Available online at www.sciencedirect.com

Journal of Organometallic Chemistry 672 (2003) 100–108

Journal of Organometallic Chemistry

www.elsevier.com/locate/jorganchem

Preparation and structural characterization of trimethylsilyl-substituted germylzinc halides, $(Me_3Si)_3GeZnX$ ($X = Cl$, Br, and I) and silylzinc chloride, $R(Me_3Si)_2SiZnCl$ ($R = SiMe_3$ and Ph)

Masato Nanjo *, Takashi Oda, Kunio Mochida *

Department of Chemistry, Faculty of Science, Gakushuin University, 1-5-1 Mejiro, Toshima-ku, Tokyo 171-8588, Japan

Received 26 December 2002; received in revised form 31 January 2003; accepted 4 February 2003

Abstract

The trimethylsilyl-substituted germylzinc halides, $(Me_3Si)_3GeZnX$ ($X = Cl$, Br, and I), and silylzinc chlorides, $R(Me_3Si)_2SiZnCl$ ($R = SiMe_3$, Ph), have been prepared and their molecular structures have been full determined by spectroscopic and single-crystal X-ray diffraction methods. The germylzinc halides and silylzinc chlorides have dimeric structures consisting of two μ-halogen atoms. The reactivity of germylzinc chloride with substrates is also examined.

Keywords: Germylzinc halides; Silylzinc chlorides; Structure; X-ray diffraction; Reactivity

1. Introduction

Organozinc compounds are useful reagents not only in organic synthesis but also in organometallic chemistry [1]. The well-known Frankland and 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. In this report we describe the first successful isolation and structural characterization of tris(trimethylsilyl)germylzinc halides, $(Me_3Si)_3GeZnX$ ($X = Cl$, **1a**; Br, **1b**; I, **1c**) and tris(trimethylsilyl)silylzinc chloride, $(Me_3Si)_3SiZnCl$ (**2a**) and bis(trimethylsilyl)phenylsilylzinc chloride, $Ph(Me_3Si)_2SiZnCl$ (**2b**). Some reactions of the germylzinc chloride **1a** with substrates are also examined.

2. Results and discussion

2.1. Synthesis of tris(trimethylsilyl)germylzinc halides, $(Me_3Si)_3GeZnX$ ($X = Cl$, Br and I)

The treatment of zinc chloride ($ZnCl_2$) with one molar equivalent of tris(trimethylsilyl)germyllithium solvated tetrahydrofuran (THF), $(Me_3Si)_3GeLi(thf)_3$ [4], in diethyl ether at room temperature for 3 h afforded colorless crystals with a composition of $(Me_3Si)_3GeZnCl(thf)$ (**1a**) in 86% isolated yield. ^{1}H-, ^{13}C- and ^{29}Si-NMR examination of a C_6D_6 solution of the colorless crystals **1a** revealed a single signal assigned to the trimethylsilyl group (Me_3Si), and one THF molecule was included for a molecule **1a** based on the ^{1}H- and ^{13}C-NMR data.

---

* Corresponding authors. Tel.: +81-3-3986-0221; fax: +81-3-5992-1029.

E-mail address: kunio.mochida@gakushuin.ac.jp (K. Mochida).

0022-328X/03/$ - see front matter © 2003 Elsevier Science B.V. All rights reserved.
doi:10.1016/S0022-328X(03)00148-7

$$(Me_3Si)_3GeLi(thf)_3 + ZnX_2(excess) \xrightarrow[r.t.]{} (Me_3Si)_3GeZnX(thf)_3$$

where X = Cl (**1a**), 86%; Br (**1b**), 71%; I (**1c**), 86%

The $(Me_3Si)_3GeLi$ $(thf)_3$ reacted with one molar equivalent of zinc bromide ($ZnBr_2$) and zinc iodide (ZnI_2) in THF under similar conditions to give the corresponding germylzinc halides, $(Me_3Si)_3GeZnBr$ (thf) (**1b**) and $(Me_3Si)_3GeZnI$ (thf) (**1c**), in 71 and 86% isolated yields, respectively. The germylzinc bromide and -iodide coordinated one THF, **1b** and **1c**, were also confirmed by ^1H-, ^{13}C- and ^{29}Si-NMR spectra.

The germylzinc chloride **1a** could be recrystallized from pentane at −20 °C as colorless needles flammable in air. The air-sensitive germylzinc bromide, **1b** and -iodide, **1c** could also be recrystallized from pentane at −20 °C as colorless needles flammable in air. The molecular structures of **1a**–**c** were unequivocally confirmed by X-ray diffraction analysis. The germylzinc halides, **1a**–**c** are dimeric structures consisting of two μ-halogen atoms in the solid states. The molecular structures of **1a**–**c** have crystallographic inversion center as Figs. 1–3. In **1a**–**c** no interaction between the dimer and another dimer was observed.

The selected bond lengths and bond angles of **1a**–**c** are summarized in Table 1. Crystallographic data of **1a**–**c** are summarized in Table 4 in experimental section. The two zinc and two halogen atoms constitute a planar four-membered ring. For **1c**, there are four independent molecules in the unit cell, and not a significant difference is found in one another. The two Zn–X distances of the four-membered ring in **1a**–**c** are 2.356(11) and 2.400(2) Å, 2.547(2) and 2.498(1) Å, and 2.710(2) and 2.727(2) Å, respectively. The X–Zn–X bond angles of **1a**–**c** are in order **1a** (92.75(4)°) < **1b** (94.93(3)°) < **1c** (98.81(3)°). On the other hand, the Zn–X–Zn bond angles for **1a**–**c** are inversely in order **1c** (81.49(4)°) < **1b** (85.07(3)°) < **1a** (87.25(4)°). The zinc atom of **1a**–**c** is solvated by coordiantion to an oxygen atom of a THF molecule with a Zn–O distance of 2.097(4), 2.092(7), and 2.105(7) Å, respectively, and has a distorted tetrahedral configuration. The Ge–Zn bond length of **1a**–**c** is within the range of 2.37–2.39 Å. The Si–Ge–Zn angle of 109.03(av.)–109.98(av.) and the Ge–Si bond length of 2.370–2.372Å are normal values.

Synthesis of tris(trimethylsilyl)silylzinc chloride, $(Me_3Si)_3SiZnCl$ and bis(trimethylsilyl)phenylsilylzinc chloride, $Ph(Me_3Si)_2SiZnCl$. The $ZnCl_2$ reacted with one molar equivalent of tris(trimethylsilyl)silyllithium solvated THF, $(Me_3Si)_3SiLi$ $(thf)_3$ [5] in THF at room temperature for 3 h to afford colorless crystals with a composition of $(Me_3Si)_3SiZnCl$ (thf) (**2a**) in 81% isolated yield. The colorless crystals **2a** were identified with NMR (^1H-, ^{13}C- and ^{29}Si-NMR) spectra, which displayed a single signal assigned to the Me_3Si group, and one THF molecule.

$$R(Me_3Si)_2SiLi(thf)_3 + ZnCl_2(excess) \xrightarrow[r.t.,\ THF]{} R(Me_3Si)_2SiZnCl(thf)_3$$

where X = $SiMe_3$ (**2a**), 81%; Ph (**2b**), 65%

The $Ph(Me_3Si)_2SiLi$ $(thf)_3$ reacted with one molar equivalent of $ZnCl_2$ in THF under similar conditions to give the corresponding silyllzinc chloride, $Ph(Me_3Si)_2SiZnCl$ (thf) (**2b**) in 65% isolated yield. Bis(Tri-

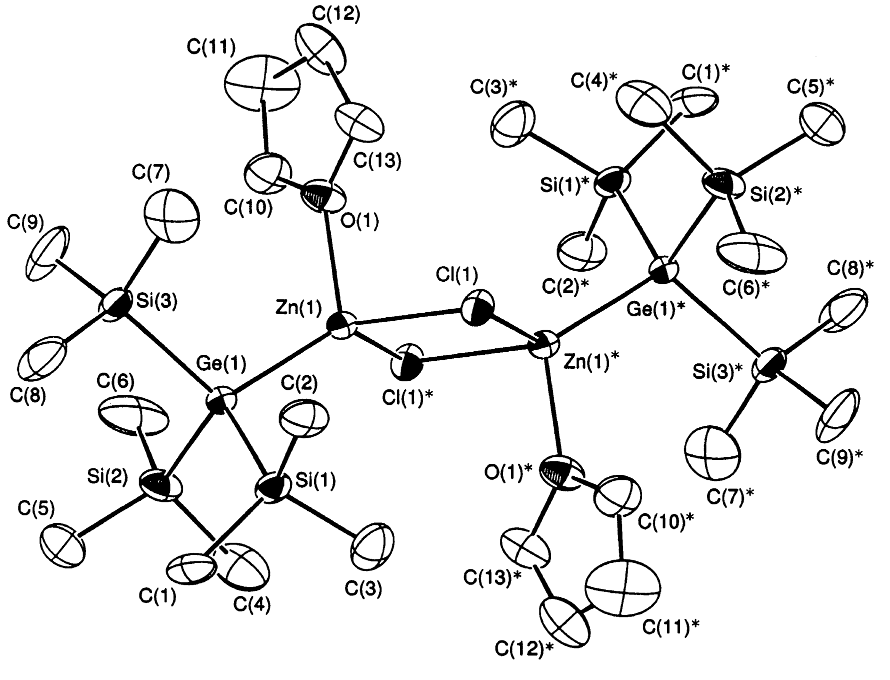

Fig. 1. An ORTEP representation of the dimeric structure of **1a** (hydrogen atoms are omitted for clarity).

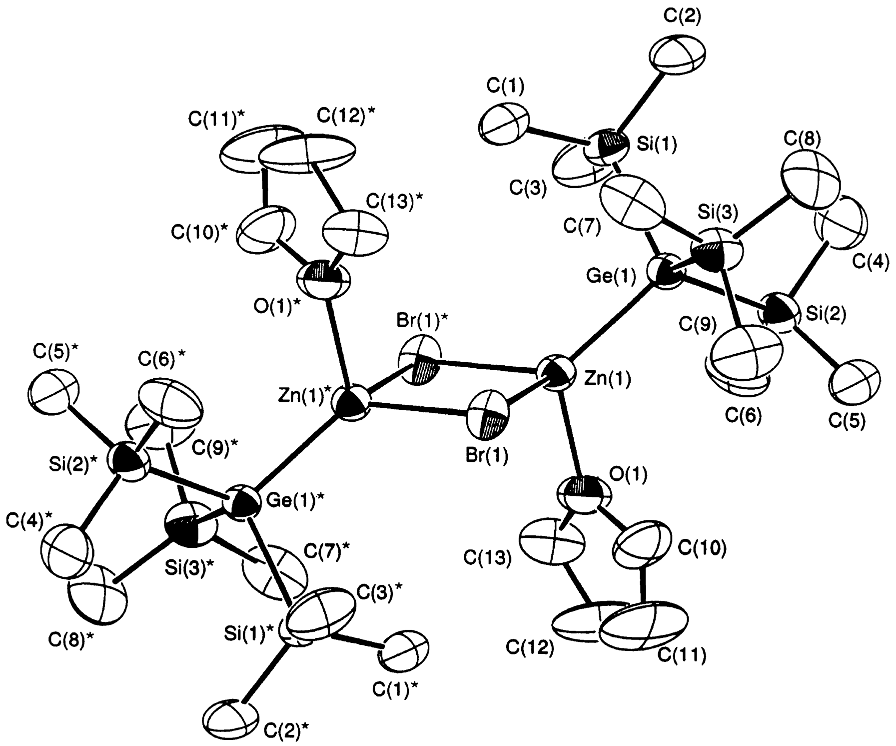

Fig. 2. An ORTEP representation of the dimeric structure of **1b** (hydrogen atoms are omitted for clarity).

methylsilyl)phenylsilane, Ph$(Me_3Si)_2$SiH was also formed as a minor product in the reaction of Ph$(Me_3Si)_2$SiLi $(thf)_3$ with $ZnCl_2$. The silylzinc chloride coordinated one THF, **2b** were also established by ^{1}H-, ^{13}C- and ^{29}Si-NMR spectra.

The silyllzinc chlorides, **2a** and **2b**, could be recrystallized from pentane at −20 °C as colorless crystals flammable in air. The molecular structures of **2a** and **2b** were fully established by X-ray diffraction analysis, as shown in Figs. 4 and 5. The silylzinc chlorides **2a** and **2b** are dimeric consisting of two μ-chlorine atoms as like as the germylzinc halides in the solid states. No interaction between the dimer and another dimer in these silylzinc chlorides was observed. The selected bond lengths and

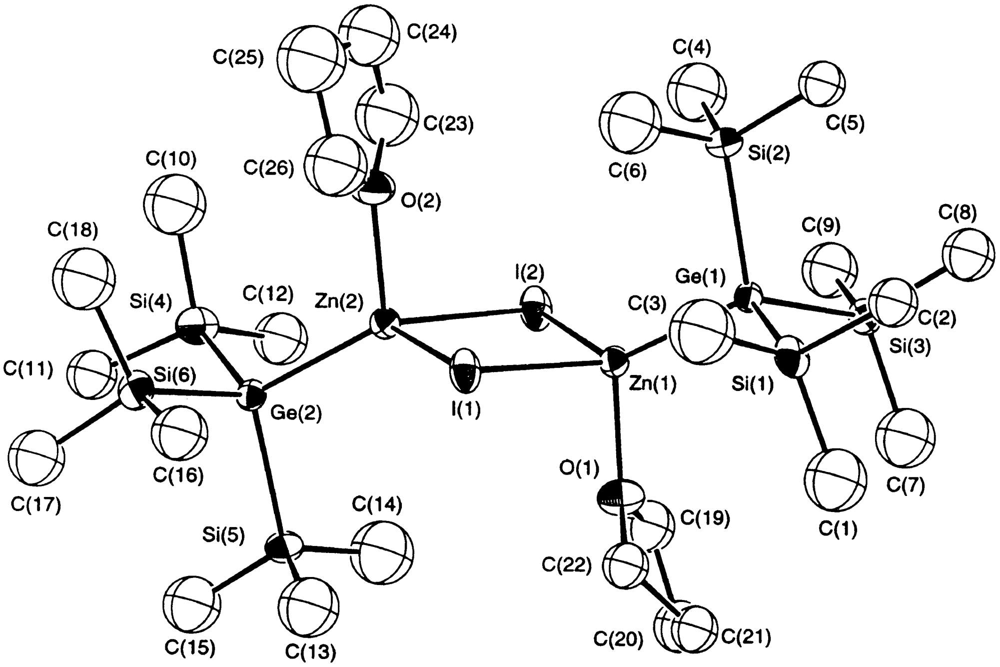

Fig. 3. An ORTEP representation of the dimeric structure of **1c** (hydrogen atoms are omitted for clarity).

Table 1
The selected bond lengths (Å) and bond angles (°) of $(Me_3Si)_3GeZnX$ (X = Cl, Br and I)

	1a (X = Cl)	**1b** (X = Br)	**1c** (X = I)
Bond lengths			
Zn–X	2.356(1)	2.547(2)	2.710(2)
	2.400(2)	2.498(1)	2.727(2)
Ge–Zn	2.377(1)	2.383(2)	2.387(2)
Zn–O	2.097(4)	2.092(7)	2.105(7)
Bond angles			
X–Zn–X	92.75(4)	94.93(3)	98.81(3)
Zn–X–Zn	87.25(4)	85.07(3)	81.49(4)
Si–Ge–Si	109.89(av.)	109.60(av.)	108.93(av.)

bond angles of **2a** and **2b** are summarized in Table 2. Crystallographic data of **2a** and **2b** are also summarized in Table 4 in Section 3.

The two zinc and two chlorine atoms in **2a** and **2b** constitute a planar four-membered ring with Zn–Cl distances of 2.3580(8) and 2.3982(8) Å, and 2.3853(14) and 2.4019(13) Å, respectively. The Cl–Zn–Cl bond angles of **2a** and **2b** are 92.62(13) and 91.49(4)°, respectively. The zinc atoms of **2a** and **2b** are solvated by coordiantion to an oxygen atom of a THF molecule with a Zn–O distance of 2.095(2) and 2.092(3) Å, respectively. The zinc atoms in these silylzinc chlorides have distorted tetrahedral configurations. The Si–Zn bond lengths of 2.3537(9) Å (**2a**) and 2.3652(12) Å (**2b**). The Si–Si–Zn angle of 108.97(av.)° (**2a**), 110.96(av.)° (**2b**), and the Si–Si bond length of 2.337(av.) Å (**2a**) and 2.347(av.) Å (**2b**) [2a] are quite normal.

Several reports on organozinc halides using highly sterically hindered silicon conpounds have been reported. The preparaton and structural characterization of $(PhMe_2Si)_3CZnCl$ have been examined by Eaborn and co-workers [6]. The zinc in the crystal was present as the dimer $[(PhMe_2Si)_3CZn(\mu\text{-}Cl)_2ZnC(SiMe_2Ph)_3]$, with the zinc three-coordinate in a planar enviromenet and the chloride bridged sligthly unsymmetrical. Wiberg and co-workers have reported the preparation of t-$Bu_3SiZnCl$ and t-$Bu_3SiZnBr$ by reactions of $(t\text{-}Bu_3Si)_2Zn$ with $BiCl_3$ and BBr_3, respectively. Structure of t-$Bu_3SiZnBr$ were tetramer with a regular cubic by X-ray diffraction analysis [2a].

2.2. Reactions of germylzinc chloride

The reactions of **1a** with some electrophiles in diethyl ether under argon atmosphere in Schlenk tube were examined at room temperature. The hydrolysis of **1a** with deoxygenated water in diethyl ether under argon atmosphere proceeded extremely slow to give tris(trimethylsilyl)germane, $(Me_3Si)_3GeH$ in only 43% yield after 7 days of stirring. The addition of hydrochloric acid of **1a** for 2 h under argon atmosphere promoted the hydrolysis reaction up to 95% yield. The germylzinc chloride **1a** reacted slowly with Me_3SiCl for 4 days under argon atmosphere gave tetrakis(trimethylsilyl)germane, $(Me_3Si)_4Ge$ in 17% yield. Unreacted **1a** was recovered as $(Me_3Si)_3GeH$ after hydrolysis with water in 83% yield. The reaction of **1a** with I_2 did not proceed at room temperature for 4 days. Unreacted **1a** was

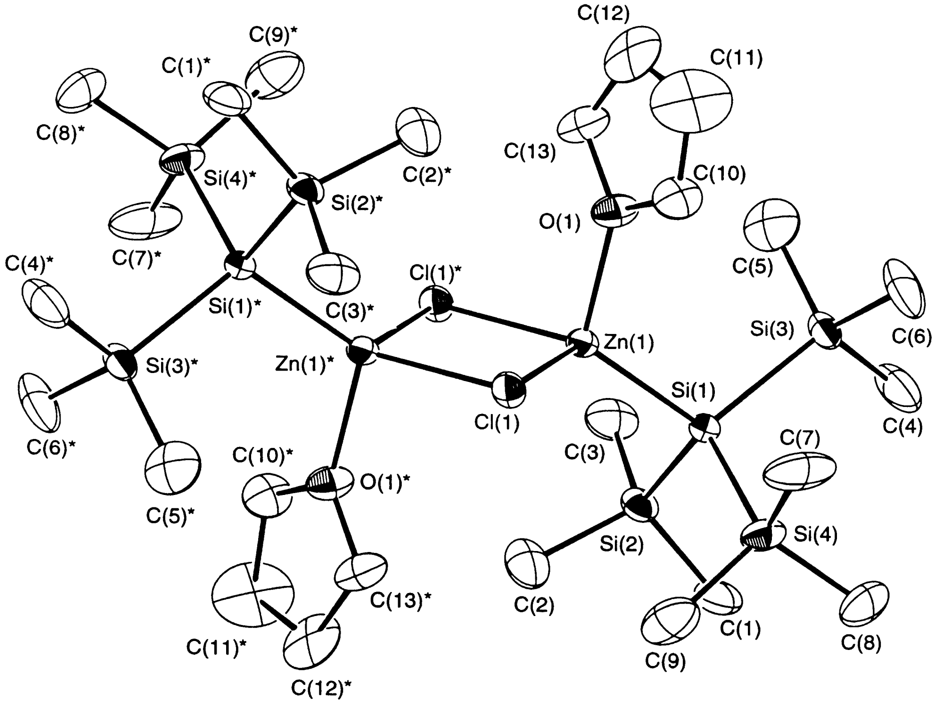

Fig. 4. An ORTEP representation of the dimeric structure of **2a** (hydrogen atoms are omitted for clarity).

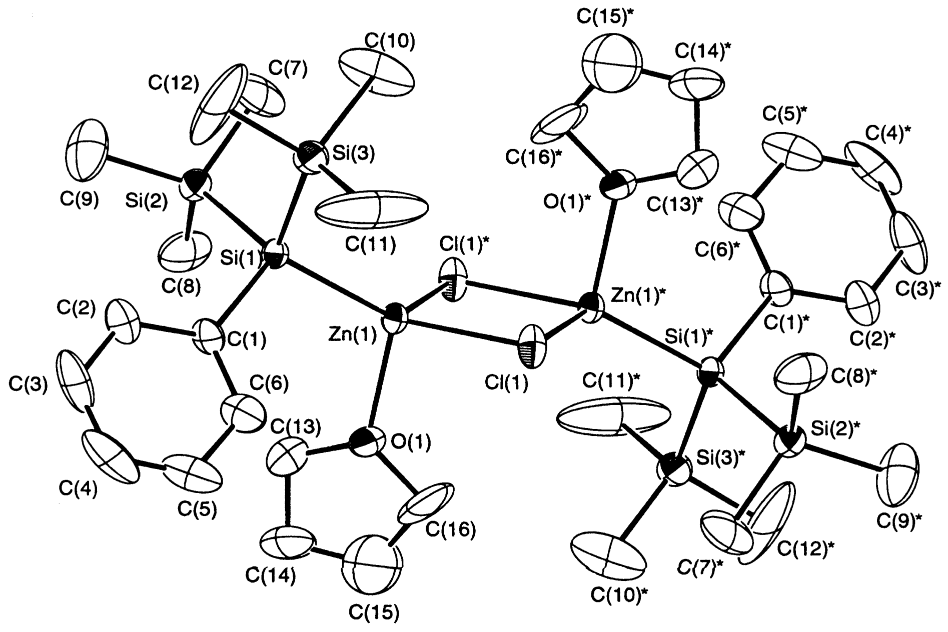

Fig. 5. An ORTEP representation of the dimeric structure of **2b** (hydrogen atoms are omitted for clarity).

Table 2
The selected bond lengths (Å) and bond angles (°) of $R(Me_3Si)_2SiZnCl$ ($R = SiMe_3$ and Ph)

	2a ($R = SiMe_3$)	**2b** ($R = Ph$)
Bond lengths		
Zn–Cl	2.3580(8)	2.3583(14)
	2.3980(8)	2.4019(13)
Si–Zn	2.3537(9)	2.3652(12)
Zn–O	2.095(2)	2.092(3)
Bond angles		
Cl–Zn–Cl	92.62(3)	91.49(4)
Zn–Cl–Zn	87.38(3)	88.50(4)
Si–Si–Si	110.99(av.)	109.22(av.)

completely recovered. All products were identified by GC, GCMS, and NMR spectra in comparison with those of authentic samples. The yields of products were determined by GC with internal standard methods.

The treatment of **1a** with one molar equivalent of $(Me_3Si)_3GeLi\ (thf)_3$ under argon atmosphere in diethyl ether at room temperature for 2 h gave bis[(trimethylsilyl)germyl]zinc, $[(Me_3Si)_3Ge]_2Zn$ [7] in 93% isolated yield. One of particular interest is the fact that the redistribution reaction happened on addition of some other organolithium reagents to germylzinc chloride **1a**. The germylzinc chloride **1a** was allowed to react with one molar equivalent of $(Me_3Si)_3SiLi\ (thf)_3$ to give not asymmetrically bis(germyl)(silyl)zinc, $(Me_3Si)_3GeZn\text{-}Si(SiMe_3)_3$ but the symmetrical products of $[(Me_3Si)_3Ge]_2Zn$ and $[(Me_3Si)_3Si]_2Zn$ [2b], quntitatively, with the ratio of 1:1. The ratio of redistribution reaction products was determined by the ^{1}H-NMR signal intensities of Me_3Si groups. The addition of one molar equivalent of methyllithium, MeLi to **1a** led to the formation of $[(Me_3Si)_3Ge]_2Zn$ and Me_2Zn quantitatively with the ratio of 1:1. Expected substitution product $(Me_3Si)_3GeZnMe$ could not be detected at all, probably due to its instability. The formation of Me_2Zn was confirmed by both NMR spectra of authentic sample and chemical trapping experiments with triphenylgermyl chloride, Ph_3GeCl. The reaction mixture of Me_2Zn reacted with Ph_3GeCl to give Ph_3GeMe in 59% yield. Reactions of **1a** with one molar equivalent of dimethylphenylsilyllithium, $PhMe_2SiLi$ or dimethylphenylgermyllithium, $PhMe_2GeLi$ afforded symmetrical product of $[(Me_3Si)_3Ge]_2Zn$ (50% yield) as a sole product in either case. In the reaction of **1a** with silyl- or germyllithium lithium, expected another symmetrical products of $(PhMe_2Si)_2Zn$ or $(PhMe_2Ge)_2Zn$, respectively, could not be detected under these reaction conditions, probably due to their instability. Of course, unsymmetrical products of $(Me_3Si)_3GeZnSiMe_2Ph$ or $(Me_3Si)_3GeZnGeMe_2Ph$ could not be detected by GC, GCMS, and NMR spectra. The unsymmetrical silyl- and germyl-substituted zinc are unknown. The reactions of **1a** with electrophiles and organolithiums are summarized in Table 3.

3. Experimental

3.1. General methods

The NMR spectra were obtained on a Varian Unity Inova 400 MHz spectrometer. The GCMS spectra were measured on a JEOL JMS-DX 303 mass spectrometer. Gas chromatography was performed on a Shimadzu GC

Table 3
Reactions of tris(trimethylsilyl)germylzinc chloride (**1a**) with substrates in diethyl ether

Substrate	Reaction conditions	Products (yield/%)
H_2O	r.t., 6 days	$(Me_3Si)_3GeH$ (43)
HCl	r.t., 2 h	$(Me_3Si)_3GeH$ (100)
I_2	r.t., 4 days	no reaction
Me_3SiCl	r.t., 4 days	$(Me_3Si)_4Ge$ (17)
$(Me_3Si)_3GeLi(thf)_3$	r.t., 2 h	$[(Me_3Si)_3Ge]_2Zn$ (100)
$(Me_3Si)_3SiLi(thf)_3$	r.t., 2 h	$[(Me_3Si)_3Ge]_2Zn$ (50) $[(Me_3Si)_3Si]_2Zn$ (50)
MeLi	r.t., 2 h	$[(Me_3Si)_3Ge]_2Zn$ (50) Me_2Zn (50)
$PhMe_2SiLi$	r.t., 2 h	$[(Me_3Si)_3Ge]_2Zn$ (50)
$PhMe_2GeLi$	r.t., 2 h	$[(Me_3Si)_3Ge]_2Zn$ (50)

8A 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_α ($\lambda = 0.71073$ 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.

3.2. Materials

$(Me_3Si)_3SiLi$ [5], $(Me_3Si)_3GeLi$ [4], $PhMe_2GeLi$ [8], $PhMe_2SiLi$ [8], $(Me_3Si)_3GeH$ [4], $(Me_3Si)_4Ge$ [4], Ph_3GeCl [9], and Ph_3GeMe [10] were prepared as reported in the literature. $ZnCl_2$, $ZnBr_2$, ZnI_2, Me_3SiCl, and MeLi are commercially available.

3.3. Structural studies

Germylzinc halides (**1a**–**c**) and silylzinc chloride (**2a**, **b**) could be obtained in the form crystals suitable for X-ray diffraction studies. A single crystal was sealed in a capillary glass tube for the collection. Diffraction data was collected at 200 K on a MacScience DIP2030 image plate diffraction employing graphite-monochromated Mo–K_α radiation ($\lambda = 0.71073$ Å). Crystallographic data for **1a**–**c** and **2a**,**b** are listed in Table 4.

3.4. Preparation of tris(trimethylsilyl)germylzinc chloride, $(Me_3Si)_3GeZnCl$ (1a)

$ZnCl_2$ (0.30 g, 2.17 mmol) reacted with one molar equivalent of $(Me_3Si)_3GeLi(thf)_3$ (1.12 g, 2.17 mmol) containing diethyl ether (10 ml) in Schlenk tube at room temperature (r.t.) for 1 day under argon atmosphere. The concentration of the reaction mixture by removal of diethyl ether followed by addition of pentane (10 ml). The organic layer was filtered. After removal of solvent under vacuum, pentane (3 ml) was added to the residue. The solution was kept at −20 °C. The colorless crystals were filtered off, dried, and shown to be $(Me_3Si)_3GeZnCl(thf)$ (**1a**) (0.88 g, 1.87 mmol) in 86% yield. ^1H-NMR (C_6D_6) δ 0.48 (s, 27H), 1.34–1.36 (m, 4H, THF), 3.60–3.62 (m, 4H, 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.

3.5. Preparation of tris(trimethylsilyl)germylzinc bromide, $(Me_3Si)_3GeZnBr$ (1b)

$ZnBr_2$ (4.05 g, 18.0 mmol) reacted with one molar equivalent of $(Me_3Si)_3GeLi(thf)_3$ (0.99 g, 1.92 mmol) containing THF (10 ml) in Schlenk tube at r.t. for 3 h under argon atmosphere. The solvent was taken off under reduced pressure. The solid residue was washed twice with pentane (10 ml). The organic layer was filtered. The solvent was concentrated (3 ml), and then kept at −20 °C. Colorless crystals separated, and these were filtered off and judged probably to be $(Me_3Si)_3GeZnBr(thf)$ (**1b**) (0.70 g, 1.37 mmol) in 71% yield. ^1H-NMR (C_6D_6) δ 0.46 (s, 27H), 1.34–1.36 (m, 4H, THF), 3.60–3.62 (m, 4H, THF); $^{13}C\{^1H\}$-NMR (C_6D_6) δ 4.6, 25.3 (THF), 68.8 (THF); $^{29}Si\{^1H\}$-NMR (C_6D_6) δ −1.0.

3.6. Preparation of tris(trimethylsilyl)germylzinc iodide, $(Me_3Si)_3GeZnI$ (1c)

ZnI_2 (6.00 g, 18.8 mmol) reacted with one molar equivalent of $(Me_3Si)_3GeLi(thf)_3$ (1.00 g, 1.94 mmol) containing THF (15 ml) in Schlenk tube at r.t. for 3 h under argon atmosphere. The solvent was taken off under reduced pressure. The solid residue was washed twice with pentane (10 ml). The organic layer was filtered. The concentration of the solvent under reduced pressure, and then kept at −20 °C. Colorless crystals separated, and these were filtered off and judged to be $(Me_3Si)_3GeZnI(thf)$ (**1c**) (0.93 g, 1.67 mmol) in 86% yield. ^1H-NMR (C_6D_6) δ 0.46 (s, 27H), 1.34–1.36 (m, 4H, THF), 3.60–3.62 (m, 4H, THF); $^{13}C\{^1H\}$-NMR (C_6D_6) δ 4.7, 25.3 (THF), 68.8 (THF).

3.7. Preparation of tris(trimethylsilyl)silylzinc chloride, $(Me_3Si)_3SiZnCl$ (2a)

$ZnCl_2$ (5.32 g, 39.0 mmol) reacted with one molar equivalent of $(Me_3Si)_3SiLi(thf)_3$ (1.64 g, 3.48 mmol) containing THF (15 ml) in Schlenk tube at r.t. for 3 h under argon atmosphere. The solvent was taken off under reduced pressure. The solid residue was washed twice with pentane (10 ml). The organic layer was filtered. The solution was concentrated (3 ml), and then kept at −20 °C. Crystals separated, and these were filtered off. Colorless crystals flammable in air with a composition of $(Me_3Si)_3SiZnCl(thf)$ (**2a**) (1.19 g, 2.83

Table 4
Crystallographic data for **1a**–**c**, **2a** and **2b**

	1a	**1b**	**1c**	**2a**	**2b**
Formula	$C_{13}H_{35}ClGeOSi_3Zn$	$C_{13}H_{35}BrGeOSi_3Zn$	$C_{13}H_{35}IGeOSi_3Zn$	$C_{13}H_{35}ClOSi_4Zn$	$C_{16}H_{31}ClOSi_3Zn$
Mol. wt.	465.09	509.55	556.55	420.59	424.50
Crystal size (mm^3)	0.25 × 0.20 × 0.20	0.45 × 0.30 × 0.30	0.40 × 0.40 × 0.20	0.45 × 0.25 × 0.25	0.40 × 0.40 × 0.20
Crystal system	Monoclinic	Triclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$P2_1/c$
Unit cell dimensions					
a (Å)	9.6390(7)	9.5250(5)	9.6080(3)	9.6130(3)	13.7680(10)
b (Å)	20.5050(91)	10.3630(10)	18.1170(10)	20.5070(12)	10.6160(4)
c (Å)	12.7720(9)	13.0280(13)	29.6050(14)	12.6970(8)	17.0490(12)
α (°)	90	92.294(5)	76.118(2)	90	90
β (°)	105.452(3)	105.931(6)	83.763(2)	105.492(4)	113.178
γ (°)	90	96.603(6)	82.980(3)	90	90
V (Å^3)	2433.1(3)	1224.91(18)	4948.4(4)	2412.1(2)	2290.8(2)
Z	4	2	2	4	4
Radiation Mo–K$_\alpha$ (λ/Å)	0.71070	0.71070	0.71070	0.71070	0.71070
Temperature (K)	200	200	200	200	200
D_{calc} (g cm^{-3})	1.270	1.382	1.494	1.158	1.231
Unique reflections	3531	3241	11528	3291	3243
Goodness-of-fit	1.104	1.836	1.817	1.360	1.829
R ($I > 2\sigma(I)$)	0.0399	0.0559	0.0645	0.0407	0.0541
wR_2	0.1255	0.2069	0.2145	0.1467	0.1994

mmol) were obtained in 81% yield. ^{1}H-NMR (C_6D_6) δ 0.44 (s, 27H), 1.34–1.36 (m, 4H, THF), 3.60–3.62 (m, 4H, THF); ^{13}C{^{1}H}-NMR (C_6D_6) δ 4.0, 25.3 (THF), 68.8 (THF).

3.8. Preparation of bis(trimethylsilyl)phenylsilylzinc chloride, ($Me_3Si)_2PhSiZnCl$ (**2b**)

$ZnCl_2$ (5.12 g, 37.6 mmol) reacted with one molar equivalent of $Ph(Me_3Si)_2SiLi$ (4.33 mmol) containing THF (20 ml) in Schlenk tube at r.t. for 1 h under argon atmosphere. The solvent was taken off under reduced pressure. The solid residue was washed twice with pentane (10 ml). The organic layer was filtered, and then removed under reduced pressure. The solid residue was dissolved with pentane (5 ml) and kept at −20 °C. Colorless crystals separated, and these were filtered off and judged probably to be a composition of $Ph(Me_3Si)_2SiZnCl(thf)$ (**2b**) (1.18 g, 2.44 mmol) in 65% yield. ^{1}H-NMR (C_6D_6) δ 0.43 (s, 18H), 1.34–1.36 (m, 4H, THF), 3.60–3.62 (m, 4H, THF), 7.09–7.81 (m, 5H); ^{13}C{^{1}H}-NMR (C_6D_6) δ 1.7, 25.3 (THF), 68.8 (THF), 127.1, 127.9, 137.6, 138.7.

3.9. Preparation of bis(trimethylsilyl)phenylsilyllithium

To a THF (5 ml) of bis(trimethylsilyl)phenylsilane, $Ph(Me_3Si)_2SiH$ (1.50 g, 5.9 mmol) in Schlenk tube, pentane solution of t-butyllithium (4.3 ml, 6.5 mmol) was introduced by stringe at −40 °C under argon atmosphere. After stirring for 1 h, the reaction mixture was concentrated by evaporation of THF. ^{1}H-NMR (C_6D_6) δ 0.60 (s, 18H), 1.34–1.36 (m, 12H, THF), 3.60–3.62 (m, 12H, THF), 7.23 (t, $J = 7.0$ Hz, 3H), 7.95 (d, $J = 3$ Hz, 2H); ^{13}C{^{1}H}-NMR (C_6D_6) δ 4.4, 25.3 (THF), 68.8 (THF), 123.5, 126.8, 137.6; ^{7}Li-NMR (C_6D_6) δ 0.58.

3.10. Preparation of dimethylzinc

THF-d_8 (7.5 ml) was introduced to a mixture of $ZnCl_2$ (0.021 g, 0.15 mmol) and MeLi (solid, 0.029 g, 0.30 mmol) in NMR tube, at low temperature under argon atmosphere. The reaction mixture was allowed to r.t. and stirred for 5 min. ^{1}H-NMR (THF-d_8) δ −1.44 (s, 9H).

3.11. Hydrolysis of tris(trimethylsilyl)germylzinc chloride (**1a**) with water

A diethyl ether solution (10 ml) of **1a** (1.00 mmol), excess amount of deoxygenated H_2O, and nonadecane as internal standard under argon atmosphere was stirred at r.t. for 6 days in Schlenk tube. Tris(trimethylsilyl)germane, $(Me_3Si)_3GeH$ (0.43 mmol) was formed in 43% GC yield. Unreacted **1a** (0.50 mmol) was recovered. $(Me_3Si)_3GeH$: ^{1}H-NMR (C_6D_6) δ 0.28 (s, 27H), 2.16 (s, 1H); ^{13}C{^{1}H}-NMR (C_6D_6) δ 3.4. GCMS m/z 294 ($[M]^+$, 20), 278 (5), 220 (40), 146 (35), 131 (40), 73 (100).

3.12. Hydrolysis of tris(trimethylsilyl)germylzinc chloride (**1a**) with hydrochloric acid

A diethyl ether solution (10 ml) of **1a** (1.00 mmol), excess amount of conc. HCl, and nonadecane as internal standard under argon atmosphere was stirred at r.t. for

2 h in Schlenk tube. Tris(trimethylsilyl)germane, $(Me_3Si)_3GeH$ (0.95 mmol) was formed in 95% GC yield.

3.13. Reaction of tris(trimethylsilyl)germylzinc chloride (1a) with trimethylchlorosilane

A diethyl ether solution (10 ml) of **1a** (1.00 mmol), excess amount of Me_3SiCl, and nonadecane as internal standard was stirred at r.t. for 4 days in Schlenk tube under argon atmosphere. Tetrakis(trimethylsilyl)germane, $(Me_3Si)_4Ge$ (0.17 mmol) was formed in 17% GC yield. Unreacted **1a** (0.80 mmol) was recovered. $(Me_3Si)_4Ge$: ^1H-NMR (C_6D_6) δ 0.30 (s, 36H; $^{13}C\{^1H\}$-NMR (C_6D_6) δ 3.5. GCMS m/z 366 ($[M]^+$ 30), 351 (20), 293 (10), 278 (100), 219 (20), 205 (15), 187 (20), 144 (10), 131 (25), 73 (90).

3.14. Reaction of tris(trimethylsilyl)germylzinc chloride (1a) with tris(trimethylsilyl)germyllithium

$(Me_3Si)_3GeLi(thf)_3$ (0.34 mmol) in THF (10 ml) was added to a THF solution (5 ml) of **1a** (0.34 mmol) in a Schlenk tube, under argon atmosphere. The reaction mixture was stirred at r.t. for 2 h. bis[Tris(trimethylsilyl)germyl]zinc, $[(Me_3Si)_3Ge]_2Zn$ (0.34 mmol) was formed quantitatively. $[(Me_3Si)_3Ge]_2Zn$: ^1H-NMR (C_6D_6) δ 0.39 (s, 54H); $^{13}C\{^1H\}$-NMR (C_6D_6) δ 5.2; $^{29}Si\{^1H\}$-NMR δ −2.3.

3.15. Reaction of tris(trimethylsilyl)germylzinc chloride (1a) with tris(trimethylsilyl)silyllithium

$(Me_3Si)_3SiLi(thf)_3$ (0.34 mmol) in THF (10 ml) was added to a THF solution (5 ml) of **1a** (0.34 mmol) in a Schlenk tube, under argon atmosphere. The reaction mixture was stirred at r.t. for 2 h. $[(Me_3Si)_3Ge]_2Zn$ (0.17mmol) and bis[tris(trimethylsilyl)silyl]zinc, $[(Me_3Si)_3Si]_2Zn$ (0.17 mmol) were formed with the ratio of 1:1 in quantitatively. $[(Me_3Si)_3Si]_2Zn$: ^1H-NMR (C_6D_6) δ 0.35 (s, 54H); $^{13}C\{^1H\}$-NMR (C_6D_6) δ 4.5.

3.16. Reaction of tris(trimethylsilyl)germylzinc chloride (1a) with methyllithium

MeLi (0.47 mmol) in THF (25 ml) was added to a THF solution (5 ml) of **1a** (0.45 mmol) in a Schlenk tube, methyllithium, under argon atmosphere. The reaction mixture was stirred at r.t. for 1.5 h. $[(Me_3Si)_3Ge]_2Zn$ (0.23 mmol) was formed. Dimethylzinc, Me_2Zn was confirmed by NMR analysis. Me_2Zn: ^1H-NMR (THF-d_8) δ −1.42 (s, 9H).

3.17. Reaction of tris(trimethylsilyl)germylzinc chloride (1a) with phenyldimethylgermyllithium

$PhMe_2GeLi$ (0.69 mmol) in THF (6 ml) was added to a THF solution (5 ml) of **1a** (0.69 mmol), phenyldimethylgermyllithium in a Schlenk tube, under argon atmosphere. The reaction mixture was stirred at r.t. for 1.5 h. $[(Me_3Si)_3Ge]_2Zn$ (0.35 mmol) was formed.

3.18. Reaction of tris(trimethylsilyl)germylzinc chloride (1a) with phenyldimethylsilyllithium

$PhMe_2SiLi$ (0.69 mmol) in THF (6 ml) was added to a THF solution (5 ml) of **1a** (0.69 mmol), phenyldimethylsilyllithium in a Schlenk tube, under argon atmosphere. The reaction mixture was stirred at r.t. for 1.5 h. $[(Me_3Si)_3Ge]_2Zn$ (0.35 mmol) was formed.

3.19. Reaction of dimethylzinc with triphenylgermyl chloride

MeLi (0.43 mmol) in THF (4 ml) was added to a THF solution (5 ml) of **1a** (0.43 mmol) in a Schlenk tube, under argon atmosphere. The reaction mixture was stirred at r.t. for 1.5 h. To a triphenylchlorogermane, Ph_3GeCl (0.58 mmol) in a Schlenk tube, the THF solution of Me_2Zn was transferred by means of vacuum line. The reaction mixture was stirred at r.t. for 1 day. Triphenylmethylgermane, Ph_3GeMe was formed in 59% yield.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 194958–194962 for compounds **1a**–**c** and **2a**,**b**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

This work was supported by a grant-in-aid for scientific research (no. 11740344) from Ministry of Education, Culture, Sports, Science, and Technology, Japan. We thank Mitsubishi Material Co. Ltd., for providing us tetrachlorogermane.

References

[1] (a) J.B. Wakefield, in: D. Barton, W.D. Ollis, D.N. Jones (Eds.), Comprehensive Organic Chemistry, vol. 3, Pergamon, Oxford, 1979, p. 987;
(b) D.A. Armitage, in: G. Wilkinson, F.G.A. Stone, E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, vol. 2, Pergamon, New York, 1982, p. 99.

[2] (a) N. Wiberg, K. Amelunxen, H.-W. Lerner, H. Noth, A. Appel, J. Knizek, K. Polborn, Z. Anorg. Allg. Chem. 623 (1861) 1997;
(b) J. Arnold, T.D. Tilley, A.L. Rheingold, S.J. Geib, J. Inorg. Chem. 26 (1987) 2106;
(c) L. Rosch, G. Altnau, Angew. Chem. Int. Ed. Engl. 18 (1979) 60;
(d) E. Wiberg, O. Stecher, H. -J. Andrasscheck, L. Kreuzbichler, E. Staude, Angew. Chem. Int. Ed. Engl. 2 (1963) 507.

[3] (a) E. Amberger, W. Stoeger, Angew. Chem. Int. Ed. Engl. 5 (1966) 522;
(b) V.T. Bychkov, N.S. Vyazankinand, G.A. Razuvaev, Zh. Obshch. Khim. 43 (1973) 793;
(c) N.S. Vyazankin, G.A. Razuvaev, O.A. Kruglaya, Organomet. Chem. Rev. A 3 (1968) 323.

[4] (a) S. Freitag, R. Nerbst-Irmer, L. Lameyer, D. Stalke, Organometallics 15 (1996) 2839;
(b) A.G. Brook, F. Abdessaken, H. Sollradl, J. Organomet. Chem. 299 (1986) 9.

[5] G. Gutekunst, A.G. Brook, J. Organomet. Chem. 225 (1982) 1.

[6] A.S. Al-Juaid, C. Eaborn, A. Habtemariam, P.B. Hitchcock, J.D. Smith, K. Tavakkoli, A.D. Webb, J. Organomet. Chem. 462 (1993) 45.

[7] M. Nanjo, T. Oda, K. Mochida, Chem. Lett. (2002) 108.

[8] D.D. Davies, Organomet. Chem. Rev. Sect. A 6 (1970) 283.

[9] E.H. Brook, G.J.D. Peddle, J. Chem. Soc. A (1966) 1241.

[10] A.G. Brook, G.J.D. Peddle, J. Am. Chem. Soc. 85 (1869) 1963.