A Silatetragallane—Classical Heterobicyclopentane or *closo*-Polyhedron?[**]

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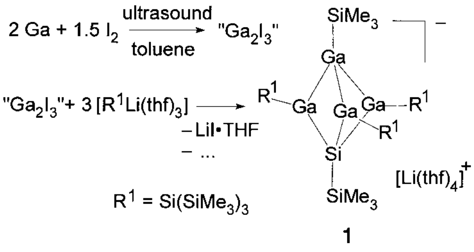
The cluster chemistry of gallium has received increasing attention during the last few years. Bulky silyl groups have proved particularly favorable for stabilizing cluster compounds, and their application has enabled the synthesis of electron-precise oligogallanes such as R_4Ga_2[1] and gallium clusters such as $(R^1GaCl)_4$[2] ($R^1 = Si(SiMe_3)_3$) and $\{R^1Ga[GaR^1(I)]_3\}^-$,[3] as well as the electron-deficient clusters $(RGa)_4$ ($R = C(SiMe_3)_3$,[4a] $Si(SiMe_3)_3$,[4b] and $Si\mathit{t}Bu_3$)[4c] and $[R^1_6Ga_9]^-$.[3] Among other known oligogallanes are $[(\mathit{t}Bu_3Si)_2GaGaSi\mathit{t}Bu_3]^{\bullet}$,[5] $M_2Ga_3Ar_3$ (M = Na, K; Ar = 2,6-dimesitylphenyl),[6] $Ga_3I_5(PEt_3)_3$,[7] $[Cl_2Ga(OEt_2)]_3[ClGa(OEt_2)_2]Ga$,[8a] and $Ga_8I_8(PEt_3)_6$.[8b] Cp*Ga, though monomeric in solution, also forms hexameric aggregates in the crystal.[9] In comparison with the rich chemistry of borane clusters this seems to be very limited, but also shows distinct differences. In spite of the wealth of heteroboranes, silaboranes have only recently been discovered and are confined to a few icosahedral clusters.[10] Herein, we describe the first example of a silagallane, that is a cluster with a III/IV framework.

The ultrasonication of gallium with 1.5 equivalents of iodine in toluene[3, 11] yields insoluble gallium subhalides together with toluene-soluble $Ga[GaI_4]$. This is also achieved with a Ga/I mixture in a 1:1 ratio, if the sonication is interrupted before the reaction is complete. Addition of tris(trimethylsilyl)silyllithium · 3THF to these gallium halide mixtures affords in a complex reaction the anionic gallium cluster **1** (Scheme 1), which is isolated as black-violet crystals.



Scheme 1.

The X-ray structure analysis of **1**[12] shows a C_3-symmetric clusteranion (Figure 1) with a trigonal-bipyramidal Ga_4Si backbone. The counterion is $[Li(thf)_4]^+$. The gallium atoms in the equatorial plane bear hypersilyl groups, the gallium atom and the silicon atom in axial positions trimethylsilyl groups. The Ga–SiMe$_3$ bond ($d_{Ga-Si} = 233.8(3)$ pm) is 4 pm shorter than the bond between gallium and the hypersilyl group. A similar difference is also observed in the only other structurally characterized compound with a Ga–SiMe$_3$ unit, that is the four-membered ring heterocyclic anion $[Ga_3SiR^1_3(SiMe_3)_3]^-$ ($R^1 = Si(SiMe_3)_3$).[13] The Ga–Si distances of the silicon atom in the cluster (240.2(2) pm) are comparable to those of the ring-silicon atoms in $[R^1_2GaSi(SiMe_3)_2]_2$.[13] The Ga–Ga distances to the apical gallium atom are 244.0 pm, and thus 14 pm shorter than in $R^1_4Ga_4$ (258.2 pm)[4b] and also markedly shorter than in $R^1_4Ga_4Cl_4$ (250.5 pm)[2] or in $R^1Ga[R^1Ga(I)]_3^-$ (253.3 pm).[3] The Ga–Ga distances of 279.0 pm in the equatorial plane are distinctly longer, but are still in a range, where Ga–Ga interactions are likely. In $[(CO)_3Fe(GaR^1)_3Fe(CO)_3]$, which also has a trigonal-bipyramidal framework, but is described without Ga–Ga interactions, the gallium atoms are 328.9 pm apart;[14] that is 50 pm more than in **1**. A consequence of the smaller equatorial Ga–Ga distances are very acute bond angles at the axial, distorted tetrahedrally coordinated cluster atoms (Ga2-Si-Ga2′ 71.00(6)°, and Ga2-Ga1-Ga2a: 69.74(4)°). The Si-Ga2-Ga1 angle (96.58(4)°) is 22° wider than the Fe-Ga-Fe angle in the above-mentioned GaFe cluster. Six cluster bonding electron pairs are available for the Ga_4Si core of **1**, thus this cluster may be described as electron-precise with six 2e2c bonds (see **A** in Figure 2). The short equatorial Ga–Ga distances are indicative of the *closo* cluster **B** with three 2e2c and three 2e3c bonds (Figure 2).

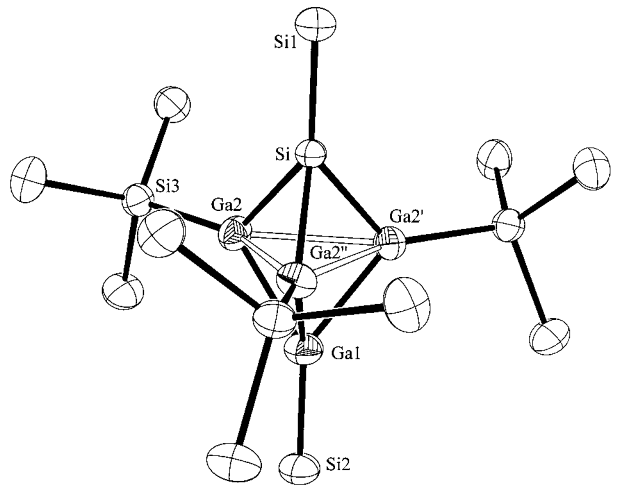


Figure 1. Structure of **1** in the crystal. Methyl groups are omitted in the drawing for clarity. Selected distances [pm] and bond angles [°]: Ga1–Ga2 244.0(1), Ga2–Ga2′ 279.0(1), Ga2–Si 240.2(2), Si–Si1 227.1(4), Ga1–Si2 233.8(3), Ga2–Si3 237.6(2); Ga2-Ga1-Ga2′ 69.74(4), Ga1-Ga2-Si 96.58(4), Ga2-Si-Ga2′ 71.00(6), Si2-Ga1-Ga2 138.69(2), Si3-Ga2-Si 128.73(6), Si3-Ga2-Ga1 134.64(5), Si3-Ga2-Ga2′ 151.58(6), Si3-Ga2-Ga2″ 148.08(6).

Density functional calculations[15] were performed on $R'Ga(R_3Ga_3)SiR'$ (Table 1) to gain a better insight. All structures were optimized in point group C_3. The substituents evidently have a negligible influence on the Ga_4Si core. Shared electron numbers (SEN) obtained from Ahlrichs–Heinzmann population analysis[16] reveal only weak two-

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Table 1. Results of RI-DFT calculations (BP86-functional, def-SV(P)-base; distances in pm, q = shared electron number).

		Ga–Si$_{ap}$	Ga$_{eq}$-Ga$_{ap}$	Ga$_{eq}$-Ga$_{eq}$	$q_{Ga–Si}$	$q_{Ga–Ga_{eq}}$	$q_{Ga_{eq}–Ga_{eq}}$	$q_{Ga-Ga-Ga}$	$q_{Ga-Ga-Si}$
[R′Ga(RGa)$_3$SiR′]$^-$	in C_3								
R	R′								
H	H	236.1	241.0	286.7	1.52	1.65	0.70	0.35	0.29
SiMe$_3$	SiMe$_3$	236.9	242.1	280.3	1.46	1.63	0.76	0.35	0.30
Si(SiMe$_3$)$_3$	SiMe$_3$	238.7	244.0	284.2	–	–	–	–	–
NH$_2$	H	238.3	242.6	294.1	1.47	1.60	0.63	0.36	0.26
HGa(H$_2$Ge)$_3$SiH		235.7^{GeSi}	245.7^{GeGa}	325.8^{GeGe}	1.30^{GeSi}	1.28^{GaGe}	0.06^{GeGe}	0.01^{GaGe2}	0.05^{Ge2Si}
[(CO)$_3$Fe]$_2$(GaH)$_3$		236.2^{GaFe}	–	323.3	–	–	0.40	–	0.25^{Ga2Fe}
tbp[H$_5$Ga$_5$]$^{2-}$		–	243.8	281.5	–	1.67	0.84	0.37	–
okt[H$_6$Ga$_6$]$^{2-}$		–	250.4	250.4	–	1.45	1.45	0.45	–
1,5-(HSi)$_2$(GaH)$_3$		239.5	–	254.1	1.29	–	1.15	–	0.33
T_d-Ga$_4$H$_4$		–	249.0		–	1.40	–	0.36	–

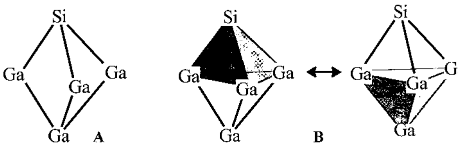

Figure 2. Classical (**A**) and *closo*-cluster representation (**B**) for a Ga$_4$Si cluster.

center interactions in the equatorial plane compared to Ga–Ga single bonds. But, those and the three-center interactions for the Ga$_2$Si and Ga$_3$ facets are markedly larger than that calculated for comparable electron-precise compounds. Similar three-center SEN (0.36) are calculated for borane clusters like H$_5$B$_3$C$_2$. Very recent theoretical[17] and experimental studies[18] on related trigonal-bipyramidal boron, aluminum, and indium compounds support the description as *closo* cluster compounds, although this is discussed controversially. As in **1**, these compounds have long distances between the equatorial atoms and short ones to the axial atoms. For example, in [(Me$_3$Si)$_3$CIn]$_4$S the axial In–In distances are 55 pm shorter than the equatorial ones.[18c]

With the characterization of **1** we present a *closo*-silagallane that promises a rich chemistry. The cleavage of the Ga–Ga bonds with iodine, for example, affords (Me$_3$Si)Si(GaR^{1}I)$_3$. This trifunctional building block, which is isolectronic to {R^{1}Ga[GaR^1(I)]$_3$}$^-$, might provide access to novel cage molecules.

Experimental Section

1: Gallium (0.38 g, 5.3 mmol) and iodine (1.01 g, 8.0 mmol) in toluene (20 mL) were treated in a ultrasonic bath until the mixture had reached a pale yellow to yellow-greenish color. A solution of LiSi(SiMe$_3$)$_3$ · 3THF[19] (3.78 g, 8.0 mmol) in toluene (40 mL) was added dropwise to this solution at −78 °C. After the mixture had been allowed to warm up slowly to ambient temperature, it was stirred for an additional 12 h. After concentration of the reaction solution to dryness, the residue was extracted with pentane (50 mL). After separation of colorless to yellow crystallizing byproducts (LiI · THF, I$_3$GaSi(SiMe$_3$)$_3$ · Li(THF)$_{2,3}$ and further not yet characterized compounds) from the violet-red solution, **1** (0.36 g, 19% with respect to Ga) precipitated as black hexagonal prismatic crystals (deep violet in thin layers). Once crystallized, **1** was no longer soluble in pentane; with THF stable, intense violet solutions of **1** were obtained. ^{1}H NMR (300 MHz,[D$_8$]THF, 300 K): $\delta = 0.51$, 0.39 (9H each, SiMe$_3$), 0.17 (81H, Si(SiMe$_3$)$_3$); ^{13}C NMR ([D$_8$]THF, 300 K): $\delta = 6.9$, 6.2 (SiMe$_3$), 3.8 (Si-(SiMe$_3$)$_3$); ^{29}Si NMR ([D$_8$]THF, 300 K): $\delta = -1.8$ (Si*Si*Me$_3$), −5.5 (Ga-SiMe$_3$), −9.1 (Si(*Si*Me$_3$)$_3$), −60.2 (*Si*SiMe$_3$), −127.1 (*Si*(SiMe$_3$)$_3$); MS (70 eV, EI, ^{69}Ga): *m/z* (%): 1191 (15) [Ga$_4$Si[Si(SiMe$_3$)$_3$]$_3$(SiMe$_3$)$_2$]$^+$ = [A]$^+$, 1118 (77) [A − SiMe$_3$]$^+$, 1045 (35) [A − 2SiMe$_3$]$^+$, 944 (82) [A − Si(SiMe$_3$)$_3$]$^+$, 871 (81) [A − Si(SiMe$_3$)$_4$]$^+$, 729 (80) [Ga$_3$Si[Si(SiMe$_3$)$_3$]$_2$]$^+$, 389 (100) [Ga[Si(SiMe$_3$)$_3$](SiMe$_3$)]$^+$. IR (KBr): $\tilde{\nu}$[cm^{-1}] = 2925, 2855, 1592, 1461, 1378, 1240, 1091, 1042, 833, 735, 682, 623; correct elemental analysis.

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[1] a) W. Uhl, *Angew. Chem.* **1993**, *105*, 1449–1461; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1386–1397; b) C. Dohmeier, D. Loos, H. Schnöckel, *ibid.* **1996**, *108*, 141–161 and **1996**, *35*, 129–149.

[2] G. Linti, W. Köstler, *Angew. Chem.* **1996**, *108*, 593–595; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 550–552.

[3] G. Linti, W. Köstler, *Angew. Chem.* **1997**, *109*, 2758–2760; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2644–2646.

[4] a) W. Uhl, W. Hiller, M. Layh, W. Schwarz, *Angew. Chem.* **1992**, *104*, 1378–1380; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1364–1367; b) G. Linti, *J. Organomet. Chem.* **1996**, *520*, 107–113; c) N. Wiberg, *Coord. Chem. Rev.* **1997**, *163*, 217–252.

[5] N. Wiberg, K. Amelunxen, H. Nöth, H. Schwenk, W. Kaim, A. Klein, T. Scheiring, *Angew. Chem.* **1997**, *109*, 1258–1261; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1213–1215.

[6] a) X.-W. Li, W. T. Pennington, G. H. Robinson, *J. Am. Chem. Soc.* **1995**, *117*, 7578–7580; b) X.-W. Li, Y. Xie, P. R. Schreiner, K. D. Gripper, R. C. Crittendon, C. F. Campana, H. F. Schaefer, G. H. Robinson, *Organometallics* **1996**, *15*, 3798–3803.

[7] A. Schnepf, C. Doriat, E. Möllhausen, H. Schnöckel, *Chem. Commun.* **1997**, 2111–2112.

[8] a) D. Loos, H. Schnöckel, D. Fenske, *Angew. Chem.* **1993**, *105*, 1124–1125; *Angew. Chem. Int. Ed. Engl.* **1993**, *32,* 1059–1060; b) C. U. Doriat, E. Baum, A. Ecker, H. Schnöckel, *ibid.* **1997**, *109*, 2057–2059 and **1997**, *36*, 1969–1971.

[9] D. Loos, E. Baum, A. Ecker, H. Schnöckel, A. J. Downs, *Angew. Chem.* **1997**, *109*, 894–896; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 860–862.

[10] z. B. a) D. Seyferth, K. Büchner, W. S. Rees, Jr., W. M. Davis, *Angew. Chem.* **1990**, *102*, 911–913; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 918–920; b) L. Wesemann, U. Englert, *ibid.* **1996**, *108*, 586–587 and **1996**, *35*, 527.

[11] Analogous to the preparation of GaI: M. L. H. Green, P. Mountford, G. J. Smout, S. R. Speel, *Polyhedron* **1990**, *9*, 2763–2765.

[12] Crystal structure analysis of **1**: STOE IPDS, Mo$_{K\alpha}$ radiation, structure solved by direct methods, and full-matrix least-squares refeinement against F^2, hydrogen atoms were included as riding model with Siemens SHELXTL 5.0 (PC) and SHELXL97. Crystal dimensions: 0.15 × 0.15 × 0.10 mm, trigonal, space group $P31c$ (no. 159), a, b = 1568.0(2), c = 1956.0(2) pm, V = 4.1650(8) nm^3, Z = 2, ρ_{calcd} = 1.189 g cm^{-3}, μ = 1.528 mm^{-1}, F(000) = 1588, 19740 measured reflections in $2\Theta = 5–52°$, 5381 [with $F > 4\sigma(F)$: 3915] independent

reflections, numerical absorption correction (min./max. transmission: 0.546/0.664), 256 parameters. $R_1 = 0.042$, $wR_2 = 0.122$ (all data), max. residual electron density 0.64 e Å^{-3}. In the refinement a merohedral twinning from 6/*m* into 6/*mmm* with volume fractions of 91:9 was considered. One THF molecule of the $[Li(thf)_4]^+$ ion is disordered over a C_3 axis. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101051. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[13] G. Linti, W. Köstler, A. Rodig, *Eur. J. Inorg. Chem.* **1998,** *745*, 749.

[14] G. Linti, W. Köstler, *Chem. Eur. J.* **1998**, *4*, 942–949.

[15] RI-DFT calculations with program package TURBOMOLE. All distances were multiplied by 0.97 to fit with experimental data of **1**: R. Ahlrichs, Universität Karlsruhe; K.Eichkorn, O. Treutler, H. Öhm, M. Häser, R. Ahlrichs, *Chem. Phys. Lett.* **1995**, *240*, 283.

[16] a) E. R. Davidson, *J. Chem. Phys.* **1967**, *46*, 3320; b) K. R. Roby, *Molec. Phys.* **1974**, *27*, 81; c) R. Heinzmann, R. Ahlrichs, *Theoret. Chim. Acta* **1976**, *42*, 33.

[17] P. von R. Schleyer, G. Subramanian, A. Dransfeld, *J. Am. Chem. Soc.* **1996**,*118*, 9988–9989.

[18] a) $[As_2(AlCp^*)_3]$: C. K. F. von Hänisch, C. Üffing, M. A. Junker, A. Ecker, B. O. Kneisel, H. Schnöckel, *Angew. Chem.* **1996**, *108*, 3003–3005; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2875–2877; b) $Et_5B_3C_2$: M. Antipin, R. Boese, D. Bläser, A. Maulitz, *J. Am. Chem. Soc.* **1997**, *119*, 326–333; c) $[(Me_3Si)_3CIn]_4S$: W. Uhl, R. Graupner, W. Hiller, M. Neumayer, *Angew. Chem.* **1997**, *109*, 62–64; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 62–64.

[19] a) H. Gilman, C. L. Smith, *J. Organomet. Chem.* **1968**, *14*, 91; b) G. Gutekunst, A. G. Brook, *ibid.* **1982**, *225*, 1; c) A. Heine, R. Herbst-Irmer, G. M. Sheldrick, D. Stalke, *Inorg. Chem.* **1993**, *32*, 2694–2698.

Olefin Epoxidation by Methyltrioxorhenium: A Density Functional Study on Energetics and Mechanisms**

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Oxygen transfer reactions mediated by transition metals, such as olefin epoxidation[1] and dihydroxylation,[2] are currently attracting much interest from both experimentalists and theoreticians. Many investigations, several of them of computational thrust, have unraveled details of olefin dihydroxylation as catalyzed by oxo complexes of the type MO_4 (M = Os, Ru).[3] Extensive experimental work has been devoted to the structurally similar compound methyltrioxorhenium (MTO) which has proven to be a highly efficient olefin epoxidation catalyst in the presence of hydrogen peroxide.[4] MTO reacts with H_2O_2 resulting in mono- and bisperoxo compounds; an additional aquo ligand has been found to stabilize the latter complex.[5] Recent experimental work shows the possibility for olefin epoxidation also by inorganic compounds like ReO_4^-, even without explicit use of H_2O_2.[6] Herrmann et al.[5] and Espenson et al.[7] have proposed reaction mechanisms for epoxidation by MTO-related complexes that involve differently oxygenated and hydrated forms of these catalysts. Also conceivable are processes in which hydroperoxo species participate.[8] However, in contrast to dihydroxylation by oxo complexes,[3] quite a few details of the reaction mechanism involving peroxo complexes remain to be clarified. Previous computational studies focused on structural aspects of MTO-related oxo complexes.[9] Here, we use density functional (DF) calculations[10, 11] to analyze structural and energetic properties of various mono-, bis-, and hydroperoxo derivatives of MTO and to estimate the activation barriers of the corresponding oxygen-transfer reactions.

We start by considering various rhenium–oxo and -peroxo complexes: MTO (**1**) as well as the corresponding monoperoxo (**2**) and bisperoxo (**3**) complexes, each of them in free (**A**) and monohydrated (**B**) form (Figure 1). The water ligand of complexes **B** was added in *cis* position to the methyl group, as suggested by an X-ray structure analysis for the bisperoxo complex.[5] A second water molecule in *trans* position is

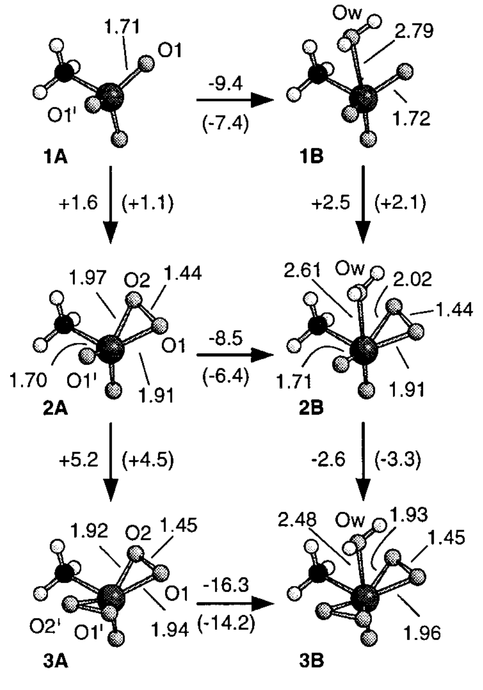

Figure 1. Optimized structures of **1A** and the corresponding monoperoxo (**2A**) and bisperoxo complexes (**3A**) as well as the mono-hydrated complexes **1B**, **2B**, and **3B**. Bond lengths in Å, energy and enthalpy (in parentheses) changes of peroxidation (columns) and hydration (rows) in kcal mol^{-1}. Experimental bond lengths for **3B**:[5] Re–O1 1.91, Re–O2 1.90, O1–O2 1.47, Re–Ow 2.25.

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