent of $Li\{CH(SiMe_3)_2\}$ and the precipitation of LiH [Eq. (1)]. The product, $[Li(OEt_2)][H_3Ga\{CH(SiMe_3)_2\}]$ **1**, is produced in high purity and almost quantitative yield.

$$LiGaH_4 + Li\{CH(SiMe_3)_2\} \xrightarrow[-LiH]{OEt_2} [Li(OEt_2)][H_3Ga\{CH(SiMe_3)_2\}]\ (\mathbf{1}) \quad (1)$$

Subsequently, a solution of compound **1** in diethyl ether was added to a cooled (−50 °C) suspension of $(H_2O_2)_2$dabco (dabco = diazabicyclooctane), which is easily available from aqueous solutions of H_2O_2.[4] Elemental hydrogen formed upon warming to room temperature; it was identified by absorption with a palladium wire and formation of molybdenum blue in a secondary reaction. Filtration of the reaction mixture afforded a colorless solution from which, upon cooling, colorless crystals of **2** precipitated in 69 % yield. An idealized reaction course is shown in Equation (2). The constitution of **2** was clarified by crystal structure determination (Figure 1).[5] Interestingly, the strongly reducing hydride functions attached to gallium were not completely oxidized by contact with hydrogen peroxide to give hydroxo groups. Instead, they were replaced by peroxo ligands, the formation of which was accompanied by deprotonation of H_2O_2 and elimination of H_2. The anionic part of the product contains an unprecedented and extraordinarily remarkable structural motif, in which three μ-1,2-peroxo groups bridge three alkyl gallium moieties to form a nine-membered, strongly corrugated heterocycle. The gallium atoms are further coordinated by a single central oxygen atom that may result from oxidation (insertion of O in a Ga−H bond) and subsequent H_2 elimination by the reaction of the hydroxide with a second Ga−H function. Hence, a chalicelike, tricyclic dianion is formed. The Ga−C bonds are not affected



(2)

2

---

[*] Prof. Dr. W. Uhl, M. Reza Halvagar
Institut für Anorganische und Analytische Chemie der Westfälischen Wilhelms-Universität Münster
Correnssstrasse 30, 48149 Münster (Germany)
Fax: (+49) 251-833-6610
E-mail: uhlw@uni-muenster.de

[**] This work was supported by the Deutsche Forschungsgemeinschaft (SFB 424) and the Fonds der Chemischen Industrie.

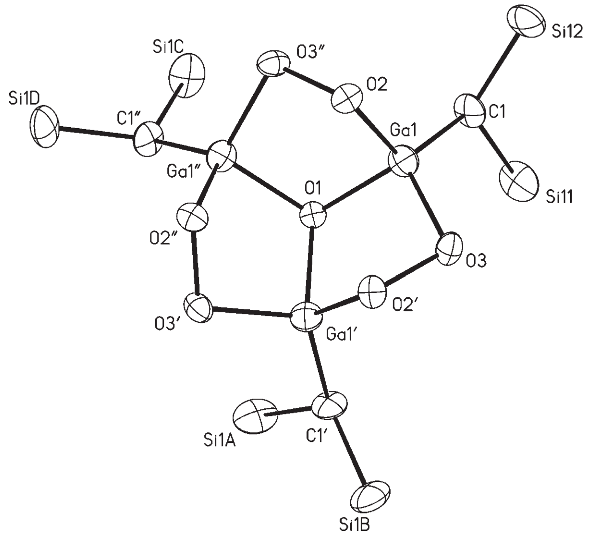


Figure 1. Structure of the $[(RGa)_3O_6]^{2-}$ ion of **2**. Thermal ellipsoids are set at the 40% probability level; methyl groups and hydrogen atoms are omitted. Selected bond lengths [pm], bond angles, and torsion angles [°] (parameters of the second unit of the cage in square brackets): Ga1-O1 189.1(2) [190.2(2)], Ga1-O2 189.5(3) [189.9(3)], Ga1-O3 188.7(3) [190.2(3)], O2-O3″ 153.2(4) [152.7(4)]; Ga1-O1-Ga1′ 106.9(1) [106.0(2)], Ga-O-O 103.9 (av), Ga-O-O-Ga 58.1 [59.8], Ga1′ and O3″ generated by $y-0.5$, $-z+0.5$, $-x$.

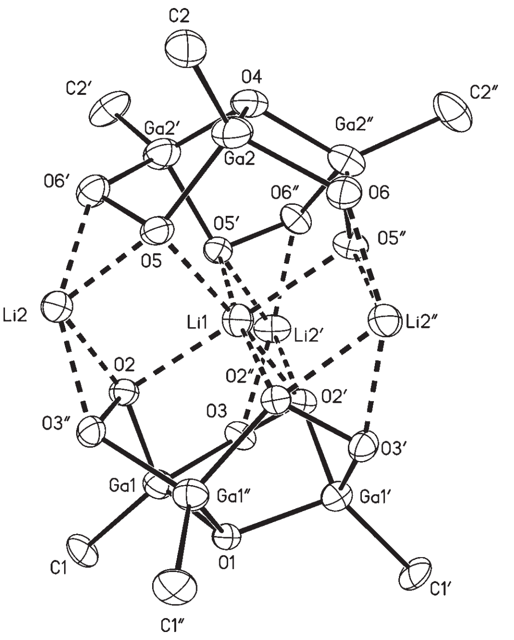


Figure 2. Structure of the dimeric formula unit of **2** including the lithium atoms (thermal ellipsoids set at the 40% probability level). $SiMe_3$ groups and the dabco ligands attached to the atoms Li2, Li2′, und Li2″ are not depicted. Selected bond lengths [pm] and angles [°]: Li1-O2 215.6(8), Li1-O5 215.9(8), Li2-O2 200.6(8), Li2-O3″ 198.9(8), Li2-O5 194.0(9), Li2-O6′ 199.4(8), O-Li1-O 85.1(1)–94.3(1) and 173.5(1); O6′ and O3″ generated by $-z$, $x+0.5$, $-y+0.5$ and $y-0.5$, $-z+0.5$, $-x$, respectively.

despite the occurrence of three closely arranged peroxo groups in the molecular core. Instead, each gallium atom has an intact bond to one carbon atom. Thus, the Ga–C bonds are remarkably resistant towards an oxidative attack and the insertion of oxygen atoms by the formation of alkoxy groups. This remarkable stability may be caused by the particular electronic properties of the bis(trimethylsilyl)methyl residue, which is suitable to act as an electron donor or acceptor through interactions with the σ or σ* orbitals of the α-C–Si bonds. That hyperconjugative electron transfer may result in a diminution of the negative charge at the carbon atoms of the Ga–C bonds and reduce their sensitivity towards oxidation. In contrast, steric shielding by the bulky substituents seems to be of only minor importance, owing to the close proximity of the oxidizing and reducing functions.

In the solid state, two of these anions are connected by four lithium atoms (Figure 2). One is in the center of the resulting cage and is octahedrally coordinated by one oxygen atom from each of the six neighboring peroxo groups (Li–O 216 pm). Three further lithium atoms bear a terminal dabco ligand and are side-on coordinated by lone pairs of electrons to the O–O bonds of two peroxo groups (Li–O 194–201 pm), resulting in a coordination number of five. These Li–O interactions probably contribute to the stability of the unusual structure of **2** by the relatively high polarizing capability of the lithium ions and the resulting reduction of electron density in the peroxo groups. Both anionic building blocks of the cage are twisted by 11° relative to the Ga–O bonds to the μ_3 oxygen atoms. This arrangement may be described as a part of a helical structure. Hence, the molecules are chiral, at least in the solid state. The O–O bond lengths (153 pm) correspond to values detected for dianionic O_2 units,[6] which often display side-on coordination of the peroxo groups to metal atoms. A shorter distance (147.7 pm) occurred in the digallium peroxide mentioned above, which had only terminal gallium atoms.[2] While the Ga-O-O-Ga moiety of that compound is almost planar, with a torsion angle of 164°, a rather acute torsion angle across the O–O bond (59.0° on average) indicates an approach to the *gauche* form in **2**. Depending on the aggregation state, hydrogen peroxide shows torsion angles between 90 and 112°.[7] The relatively small value observed for **2** is caused by the particular bridging situation of the peroxo ligands. Three bridging peroxo units also occurred in the highly explosive acetone peroxide.[8]

Compound **2** decomposed slowly in the solid state at room temperature over several hours and adopted a yellow color. In contrast, solutions in benzene remained unchanged over several days. Gas evolution occurred in paraffin. Hence, IR data are not reported. The singular Ga_3O_6 structural motif with its high density of peroxo groups in close proximity, the easy availability, and the relatively high thermal stability make compound **2** a very promising reagent for oxygen-transfer reactions. Moreover, the simple synthetic procedure, which comprises the treatment of alkyl element hydrides with hydrogen peroxides under hydrogen elimination, opens the facile access to the synthesis of further derivatives possessing unprecedented and spectacular coordination modes.

Experimental Section

n-Hexane was dried over $LiAlH_4$, diethyl ether over Na/benzophenone.

Synthesis of **1**: A solution of $Li\{CH(SiMe_3)_2\}$ (0.834 g, 5.02 mmol),[9] which was purified by sublimation in vacuum, in diethyl ether (15 mL) was added dropwise at room temperature to a suspension of $LiGaH_4$[10] (0.500 g, 6.20 mmol, excess) in the same solvent (15 mL). The mixture was stirred for 5 h and filtered. The solvent of the filtrate was completely removed in vacuum. A highly viscous residue remained, which crystallized upon thorough evacuation over several hours. As shown by NMR spectroscopy, the product (**1**) was formed directly in high purity; it could be used in secondary reactions without further purification. Recrystallization from *n*-hexane afforded colorless crystals (Yield: 1.53 g, 97 %). M.p. (under argon, sealed capillary): 87–89 °C (decomp); ^{1}H NMR (400 MHz, C_6D_6): $\delta = 3.20$ (4H, q, $^3J_{H\text{-}H} = 7.0$ Hz, OCH_2), 3.00 (3H, br s, GaH), 1.02 (6H, t, $^3J_{H\text{-}H} = 7.0$ Hz, CH_3 of ether), 0.35 (18H, s, $SiMe_3$), −0.77 ppm (1H, s, GaCH); ^{13}C NMR (100 MHz, C_6D_6): $\delta = 66.5$ (OCH_2), 14.7 (CH_3 of ether), 3.1 ($SiMe_3$), −4.2 ppm (GaC); ^{29}Si NMR (79.5 MHz, C_6D_6): $\delta = 0.63$ ppm; ^{7}Li NMR (155.5 MHz, C_6D_6): $\delta = 0.41$ ppm; IR (paraffin, CsBr): $\tilde{\nu} = 1770$ vs, br νGaH, 1483 w, 1449 s (paraffin), 1422 w δCH, 1387 s (paraffin), 1300 m, 1242 vs δCH_3, 1184 m, 1153 m, 1093 vs, 1065 vs νCC, νCO, 1024 vs $\delta CH(Si_2)$, 924 s, 833 vs, 790 s, 770 vs, 754 vs $\rho CH_3(Si)$, 683 m, 667 vs $\nu_{as}SiC$, 611 s, 596 s ν_sSiC, 505 cm^{-1} w νGaC.

Synthesis of **2**: Solid $(H_2O_2)_2$dabco[4] (0.72 g, 4.00 mmol, excess) was suspended in diethyl ether (25 mL) at 0 °C and intensively stirred at that temperature for 10 min. The mixture was cooled to −50 °C and slowly treated with a solution of the gallium hydride **1** (0.62 g, 1.98 mmol) in diethyl ether (10 mL). The suspension was allowed to warm to room temperature over a period of 20 min. Gas evolution occurred. Hydrogen was detected by absorption with a palladium wire and subsequent reduction of molybdate to give a deep blue aqueous solution.[11] Filtration and cooling of the filtrate to −15 °C afforded colorless crystals of **2**. The solid was washed twice with *n*-hexane (5 mL) to remove excess dabco (Yield: 0.91 g, 69 %). The peroxide content was determined by hydrolysis of **2** in dilute HNO_3 and subsequent addition of iodide to give iodine, which was determined quantitatively by titration with thiosulfate. We reproducibly obtained greater than 90 % of the calculated peroxide concentration. M.p. (under argon, sealed capillary): slow decomposition at room temperature; ^{1}H NMR (400 MHz, $[D_8]$toluene, 220 K): $\delta = 2.63$ (36H, dabco), 0.11 (108H, s, $SiMe_3$), −0.42 ppm (6H, s, GaCH); ^{13}C NMR (100 MHz, $[D_8]$toluene, 220 K): $\delta = 48.3$ (dabco), 3.9 ($SiMe_3$), 0.5 ppm (GaC); ^{29}Si NMR (79.5 MHz, $[D_8]$toluene): $\delta = -1.3$ ppm; ^{7}Li NMR (155.5 MHz, C_6D_6): $\delta = 0.71$ ppm.

Received: October 15, 2007

Keywords: cage structures · gallium · hydrides · lithium · peroxides

---

[1] W. M. Cleaver, A. R. Barron, *J. Am. Chem. Soc.* **1989**, *111*, 8966; M. B. Power, W. M. Cleaver, A. W. Apblett, A. R. Barron, J. W. Ziller, *Polyhedron* **1992**, *11*, 477; M. B. Power, J. W. Ziller, A. R. Barron, *Organometallics* **1993**, *12*, 4908; A. R. Barron, *Chem. Soc. Rev.* **1993**, *22*, 93.

[2] W. Uhl, S. Melle, M. Prött, *Z. Anorg. Allg. Chem.* **2005**, *631*, 1377.

[3] J. Lewinski, J. Zachara, E. Grabska, *J. Am. Chem. Soc.* **1996**, *118*, 6794; J. Lewinski, J. Zachara, P. Gos, E. Grabska, T. Kopec, I. Madura, W. Marciniak, I. Prowotorow, *Chem. Eur. J.* **2000**, *6*, 3215; S. S. Kumar, S. Singh, H. W. Roesky, J. Magull, *Inorg. Chem.* **2005**, *44*, 1199. Matrix-isolated peroxides: J. Bahlo, H.-J. Himmel, H. Schnöckel, *Inorg. Chem.* **2002**, *41*, 2678; J. Bahlo, H.-J. Himmel, H. Schnöckel, *Angew. Chem.* **2001**, *113*, 4820; *Angew. Chem. Int. Ed.* **2001**, *40*, 4696; G. Stößer, H. Schnöckel, *Angew. Chem.* **2005**, *117*, 4334; *Angew. Chem. Int. Ed.* **2005**, *44*, 4261.

[4] P. Dembech, A. Ricci, G. Seconi, M. Taddei, C. S. Brook, M. Guzman, A. B. Smith, *Org. Synth.* **1997**, *74*, 84.

[5] Crystal structure of **2**: Crystals from diethyl ether at −15 °C; $C_{60}H_{150}Ga_6Li_4N_6O_{14}Si_{12}$, cubic, space group $P2_13$, $a = 2202.23(3)$ pm, $V = 10680.4(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.221$ g cm^{-3}, crystal dimensions: 0.10 × 0.10 × 0.20 mm, Bruker APEX diffractometer, $Mo_{K\alpha}$ radiation, 153 K, measurement range: $2.6 < 2\Theta < 52.1°$, 7022 independent reflections, 6355 reflections $F > 4\sigma(F)$, $\mu = 1.674$ mm^{-1}, programs SHELXTL PLUS REL 4.1 and SHELXL-98, 397 parameters, $R1 = 0.056$ and $wR2$ (all data) = 0.147, max/min residual electron density: $1.054/-0.374 \times 10^{30}$ e m^{-3}. One $SiMe_3$ residue and the dabco ligands are disordered. Their atoms were refined on split positions. The arrangement of the cages in the crystal structure resembles that of a cubic closed-packed lattice. CCDC-663036 (**2**) contains 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.

[6] G. C. Forbes, A. R. Kennedy, R. E Mulvey, R. B. Rowlings, W. Clegg, S. T. Liddle, C. C. Wilson, *Chem. Commun.* **2000**, 1759; A. R. Kennedy, R. E. Mulvey, R. B. Rowlings, *J. Am. Chem. Soc.* **1998**, *120*, 7816; C. Drost, C. Jäger, S. Freitag, U. Klingebiel, M. Noltemeyer, G. M. Sheldrick, *Chem. Ber.* **1994**, *127*, 845; H. Föppl, *Z. Anorg. Allg. Chem.* **1957**, *291*, 12; J. H. Yates, R. M. Pitzer, *J. Chem. Phys.* **1977**, *66*, 3592.

[7] J.-M. Savariault, M. S. Lehmann, *J. Am. Chem. Soc.* **1980**, *102*, 1298; S. Samdal, V. S. Mastryukov, J. E. Boggs, *J. Mol. Struct.* **1995**, *346*, 35, and references therein.

[8] F. Dubnikova, R. Kosloff, J. Almog, Y. Zeiri, R. Boese, H. Itzhaky, A. Alt, E. Keinan, *J. Am. Chem. Soc.* **2005**, *127*, 1146.

[9] P. J. Davidson, D. H. Harris, M. F. Lappert, *J. Chem. Soc. Dalton Trans.* **1976**, 2268.

[10] A. E. Shirk, D. F. Shriver, *Inorg. Synth.* **1977**, *17*, 45.

[11] C. Zhengelis, *Z. Anal. Chem.* **1911**, *49*, 729.