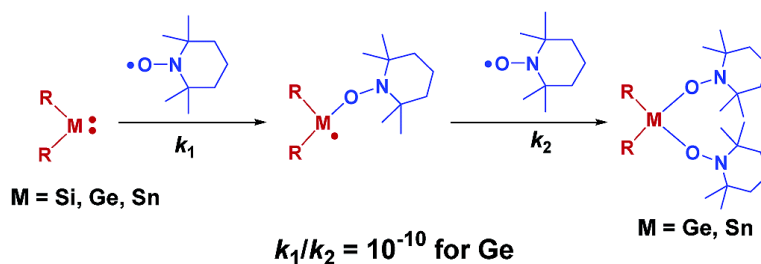Communication

Addition of Stable Nitroxide Radical to Stable Divalent Compounds of Heavier Group 14 Elements

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Addition of Stable Nitroxide Radical to Stable Divalent Compounds of Heavier Group 14 Elements

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Because both doublet radicals and group 14 divalent compounds[1] are usually reactive intermediates, reactions between these electron-deficient species have been very poorly studied. The reaction of triplet diphenylcarbene with a persistent nitroxide radical such as 2,2,6,6-tetramethylpiperidine *N*-oxide (TEMPO) was found by Scaiano and co-workers[2] to be very fast, giving benzophenone and 2,2,6,6-tetramethylpiperidine; the second-order rate constant was 2.7×10^8 M^{-1} s^{-1} in acetonitrile at room temperature. Despite the fundamental importance, the reactions between doublet radicals and heavier group 14 divalent species with singlet electronic configuration have not been investigated thus far. We wish herein to report the characteristics of the reactions of TEMPO with stable metallylenes **1**,[3] **2**,[4] and **3**.[5]
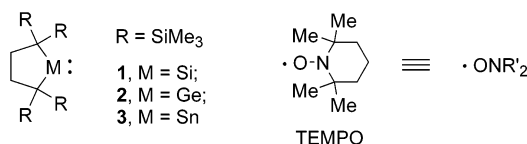
The reactions of germylene **2** and stannylene **3** with 2 equiv of TEMPO gave the corresponding 1:2 adducts **4** and **5**, respectively (eq 1).[6,7]
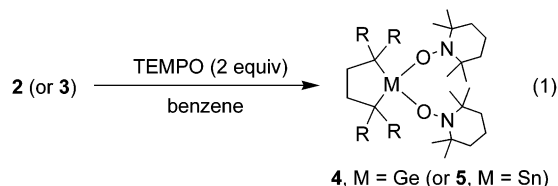
Molecular structure of adduct **4** determined by X-ray crystallography[8] is shown in Figure 1. The Ge—C bond distances are slightly longer than those of germylene **2** (2.010 and 2.020 Å).[4] The Ge—O bond distances are significantly lengthened compared to a typical Ge—O bond distance (1.76 Å),[9] probably due to the steric congestion around the germanium atom, while the N—O bond distances are within those reported for N—O(Ge) bonds.[10] For the details of X-ray structures of **4** and **5**, see the Supporting Information.

The reactions of **2** and **3** with TEMPO are easily understood by the stepwise addition of TEMPO to **2** and **3** via intermediary radicals **6** and **7**, respectively (eq 2).
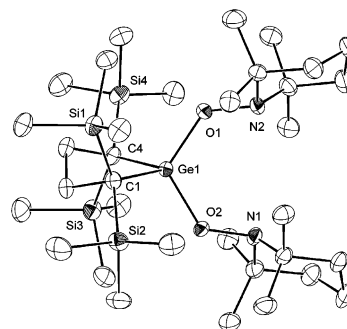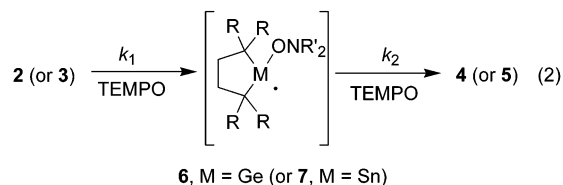

Figure 1. Molecular structure of **4**. Hydrogen atoms are omitted for clarity. Selected bond length (Å) and angles (deg): Ge1—O2 1.824(2), Ge1—O2 1.826(2), Ge1—C1 2.060(3), Ge1—C4 2.056(4), O1—N1 1.483(4), O2—N2 1.480(4), O1—Ge1—O2 115.7(1), C1—Ge—C4 95.0(1), Ge1—O1—N1 126.9(2), Ge1—O2—N2 127.1(2).

The rate profile of the reaction of TEMPO with germylene **2** was investigated in more detail. Even though the reaction was performed using a large excess amount of TEMPO, no ESR signals due to germyl radical **6** were observed. The result indicates that the rate for the second step (k_2) is much faster than that of the first step (k_1) to allow the use of the steady-state approximation for intermediate radical **6**. The decay of TEMPO monitored by ESR spectroscopy obeyed pseudo-first-order kinetics with rate constant k_{obs} (eq 3), when the initial concentrations of **2** were ca. 20 times larger than those of TEMPO. Second-order rate constant k_1 was determined as a half of the slope of a linear relationship between k_{obs} and the initial concentrations of **2**.

$$-\frac{d[\text{TEMPO}]}{dt} = k_{obs}[\text{TEMPO}] = 2k_1[\mathbf{2}][\text{TEMPO}] \quad (3)$$

Rate constant k_1 for the addition of TEMPO to germylene **2** was determined to be about 1.5×10^{-2} M^{-1} s^{-1} at 274 K. From the temperature dependence of k_1, the activation parameters were determined as follows: $\Delta H^{\ddagger} = 9.7 \pm 0.5$ kcal mol^{-1} and $\Delta S^{\ddagger} = -32 \pm 2$ cal mol^{-1} K^{-1}. Rate constant k_2 for the second step was not determined in the present reaction but was supposed to be quite large. While usual radical coupling rates range in solution between 10^9 and 10^{10} M^{-1} s^{-1}, the rates have been reported to be 7.2×10^8 and 3.4×10^8 M^{-1} s^{-1} for the reactions of TEMPO with Bu$_3$Ge• and Ph$_3$Ge•, respectively.[11] On this basis, k_1 is estimated to be about 10^{10} times slower than the second step.[12]

The observed huge difference between k_1 and k_2 is interesting but would be explained as a consequence of a simple perturbation theory. The second step, a radical–radical coupling, involves a SOMO–SOMO interaction between two radicals (two-electron interaction) resulting large stabilization of the system, and hence, the reaction rate is usually close to that for a diffusion-controlled reaction. On the other hand, because germylene **2** has a high-lying nonbonding HOMO and a low-lying pπ LUMO, the important

orbital interaction between TEMPO and **2** during the first step should involve either a SOMO−HOMO (three-electron) interaction or a SOMO−LUMO (one-electron) interaction depending on the direction of the approach of the two substrates.[13] The stabilization energy for each interaction is much smaller than the SOMO−SOMO interaction, which makes the first-step reaction much slower than the second radical coupling reaction.[13]

Interestingly, 1,3-dioxadisiletane derivative **8** was obtained in 66% yield together with 2,2,6,6-piperidine (**9**, 71%) during the reaction of **1** with 1 equiv of TEMPO in benzene (eq 4).[15] Even when a large excess amount of TEMPO was used, a 1:2 adduct, a silicon analogue of **4** (or **5**), was never produced.
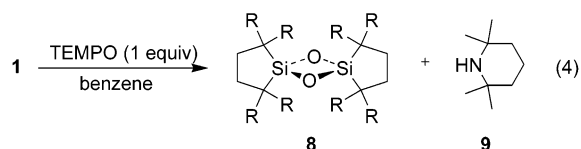
Dioxadisiletane **8** will form via a cleavage of the N−O bond of an initial radical adduct **10**, giving silanone **11**[16] followed by the dimerization (eq 5).
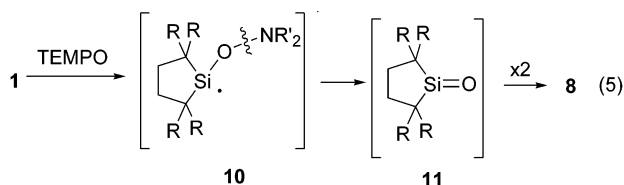
Radical **10** is suggested to undergo preferably a unimolecular N−O bond cleavage rather than an expected coupling with TEMPO, in contrast to the corresponding germanium and tin radicals (**6** and **7**). In agreement with this explanation, theoretical calculations for model reactions (eq 6) at the B3LYP/6-311+G(2d,p) level showed that the reaction for M = Si is slightly exothermic with $\Delta E = -2.0$ kcal mol^{-1}, while the reaction for M = Ge is highly endothermic with $\Delta E = 13.8$ kcal mol^{-1}. Further works are in progress.
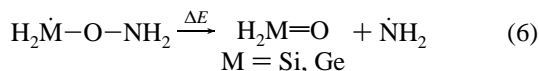
$$H_2\dot{M}-O-NH_2 \xrightarrow{\Delta E} H_2M=O + \dot{N}H_2 \qquad (6)$$
$$M = Si, Ge$$

Supporting Information Available: Experimental details for the reactions of **1**−**3** with TEMPO and tables giving the details of the X-ray structure determination, bond lengths, and bond angles of **4**, **5**, and **8** (PDF). X-ray crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(6) A 1:2 adduct of a stable diaminogermylene to TEMPO was detected in the quenching of the polymerization of quinones with the diaminogermylene by TEMPO. Kobayashi, S.; Iwata, S.; Abe, M.; Shoda, S. *J. Am. Chem. Soc.* **1995**, *117*, 2187.

(7) Typically, when a mixture of dialkylgermylene **2** (0.0685 mmol) with TEMPO (0.17 mmol) dissolved into dry benzene (0.5 mL), the solution turned from original orange to colorless within a minute at room temperature with the formation of colorless precipitates. After stirring for 30 min, evaporation of solvents and excess TEMPO afforded the white precipitates of **4** in 70% yield. Recrystallization from benzene gave single crystals of **4** suitable for X-ray analysis. **4**: colorless crystals, mp 122 °C dec; ¹H NMR (THF-d_8, 273 K, δ) 0.33 (br s, 36H, SiMe₃), 1.19 (s, 6H, CH₃), 1.23 (s, 6H, CH₃), 1.33 (s, 6H, CH₃), 1.50−1.75 (m, 12H, CH₂), 1.80 (s, 6H, CH₃), 2.52 (br s, 2H, CH₂), 2.55 (br s, 2H, CH₂); ¹³C NMR (THF-d_8, 248 K, δ) 3.5, 5.8, 6.7, 9.4, 17.5, 22.6, 24.2, 26.9, 35.3, 35.8, 35.9, 42.4, 42.7, 61.3, 62.3; ²⁹Si NMR (THF-d_8, 248 K, δ) 3.4, 6.0; MS (FAB, 3-nitrobenzyl alcohol) m/z (%) 731 (4.8, M + H⁺), 588 (11.2), 574 (55.9), 419 (100); Anal. Calcd for C₃₄H₇₆GeN₂O₂Si₄: C, 55.95; H, 10.49; N, 3.84%. Found: C, 55.65; H, 10.61; N, 3.76%. **5**: 45% isolated yield; air-sensitive pale yellow crystals, mp 145 °C; ¹H NMR (C₆D₆, δ) 0.41 (s, 36H, SiMe₃), 1.28 (s, 12H, CH₃), 1.47−1.70 (m, 24H, CH₃ + CH₂), 2.00 (m, 2H, CH₂), 2.10 (br s, 2H, CH₂); ¹³C NMR (C₆D₆, δ) 4.9, 17.4, 21.4, 33.6, 34.6, 41.4, 60.8; ²⁹Si NMR (C₆D₆, δ) 4.9; Anal. Calcd for C₃₄H₇₆N₂O₂Si₄Sn: C, 52.62; H, 9.87; N, 3.61%. Found: C, 52.32; H, 9.59; N, 3.44%.

(8) X-ray analysis of **4** (293 K): C₃₄H₇₆O₂GeSi₄N₂·(C₆H₆); colorless prism; monoclinic; space group $P2_1/c$ (No. 14); $a = 11.4137(5)$ Å, $b = 18.247(1)$ Å, $c = 22.1105(8)$ Å, $\beta = 96.798(2)°$, $V = 4572.5(4)$ Å³; $Z = 4$; D_{calcd} 1.174 g/cm³; μ(MoKα) = 8.07 cm^{-1}; $2\theta_{max} = 54.7°$; of 36422 measured reflections, 9211 were independent and 5878 observed with $I > 2\sigma(I)$. R1 = 0.053, wR2 (all data) 0.156 for 442 parameters.

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(12) In reality, rate constant k_2 would be somewhat smaller than 10⁸ M^{-1} s^{-1} because of the highly sterically hindered environment around the radical center.

(13) If we assume TEMPO is an electrophilic radical because of the electronegativity of oxygen, the reaction should be controlled by the SOMO−HOMO interaction. According to the perturbation theory including overlap,[14] the destablization energy of the SOMO is much larger than the stabilization energy of the HOMO after the SOMO−HOMO interation, and hence, the stabilization of the whole system may be not very large.

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(15) **8**: colorless crystals; mp 258 °C dec; ¹H NMR (C₆D₆, δ) 0.38 (s, 72H, SiMe₃), 2.01 (s, 8H, CH₂); MS (EI, 70 eV) m/z (%) 776 (2.0, M⁺), 761 (3.2), 531 (17.8), 373 (60.3), 147 (15.8), 73 (100); Anal. Calcd for C₃₂H₈₀O₂Si₁₀: C, 49.41; H, 10.37%. Found: C, 49.64; H, 10.45%. Measurement of the ¹³C and ²⁹Si NMR spectra of **5** was unsuccessful because of very low solubility of **8** in organic solvents. For X-ray data, see the Supporting Information.

(16) For a recent review on silanone derivatives generated as reactive intermediates, see: Tokitoh, N.; Okazaki, R. In *The Chemistry of Organic Silicon Compounds*, *Volume 2*; Rappoport, Z., Apeloig, Y., Eds.; John Wiley & Sons: New York, 1999; Part 2, p 1063−1103. See also: Takeda, N.; Tokitoh, N.; Okazaki, R. *Chem. Lett.* **2000**, 244. Khabashesku, V. N.; Kudin, K. M.; Margrave, J. L.; Fredin, L. *J. Organomet. Chem.* **2000**, *595*, 248.

(17) Since the environment around the ring silicon atom in **10** is much more crowded than that around ring germanium in **6**, the radical coupling between **10** and TEMPO will be somewhat slower than that between **6** and TEMPO.

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