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

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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  $\mu$ -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.<sup>1</sup> 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- $Bu_3Si)_2Zn^{2a}$  $[(Me_3Si)_3Si]_2Zn,^{2b}$ (Me<sub>3</sub>Si)<sub>2</sub>Zn,<sup>2c</sup> and  $(Ph_3Si)_2Zn^{2d}$  and two silvlzinc halides {(t-Bu<sub>3</sub>Si)ZnCl<sup>2a</sup> and  $(t\mathchar`Bu_3Si)ZnBr^{2a}\}$  have been prepared and only three X-ray crystal structures of (t-Bu<sub>3</sub>Si)<sub>2</sub>Zn, [(Me<sub>3</sub>Si)<sub>3</sub>Si]<sub>2</sub>Zn, and (t-Bu<sub>3</sub>Si)ZnBr have been determined. Although a few example of bis(germyl)zinc, (Ph<sub>3</sub>Ge)<sub>2</sub>Zn and (Et<sub>3</sub>Ge)<sub>2</sub>Zn, are known,<sup>3a-c</sup> no solid state structure or few reactivities of bis(germyl)zinc derivatives have been reported. Furthermore, the Reformatsky-type germylzinc halides  $R_3$ GeZnX (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 Reformatskytype metallozinc compound  $(Me_3Si)_3GeZnCl$  (1) as colorless crystals in 86% isolated yield (eq 1).<sup>5</sup> As expected, the <sup>1</sup>H, <sup>13</sup>C, and <sup>29</sup>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 <sup>1</sup>H and <sup>13</sup>C NMR.<sup>6</sup>

$$ZnCl_{2} + (Me_{3}Si)_{3}GeLi (thf)_{3} \xrightarrow{Et_{2}O} \underbrace{t}_{rt}$$

$$(Me_{3}Si)_{3}GeZnCl (thf) + LiCl \quad (1)$$

$$1 (thf)$$

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.<sup>7</sup> 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



**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-Cl1\* 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).

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<sub>3</sub>Si)<sub>3</sub>GeH 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<sub>3</sub>SiCl in diethyl ether for 4 days to yield (Me<sub>3</sub>Si)<sub>4</sub>Ge (17%). The treatment of 1 with additional (Me<sub>3</sub>Si)<sub>3</sub>GeLi(thf)<sub>3</sub> in diethyl ether gave [(Me<sub>3</sub>Si)<sub>3</sub>Ge]<sub>2</sub>Zn (2)<sup>8</sup> in 93% isolated yield, suggesting that germylzinc chloride 1 is an intermediate to form the bis(germyl)zinc. The <sup>1</sup>H, <sup>13</sup>C, and <sup>29</sup>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<sub>3</sub>Si)<sub>3</sub>SiLi(thf)<sub>3</sub> to give not asymmetrically bis(germyl)(silyl)zinc (Me<sub>3</sub>Si)<sub>3</sub>GeZnSi(SiMe<sub>3</sub>)<sub>3</sub> but the symmetrical products of [(Me<sub>3</sub>Si)<sub>3</sub>Ge]<sub>2</sub>Zn and [(Me<sub>3</sub>Si)<sub>3</sub>Si]<sub>2</sub>Zn, quantitatively, with the ratio of 1 : 1 determined by the <sup>1</sup>H NMR signal intensities. The addition of methyllithium to 1 led to the formation



of [(Me<sub>3</sub>Si)<sub>3</sub>Ge]<sub>2</sub>Zn and Me<sub>2</sub>Zn (1:1),<sup>10</sup> (Me<sub>3</sub>Si)<sub>3</sub>GeZnMe could not be detected at all.<sup>11</sup>

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).<sup>12</sup> 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<sup>\*</sup> =  $180.0(0)^{\circ}$ ) 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  $(1)^{\circ}$ , 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<sub>3</sub>Si)<sub>3</sub>GeI (91%), whereas trimethylchlorosilane did not react with 2 at all. The reaction of 2 with iodomethane included two steps. In 4h, the bis(germyl)zinc 2 reacted with idomethane to form (Me<sub>3</sub>Si)<sub>3</sub>GeI (50%) and Me<sub>2</sub>Zn as reactive intermediates.<sup>13</sup> Further stirring for two days led to the final formation of  $(Me_3Si)_3GeMe$  (75%) with precipitation of  $ZnI_2$ salt.

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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<sub>3</sub>Si)<sub>3</sub>GeLi(thf)<sub>3</sub> (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.
- Spectroscopic data for 1: <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  0.48 (s, 27 H), 1.34-6 1.36 (m, 4 H, THF), 3.60–3.62 (m, 4 H, THF);  $^{13}C{^{1}H}$  NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  4.7, 25.3 (THF), 68.8 (THF);  $^{29}$ Si { $^{1}H$ } NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  0.2.
- Crystal structure analysis of 1: A single crystal  $(0.25 \times 0.20 \times$  $0.20\,\text{mm})$  was sealed in a capillary glass tube for the data collection. Diffraction data were collected at 200 K on a MacScience DIP2030 image plate diffractiometer employing graphite-monochromated Mo (K $\alpha$ ) radiation ( $\lambda = 0.71073 \text{ Å}$ ); MF = C<sub>13</sub>H<sub>35</sub>ClGeOSi<sub>3</sub>Zn, 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<sup>3</sup>, Z = 4,  $D_{calcd} = 1.270 \text{ g} \cdot \text{cm}^{-3}$ . 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<sub>2</sub> (0.13 g, 0.95 mmol) with two mol amounts of (Me<sub>3</sub>Si)<sub>3</sub>GeLi(thf)<sub>3</sub> (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. Spectroscopic data for **2**: <sup>1</sup>H NMR ( $C_6D_6$ )  $\delta$  0.39 (s, 54 H); <sup>13</sup>C{<sup>1</sup>H}
- 9 NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  5.2; <sup>29</sup>Si {<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  – 2.3.
- Spectroscopic data for Me<sub>2</sub>Zn at 25 °C: <sup>1</sup>H NMR (THF-d<sub>8</sub>)  $\delta 1.44$  (s, 6 H); <sup>13</sup>C{<sup>1</sup>H} NMR (THF-d<sub>8</sub>)  $\delta 7.3$ . For <sup>1</sup>H NMR 10 chemical shift of Me<sub>2</sub>Zn at -20 °C, see: M. Uchiyama, M. Kameda, O. Mishima, N. Yokoyama, M. Koike, Y. Kondo, and T. Sakamoto, I. Am. Chem. Soc., 120, 4934 (1998).
- 11 The formation of the unsymmetrical (alkyl)(germyl)zinc compound was reported in Ref. 3b. Ph3GeZnEt was generated by the reaction of Ph<sub>3</sub>GeH with Et<sub>2</sub>Zn in bis(2-methoxylethyl)ether.
- 12 Crystal structure analysis of 2: A single crystal  $(0.30 \times$  $0.30 \times 0.30$  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 diffractiometer 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<sup>3</sup>, Z = 1,  $D_{calcd} =$ 1.222 g·cm<sup>-3</sup>. 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, Ph3GeCl was added to the reaction mixture to form Ph3GeMe together with (Me3Si)3GeI.