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Preparation and Structural Characterization of Bis[tris(trimethylsilyl)germyl]zinc, $[(\mathrm{Me_3Si})_3\mathrm{Ge}]_2\mathrm{Zn}$

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Bis[tris(trimethylsilyl)germyl]zinc, $[(\mathrm{Me_3Si})_3\mathrm{Ge}]_2\mathrm{Zn}$, was prepared by the reaction of [tris(trimethylsilyl)germyl]lithium, $(\mathrm{Me_3Si})_3\mathrm{GeLi(thf)}$, with zinc chloride, $\mathrm{ZnCl_2}$, and by the reaction of tris(trimethylsilyl)germane, $(\mathrm{Me_3Si})_3\mathrm{GeH}$, with diethylzinc, $\mathrm{Et_2Zn}$. The molecular structure of $[(\mathrm{Me_3Si})_3\mathrm{Ge}]_2\mathrm{Zn}$ was determined by spectroscopic and X-ray diffraction methods. In $[(\mathrm{Me_3Si})_3\mathrm{Ge}]_2\mathrm{Zn}$, the two tris(trimethylsilyl)germyl ligands, $(\mathrm{Me_3Si})_3\mathrm{Ge}$, are bonded in a linear fashion to the zinc atom and are staggered with respect to each other. The reactions of bis(germyl)zinc with substrates were also examined.

The chemistry of organozinc compounds has been a major research theme in organic synthesis and organometallic chemistry.[1] Despite the large number of reports on organozinc reagents, far less attention has been devoted to silyl- or germyl-substituted zinc compounds. Up to now, four bis(silyl)zinc derivatives $\{(t\text{-}\mathrm{Bu_3Si})_2\mathrm{Zn}$,[2a] $[(\mathrm{Me_3Si})_3\mathrm{Si}]_2\mathrm{Zn}$,[2b] $(\mathrm{Me_3Si})_2\mathrm{Zn}$,[2c] and $(\mathrm{Ph_3Si})_2\mathrm{Zn}$[2d]$\}$ have been prepared, and only two X-ray crystal structures of $(t\text{-}\mathrm{Bu_3Si})_2\mathrm{Zn}$ and $[(\mathrm{Me_3Si})_3\mathrm{Si}]_2\mathrm{Zn}$ have been determined. Although a few examples of bis(germyl)zinc, $(\mathrm{Ph_3Ge})_2\mathrm{Zn}$ and $(\mathrm{Et_3Ge})_2\mathrm{Zn}$, are known,[3a–c] no solid state structure, or few reactivities, of bis(germyl)zinc derivatives have been reported.

In this report we describe the first successful isolation of bis[tris(trimethylsilyl)germyl]zinc, $[(\mathrm{Me_3Si})_3\mathrm{Ge}]_2\mathrm{Zn}$ (**1**), prepared by several methods, and its structural characterization by X-ray diffraction analysis. Some reactions of the bis(germyl)zinc **1** with substrates are also examined.

Results and Discussion

Preparation of Bis[tris(trimethylsilyl)germyl]zinc, $[(\mathrm{Me_3Si})_3\mathrm{Ge}]_2\mathrm{Zn}$. Bis[tris(trimethylsilyl)germyl]zinc, $[(\mathrm{Me_3Si})_3\mathrm{Ge}]_2\mathrm{Zn}$, **1** was prepared by several methods. The treatment of zinc chloride ($\mathrm{ZnCl_2}$) with two molar amounts of [tris(trimethylsilyl)germyl]lithium solvated by tetrahydrofuran (THF), $(\mathrm{Me_3Si})_3\mathrm{GeLi(thf)}_3$,[4] prepared by the reaction of tetrakis(trimethylsilyl)germane, $(\mathrm{Me_3Si})_4\mathrm{Ge}$, with THF solution of MeLi, in diethyl ether at room temperature for 1 day afforded colorless crystals with a composition of $[(\mathrm{Me_3Si})_3\mathrm{Ge}]_2\mathrm{Zn}$ (**1**) in 83% isolated yield. ^{1}H, ^{13}C, and ^{29}Si NMR examinations of a $\mathrm{C_6D_6}$ solution of the colorless crystals **1** revealed a single assigned to the trimethylsilyl group ($\mathrm{Me_3Si}$). No coordinating THF in **1** was observed. The symmetrical bis(germyl)zinc **1** could be recrystallized from pentane at −20 °C as colorless needles that are very flammable in air. The bis(germyl)zinc **1** are thermally stable for prolonged periods in the absence of air at room temperature.

$$2(\mathrm{Me_3Si})_3\mathrm{GeLi(thf)}_3 + \mathrm{ZnCl_2} \xrightarrow[\substack{\text{r.t., 1 day}\\ \text{diethyl ether}}]{} \underset{\mathbf{1}}{[(\mathrm{Me_3Si})_3\mathrm{Ge}]_2\mathrm{Zn}} \tag{1}$$

The treatment of [tris(trimethylsilyl)germyl]zinc chloride solvated by THF, $(\mathrm{Me_3Si})_3\mathrm{GeZnCl(thf)}$,[5] which was prepared by the reaction of $\mathrm{ZnCl_2}$ with one molar amount of $(\mathrm{Me_3Si})_3\mathrm{GeLi(thf)}$, with additional $(\mathrm{Me_3Si})_3\mathrm{GeLi(thf)}_3$ in diethyl ether at room temperature for 1 h, also gave bis(germyl)zinc **1** in 93% isolated yield. This result suggests that $(\mathrm{Me_3Si})_3\mathrm{GeZnCl(thf)}$ is an intermediate in the formation of the bis(germyl)zinc **1** by the reaction of $\mathrm{ZnCl_2}$ with two molar amounts of $(\mathrm{Me_3Si})_3\mathrm{GeLi(thf)}$:

$$(\mathrm{Me_3Si})_3\mathrm{GeZnCl(thf)} + (\mathrm{Me_3Si})_3\mathrm{GeLi(thf)}_3 \xrightarrow[\substack{\text{r.t., 1 day}\\ \text{diethyl ether}}]{} \mathbf{1} \tag{2}$$

Two molar amounts of tris(trimethylsilyl)germane, $(\mathrm{Me_3Si})_3\mathrm{GeH}$, reacted with diethylzinc, $\mathrm{Et_2Zn}$, in diethyl ether (or THF) at room temperature for 1 day to give bis(germyl)zinc **1** quntitatively:

$$2(\mathrm{Me_3Si})_3\mathrm{GeH} + \mathrm{Et_2Zn} \xrightarrow[\substack{\text{r.t., 1 day}\\ \text{diethyl ether}}]{} \mathbf{1} \tag{3}$$

This method is experimentally easier and gives higher yields of **1** than the $\mathrm{ZnCl_2}$–$(\mathrm{Me_3Si})_3\mathrm{GeLi(thf)}$ methods. Attempts to prepare ethyltris(trimethylsilyl)germylzinc, $(\mathrm{Me_3Si})_3\mathrm{GeZnEt}$, as an intermediate in the formation of the bis(germyl)zinc **1** have failed, probably due to its thermodynamically instability.

The formation and the mechanism of bis(triphenylgermyl)zinc, $(\mathrm{Ph_3Ge})_2\mathrm{Zn}$, by a treatment of $\mathrm{Et_2Zn}$ with triphenylgermane, $\mathrm{Ph_3GeH}$, in diglyme at 150 °C for 1.5 h were reported

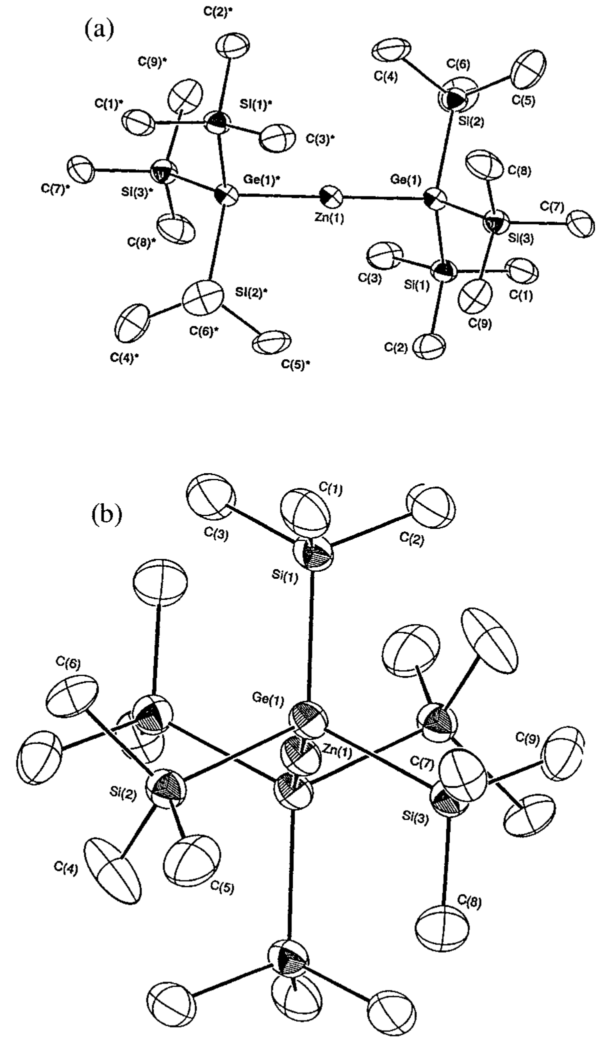

Fig. 1. An ORTEP representation of bis[(tris(trimethylsilyl)germyl]zinc **1** (hydrogen atoms are omitted for clarity).

by Bychkov and co-workers.[3b]

Several studies on the preparation of a binary group 12-element germyl derivatives by reactions of organogermanium hydrides with diorganometals have been reported.[6–8] The easiness of the reaction is in the order Zn < Cd < Hg.

Crystal Structure. The molecular structure of **1** was unequivocally confirmed by an X-ray diffraction analysis. The molecular structure of **1** is shown in Fig. 1. The bis(germyl)zinc **1** has a crystallographic inversion center on the zinc atom. The two tris(trimethylsilyl)germyl, $(Me_3Si)_3Ge$, ligands are bonded in a linear fashion to the zinc atom, and are staggered with respect to each other, as shown in Fig. 1. The structual features are similar to that found in $[(Me_3Si)_3Si]_2Zn$.[2b] The bond angle of Ge1–Zn–Ge1* is 180°. No solvent coordinating to the zinc metal of **1** was observed due to the steric hindrance of the $(Me_3Si)Ge$ ligand. The Ge–Zn bond length of 2.3818(3) Å is somewhat longer than that found in $(Me_3Si)_3GeZnCl(thf)$.[5] The average Si–Ge–Zn angle of 106.65(1) Å is smaller than that found in Si–Ge–Si angles (av 112.13(2)°). The mean Ge–Si bond length of 2.3804 Å is quite normal.

The selected bond lengths and bond angles of **1** are summarized in Table 1. Crystallographic data of **1** are summarized in the experimental section.

Table 1. The Selected Bond Lengths (Å) and Bond Angles (°) of $[(Me_3Si)_3Ge]_2Zn$ (**1**)

Ge1–Si1	2.3788(6)	Ge1–Si3	2.3761(7)
Ge1–Zn1	2.3818(2)	Ge1–Si2	2.3863(6)
Zn1–Ge1*	2.3818(3)	Si1–C3	1.875(3)
Si1–C2	1.876(3)	Si1–C1	1.879(3)
Si2–C6	1.867(3)	Si2–C4	1.869(3)
Si2–C5	1.880(3)	Si3–C8	1.869(3)
Si3–C9	1.879(3)	Si3–C7	1.879(3)
Si3–Ge1–Si1	112.55(2)	Si3–Ge1–Zn1	107.599(18)
Si1–Ge1–Zn1	107.842(17)	Si3–Ge1–Si2	110.29(2)
Si1–Ge1–Si2	113.54(2)	Zn1–Ge1–Si2	104.495(17)
Ge1–Zn1–Ge1*	179.999(2)	C3–Si1–C2	108.07(13)
C3–Si1–C1	109.18(15)	C2–Si1–C1	108.54(12)
C3–Si1–Ge1	109.09(9)	C2–Si1–Ge1	109.66(9)
C1–Si1–Ge1	112.22(9)	C6–Si2–C4	108.91(18)
C6–Si2–C5	108.11(16)	C4–Si2–C5	107.78(19)
C6–Si2–Ge1	111.23(9)	C4–Si2–Ge1	108.47(10)
C5–Si2–Ge1	112.25(9)	C8–Si3–C9	108.01(15)
C8–Si3–C7	108.52(13)	C9–Si3–C7	108.11(13)
C8–Si3–Ge1	109.93(10)	C9–Si3–Ge1	110.88(9)
C7–Si3–Ge1	111.30(9)		

The crystal structure of bis(germyl)zinc **1** is different from that of $(Me_3Si)_3GeZnCl(thf)$. The germylzinc chloride has dimeric structures consisiting of two μ-chlorine atoms.[5]

Reactivity. The reactions of bis(germyl)zinc **1** with some electrophiles in diethyl ether under an argon atmosphere in a Schlenk tube were examined at room temperature. All of the products were identified by GC, GC-MS, and NMR spectra compared with those of authentic samples. The yields of the products were determined by GC with internal-standard methods.

The bis(germyl)zinc **1** could be preserved under an argon atmosphere at room temperature. The hydrolysis of bis(germyl)zinc **1** in diethyl ether with deoxygenated water proceeded extremely slowly to give tris(trimethylsilyl)germane, $(Me_3Si)_3GeH$, in only 38% yield after 7 days of stirring under an argon atmosphere at room temperature. Unreacted **1** still remained. The addition of hydrochloric acid of **1** under an argon atmosphere for 2 h completely promoted the hydrolysis reaction to give $(Me_3Si)_3GeH$. This reactivity contrasts with that of the analogous silyl derivatives, $[(Me_3Si)_3Si]_2Zn$,[2b] which appear to be more reactive. The bis(germyl)zinc **1** did not react with an excess amount of Me_3SiCl at all for 2 days. Unreacted **1** was completely recovered. On the other hand, the bis(germyl)zinc **1** reacted easily with I_2 to afford iodotris(trimethylsilyl)germane, $(Me_3Si)_3GeI$ in 91% yield after 3 h of stirring under an argon atmosphere at room temperature. In 4 h of stirring under an argon atmosphere, the reaction of bis(germyl)zinc **1** with MeI proceeded to form $(Me_3Si)_3GeI$ in 93% yield. The reaction took place even in a dark condition. The presence of $(Me_3Si)_3GeI$ suggests that Me_2Zn is simultaneously formed as a reactive species. Further stirring for 3 days led to the final formation of methyltris(trimethylsilyl)germane, $(Me_3Si)_3GeMe$ (50% yield), with the precipitation of ZnI_2 salt:

Table 2. Reactions of Bis[tris(trimethylsilyl)germyl]zinc (**1**) with Substrates in Diethyl Ether

Substrate	Reaction conditions	Products (Yield/%)
H_2O	r.t., 7 d	$(Me_3Si)_3GeH$ (38)
HCl	r.t., 2 h	$(Me_3Si)_3GeH$ (100)
I_2	r.t., 3 h	$(Me_3Si)_3GeI$ (91)
Me_3SiCl	r.t., 2 d	No reaction
MeI	r.t., 1 h	$(Me_3Si)_3GeI$ (93)
	r.t., 3 d	$(Me_3Si)_3GeMe$ (50)

$$\mathbf{1} + \mathrm{MeI} \xrightarrow[\text{r.t., 4 h}]{} (\mathrm{Me_3Si})_3\mathrm{GeI} + \mathrm{Me_2Zn} \xrightarrow[\text{r.t., 3 d}]{} (\mathrm{Me_3Si})_3\mathrm{GeMe} + \mathrm{ZnI_2} \quad (4)$$

The formation of Me_2Zn was confirmed by the ^1H NMR spectra ($\delta = -1.44$ in THF-d_8) and a chemical trapping experiment with chlorotriphenylgermane, Ph_3GeCl. The Me_2Zn was quenched with Ph_3GeCl to yield methyltriphenylgermane, Ph_3GeMe, in 59% yield. The formation of $(Me_3Si)_3GeI$ and Me_2Zn may be explained by electron-transfer processes as one possible reaction mechanism. Since bis(germyl)zinc **1** with low ionization oxidative potentials is an excellent electron donor, electron-transfer from **1** to MeI with high reductive potentials generates geminate radical anions composed of the radical cation of **1** and the radical anion of MeI. The radical cation of **1** possibly reacts with the radical anion of MeI to afford $(Me_3Si)_3GeI$ and Me_2Zn.[9] The reaction mechanism for the formation of $(Me_3Si)_3GeMe$ and ZnI_2 is unclear.

Taking these results of reaction of **1** with H_2O and Me_3SiCl into consideration, bis(germyl)zinc **1** is not only a very weak base, but also a weak nucleophile. These results are summarized in Table 2.

Experimental

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 GC 8A with a 1 m 20% SE30 column. X-ray crystallographic data and diffraction intensities were collected on a MacScience DIP2030 diffraction utilizing graphite-monochromated Mo Kα ($\lambda = 0.71073$ Å) radiation. The structures were solved by direct methods using the program system SIR-92. A refinement was performed by a SILICON Graphics O_2 with maXus. THF, diethyl ether, and other solvents were purified and dried as reported in the literature.

Materials. $(Me_3Si)_3GeLi(thf)_3$,[4] $(Me_3Si)_3GeH$,[4] $(Me_3Si)_3GeI$,[4] $(Me_3Si)_3GeMe$,[4] Ph_3GeCl,[10] and Ph_3GeMe[11] were prepared as reported in the literature. Me_2Zn, Et_2Zn, $ZnCl_2$, Me_3SiCl, and MeI were commercially available.

Structural Studies. Bis(germyl)zinc **1** 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 collection. Diffraction data were collected at 293 K on a MacScience DIP2030 image plate diffraction employing graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). MF = $C_{18}H_{54}Ge_2Si_6Zn$, MW = 649.70, cryst size = 0.30 × 0.30 × 0.30 mm, triclinic, $P1$, $a = 9.3840(7)$, $b = 9.4960(6)$, $c = 12.2610(6)$ Å, $\beta = 70.174(5)$, $\gamma = 62.489(4)^\circ$, $V = 882.80(10)$ Å^3, $Z = 1$, $D_{\mathrm{calcd}} = 1.222$ g cm^{-3}, Temp/K = 293. The final R factor and the goodness-of-fit indicator were 0.0399 ($R_w = 0.1255$ for all data, 3506 reflections) and 1.141, respectively, for 3357 reflcetion with $I > 2\sigma(I)$.

Preparation of Bis[tris(trimethylsilyl)germyl]zinc (1) by Treatment of [Tris(trimethylsilyl)germyl]lithium with Zinc Chloride. Zinc chloride, $ZnCl_2$, (0.13 g, 0.95 mmol) reacted with two molar amounts of [tris(trimethylsilyl)germyl]lithium solvated by THF, $(Me_3Si)_3GeLi(thf)_3$ (0.88 g, 1.70 mmol) containing diethyl ether (10 mL) in a Schlenk tube at room temperature for 1 day under an argon atmosphere. The concentration of the reaction mixture by the removal of diethyl ether, followed by recrystallization from pentane at −20 °C, gave colorless crystals flammable in air with a composition of bis[tris(trimethylsilyl)germyl]zinc, $[(Me_3Si)_3Ge]_2Zn$ (**1**) (0.52 g, 0.80 mmol) in 83% yield. ^1H NMR (C_6D_6) δ 0.39 (s, 54 H); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 5.2; $^{29}Si\{^1H\}$ NMR (C_6D_6) δ −2.3.

Preparation of Bis[tris(trimethylsilyl)germyl]zinc (1) by the Treatment of [Tris(trimethylsilyl)germyl]zinc Chloride with [Tris(trimethylsilyl)germyl]lithium. To a THF solution (10 mL) of [tris(trimethylsilyl)germyl]zinc chloride, $(Me_3Si)_3GeZnCl$ (0.10 g, 0.21 mmol), in a Schlenk tube $(Me_3Si)_3GeLi(thf)_3$ (0.11 g, 0.21 mmol) in diethyl ether (10 mL) was added under an argon atmosphere. The reaction mixture was stirred at room temperature for 1 h. After the removal of diethyl ether, $[(Me_3Si)_3Ge]_2Zn$ (**1**) (0.13 g, 0.20 mmol) was formed quantitatively. $[(Me_3Si)_3Ge]_2Zn$: ^1H NMR (C_6D_6) δ 0.39 (s, 54 H); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 5.2; $^{29}Si\{^1H\}$ NMR δ −2.3.

Preparation of Bis[tris(trimethylsilyl)germyl]zinc (1) by Treatment of Tris(trimethylsilyl)germane with Diethylzinc. To a diethyl ether (3 mL) solution of $(Me_3Si)_3GeH$ (0.30 g, 1.0 mmol) in a Schlenk tube, Et_2Zn in hexane (0.5 mL, 0.5 mmol) was added under an argon atmosphere. The reaction mixture was stirred at room temperature for 1 day. After removal of diethyl ether, $[(Me_3Si)_3Ge]_2Zn$ (**1**) (0.32 g, 0.5 mmol) was formed quantitatively.

Hydrolysis of Bis[tris(trimethylsilyl)germyl]zinc (1) with Water. A diethyl ether solution (10 mL) of **1** (1.00 mmol), an excess amount of deoxygenated H_2O, and nonadecane as internal standard in a Schlenk tube was stirred under an argon atmosphere at room temperature for 7 days. Tris(trimethylsilyl)germane, $(Me_3Si)_3GeH$ (0.38 mmol) was formed in 38% GC yield. $(Me_3Si)_3GeH$: ^1H NMR (C_6D_6) δ 0.28 (s, 27 H), 2.16 (s, 1 H); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 3.4. GC-MS m/z 294 (M^+, 20), 278 (5), 220 (40), 146 (35), 131 (40), 73 (100).

Hydrolysis of Bis[tris(trimethylsilyl)germyl]zinc (1) with Hydrochloric Acid. A diethyl ether solution (10 mL) of **1** (1.00 mmol), an excess amount of conc. HCl, and nonadecane as internal standard in a Schlenk tube was stirred under argon atmosphere at room temperature for 2 h. Tris(trimethylsilyl)germane, $(Me_3Si)_3GeH$ (2.00 mmol) was formed quantitatively.

Reaction of Bis[tris(trimethylsilyl)germyl]zinc (1) with Iodine. A diethyl ether solution of **1** (1.00 mmol), an excess amount of I_2, and nonadecane as an internal standard in a Schlenk tube was stirred under an argon atmosphere at room temperature for 3 h. Iodotris(trimethylsilyl)germane, $(Me_3Si)_3GeI$ (1.82 mmol) was formed in 91% GC yield. $(Me_3Si)_3GeI$: ^1H NMR (C_6D_6) δ 0.29 (s, 27 H); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 0.81. GC-MS m/z 420 (M^+, 5), 220 (10), 146 (10), 73 (100).

Reaction of Dimethylzinc with Chlorotriphenylgermane. To a diethyl ether solution (10 mL) of **1** (0.26 g, 0.40 mmol) in a Schlenk tube, MeI (0.62 g, 4.3 mmol) was added under an argon atmosphere. The reaction mixture was stirred at room temperature for 4 h. Then, chlorotriphenylgermane, Ph_3GeCl (0.27 g, 0.80 mmol) was added to this solution. The reaction mixture was stirred at room temperature for 1 day. Methyltriphenylgermane, Ph_3GeMe, was formed in 59% yield.

X-ray Crystallographic Data. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number 205945.

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