Notes

Synthesis and Characterization of $[t\text{-Bu}_2\text{Ga}(\mu\text{-OH})]_3$

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Introduction

Recently we reported the synthesis and characterization of $[t\text{-Bu}_2\text{GaP}(i\text{-Pr})_2]_2$ (**1**) and $t\text{-Bu}_2\text{GaP}(t\text{-Bu})_2$ (**2**), formed by means of reaction 1.[1] Both **1** and **2** are volatile (**2** subliming slowly at

$$\text{LiPR}_2 + t\text{-Bu}_2\text{GaCl} \longrightarrow \text{LiCl} + [t\text{-Bu}_2\text{GaPR}_2]_n \qquad (1)$$

$$\begin{array}{l} \mathbf{1},\ \text{R} = i\text{-Pr},\ \text{n} = 2 \\ \mathbf{2},\ \text{R} = t\text{-Bu},\ \text{n} = 1 \end{array}$$

room temperature at 1 × 10^{-3} torr) and serve as single-source precursors for the preparation of GaP.[1]

$$\begin{array}{c} \mathbf{1} \\ \text{or} \\ \mathbf{2} \end{array} \xrightarrow{\Delta} \text{GaP} \qquad (2)$$

Compound **2** has been successfully utilized for the impregnation of ZnS by GaP to form a nanocomposite.[2] Here we report that the hydrolyses of **1** and **2** give the cyclic trimers $[t\text{-Bu}_2\text{Ga}(\mu\text{-OH})]_3$ (**3**) and $[t\text{-Bu}_2\text{Ga}(\mu\text{-OD})]_3$ (**4**). While this work was underway, a recent report by Barron and co-workers on the synthesis of **3** by the hydrolysis of $t\text{-Bu}_3\text{Ga}$ or $t\text{-Bu}_2\text{GaCl(THF)}$ appeared,[3] followed by a paper by Cowley et al. describing the structure determination of **3** and the preparations of **3** and **4** by the hydrolysis of $t\text{-Bu}_3\text{Ga}$.[4] Interestingly, Higa et al. had observed earlier that $t\text{-Bu}_2\text{GaAs}(t\text{-Bu})_2$ decomposes to a white solid in air, but reported no characterization of the product.[5]

Experimental Section

General Procedure. All reactions were carried out under an atmosphere of prepurified argon using standard inert-atmosphere and Schlenk techniques.[6] Benzene, Et_2O, and pentane were distilled from Na/benzophenone under N_2. ^1H and ^{13}C NMR spectra were recorded on a Nicolet NT-300 or a Varian VXR-300 instrument. FTIR spectra were recorded on an IBM-ZR 98 spectrometer using Nujol mulls. Mass spectra were obtained on a Finnigan 4000 instrument. Compounds **1** and **2** were prepared according to a published method.[1]

$[t\text{-Bu}_2\text{Ga}(\mu\text{-OH})]_3$ (3). Distilled water (11 μL, 0.60 mmol) was added dropwise to an ether solution of 0.18 g (0.61 mmol) of **1** or 0.20 g (0.61 mmol) of **2**. The reaction mixture was stirred for 10 min, all the volatiles were removed under vacuum, and the residue was extracted by benzene. Yield: 83% using **1** and 86% using **2**. Mp: 252–254 °C dec. ^1H NMR (CDCl_3): δ 1.06 (s, 18 H, *t*-BuGa), 0.77 (s, 1 H, GaOH). ^{13}C NMR (CDCl_3): δ 30.91 ($(\text{CH}_3)_3$CGa), 25.75 $(\text{CH}_3)_3$*C*Ga. MS, *m/e* (relative intensity): 545 (2, M^+ − *t*-Bu), 529 (4, M^+ − *t*-BuO), 345 (4, M^+ − $t\text{-Bu}_2\text{GaOH}$ − *t*-Bu). IR (Nujol mull): 3610 (m, sh), 3350 (m), 2947 (s), 2840 (s), 2768 (m), 2740 (m), 2704 (m), 2644 (m), 1464 (s), 1361 (m), 1092 (m), 940 (m), 721 (m) cm^{-1}.

Table I. Crystallographic Data for **3**

formula	$\text{Ga}_3\text{O}_3\text{C}_{24}\text{H}_{57}$
fw	602.88
space group	$R\bar{3}c$
a, Å	10.297(1)
c, Å	50.685(20)
V, Å^3	4654(3)
Z	6
d_{calc}, g/cm^3	1.29
μ(Mo Kα), cm^{-1}	26.1
data collecn instrument	Siemens P4/RA
temp, °C	−50.0
scan method	θ–2θ
data collcn range, 2θ, deg	3.5, 50.0
unique data total	933
unique data, with $F_o^2 > 3\sigma(F_o^2)$	678
R^a	0.053
$R_w{}^b$	0.063

[a] $R = \sum||F_o| - |F_c|| / \sum|F_o|$. [b] $R_w = [\sum(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$, $w = 1/(|F_o|)$.

Crystals suitable for X-ray diffraction were grown in a septum-capped NMR tube containing compound **2** and benzene-d_6 which was exposed to moist air for a period of 2 weeks at room temperature.

$[t\text{-Bu}_2\text{Ga}(\mu\text{-OD})]_3$ (4). The procedure for the preparation of **4** is the same as that for **3** except for the use of D_2O instead of H_2O and a scale-down of the reaction by 50%. Yield: 86% from **1**, 92% from **2**. Mp: 252–254 °C dec. ^1H NMR (CDCl_3): δ 1.07 (s, 18 H, *t*-BuGa). ^{13}C NMR (CDCl_3): δ 30.92 ($(\text{CH}_3)_3$CGa), 25.79 $(\text{CH}_3)_3$*C*Ga). MS, *m/e* (relative intensity): 548 (4, M^+ − *t*-Bu), 532 (1, M^+ − *t*-BuO), 347 (11, M^+ − $t\text{-Bu}_2\text{GaO}$ − *t*-Bu). IR (Nujol mull): 2960 (s), 2932 (s), 2873 (s), 2840 (s), 2720 (m), 2673 (m, sh), 1470 (m), 1400 (m), 1360 (m), 1010 (m), 931 (m), 870 (m), 810 (m), 765 (m) cm^{-1}.

X-ray Structure Determination of 3. A colorless crystal of dimensions 0.35 mm × 0.035 mm × 0.30 mm was glued to the tip of a glass fiber and mounted on a Siemens P4/RA single-crystal diffractometer for data collection at −50 ± 1 °C. The cell constants for data collection were determined from a set of 20 reflections found from a rotation photograph. Pertinent data collection and reduction information is given in Table I. Lorentz and polarization corrections were applied. A correction based on decay of 2.4% in the standard reflections was applied to the data. An absorption correction based on a series of ψ-scans was applied by using XEMP.[7] The agreement factor the averaging of observed reflections was 3.6% (based on F^2). The data set was determined to have both obverse ($-h + k + 1 = 3n$) and reverse ($h - k + 1 = 3n$) contributions. Hexagonal solutions were attempted, but none gave a suitable result. $R\bar{3}c$ was selected as the space group, assuming the sample collected was a merihedral twin. The positions of all non-hydrogen atoms were determined by direct methods using XS.[7] Refinement proceeded using SHELXTL-Plus.[7] All non-hydrogen atoms were refined anisotropically. Refinement results at this stage were poor with $R = 0.178$ and $R_w = 0.201$ for 678 observed reflections. The worst group of reflections was that which had the possibility of a contribution from both twins. The refinement was transferred to GSAS, which allows for twin refinements.[8] All non-hydrogen atoms were refined anisotropically. All methyl hydrogen atoms were refined as riding atoms. The final residuals are $R = 0.053$ and $R_w = 0.063$.

Results and Discussion

Since we discovered crystals of **3** growing in an NMR tube wherein **2** was undergoing slow hydrolysis, we decided to determine whether both **1** and **2** would provide **3** in high yield in a more rapid synthetic procedure (reaction 3). This is indeed the case

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(1) Naiini, A. A.; Han, Y.; Akinc, M.; Verkade, J. G. Submitted for publication.

(2) Han, Y.; Naiini, A. A.; Voiles, T.; Chumbley, L. S.; Akinc, M.; Verkade, J. G. Manuscript in preparation.

(3) Power, M. B.; Cleaver, W. M.; Apblett, A. W.; Barron, A. R.; Ziller, J. W. *Polyhedron* **1992**, *11*, 477.

(4) Atwood, D. A.; Cowley, A. H.; Harris, P. R.; Jones, R. A.; Koschmieder, S. U.; Nunn, C. M.; Atwood, J. L.; Bott, S. G. *Organometallics* **1993**, *12*, 24.

(5) Higa, K. T.; George, C. *Organometallics* **1990**, *9*, 275.

(6) Shriver, D. F.; Dresdon, M. A. *The Manipulation of Air-Sensitive Compounds*; Wiley and Sons: New York, 1986.

(7) SHELXTL-Plus, Siemens Analytical X-ray Instruments, Inc., Madison, WI.

(8) GSAS: Larson, A. C.; VonDreele, R. B. *LANSCE*. Report MS-H805; Los Alamos National Laboratory: Los Alamos, NM 87545. Copyright 1985–1993: The Regents of the University of California.

0020-1669/93/1332-3781$04.00/0

$$1 \text{ or } 2 \xrightarrow{H_2O,\,(D_2O)} 3,\,(4) + HPR_2 \text{ or } DPR_2 \qquad (3)$$

and the reactions are complete within 2 min at room temperature. This can be inferred from the color change of **2** from yellow to colorless during that time period.

The ^1H NMR spectrum of **3** in $CDCl_3$ shows two singlets at 1.06 and 0.77 ppm and their 18:1 ratios indicative of the *tert*-butyl and hydroxy protons, respectively, whereas the ^1H NMR spectrum of **4** in the same solvent displays only the singlet at 1.07 ppm. The ^{13}C NMR spectra of both compounds are similar, displaying peaks at 30.71 and 25.75 ppm, which can be assigned to the methyl carbons and the tertiary carbons, respectively. IR spectral data confirmed the presence of OH (3610 (m, sh) cm^{-1}) and OD (2673 (m, sh) cm^{-1}) groups in **3** and **4**, respectively, and mass spectrometry provided a peak for the trimeric structures of **3** and **4** minus a *tert*-butyl group. While **3** appears to be stable in air for a few hours, we found that, over a period of several days in a capped sample vial, the compound decomposed, giving a very different mass spectrum.

The ORTEP drawing of **3** shown in Figure 1 reveals its cyclic trimeric structure in which three Ga and three oxygen atoms form a six-membered planar ring with the six *t*-Bu groups located above and below the plane of the ring. The geometry around Ga is a distorted tetrahedron with average angles ranging from 96.3(5)° for O–Ga–O to 121.9(7)° for C–Ga–C. The average Ga–C (2.00(2) Å) and Ga–O distances (1.935(3) Å) closely match those reported for the related tetrameric structure $[Me_2Ga(\mu\text{-}OH)]_4$ (1.97(4) and 1.94–1.99 Å, respectively).[9] In contrast to compound **3**, $[Me_2Ga(\mu\text{-}OH)]_4$ contains a larger (eight-membered) ring: one that is puckered rather than planar. While the O–Ga–O bond angles are within 3° in both compounds, the average Ga–O–Ga angle in **3** (143.7(5)°) is about 10° larger than that in the tetramer (133.1°) and the average C–Ga–C angle (121.9(7)°) is about ca. 6° smaller than that in the tetramer (129.2°).[9]

A comparison of the structures of **3** and $[Me_2Ga(\mu\text{-}OH)]_4$ suggests a reason for the trimeric configuration of the former and the tetrameric constitution of the latter. Since the O–Ga–O angles are very similar in both compounds (while the C–Ga–C and Ga–O–Ga angles are not), let us assume for the sake of argument that the O–Ga–O angle is the least flexible. Thus the puckering of the eight-membered ring in $[Me_2Ga(\mu\text{-}OH)]_4$ is accommodated mainly by the Ga–O–Ga angles. The consequences are that the distance between closest pairs of methyl carbons on neighboring Ga atoms is 3.59(30) Å in **3**,[10] which corresponds to the sum of the van der Waals radii of two Me groups (ca. 4.0 Å[11]), and the Ga–O–Ga angle can close down to a relatively unstrained angle of 133.1°.[9]

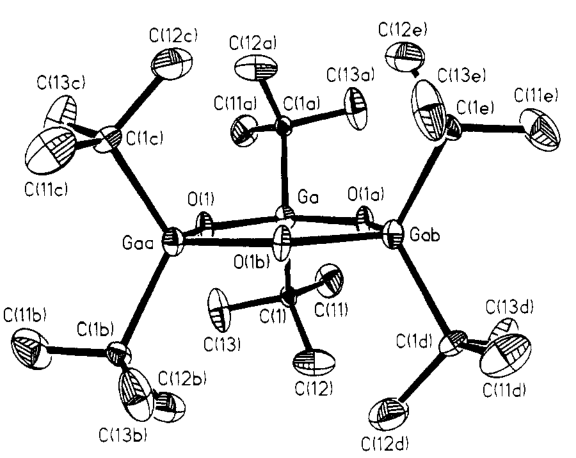

Figure 1. Structure of $[(t\text{-}Bu)_2Ga(\mu\text{-}OH)]_3$ (**3**) with hydrogen atoms are ommited for clarity. Ellipsoids are drawn at the 50% probability level.

Table II. Positional Parameters and Their Estimated Standard Deviations for 3

atom	*x*	*y*	*z*	*U*, Å^2	frac
Ga	0.666667	0.5395(2)	0.083333	0.0307	0.5
O	0.5050(9)	0.333333	0.083333	0.0422	0.5
C1	0.6707(8)	0.6358(8)	0.0488(3)	0.0288	1.0
C11	0.761(4)	0.804(5)	0.0506(5)	0.0408	1.0
C12	0.724(2)	0.577(2)	0.0253(2)	0.0561	1.0
C13	0.512(5)	0.599(4)	0.0413(4)	0.0515	1.0

In **3**, the methyl groups of *t*-Bu moieties on the same Ga are staggered in order to accommodate their van der Waals radii. This also leads to "meshing" of methyl groups extending over and under the planar six-membered ring. In response, the average C–Ga–C angle is compressed relative to that in the tetrameric structure of $[Me_2Ga(\mu\text{-}OH)]_4$ and the average Ga–O–Ga angle can enlarge. It would appear that puckering of the six-membered ring to a chair form in **3** is precluded by severe 1,3-syn diaxial steric interactions of *t*-Bu groups which would result and also by the requirement for the Ga–O–Ga angle to close down to a virtually tetrahedral angle. A tetrameric structure analogous to that of $[Me_2Ga(\mu\text{-}OH)]_4$ would be inhibited by strong steric interactions of the closest pairs of *t*-Bu groups on adjacent Ga atoms. A planar tetrameric structure would possess Ga–O–Ga angles even larger than those in the trimer, and hence also greater steric interactions would be operative between pairs of *t*-Bu groups above (and below) the ring that reside on neighboring Ga atoms.

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Supplementary Material Available: Tables of crystallographic data, hydrogen positional parameters, general displacement parameters, and bond distances and angles and further textual details of the twin refinement (5 pages). Ordering information is given on any current masthead page.

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[9] Smith, G. S.; Hoard, J. L. *J. Am. Chem. Soc.* **1959**, *81*, 3907.

[10] The distance was calculated from the structural parameters given in ref 9, using SHELXTL-Plus.[7]

[11] Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960.