

# Synthesis and oxidation of bis(triphenylgermyl)zinc

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## Abstract

Bis(triphenylgermyl)zinc ( $\text{Ph}_3\text{Ge}$ )<sub>2</sub>Zn (**1**), prepared by the reaction of diethylzinc ( $\text{Et}_2\text{Zn}$ ) with two molar amounts of triphenylgermane ( $\text{Ph}_3\text{GeH}$ ), was easily reacted by a small amount of oxygen to give tetrameric oxide ( $\text{Ph}_3\text{GeZnO}$ )<sub>4</sub> (**2**). Four zinc and four oxygen atoms in **2** are arranged such that a cube is formed as determined by X-ray diffraction analysis. Further oxidation of **2** led to the formation of digermoxane, ( $\text{Ph}_3\text{Ge}$ )<sub>2</sub>O as a final product.

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*Keywords:* Germylzinc; X-ray diffraction; Oxidation

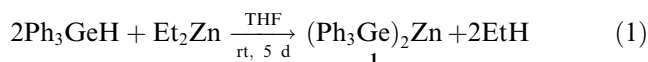
## 1. Introduction

Organozinc compounds are useful reagents not only in organic synthesis but also in organometallic chemistry [1]. The well-known Reformatsky zinc alkylation and the Simons–Smith reaction proceed via organozincs assumed as key intermediates. Despite the large number of reports on organozinc reagents, far less attention has been given to silyl- or germyl-substituted zinc compounds [2,3]. Up to now, several bis(silyl)- or bis(germyl)-substituted zinc derivatives {( $\text{Ph}_3\text{Si}$ )<sub>2</sub>Zn [2a], ( $\text{Me}_3\text{Si}$ )<sub>2</sub>Zn [2b], [( $\text{Me}_3\text{Si}$ )<sub>3</sub>Si]<sub>2</sub>Zn [2c], (*t*- $\text{Bu}_3\text{Si}$ )<sub>2</sub>Zn [2d], ( $\text{Ph}_3\text{Ge}$ )<sub>2</sub>Zn [3a], ( $\text{Et}_3\text{Ge}$ )<sub>2</sub>Zn [3b], and [( $\text{Me}_3\text{Si}$ )<sub>3</sub>-Ge]<sub>2</sub>Zn [3c]} and silyl- or germyl-substituted zinc halides {*t*- $\text{Bu}_3\text{SiZnCl}$  [2d], *t*- $\text{Bu}_3\text{SiZnBr}$  [2d], ( $\text{Me}_3\text{Si}$ )<sub>3</sub>GeZnX (X = Cl, Br, I) [3d]} have been prepared and a few X-ray crystal structures of [( $\text{Me}_3\text{Si}$ )<sub>3</sub>Si]<sub>2</sub>Zn, (*t*- $\text{Bu}_3\text{Si}$ )<sub>2</sub>Zn, *t*- $\text{Bu}_3\text{SiZnBr}$ , [( $\text{Me}_3\text{Si}$ )<sub>3</sub>Ge]<sub>2</sub>Zn, and ( $\text{Me}_3\text{Si}$ )<sub>3</sub>GeZnX have been determined. However, reports on the reactivities of silyl- or germyl-zinc derivatives are limited [3c]. We describe herein the first oxidation of bis(germyl)zinc

(**1**). In the oxidation of **1** we found a novel tetrameric germylzinc oxide, ( $\text{Ph}_3\text{GeZnO}$ )<sub>4</sub> (**2**). Further oxidation of **2** finally led to the formation of digermoxane, ( $\text{Ph}_3\text{Ge}$ )<sub>2</sub>O.

## 2. Results and discussion

Treatment of diethylzinc ( $\text{Et}_2\text{Zn}$ ) with two molar amounts of triphenylgermane ( $\text{Ph}_3\text{GeH}$ ) in THF at room temperature for 5 days of stirring afforded flammable colorless crystals with a composition of ( $\text{Ph}_3\text{Ge}$ )<sub>2</sub>Zn (**1**) in 26% isolated yield (based on the concentration of  $\text{Et}_2\text{Zn}$ ) (Eq. (1)). Unreacted  $\text{Ph}_3\text{GeH}$  was mostly recovered. The bis(germyl)zinc (**1**) is thermally stable for prolonged periods in the absence of air at room temperature.



The bis(germyl)zinc (**1**) was identified with the <sup>1</sup>H, and <sup>13</sup>C NMR spectra. Two THF molecules were included for a molecule **1** based on the <sup>1</sup>H and <sup>13</sup>C NMR data. Bychkov et al. [3b] described the formation of ( $\text{Et}_3\text{Ge}$ )<sub>2</sub>Zn by treatment of  $\text{Et}_2\text{Zn}$  with two molar amounts

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of  $\text{Et}_3\text{GeH}$  in diglyme at  $150^\circ\text{C}$  for 1.5 h. The bis(germyl)zinc (**1**) was prepared by another method, namely, the reaction of  $\text{ZnCl}_2$  with two molar amounts of triphenylgermylalkali metals ( $\text{Ph}_3\text{GeM}$ ,  $\text{M} = \text{Na}, \text{K}$ ) in liquid  $\text{NH}_3$  [3a].

The air-sensitive bis(germyl)zinc (**1**) could be recrystallized from pentane at  $-20^\circ\text{C}$ . The molecular structure of **1** was unequivocally confirmed by X-ray diffraction analysis. The molecular structure of **1** is shown in Fig. 1. The selected bond lengths and bond angles of **1** are summarized in Table 1. Crystallographic data of **1** are summarized in Section 3. **1** has a bent structure with  $\text{Ge-Zn-Ge}$  bond angle of  $135.42(2)^\circ$ . Two THF molecules are coordinated to the zinc atom with  $\text{Zn-O}$  bond length of  $2.148 \text{ \AA}$  (av). The bond angle of  $\text{O-Zn-O}$  is  $91.47(11)^\circ$  and the  $\text{Ge-Zn-O}$  bond angles range from  $103.52(7)$ – $105.87(7)^\circ$ . The bond lengths of  $\text{Ge-Zn}$  ( $2.4331 \text{ \AA}$  (av)) is almost equal within experimental error with the sum ( $2.47 \text{ \AA}$ ) of the covalent radii [7] and is longer than those of  $(\text{Me}_3\text{Si})_3\text{GeZnX}$  and  $[(\text{Me}_3\text{Si})_3\text{Ge}]_2\text{Zn}$  [3c,3d]. The bond length of  $\text{Zn-O}$  are also longer than those of  $(\text{Me}_3\text{Si})_3\text{GeZnX}$  and  $[(\text{Me}_3\text{Si})_3\text{Ge}]_2\text{Zn}$  [3c,3d].

We have previously reported on a molecular structure of bis[tris(trimethylsilyl)germyl]zinc,  $[(\text{Me}_3\text{Si})_3\text{Ge}]_2\text{Zn}$  [3c]. In  $[(\text{Me}_3\text{Si})_3\text{Ge}]_2\text{Zn}$ , the two tris(trimethylsilyl)germyl ligands,  $(\text{Me}_3\text{Si})_3\text{Ge}$ , were bonded in a linear fashion to the zinc atom and staggered with respect to each other. The difference of these geometries are considered to be caused by steric repulsion between the bulky  $\text{Ph}_3\text{Ge}$  groups.

Bis(germyl)zinc (**1**) was easily oxidized in air to give hexaphenyldigermoxane in high yield (Eq. (2)).



A small amount of oxygen was added to bis(germyl)zinc (**1**) in  $\text{C}_6\text{D}_6$  at room temperature, and the oxidation process of **1** was investigated by  $^{13}\text{C}$  NMR spectra.

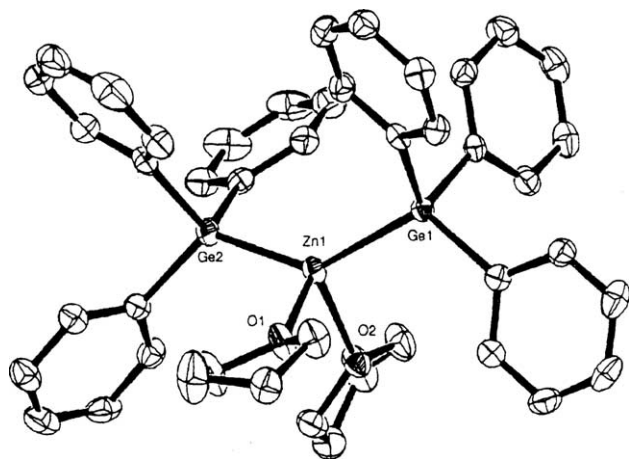
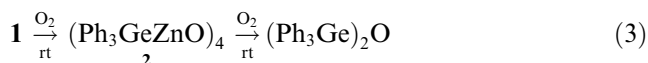


Fig. 1. Molecular structure of **1**. Hydrogen atoms are omitted for clarity.

$\text{Zn(1)-Ge(1)}$	2.4315(6)	$\text{Zn(1)-Ge(2)}$	2.4346(6)
$\text{Zn(1)-O(1)}$	2.179(3)	$\text{Zn(1)-O(2)}$	2.17(3)
$\text{Ge(1)-Zn(1)-Ge(2)}$	135.24(2)	$\text{Ge(1)-Zn(1)-O(1)}$	103.52(7)
$\text{Ge(1)-Zn(1)-O(2)}$	105.87(7)	$\text{O(1)-Zn(1)-O(2)}$	91.47(11)

The signals of **1** completely disappeared after 1 h, resulting in the build-up of new signals of an intermediate **2**:  $^{13}\text{C}$  NMR ( $\delta$ ,  $\text{C}_6\text{D}_6$ ) 26.0 (THF), 67.9 (THF), 128.2, 128.7, 136.1, 143.2. which were apparently different from that found in the starting material **1**, together with digermoxane,  $(\text{Ph}_3\text{Ge})_2\text{O}$ . Finally, the signals of  $(\text{Ph}_3\text{Ge})_2\text{O}$  alone were observed after 10 h.



Fortunately, the intermediate **2**, prepared by the reaction of  $\text{Ph}_3\text{GeH}$  and  $\text{Et}_2\text{Zn}$ , could be isolated and recrystallized from THF at  $-20^\circ\text{C}$  as unstable colorless crystals with a composition of  $(\text{Ph}_3\text{GeZnO})_4$ . The germylzinc oxide (**2**) was characterized by the  $^1\text{H}$ , and  $^{13}\text{C}$  NMR spectra. The germylzinc oxide (**2**) is first group 14 element-substituted zinc oxide. Four THF molecules were included for a molecule **2** based on the  $^1\text{H}$  and  $^{13}\text{C}$  NMR data. The molecular structure of **2** was analyzed by X-ray diffraction method. The molecular structure of **2** is shown in Fig. 2. The selected bond lengths and bond angles of **2** are summarized in Table 2. Crystallographic data of **2** are also summarized in Section 3.

Interestingly, germylzinc oxide (**2**) is tetrameric germylzinc oxide, and four zinc atoms and four oxygen atoms make a distorted cubic center with  $\text{Zn-O}$  bond length of  $2.054 \text{ \AA}$  (av). The distortion can be described in terms of an inward movement of the O atoms along the threefold axes of the cube, resulting in  $\text{Zn-O-Zn}$  angles  $>90^\circ$ . The largest deviations from the tetrahedron values are found for the angles at Zn. The bond angle of  $\text{Zn-O-Z}$  and  $\text{O-Zn-O}$  is  $95.69^\circ$  (av) and  $84.0^\circ$  (av), respectively. The bond length of  $\text{Zn-O}$  of **2** is larger than the  $1.97 \text{ \AA}$  obtained from the sum of the tetrahedral covalent radii and shorter than those ( $2.089$ – $2.105 \text{ \AA}$ ) of organozinc oxides such as  $(\text{Me}_2\text{ZnO})_4$  [4] and  $\text{Me}_{14}\text{Zn}_7\text{O}_8$  [5]. The bond length of **2** is indeed in better agreement with  $\text{Zn-O}$  distances ( $2.04 \text{ \AA}$ ) complexes where Zn is octahedrally coordinated [6]. The bond length of  $\text{Zn-Ge}$  is less than the sum ( $2.47 \text{ \AA}$ ) of the covalent radii [7]. This shortening may be explained by invoking hyperconjugation between Zn and Ge [4]. The bond length of  $\text{Zn-Zn}$  ( $3.042 \text{ \AA}$  (av)) is also shorter than those of organozinc oxides ( $3.068$ – $3.094 \text{ \AA}$ ) [4,5]. Four THF molecules are included in the crystal; however, no interaction between the zinc atom and THF was observed ( $\text{Zn-O}_{\text{THF}} > 4.0 \text{ \AA}$ ). Molecular structures of organozinc oxides  $(\text{Me}_2\text{ZnO})_4$  and  $\text{Me}_{14}\text{Zn}_7\text{O}_8$  have cubic and cuban geometries, respectively.

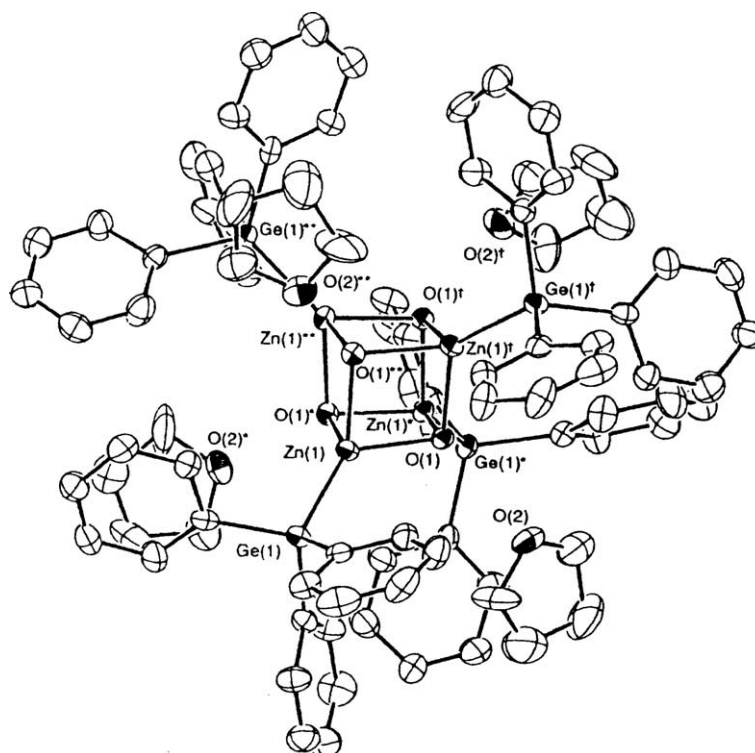


Fig. 2. Molecular structure of **2**. Hydrogen atoms are omitted for clarity.

Table 2

The selected bond length (Å) and bond angles (°) of  $(\text{Ph}_3\text{GeOZn})_4$  (**2**)

Zn(1)–Ge(1)	2.3759(7)	Zn(1)–O(1)	2.049(3)
Zn(1)–O*(1)	2.054(3)	Zn(1)–O**(1)	2.059(3)
Ge(1)–Zn(1)–O(1)	129.10(9)	Ge(1)–Zn(1)–O*(1)	128.03(9)
Ge(1)–Zn(1)–O**(1)	131.06(9)	O(1)–Zn(1)–O*(1)	84.47(13)
O(1)–Zn(1)–O**(1)	83.85(13)	O*(1)–Zn(1)–O**(1)	83.70(12)
Zn(1)–O(1)–Zn*(1)	95.12(13)	Zn(1)–O(1)–Zn**(1)	96.06(12)
Zn*(1)–O(1)–Zn***(1)	95.88(13)		

Addition of oxygen at room temperature for 10 h led to complete decomposition of **2** with the formation of  $(\text{Ph}_3\text{Ge})_2\text{O}$  quantitatively.

### 3. Experimental

#### 3.1. General methods

The NMR spectra were obtained on a Varian Unity Inova 400 MHz spectrometer. The GC-MS spectra were measured on a JEOL JMS-DX 303 mass spectrometer. Gas chromatography was performed on a Shimadzu GC8A with a 1 m 20% SE30 column. X-ray crystallographic data and diffraction intensities were collected on a MacScience DIP2030 diffractometer utilizing graphite-monochromated Mo  $K\alpha$  ( $\lambda = 0.71073$  Å) radiation. The structures were solved by direct methods using the program system SIR-92. Refinement was performed

by a SILICON graphics O<sub>2</sub> with MAXUS. THF, diethyl ether and other solvents were purified and dried as reported in the literature.

#### 3.2. Materials

$\text{Ph}_3\text{GeH}$  [8],  $\text{Et}_2\text{Zn}$  [3c], and  $(\text{Ph}_3\text{Ge})_2\text{O}$  [9] were prepared as reported in the literature.

#### 3.3. Structural studies

Bis(germyl)zinc (**1**) and germylzinc oxide (**2**) could be obtained in the form of crystals suitable for X-ray diffraction studies. A single crystal was sealed in a capillary glass tube for the collection. Diffraction data were collected at 200 K on a MacScience DIP2030 image plate diffraction employing graphite-monochromated Mo  $K\alpha$  radiation ( $\lambda = 0.71073$  Å). Crystallographic data for **1** and **2** are listed in Table 3.

Table 3  
Crystallographic data for **1** and **2**

	<b>1</b>	<b>2</b>
Formula	C <sub>44</sub> H <sub>46</sub> Ge <sub>2</sub> ZnO <sub>2</sub>	C <sub>22</sub> H <sub>23</sub> Ge <sub>2</sub> ZnO <sub>2</sub>
Molecular weight	817.41	457.36
Crystal size (mm <sup>3</sup> )	0.35 × 0.30 × 0.25	0.30 × 0.30 × 0.35
Crystal system	Monoclinic	Tetragonal
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> -42 <sub>1</sub> <i>c</i>
Unit cell dimensions		
<i>a</i> (Å)	10.0687(6)	15.7770(5)
<i>b</i> (Å)	19.408(1)	
<i>c</i> (Å)	19.871(1)	16.7830(2)
$\beta$ (°)	101.408(3)	
<i>V</i> (Å <sup>3</sup> )	3806.5(4)	4177.5(1)
<i>Z</i>	4	8
Radiation Mo K $\alpha$ ( $\lambda$ /Å)	0.71070	0.71070
Temperature (K)	200	200
<i>D</i> <sub>calc</sub> (g cm <sup>-3</sup> )	1.426	1.454
Unique reflections	4964	2940
Goodness-of-fit	0.926	1.078
<i>R</i> ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	0.0300	0.0435
<i>wR</i> <sub>2</sub>	0.0400	0.1271 (all data)

#### 3.4. Preparation of bis(triphenylgermyl)zinc (Ph<sub>3</sub>Ge)<sub>2</sub>Zn (**1**)

Et<sub>2</sub>Zn (0.5 ml, 0.5 mmol) in hexane reacted with two molar amounts of Ph<sub>3</sub>GeH (0.30 g, 1.0 mmol) containing THF (1.5 ml) in a Schlenk tube at room temperature for 5 days under argon atmosphere. The concentration of the reaction mixture by removal of THF was followed by addition of pentane (5 ml). The organic layer was filtered. After removal of the solvent under vacuum, pentane (3 ml) was added to the residue. The solution was kept at -20 °C. The colorless crystals were filtered off, and shown to be (Ph<sub>3</sub>Ge)<sub>2</sub>Zn(2THF) (**1**) (0.11 g, 0.13 mmol) in 26% yield (based on the concentration of Et<sub>2</sub>Zn). <sup>1</sup>H NMR ( $\delta$ , C<sub>6</sub>D<sub>6</sub>) 1.08–1.4 (m, 8H, THF), 3.42–3.48 (m, 8H, THF), 7.12–7.21 (m, 18H), 7.36–7.45 (m, 12H); <sup>13</sup>C NMR ( $\delta$ , C<sub>6</sub>D<sub>6</sub>) 25.6 (THF), 70.1 (THF), 127.2, 127.7, 136.0, 145.1.

#### 3.5. Preparation of germylzinc oxide (Ph<sub>3</sub>GeZnO)<sub>4</sub> (**2**)

Et<sub>2</sub>Zn (0.5 ml, 0.5 mmol) in hexane reacted with two molar amounts of Ph<sub>3</sub>GeH (0.30 g, 1.0 mmol) containing diethyl ether (2.5 ml) in a Schlenk tube at room temperature for 2 days under argon atmosphere. The concentration of the reaction mixture by removal of diethyl ether was followed by addition of pentane (5 ml). The organic layer was filtered. After removal of the solvent under vacuum, pentane (3 ml) was added to the residue. The solution was kept at -20 °C. The col-

orless crystals were filtered off, and shown to be (Ph<sub>3</sub>GeZnO)<sub>4</sub> (4THF) (0.17 g, 0.09 mmol) in 18% yield (based on the concentration of Et<sub>2</sub>Zn). <sup>1</sup>H NMR ( $\delta$ , C<sub>6</sub>D<sub>6</sub>) 1.34–1.41 (m, 16H, THF), 3.48–3.56 (m, 16H, THF), 7.31–7.39 (m, 24H), 7.62–7.68 (m, 24H); <sup>13</sup>C NMR ( $\delta$ , C<sub>6</sub>D<sub>6</sub>) 26.0 (THF), 67.9 (THF), 128.2, 128.7, 136.1, 143.2.

#### 3.6. Reaction of bis(germyl)zinc oxide (**1**) with oxygen

A C<sub>6</sub>D<sub>6</sub> (0.6 ml) solution of bis(germyl)zinc (**1**) (0.08 mmol) was bubbled with a small amount of oxygen in an NMR tube. After 10 h, the solvent was removed under vacuum. Crude colorless crystals of (Ph<sub>3</sub>Ge)<sub>2</sub>O were obtained quantitatively.

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