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Diverse reactions of nitroxide-radical adducts of silylene, germylene, and stannylene

Takeaki Iwamoto, Hidenori Masuda, Shintaro Ishida, Chizuko Kabuto, Mitsuo Kira *

Department of Chemistry, Graduate School of Science, Tohoku University, Aoba-ku, Sendai 980-8578, Japan

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Abstract

The results of the thermolysis of 1:2 adducts of stable group-14 element divalent compounds [R_2M:, $R_2 = $ 1,1,4,4-tetrakis(trimethylsilyl)butane-1,4-diyl; **1b**, M = Ge; **1c**, M = Sn] to TEMPO radical are discussed in detail. Whereas the thermal reactions of the 1:2 adducts [$R_2M(OR')_2$, $R' = $ 2,2,6,6-tetramethylpiperidin-*N*-yl; **3b**, M = Ge; **3c**, M = Sn] are understood to proceed by the initial homolysis of an M–O bond to give the corresponding aminoxy-substituted group-14 element radicals [$R_2(R'O)M\cdot$; **2b**, M = Ge; **2c**, M = Sn] and TEMPO, the subsequent reactions of **2b** and **2c** were remarkably different to each other; **2b** favors the N–O bond fission (path b) to give the corresponding germanone, while **2c** prefers the M–O bond fission (path a) to give stannylene (**1c**). In combining with our previous results for aminoxysilyl radical (**2a**) [$R_2(R'O)Si\cdot$], the origin of the remarkable differences in the reactivity among group-14 element radicals **2a**–**2c** is discussed on the basis of the theoretical calculations for model reactions.

Improved syntheses of the precursor dichlorogermane and dichlorostannane of germylene (**1b**) and stannylene (**1c**), respectively, are described in Section 3.

Keywords: Silicon; Germanium; Tin; Stable silylene; Stable germylene; Stable stannylene; Nitroxide radical; Bond fission; X-ray structural analysis

1. Introduction

Much attention has been focused on the structure and reactions of stable silylenes and related group-14 element divalent compounds [1]. Since silylene, germylene, and stannylene having the same cyclic dialkyl substituent, **1a**–**1c** (Scheme 1) have now been available as thermally stable compounds [2], the reactivity of the series of the divalent compounds is able to be compared systematically. During the course of our studies of the reactions between doublet radicals and the heavier group-14 divalent species with singlet electronic configuration, we have recently found the unique characteristics of the reactions of 2,2,6,6-tetramethylpiperidine *N*-oxide (TEMPO) with **1a**–**1c** (Scheme 1) [3]. The reactions of stable germylene (**1b**) and stannylene (**1c**) with TEMPO (2 eq) gave the corresponding 1:2 adducts **3b** and **3c**, respectively, in quantitative yields. The rate constant (k_1) of the addition of TEMPO to **1b** to give aminoxygermyl radical **2b** was estimated to be about 1.5×10^{-2} $M^{-1}\,s^{-1}$ at 274 K with $\Delta H^{\ddagger} = 9.7 \pm 0.5$ kcal mol^{-1} and $\Delta S^{\ddagger} = -32 \pm 2$ cal mol^{-1} K^{-1}. In good accord with the singlet nature of **1b**, the rate constant is far smaller than that for the reaction of TEMPO with triplet diphenyl carbene ($k = 2.7 \times 10^8$ $M^{-1}\,s^{-1}$) in acetonitrile at room temperature [4]. On the other hand, the reaction of stable silylene (**1a**) with TEMPO (1 eq) proceeded in a different way to afford 1,3-disiladioxetane derivative **5a**; even when a large excess amount of TEMPO was used, 1:2 adduct **3a** was never produced. The formation of disiladioxetane (**5a**) is explained by a facile cleavage of the N–O bond of intermediate aminoxysilyl radical **2a** giving silanone (**4a**) followed by the dimerization, while attempted detection of silanone (**4a**) by NMR spectroscopy failed.

In this paper, the results of the thermolysis of 1:2 adducts **3b** and **3c** were discussed in detail. The diversity of the addition reactions of group-14 element divalent

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* Corresponding author. Tel.: + 81-2221-76585; fax: + 81-2221-76589.

E-mail address: mkira@si.chem.tohoku.ac.jp (M. Kira).

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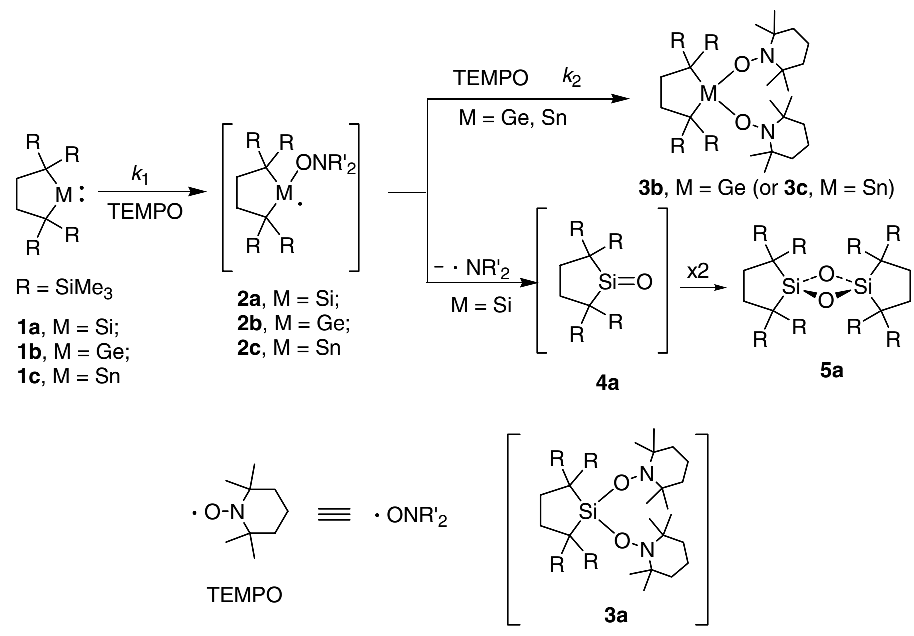


Scheme 1.

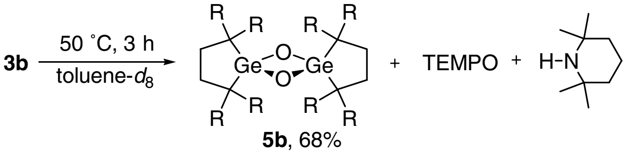
compounds **1a**–**1c** with TEMPO and their reverse reactions was explained by the systematic change of the reactivities among intermediate radicals **2a**–**2c**.

Improved syntheses of the precursor dichlorogermane and dichlorostannane of germylene (**1b**) and stannylene (**1c**), respectively, are described in Section 3.

2. Results and discussion

2.1. Thermal reaction of germylene-TEMPO 1:2 adduct 3b

When a toluene-d_8 solution of adduct **3b** was heated at 50 °C for 3 h, 1,3-digermadioxetane (**5b**) was produced as white crystals in 68% yield together with TEMPO and piperidine (90%) (Eq. 1); the yield of TEMPO was not determined but the existence of TEMPO was confirmed by ESR spectroscopy. The structure was determined by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopies and X-ray crystallography.



(1)

A single crystal of **5b** suitable for X-ray structural analysis was obtained by recrystallization from toluene. While a number of 1,3-digermadioxetanes have been known [5], **5b** is the first tetraalkyl-substituted 1,3-digermadioxetane analyzed by X-ray crystallography. Molecular structure of **5b** together with selected geometrical parameters is shown in Fig. 1. The ring structure of **5b** is quite similar to that of the corresponding 1,3-disiladioxetane (**5a**) [3]. The M–O–M and O–M–O angles are 94.5° and 85.5°, respectively, for **5b**, while they are 93.5° and 86.5°, respectively, for **5a**. The four-membered rings of **5a** and **5b** are both planar. The M–O distance for **5b** (M = Ge, 1.821 Å) is reasonably longer than that for **5a** (M = Si, 1.69 Å).

The thermal reaction of **3b** would proceed via the initial cleavage of a Ge–O bond to give aminoxygermyl radical **2b**, which was assumed as a key reactive intermediate during the addition of TEMPO to germylene (**1b**) (Scheme 2). Similarly to the formation of **5a** during the reaction of silylene (**1a**) with TEMPO, homolysis of N–O bond in **2b** would produce the transient germanone

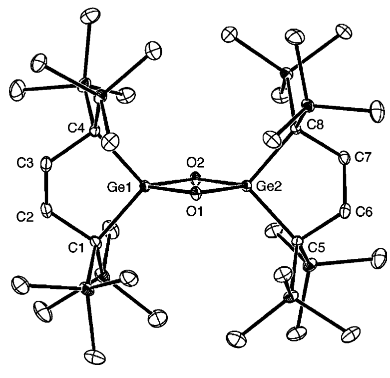
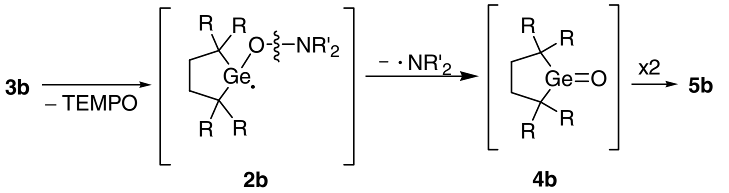


Fig. 1. Molecular structure of digermadioxetane (**5b**). Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ge1–O1 1.821(2), Ge1–O2 1.822(2), Ge2–O1 1.820(2), Ge2–O2 1.822(2), Ge1–O1–Ge2 94.54(8), Ge1–O2–Ge2 94.45(8), O1–Ge1–O2 85.49(8), O1–Ge2–O2 85.52(8). Distance between Ge1 and Ge2 atoms is 2.6748(3) Å.

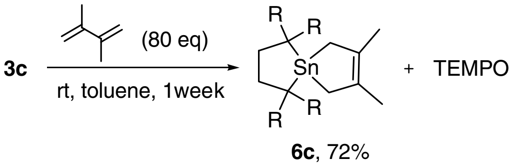


Scheme 2.

(**4b**), whose dimerization will give 1,3-digermadioxetane (**5b**).

2.2. Thermal reaction of stannylene-TEMPO 1:2 adduct 3c

Whereas the production of a distannadioxetane by the reaction of bis[bis(trimethylsilyl)methyl]stannylene dimer with trimethylamine-*N*-oxide has been reported [6], thermolysis of stannylene-TEMPO 1:2 adduct **3c** at 50 °C for 14.5 h in benzene-d_6 showed apparently no reaction; **3c** was recovered quantitatively without formation of the corresponding distannadioxetane. However, when **3c** was kept in toluene in the presence of excess 2,3-dimethyl-1,3-butadiene at room temperature, an adduct of stannylene (**1c**) to the butadiene was obtained in 72% yield (Eq. 2) together with TEMPO, which was detected by ESR. A similar reaction of a stannylene by 2,3-dimethylbutadiene is well established [6].



(2)

$$\mathbf{3c} \underset{+\text{TEMPO}}{\overset{-\text{TEMPO}}{\rightleftharpoons}} \mathbf{2c} \underset{+\text{TEMPO}}{\overset{-\text{TEMPO}}{\rightleftharpoons}} \mathbf{1c}$$

Scheme 3.

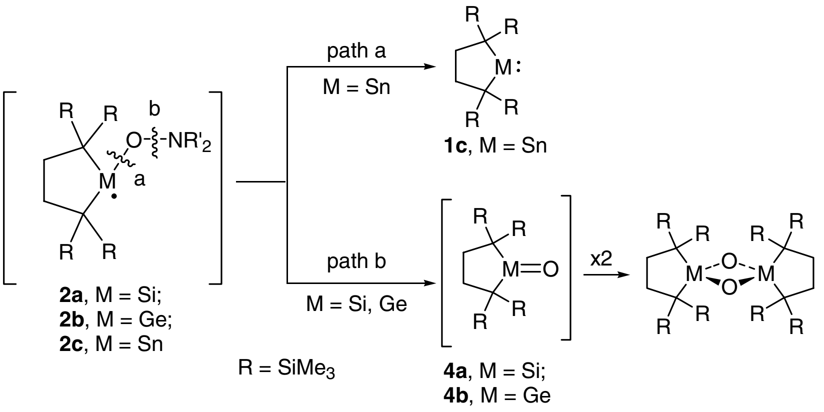
These behaviors are suggestive of the thermal equilibrium among stannylene (**1c**), aminoxystannyl radical **2c**, and 1:2 adduct **3c** occurring even at room temperature (Scheme 3).

2.3. Comparison of the fate of aminoxy-substituted group-14 element radicals 2a–2c

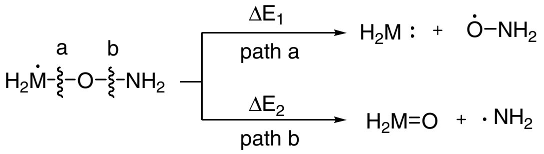
The present results suggest that there are two possible unimolecular decomposition pathways of radicals **2a**–**2c** in the absence of excess TEMPO as shown in Scheme 4. When M = Si and Ge, N–O bond fission (path b) is preferred, while M–O bond fission (path a) is favored when M = Sn.

In combining the previous results [3], the fate of radicals **2a**–**2c** is diverse as follows: (1) Aminoxysilyl radical **2a** favors the N–O bond fission (path b) to give the corresponding silanone (**4a**). The N–O bond fission of **2a** is too fast to compete with the addition of extra TEMPO giving 1:2 adduct **3a**. (2) Aminoxygermyl radical **2b** also favors the N–O bond fission but in the presence of excess TEMPO, addition of TEMPO to **2b** occurs to give **3b** preferably. (3) Aminoxystannyl radical **2c** favors the M–O bond fission (path a) rather than the N–O bond fission to afford stannylene (**1c**), while addition of TEMPO to **2c** occurs competitively to afford **3c**.

To elucidate the origin of the selectivity, DFT calculations were carried out for the model reactions by using GAUSSIAN 98 program [7] (Scheme 5). The reaction energies of ΔE_1 and ΔE_2 for path a and path b, respectively, are summarized in Table 1.



Scheme 4.



Scheme 5.

Table 1
Theoretical energies for M–O and N–O bond fissions in the reactions in Scheme 5

M	ΔE_1 (kcal/mol)[a]	ΔE_2 (kcal/mol)[a]
Si	42.1 (49.6)	11.4 (−2.0)
Ge	28.6 (28.0)	20.0 (13.8)
Sn	23.0	31.2

[a] Calculations were performed at the B3LYP/LANL2DZ level and at the ROB3LYP/LANL2DZ levels for closed-shell and open-shell molecules, respectively. In parentheses are shown the results obtained by the calculations at the B3LYP/6-311+G(2d,p) and ROB3LYP/6-311+G(2d,p) levels for closed-shell and open-shell molecules, respectively.

The ΔE_1 of path a decreases in the order Si > Ge > Sn, while that of path b decrease in the inverse order; Sn > Ge > Si. The results are qualitatively acceptable. A major factor determining the order of ΔE_1 will be the relative stability of H_2M, which is larger in the order Sn > Ge > Si. Because relative stability of M=O bond is larger in the order Si > Ge > Sn, the tendency is reflected to the order of ΔE_2. The theoretical calculations showed clearly ΔE_1 is larger than ΔE_2 for M = Si and Ge, while ΔE_1 is smaller than ΔE_2 for M = Sn. The results predict the favorable N–O bond fission (path b) for M = Si and Ge and the favorable M–O bond fission (path a) for M = Sn, being in good accord with our experimental results. At the higher level of calculations, ΔE_2 for M = Si is slightly exothermic, while ΔE_2 for M = Ge is significantly endothermic, as shown in parentheses in Table 1. The results may explain the difference in the reactions between **2a** and **2b** in the presence of excess TEMPO; path b for **2a** is too rapid to compete the addition of TEMPO, while path b for **2b** is endothermic, and hence, can compete with the addition of TEMPO. Apparent diversity of the addition reactions among **1a**–**1c** with TEMPO and of their reverse decompositions were understood by the systematic change of the intrinsic properties of the group-14 elements.

3. Experimental

3.1. General methods

^{1}H, ^{13}C, ^{29}Si, and ^{119}Sn NMR spectra were measured on a Bruker AC300P NMR and/or a Bruker AVANCE400 spectrometers. EI mass spectra were recorded on a JEOL JMS-600D and a HX-110 mass spectrometers.

3.1.1. Improved synthesis of dichlorogermacyclopentane (*7b*) and dichlorostannacyclopentane (*7c*)

Dialkylgermylene (**1b**) and dialkylstannylene (**1c**) were synthesized by the reduction of the corresponding dichlorogermane (**7b**) [2b] and dichlorostannane (**7c**) [8] using potassium graphite. Although the reactions of 1,4-dilithio-1,1,4,4-tetrakis(trimethylsilyl)butane (**8**) with tetrachlorogermane and tetrachlorostannane in THF gave **7b** and **7c** in the very low yields of 15–25% and 22%, respectively, the yields were remarkably improved by using copper cyanide (I) as an additive.

In a Schlenk tube (100 ml) equipped with a magnetic stirrer bar, a mixture of lithium wire (252 mg, 36 mmol), 1,1-bis(trimethylsilyl)ethylene (5.01 g, 29 mmol), and THF (20 ml) was stirred for a day under argon. When the resulted solution of 1,4-dilithiobutane (**8**) was added to copper cyanide (I) (3.45 g, 39 mmol) in another Schlenk tube (100 ml) equipped with a stirrer bar, an exothermic reaction took place to give a black solution, to which tetrachlorogermane (3.14 g, 15 mmol) was added at 0 °C and then the mixture was stirred overnight. Removal of the resulting salts after changing the solvent to hexane and the Kugel–Rohr distillation afforded **7b** in 63% yield (4.48 g, 9.2 mmol) as colorless crystals. By applying a similar procedure as stated above, **7c** was obtained in 66% yield as a while solid. The spectral data for **7b** [2b] and **7c** [8] were in agreement with those reported.

3.2. Thermolysis of germylene-TEMPO 1:2 adduct *3b* at 50 °C

An NMR tube containing adduct **3b** (26.0 mg, 3.56×10^{-5} mol) in toluene-d_8 (0.5 ml) sealed under vacuum was heated at 50 °C for 3 h. A ^{1}H NMR spectrum of the reaction mixture showed almost quantitative formation of 1,3-digermadioxetane (**5b**) and 2,2,6,6-tetramethylpiperidine. Evaporation of toluene-d_8 and tetramethylpiperidine in vacuo afforded **5b** in 68% yield. **5b**: colorless crystals; m.p. 292–293 °C; ^{1}H NMR (300 MHz, C_6D_6, δ) 0.38 (s, 72H, $SiMe_3$), 1.97 (s, 8H, CH_2); ^{13}C NMR (75.4 MHz, C_6D_6, δ) 4.3, 19.7, 35.7; ^{29}Si NMR (59.6 MHz, C_6D_6, δ) 4.5; MS (EI, 70 eV) m/z (%) 868 (100, M^+), 507 (94), 419 (68), 344 (81); Anal. Calc. for $C_{32}H_{80}Ge_2O_2Si_8$: C, 44.34; H, 9.30%. Found: C, 44.14; H, 9.03%.

3.3. X-ray crystallography of 1,3-digermadioxetane (*5b*)

A single crystal of **5b** suitable for X-ray diffraction study was obtained by recrystallization from toluene. X-Ray data were collected on a Rigaku/MSC Mercury CCD diffractometer with graphite monochromated Mo Kα radiation (λ 0.71073 Å). The data were corrected for Lorentz and polarization effects. The structures were solved by direct methods and refined by full-matrix leastsquares against F^2 using all data [9]. Crystallographic data for **5b**: $C_{32}H_{80}Ge_2O_2Si_8$: mw 866.85, triclinic, primitive, $a = 9.4641(1)$, $b = 11.8249(2)$, $c = 22.609(1)$ Å, $\alpha = 82.96(1)°$, $\beta = 84.54(1)°$, $\gamma = 67.082(8)°$, $V = 2309.8(2)$ Å^3, Temperature = −100.0 °C, space group $P\bar{1}$ (no. 2), $Z = 2$, $D_{calc} = 1.246$ g/cm^3; μ(Mo Kα) = 15.34 cm^{-1}; 31,536 reflections measured, 12,933 unique ($R_{int} = 0.040$). No. reflections $[I > 2\sigma(I)]$ 8167. The final R_1 and wR_2 values were 0.040 and 0.088, respectively.

3.4. Thermolysis of stannylene-TEMPO 1:2 adduct **3c** at 50 °C

An NMR tube containing adduct **3c** (21.0 mg, 2.72×10^{-5} mol) in benzene-d$_6$ (0.5 ml) sealed under vacuum was heated at 50 °C for 14.5 h. A ^{1}H NMR spectrum of the reaction mixture showed no apparent decomposition of **3c**.

3.5. Thermal reaction of stannylene-TEMPO 1:2 adduct **3c** in the presence of 2.3-dimethyl-1,3-butadiene

To stannylene-TEMPO adduct **3c** (23.9 mg, 3.1×10^{-5} mol) in a degassed glass-tube, 2,3-dimethyl-1,3-butadiene (208 mg, 2.5×10^{-3} mol) and toluene (1 ml) were transferred by the vacuum-line distillation. After the mixture was kept at room temperature for a week, toluene and excess 2,3-dimethylbutadiene were removed in vacuo and then benzene-d$_6$ (0.5 ml) was introduced to the mixture. The yield of adduct **6c** was determined to be 72% by ^{1}H NMR spectroscopy using durene as an internal standard. **6c**: colorless crystals; m.p. 106 °C (decomp.); ^{1}H NMR (400 MHz, C_6D_6, δ) 0.17 (s, 36H, SiMe$_3$), 1.78 (s, 6H, CH$_3$), 2.01 [s, 4H, $^2J(^1\text{H}–^{119}\text{Sn}) = 65.2$ Hz, CH$_2$], 2.02 [s, 4H, $^3J(^1\text{H}–^{119}\text{Sn}) = 31.0$ Hz, CH$_2$]; ^{13}C NMR (100.6 MHz, C_6D_6, δ) 3.7 (SiMe$_3$), 12.5 (C), 21.5 (CH$_3$), 27.9 [CH$_2$, $^1J(^{13}\text{C}–^{119}\text{Sn}) = 260.6$ Hz, $^1J(^{13}\text{C}–^{117}\text{Sn}) = 248.5$ Hz], 35.0 [CH$_2$, $^2J(^{13}\text{C}–^{119}\text{Sn}) = 12.1$ Hz], 131.4 (C=C); ^{29}Si NMR (79.5 MHz, C_6D_6, δ) 3.6, ^{119}Sn NMR (149.2 MHz, C_6D_6, δ) 166.2; MS (70eV, EI) *m/z* (%) 531 ($M^+ - 15$, 6.1), 464 (57.8), 292 (100); Anal. Calc. for $C_{22}H_{50}Si_4Sn$: C, 48.42; H, 9.24% Found: C, 48.16; H, 9.11%.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 223660, for compound **5b**. 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).

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