Preparation and Characterization of Tris(trimethylsilyl)germylzinc Chloride and Bis[tris(trimethylsilyl)germyl]zinc

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(Received October 22, 2001; CL-011029)

The molecular structure of $(Me_3Si)_3GeZnCl$ (**1**) has been determined by single-crystal X-ray diffraction. The germylzinc chloride **1** has a dimeric structure consisting of two μ-Cl atoms. The compound **1** reacted with $(Me_3Si)_3GeLi$ in diethyl ether to give $[(Me_3Si)_3Ge]_2Zn$ (**2**), quantitatively. The structure of bis(germyl)zinc **2** has been also elucidated by X-ray diffraction.

Organozinc compounds are useful reagents in organic synthesis and organometallic chemistry.[1] The well-known Reformatsky zinc alkylation and Simmons-Smith reaction proceed *via* organozincs assumed as key intermediates. 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 $\{(t\text{-}Bu_3Si)_2Zn$,[2a] $[(Me_3Si)_3Si]_2Zn$,[2b] $(Me_3Si)_2Zn$,[2c] and $(Ph_3Si)_2Zn$[2d]} and two silylzinc halides $\{(t\text{-}Bu_3Si)ZnCl$[2a] and $(t\text{-}Bu_3Si)ZnBr$[2a]} have been prepared and only three X-ray crystal structures of $(t\text{-}Bu_3Si)_2Zn$, $[(Me_3Si)_3Si]_2Zn$, and $(t\text{-}Bu_3Si)ZnBr$ have been determined. Although a few example of bis(germyl)zinc, $(Ph_3Ge)_2Zn$ and $(Et_3Ge)_2Zn$, are known,[3a–c] no solid state structure or few reactivities of bis(germyl)zinc derivatives have been reported. Furthermore, the Reformatsky-type germylzinc halides R_3GeZnX (X = halogen) have never been isolated and characterized. We report herein the first successful isolation and full characterization of tris(trimethylsilyl)germylzinc chloride (**1**) and bis[tris(trimethylsilyl)germyl]zinc (**2**), together with some reactions of **1** and **2**.

The treatment of zinc chloride with one mol amount of $(Me_3Si)_3GeLi(thf)_3$[4] in diethyl ether produces the Reformatsky-type metallozinc compound $(Me_3Si)_3GeZnCl$ (**1**) as colorless crystals in 86% isolated yield (eq 1).[5] As expected, the ^1H, ^{13}C, and ^{29}Si NMR of the colorless crystals of **1** gave a single signal assigned to the trimethylsilyl group, and one THF molecule was included for a molecule **1** based on the ^1H and ^{13}C NMR.[6]

$$ZnCl_2 + (Me_3Si)_3GeLi\,(thf)_3 \xrightarrow[rt]{Et_2O} \underset{\mathbf{1}\,(thf)}{(Me_3Si)_3GeZnCl\,(thf)} + LiCl \qquad (1)$$

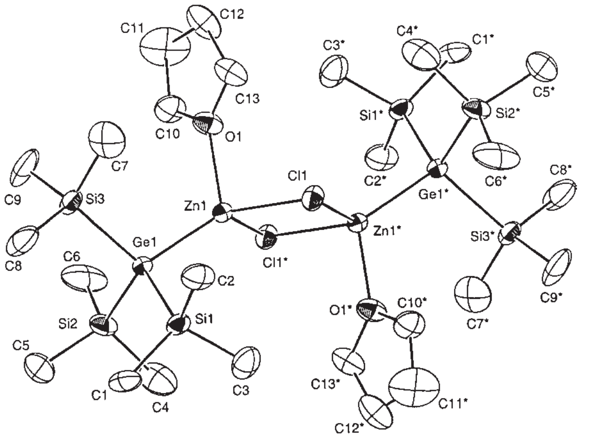
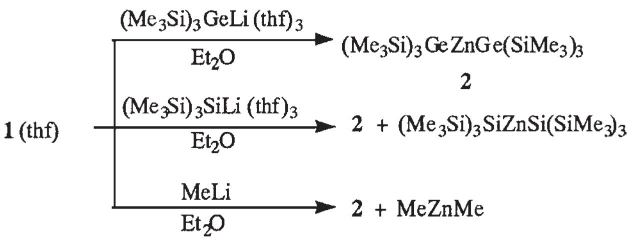


Figure 1. An ORTEP representation of the dimeric structure of **1** (hydrogen atoms are omitted for clarity). Selected bond length (Å) and angles (°): Ge1-Zn1 2.3778 (6), Ge1-Si1 2.369 (1), Ge1-Si2 2.365 (1), Ge1-Si3 2.3749 (12), Zn1-Cl1 2.3560 (11), Zn1-Cl1* 2.3999 (10), Zn1-O1 2.096 (3); Ge1-Zn1-Cl1 126.07 (3), Ge1-Zn1-Cl1* 122.40 (3), Cl1-Zn1-Cll* 92.75 (4), Ge1-Zn1-O1 117.51 (10), O1-Zn1-Cl1 96.78 (10), O1-Zn1-Cl1* 93.85 (10), Si1-Ge1-Zn1 107.36 (4), Si2-Ge1-Zn1 108.40 (4), Si3-Ge1-Zn1 111.33 (4).

The Reformatsky-type metallozinc compound **1** could be recrystallized from THF at −20 °C as air-sensitive colorless needles. The molecular structure of **1** was unequivocally confirmed by X-ray diffraction.[7] The compound **1** is dimeric in the solid state and its molecular structure has a crystallographic inversion center (Figure 1). No interaction between the dimer and another dimer was observed. The two zinc and two chlorine atoms constitute a planar four-membered ring with Zn-Cl distances of 2.3560 (11) and 2.3999 (10) Å, a Cl-Zn-Cl bond angle of 92.75 (4) °, and a Zn-Zn distance of 3.2827 (6) Å. The zinc atom is solvated by coordination to an oxygen atom of a THF molecule with a Zn-O distance of 2.096 (3) Å and has a distorted tetrahedral configuration. The Ge-Zn bond length of 2.3778 (6) Å is obviously shorter than that expected on the basis of the sum of their covalent radii (2.47 Å), suggesting that the Ge-Zn bond is comprised of a covalent one with a small ionic character due to the attachment of the electronegative chlorine atom to the zinc metal. The Si-Ge-Zn angle of 109.03 (4) ° (av.) and the Ge-Si bond length of 2.370 (1) Å (av.) are quite normal.

The hydrolysis of **1** proceeded extremely slow to give $(Me_3Si)_3GeH$ in only 43% yield after 7 days of stirring. The addition of hydrochloric acid to **1** promotes the hydrolysis reaction up to 95% (2 h) yield. The compound **1** reacted slowly with Me_3SiCl in diethyl ether for 4 days to yield $(Me_3Si)_4Ge$ (17%). The treatment of **1** with additional $(Me_3Si)_3GeLi(thf)_3$ in diethyl ether gave $[(Me_3Si)_3Ge]_2Zn$ (**2**)[8] in 93% isolated yield, suggesting that germylzinc chloride **1** is an intermediate to form the bis(germyl)zinc. The ^1H, ^{13}C, and ^{29}Si NMR of **2** gave a single signal assigned to the trimethylsilyl group.[9] One of particular interest is the fact that the redistribution reaction happened on addition of some other lithium reagents to germylzinc chloride **1** (Scheme 1). The germylzinc chloride **1** was allowed to react with one mol amount of $(Me_3Si)_3SiLi(thf)_3$ to give not asymmetrically bis(germyl)(silyl)zinc $(Me_3Si)_3GeZnSi(SiMe_3)_3$ but the symmetrical products of $[(Me_3Si)_3Ge]_2Zn$ and $[(Me_3Si)_3Si]_2Zn$, quantitatively, with the ratio of 1 : 1 determined by the ^1H NMR signal intensities. The addition of methyllithium to **1** led to the formation



Scheme 1.

of $[(Me_3Si)_3Ge]_2Zn$ and Me_2Zn (1 : 1),[10] $(Me_3Si)_3GeZnMe$ could not be detected at all.[11]

Symmetrical bis(germyl)zinc **2** could be recrystallized from pentane at −20 °C to give colorless single crystals. The structure of **2** was determined by X-ray diffraction (Figure 2).[12] Bis(germyl)zinc **2** has a crystallographic inversion center on the zinc atom. The two tris(trimethylsilyl)germyl ligands are bonded in a linear fashion to the zinc atom (Ge1-Zn1-Ge1* = 180.0(0) °) and are staggered with respect to each other. No coordinated solvent to the zinc metal was observed due to the steric hindrance between the two tris(trimethylsilyl)germyl ligands. The Ge-Zn bond length of 2.3817 (2) Å is somewhat longer than that found in germylzinc chloride **1**. The average Si-Ge-Zn angle is 106.65 (1) °, and the mean Ge-Si bond length is 2.3804 Å.

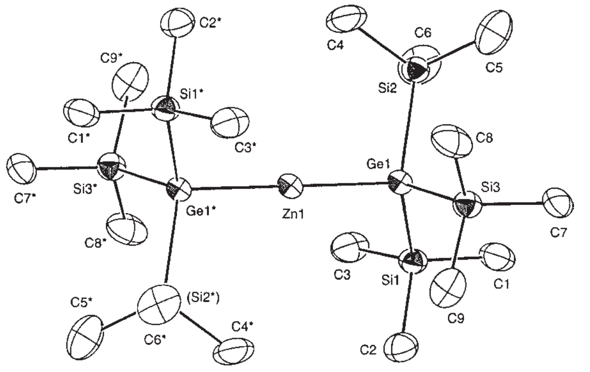


Figure 2. An ORTEP representation of the structure of **2** (hydrogen atoms are omitted for clarity). Selected bond length (Å) and angles (°): Ge1-Zn1 2.3817 (2), Ge1-Si1 2.3788 (6), Ge1-Si2 2.3863 (6), Ge1-Si3 2.3761 (6); Ge1-Zn1-Ge1* 180.0 (0), Si1-Ge1-Zn1 107.847 (18), Si2-Ge1-Zn1 104.496 (17), Si3-Ge1-Zn1 107.600 (18), Si1-Ge1-Si2

Bis(germyl)zinc **2** rapidly reacted with iodine in diethyl ether to yield $(Me_3Si)_3GeI$ (91%), whereas trimethylchlorosilane did not react with **2** at all. The reaction of **2** with iodomethane included two steps. In 4 h, the bis(germyl)zinc **2** reacted with idomethane to form $(Me_3Si)_3GeI$ (50%) and Me_2Zn as reactive intermediates.[13] Further stirring for two days led to the final formation of $(Me_3Si)_3GeMe$ (75%) with precipitation of ZnI_2 salt.

This work was supported by a Grant-in-Aid for Scientific research (No. 11740344) from Ministry of Education, Culture, Sports, Science, and Technology, Japan.

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5 The germylzinc chloride **1** could be prepared by the following procedure. The treatment of $ZnCl_2$ (0.30 g, 2.2 mmol) with one mol amount of $(Me_3Si)_3GeLi(thf)_3$ (1.14 g, 2.2 mmol) in diethyl ether produces **1** (0.88 g, 1.9 mmol) as flammable colorless crystals in 86% isolated yield.

6 Spectroscopic data for **1**: ^1H NMR (C_6D_6) δ 0.48 (s, 27 H), 1.34-1.36 (m, 4 H, THF), 3.60–3.62 (m, 4 H, THF); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 4.7, 25.3 (THF), 68.8 (THF); $^{29}Si\{^1H\}$ NMR (C_6D_6) δ 0.2.

7 Crystal structure analysis of **1**: A single crystal (0.25 × 0.20× 0.20 mm) was sealed in a capillary glass tube for the data collection. Diffraction data were collected at 200 K on a MacScience DIP2030 image plate diffractometer employing graphite-monochromated Mo ($K\alpha$) radiation ($\lambda = 0.71073$ Å); MF = $C_{13}H_{35}ClGeOSi_3Zn$, MW = 465.09, monoclinic, $P2_1/n$, $a = 9.6390$ (7), $b = 20.5050$ (9), $c = 12.7720$ (9) Å, $\beta = 105.452$ (3) °, $V = 2433.1$ (3) Å^3, $Z = 4$, $D_{calcd} = 1.270$ g·cm^{-3}. The final R factor and goodness of fit indicator were 0.0399 ($R_w = 0.1327$ for all data, 3531 reflections) and 1.104, respectively, for 3137 reflections with $I > 2\sigma(I)$.

8 The binary germylzinc **2** could be also prepared by the following procedure. The treatment of $ZnCl_2$ (0.13 g, 0.95 mmol) with two mol amounts of $(Me_3Si)_3GeLi(thf)_3$ (0.88 g, 1.7 mmol) in diethyl ether produces **2** (0.52 g, 0.80 mmol) as flammable colorless crystals in 94% isolated yield.

9 Spectroscopic data for **2**: ^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.

10 Spectroscopic data for Me_2Zn at 25 °C: ^1H NMR (THF-d_8) δ − 1.44 (s, 6 H); $^{13}C\{^1H\}$ NMR (THF-d_8) δ − 7.3. For ^1H NMR chemical shift of Me_2Zn at −20 °C, see: M. Uchiyama, M. Kameda, O. Mishima, N. Yokoyama, M. Koike, Y. Kondo, and T. Sakamoto, *J. Am. Chem. Soc.*, **120**, 4934 (1998).

11 The formation of the unsymmetrical (alkyl)(germyl)zinc compound was reported in Ref. 3b. $Ph_3GeZnEt$ was generated by the reaction of Ph_3GeH with Et_2Zn in bis(2-methoxylethyl)ether.

12 Crystal structure analysis of **2**: A single crystal (0.30× 0.30 × 0.30 mm) was sealed in a capillary glass tube for the data collection. Diffraction data were collected at 120 K on a MacScience DIP2030 image plate diffractometer employing graphite-monochromated Mo ($K\alpha$) radiation ($\lambda = 0.71073$ Å); MF = $C_{18}H_{54}Ge_2Si_6Zn$, MW = 649.70, triclinic, $P1$, $a = 9.3840$ (7), $b = 9.4960$ (6), $c = 12.2610$ (6) Å, $\alpha = 68.174$ (4), $\beta = 70.732$ (5), $\gamma = 62.489$ (4) °, $V = 882.8$ (1) Å^3, $Z = 1$, $D_{calcd} = 1.222$ g·cm^{-3}. The final R factor and goodness of fit indicator were 0.0399 ($R_w = 0.1255$ for all data, 3506 reflections) and 1.141, respectively, for 3357 reflections with $I > 2\sigma(I)$.

13 The formation of Me_2Zn was confirmed by both NMR spectra and cross reaction. The cross reaction is described. After the treatment of **2** with MeI in diethyl ether for 4 h stirring, Ph_3GeCl was added to the reaction mixture to form Ph_3GeMe together with $(Me_3Si)_3GeI$.