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Photolysis of cyclotrigermane. Synthesis and chemistry of digermiranes and digermetanes containing sulfur and selenium

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parameter shifts to standard deviations being all less than 0.1 and no significant features in the final difference maps. Main features of the refinements appear in Table IV. Atomic coordinates are given in Table V and VI.

Registry No. 1, 115590-65-3; 2, 115590-66-4; 3, 115590-67-5; $Fe_2(CO)_9$, 15321-51-4; $CH_3(\equiv CN(C_2H_5)_2$, 4231-35-0; Me_3NO, 1184-78-7; $(C_6H_5)_2CN_2$, 883-40-9; diphenylacetylene, 501-65-5.

Supplementary Material Available: Tables of anisotropic temperature factors, important least-squares planes, and hydrogen coordinates (6 pages); listings of observed and calculated structure factors (37 pages). Ordering information is given on any current masthead page.

Photolysis of Cyclotrigermane. Synthesis and Chemistry of Digermiranes and Digermetanes Containing Sulfur and Selenium

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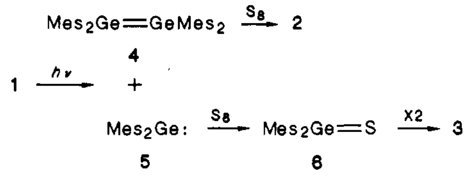
Photolysis of hexamesitylcyclotrigermane (**1**) produces tetramesityldigermene (**4**) and dimesitylgermylene (**5**) which react with elemental sulfur to give 2,2,3,3-tetramesitylthiadigermirane (**2**) and 2,2,4,4-tetramesityl-1,3,2,4-dithiadigermetane (**3**). Selenium also reacts with digermene **4** to afford 2,2,3,3-tetramesitylselenadigermirane (**7**). Photolysis of **2** with 2,3-dimethyl-1,3-butadiene produces only products from dimesitylgermylene (**5**) and dimesitylgermanethione (**6**). The reactions of **2** with pyridine *N*-oxide, sulfur, and selenium yield digermetanes containing O, S, and Se.

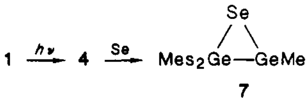
Introduction

In recent years interest in the chemistry of small-ring compounds has remarkably increased because of their unique properties resulting from strain energy. In contrast to rather extensive studies of the chemistry of small-ring silanes,[2] very little is known about germanium analogues.[3-8] Few small-ring compounds containing Ge–Ge bonds[3c,d,4-8] have been studied, and direct reaction of a digermene with sulfur and selenium appears to be the most suitable method for the synthesis of thia- and selenadigermiranes. We report here a convenient synthesis and some chemistry of thia- and selenadigermiranes, which cleanly reacted with pyridine *N*-oxide, sulfur, and selenium to afford heteroatom-containing digermetanes.

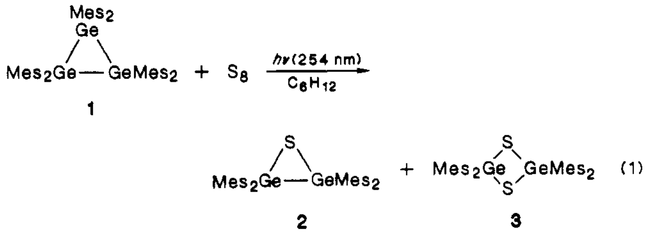
Scheme I



Scheme II



Results and Discussion



Mes = 2,4,6-trimethylphenyl

Synthesis of Thiadigermirane and Selenadigermirane.[4] Irradiation of a cyclohexane solution of hexamesitylcyclotrigermane (**1**, 0.1 mmol) and elemental sulfur (0.8 mmol) in a quartz tube at room temperature with a low-pressure mercury lamp produced a colorless crystalline product, 2,2,3,3-tetramesitylthiadigermirane (**2**), in 26% yield. Also formed was 2,2,4,4-tetramesityl-1,3,2,4-dithiadigermetane (**3**) in 24% yield (eq 1). Thiadigermirane **2** was readily separated from **3** by flash column chromatography, and its structure was confirmed by ^1H NMR and mass spectroscopic analyses and also by an X-ray diffraction study. Thiadigermirane **2** thus obtained is stable

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(1) (a) The University of Tsukuba. (b) Sankyo Co., Ltd.

(2) (a) Lambert, R. L.; Seyferth, D. *J. Am. Chem. Soc.* **1972**, *94*, 9246. (b) Conlin, R. T.; Gaspar, P. P. *J. Am. Chem. Soc.* **1976**, *98*, 3715. (c) Baudler, M.; Jongebloed, H. *Z. Anorg. Allg. Chem.* **1979**, *458*, 9. (d) Hluchy, J.; Klingebiel, U. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 301. (e) Masamune, S.; Hanzawa, Y.; Murakami, S.; Bally, T.; Blount, J. F. *J. Am. Chem. Soc.* **1982**, *104*, 1150. (f) Ishikawa, M.; Sugisawa, H.; Kumada, M.; Higuchi, T.; Matsui, K.; Hirotsu, K.; Iyoda, J. *Organometallics* **1983**, *2*, 174. (g) Masamune, S.; Murakami, S.; Tobita, H.; Williams, D. J. *J. Am. Chem. Soc.* **1983**, *105*, 7776. (h) Ando, W.; Hamada, Y.; Sekiguchi, A.; Ueno, K. *Tetrahedron Lett.* **1982**, *23*, 5323. (i) Ando, W.; Hamada, Y.; Sekiguchi, A.; Ueno, K. *Tetrahedron Lett.* **1983**, *24*, 4033. (j) Michalczyk, M. J.; West, R.; Michl, J. *J. Chem. Soc., Chem. Commun.* **1984**, 1525. (k) West, R.; De Young, D. J.; Haller, K. J. *J. Am. Chem. Soc.* **1985**, *107*, 4942. (l) Yokelson, H. B.; Millevolte, A. J.; Gillette, G. R.; West, R. *J. Am. Chem. Soc.* **1987**, *109*, 6865.

(3) (a) Baudler, M. *Pure Appl. Chem.* **1980**, *52*, 755. (b) Krebs, A.; Berndt, J. *Tetrahedron Lett.* **1983**, *24*, 4083. (c) Ando, W.; Tsumuraya, T.; Sekiguchi, A. *Tetrahedron Lett.* **1985**, *26*, 4523. (d) Ando, W.; Tsumuraya, T. *Tetrahedron Lett.* **1986**, *27*, 5105.

(4) Preparation of thiadigermirane and selenadigermirane was partly reported previously; Ando, W.; Tsumuraya, T. *Tetrahedron Lett.* **1986**, *27*, 3251.

(5) Masamune, S.; Hanzawa, Y.; Williams, D. J. *J. Am. Chem. Soc.* **1982**, *104*, 6136.

(6) Snow, J. T.; Murakami, S.; Masamune, S.; Williams, D. J. *Tetrahedron Lett.* **1984**, *25*, 4191.

(7) Ando, W.; Tsumuraya, T. *J. Chem. Soc., Chem. Commun.* **1987**, 1514.

(8) (a) Espenbetov, A. A.; Struchkov, Yu. Y.; Kolesnikov, S. P.; Nefedov, O. M. *J. Organomet. Chem.* **1984**, *275*, 33. (b) Nefedov, O. M.; Egorov, M. P.; Gal'minas, A. M.; Kolesnikov, S. P.; Krebs, A.; Berndt, J. *J. Organomet. Chem.* **1986**, *301*, C21.

(9) Germylene was reported to react with elemental sulfur to yield germathione intermediate: Lange, L.; Meyer, B.; du Mont, W.-W. *J. Organomet. Chem.* **1987**, *329*, C17.

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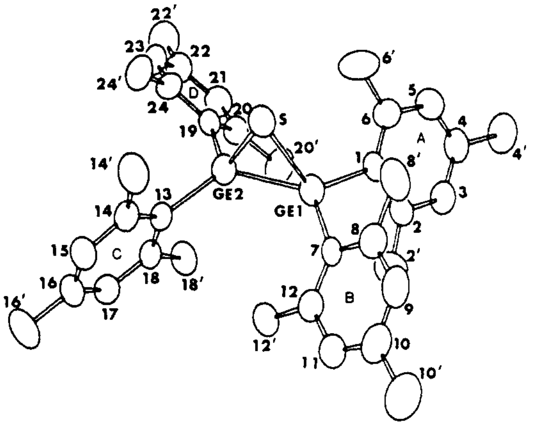


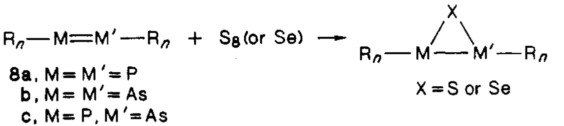
Figure 1. Molecular conformation and atomic labeling of **2**.

toward atmospheric oxygen and moisture and does not react with alcohol at room temperature. The products **2** and **3** are best rationalized as arising from tetramesityldigermene (**4**) and dimesitylgermylene (**5**) generated from the photolysis of cyclotrigermane **1**. Digermene **4** would by precedent[2k] be expected to react with elemental sulfur to afford **2**. The formation of dithiadigermetane **3** is not surprising. We suggest a route involving the reaction of dimesitylgermylene (**5**) and sulfur to dimesitylgermanethione (**6**). Germanethione **6** would be expected to dimerize in a head-to-tail fashion to produce **3** (Scheme I).

Similar results were obtained from the photolysis of **1** (0.3 mmol) and selenium (1.2 mmol) in cyclohexane at room temperature. In this reaction colorless crystals identified as 2,2,3,3-tetramesitylselenadigermirane (**7**) was obtained in 66% yield, and no adducts from dimesitylgermylene (**5**) and selenium could be found (Scheme II).

Although it has been well-known that seleniranes are unstable molecules,[10] selenadigermirane **7** is thermally stable and does not decompose when heated to its melting point at 217–219 °C.

Under normal conditions alkenes do not react with sulfur or selenium, but recently, diphosphene **8a**,[11a-c] diarsene **8b**,[11d] phosphaarsene **8c**,[11e] and disilene **9**[2k] were reported to react with sulfur or selenium to yield the corresponding three-membered ring compounds (eq 2).



(2)

Crystal Structure of 2. The structure of **2** was confirmed by an X-ray diffraction study. The molecular structure with an atomic labeling scheme is shown in Figure 1.

The thiadigermirane ring is a somewhat distorted equilateral triangle, and the bond lengths in the three-membered ring are 2.376 (2) Å for the Ge–Ge bond and 2.277 (3) and 2.263 (3) Å for the Ge–S bonds. The endocyclic bond angles of Ge(1), Ge(2), and S are 58.2 (1), 58.7 (1), and 63.1 (1)°, respectively. The four aryl substituents (rings A, B, C, and D) are each twisted about the C_{Ar}–Ge bond in the same direction, forming dihedral angles of 69.9, 55.2, 58.3, and 54.6° with the central thiadigermirane ring. The dihedral angles between mesityl rings are 69.3 (A:B), 57.6 (A:D), 76.7 (B:C), and 89.3 (C:D)°. The independent Ge–C_{Ar} bond lengths are 2.015 (9), 1.951 (8), 1.953 (7), and 1.947 (9) Å. The bond length of Ge(1)–C(1) is longer than other Ge–C_{Ar} bonds. The p orbital on C(1) is directed toward the methyl groups of C(8′) and C(20′), and to prevent these interactions the Ge(1)–C(1) bond is probably lengthened. Other bond lengths and angles for **2** are listed in Tables I and II.

Table I. List of Bond Lengths (Å) in 2 (Esd's in Parentheses)

Ge(1)–Ge(2)	2.376 (2)	C10)–C(10′)	1.508 (15)
Ge(1)–S	2.277 (3)	C(11)–C(12)	1.383 (12)
Ge(1)–C(1)	2.015 (7)	C(12)–C(12′)	1.534 (10)
Ge(1)–C(7)	1.951 (8)	C(13)–C(14)	1.433 (10)
Ge(2)–S	2.263 (3)	C(13)–C(18)	1.384 (11)
Ge(2)–C(13)	1.953 (7)	C(14)–C(15)	1.380 (11)
Ge(2)–C(19)	1.947 (9)	C(14)–C(14′)	1.490 (13)
C(1)–C(2)	1.409 (12)	C(15)–C(16)	1.357 (12)
C(1)–C(6)	1.352 (13)	C(16)–C(17)	1.409 (11)
C(2)–C(3)	1.412 (10)	C(16)–C(16′)	1.500 (12)
C(2)–C(2′)	1.446 (14)	C(17)–C(18)	1.391 (10)
C(3)–C(4)	1.359 (14)	C(18)–C(18′)	1.527 (11)
C(4)–C(5)	1.357 (13)	C(19)–C(20)	1.481 (12)
C(4)–C(4′)	1.547 (11)	C(19)–C(24)	1.365 (11)
C(5)–C(6)	1.425 (11)	C(20)–C(21)	1.384 (13)
C(6)–C(6′)	1.476 (14)	C(20)–C(20′)	1.487 (12)
C(7)–C(8)	1.407 (10)	C(21)–C(22)	1.365 (12)
C(7)–C(12)	1.374 (12)	C(22)–C(23)	1.414 (14)
C(8)–C(9)	1.372 (13)	C(22)–C(22′)	1.472 (15)
C(8)–C(8′)	1.522 (14)	C(23)–C(24)	1.381 (14)
C(9)–C(10)	1.388 (14)	C(24)–C(24′)	1.534 (13)
C(10)–C(11)	1.372 (10)		

Table II. Significant Bond Angles (deg) in 2 (Esd's in Parentheses)

Ge(2)–Ge(1)–S	58.2 (1)	C(1)–Ge(1)–C(7)	110.6 (3)
Ge(2)–Ge(1)–C(1)	122.7 (3)	C(13)–Ge(2)–C(19)	109.4 (1)
Ge(2)–Ge(1)–C(7)	124.0 (2)	Ge(1)–S–Ge(2)	63.1 (1)
S–Ge(1)–C(1)	118.7 (3)	Ge(1)–C(1)–C(2)	113.7 (6)
S–Ge(1)–C(7)	110.5 (3)	Ge(1)–C(1)–C(6)	123.9 (7)
C(1)–Ge(1)–C(7)	110.6 (3)	Ge(1)–C(7)–C(12)	123.9 (4)
Ge(1)–Ge(2)–S	58.7 (1)	Ge(1)–C(7)–C(8)	118.5 (6)
Ge(1)–Ge(2)–C(13)	124.5 (2)	Ge(2)–C(13)–C(14)	126.0 (6)
Ge(1)–Ge(2)–C(19)	122.8 (3)	Ge(2)–C(13)–C(18)	116.1 (3)
S–Ge(2)–C(13)	118.3 (2)	Ge(2)–C(19)–C(20)	121.9 (6)
S–Ge(1)–C(19)	112.4 (3)	Ge(2)–C(19)–C(24)	120.3 (5)

It is worth noting that the Ge–Ge bond length of 2.376 (2) Å is remarkably shorter than the normal bond lengths of 2.44 Å. The short Ge–Ge bond distance is not characteristic of three-membered rings because hexakis(2,6-dimethylphenyl)cyclotrigermane has longer than normal Ge–Ge bond lengths of 2.537–2.543 Å. Another structural feature of **2** is the nearly planar arrangement of the bonded carbon and germanium atoms around each germanium. The sum of the bond angles of C_{Ar}–Ge–Ge′, C'_{Ar}–Ge–Ge′, and C_{Ar}–Ge–C'_{Ar} around each germanium atom are 357.3 and 356.7°, respectively.

These results are interpreted in terms of Dewar's model of metal–olefin bonding.[12] In this model the bonding is viewed in terms of donation from the π orbitals of the olefin into a vacant orbital on the metal (σ bonding), accompanied by back-donation from a filled metal orbital into the π^* orbitals of the olefin (π bonding). Cremer and Kraka have used this model to describe the continuum

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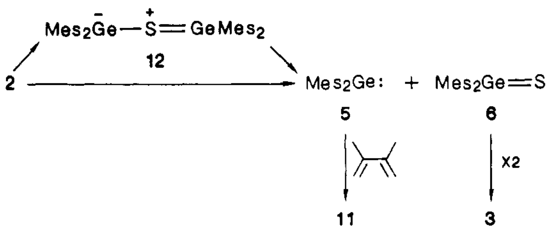
[10] Although seleniranes were known to decompose easily to olefins with the extruction of selenium, recently, we succeeded in the isolation of a stable selenirane: Ando, W.; Kumamoto, Y.; Tokitoh, N. *Tetrahedron Lett.* **1987**, *28*, 2867.

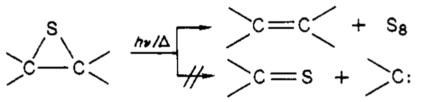
[11] (a) Escudié, J.; Couret, C.; Ranaivonjatavo, H.; Satgé, J.; Jaud, J. *Phosphorus Sulfur* **1983**, *17*, 221. (b) Yoshifuji, M.; Shibayama, K.; Inamoto, N.; Hirotsu, K.; Higuchi, T. J. *J. Chem. Soc.*, Chem. *Commun.* **1983**, 862. (c) Yoshifuji, M.; Shibayama, K.; Inamoto, N. *Chem. Lett.* **1984**, 603. (d) Couret, C.; Escudié, J.; Maudaule, Y.; Ranaivonjatavo, H.; Wolf, J.-G. *Tetrahedron Lett.* **1983**, *24*, 2769. (e) Escudié, J.; Couret, C.; Ranaivonjatavo, H.; Wolf, J.-G. *Tetrahedron Lett.* **1983**, *24*, 3625.

[12] (a) Dewar, M. J. S. *Bull. Soc. Chim. Fr.* **1951**, *18*, C71. (b) Chatt, J.; Duncanson, L. A. *J. Chem. Soc.* **1953**, 2939.

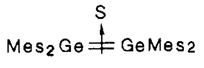
Scheme III



Scheme IV



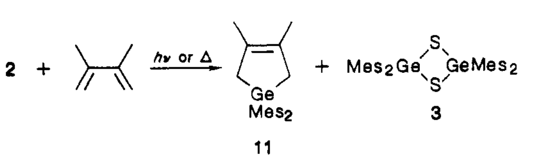
between three-membered rings and π complexes in the three-membered monosubstituted hydrocarbon rings, $\overline{\text{C–C–X}}$.[13] They predict that π-complex character is increased if the electron-acceptor ability of X toward an ethylene unit is increased. This model may apply to three-membered rings containing two germanium atoms, $\overline{\text{Ge–Ge–X}}$. In the case of 2, the Ge–Ge bond should be a better donor of π-electron density to the substituent and a better acceptor of electron density through back-donation. On the other hand, sulfur is more electronegative than germanium and should act as a better acceptor of electron density but a poor donor. All these facts suggest that 2 has some of the character of π-complex **10**. Re-



10

cently, West et al. reported similar structural features of thiadisilirane[2k] and oxadisilirane,[21] and Grev et al. reported a theoretical investigation of three-membered rings containing two silicon atoms, $\overline{\text{Si–Si–X}}$.[14]

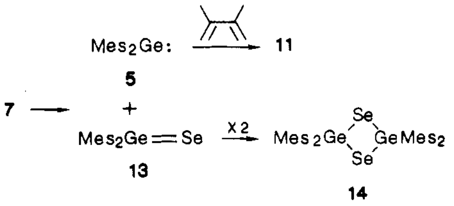
Photolysis and Pyrolysis of 2 and 7. Irradiation of a cyclohexane solution of **2** (0.1 mmol) and 2,3-dimethyl-1,3-butadiene (5 mmol) with a low-pressure mercury lamp at room temperature resulted in complete disappearance of **2** and the formation of germacyclopentene **11** and **3** in 42% and 18% yields, respectively. Tetramesityldigermene **4** was not be detected even spectroscopically.[15] Similar results were obtained in a flow copyrolysis of **2** and 2,3-dimethyl-1,3-butadiene at 500 °C (eq 3).



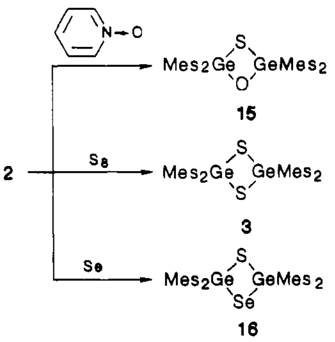
(3)

Precedent dictates that **11** arises from addition of dimesitylgermylene (**5**) to the butadiene, and **3** is produced by the dimerization of dimesitylgermanethione (**6**). It is thus clear that **2** undergoes cycloelimination to produce **5** and **6** either via the simultaneous cleavage of both the Ge–Ge and Ge–S bonds or via the germylenegermanethione ylide **12** (Scheme III). An attempt to observe **12** by a low-temperature matrix-isolation technique was not successful, since **2** did not decompose at 77 K in a hydrocarbon matrix on irradiation with a low-pressure mercury lamp.

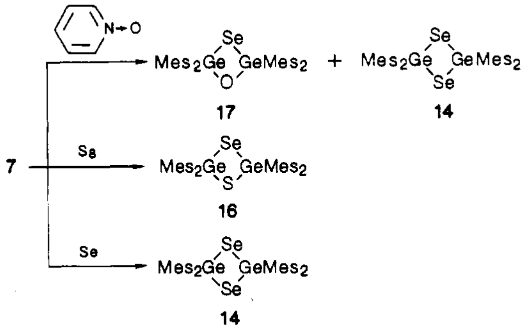
Scheme V



Scheme VI



Scheme VII



The above results are in contrast to those obtained from the photochemical or thermal decomposition of thiiranes; usually thiiranes decompose to olefins and sulfur, and the generation of carbenes cannot be observed (Scheme IV).[16]

Selenadigermirane **7** was copyrolyzed with 2,3-dimethyl-1,3-butadiene at 470 °C under flowing nitrogen. Two major products, germacyclopentene **11** and diselenadigermetane **14**, which is a dimer of germaneselone **13**, were isolated and identified by ^{1}H NMR and mass spectroscopic analyses. Thus it would be appear that selenadigermirane **7** is a precursor of germylene **5** and germaneselone **13** as illustrated in Scheme V. Photochemical generation of germylene **5** is even more efficient. Irradiation of **7** in a cyclohexane solution with 2,3-dimethyl-1,3-butadiene produced germacyclopentene **11** in 36% yield, but **14** was not isolated because of the low stability under the photochemical conditions.[17] Although the chemistry of reactive intermediates with multiple bonds to germanium such as germenes ($R_2Ge{=}CR_2$), digermenes ($R_2Ge{=}GeR_2$), germanimines ($R_2Ge{=}NR$), germaphosphenes ($R_2Ge{=}PR$), germanones ($R_2Ge{=}O$), and germanethiones ($R_2Ge{=}S$) has been investigated,[18] there

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[13] Kremer, D.; Kraka, E. *J. Am. Chem. Soc.* **1985**, *107*, 3800.

[14] Grev, R. S.; Schaefer, H. F. *J. Am. Chem. Soc.* **1987**, *109*, 6577.

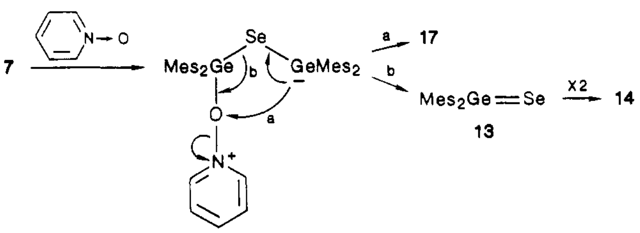
[15] Since tetramesityldigermene 4 does not react with 2,3-dimethyl-1,3-butadiene at room temperature, if 4 is generated in the reaction, it should be detected by UV spectrometry (4, λ_{max} 410 nm in cyclohexane at room temperature: Ando, W.; Tsumuraya, T., unpublished results).

[16] Griffin, G. W. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 537.

[17] Indeed, 14 was easily decomposed by the irradiation with a low-pressure mercury lamp.

[18] Satgé, J. *Adv. Organomet. Chem.* **1982**, *21*, 241.

Scheme VIII



are no reports of germaneselones ($R_2Ge{=}Se$). This is the first generation of germaneselone.

Reactions of 2 and 7 with Pyridine *N*-Oxide, Sulfur, and Selenium. Although compound 2 is fairly air-stable, the Ge–Ge bond of 2 was easily oxidized to 1,3-oxathiadigermetane 15 in 60% yield by treating 2 with pyridine *N*-oxide in benzene at 80 °C. We were unable to detect 15 in the reaction of 2 with *m*-chloroperbenzoic acid, probably due to the decomposition of 15 under acidic conditions. Elemental sulfur and selenium also reacted with 2 in refluxing toluene to give the corresponding ring expansion products 3 and 16 in 46% and 28% yields, respectively (Scheme VI).

Similarly, 7 reacted with pyridine *N*-oxide, sulfur, and selenium to yield the four-membered ring products 17, 16, and 14 in 34%, 58%, and 47% yields, respectively (Scheme VII). In the reaction with pyridine *N*-oxide, 14 was also obtained in 38% yield. The mechanism for the formation of 14 is not clear at present, but we consider that 14 was derived from the dimerization of dimesitylgermaneselone (13) generated as shown in Scheme VIII. These results indicate that the Ge–Ge bonds of 2 and 7 are more reactive than the normal Ge–Ge bond because of their ring strain. This method is useful for the preparation of the four-membered rings 1,3-disubstituted with heteroatoms.

Experimental Section

General Procedure. All reactions were carried out under an atmosphere of dry argon. The NMR spectra were recorded on Varian EM 360A and JEOL PMX 60 SI spectrometers. Mass spectra were obtained on a Hitachi RMU-6M mass spectrometer. UV spectra were measured in cyclohexane on a Shimazu UV-365 spectrometer. All melting points were uncorrected.

Materials. Hexamesitylcyclotrigermane (1) was prepared by reductive coupling of Mes_2GeCl_2 with Mg and $MgBr_2$ in THF as reported previously.[7] Benzene and cyclohexane used as solvents were dried over lithium aluminium hydride and distilled before use. Toluene and xylene were dried over calcium hydride and distilled before use. Pyridine *N*-oxide, elemental sulfur, or selenium were purchased from Wako Pure Chemical Industries, Ltd., and were used as received.

Preparation of 2,2,3,3-Tetramesitylthiadigermirane (2). A solution of 1 (373 mg, 0.4 mmol), sulfur (26 mg, 0.8 mmol), and cyclohexane (7 mL) was irradiated with a low-pressure mercury lamp for 5 h at room temperature. The solvent was evaporated at room temperature under reduced pressure, and the residue was separated by flash column chromatography (silica gel, benzene/hexane = 1/3, N_2 pressure) to give 2 (26%) and 3 (24%). For 2: mp 205–209 °C; ^1H NMR ($CDCl_3$) δ 2.21 (s, 12 H), 2.37 (s, 24 H), 6.80 (s, 8 H); MS, *m/e* (relative intensity) 654 (4, M^+), 431 (100, Mes_3Ge), 344 (17, $Mes_2Ge{=}S$), 312 (14, Mes_2Ge), 193 (27, MesGe); UV λ_{max} 278 nm (log ϵ 4.37). Anal. Calcd for $C_{36}H_{44}SGe_2$: C, 66.11; H, 6.78. Found: C, 66.12; H, 6.86. For 3: mp 220–222 °C; ^1H NMR ($CDCl_3$) δ 2.11 (s, 12 H), 2.32 (s, 24 H), 6.74 (s, 8 H); MS, *m/e* (relative intensity) 567 (29, M^+ − Mes), 431 (5, Mes_3Ge), 344 (24, $Mes_2Ge{=}S$), 312 (6, Mes_2Ge), 193 (9, MesGe), 105 (100). Anal. Calcd for $C_{36}H_{44}S_2Ge_2$: C, 63.02; H, 6.46. Found: C, 62.65; H, 6.48.

Preparation of 2,2,3,3-Tetramesitylselenadigermirane (7). A mixture of 1 (280 mg, 0.3 mmol), selenium (94.8 mg, 1.2 mmol), and cyclohexane (8 mL) was irradiated with a low-pressure mercury lamp for 4.5 h at room temperature. The solvent was evaporated at room temperature under reduced pressure, and the residue was subjected to flash column chromatography (silica gel, benzene/hexane = 1/3, N_2 pressure) to give 7 (57%) and unreacted 1 (18%). For 1: mp 217–219 °C; ^1H NMR ($CDCl_3$) δ 2.20 (s, 6 H), 2.37 (s, 12 H), 6.82 (s, 4 H); MS, *m/e* (relative intensity) 700 (3, M^+), 431 (72, Mes_3Ge), 390 (4, $Mes_2Ge{=}Se$), 312 (20, Mes_2Ge), 193 (57, MesGe), 105 (100); UV λ_{max} 274 nm (log ϵ 4.27). Anal. Calcd for $C_{36}H_{44}SeGe_2$: C, 61.69; H, 6.32. Found: C, 61.83; H, 6.37.

Table III. Crystal and Experimental Data for 2

formula	$C_{36}H_{44}SGe_2$
system	monoclinic
a, Å	31.873 (6)
b, Å	8.899 (2)
c, Å	11.773 (2)
α, deg	90.00
β, deg	99.82 (2)
γ, deg	90.00
V, $Å^3$	3290.3
M_r	654.0
D(calcd), g cm^{-3}	1.32
space group	$P2_1/a$
Z	4
cryst size, mm	0.4 × 0.3 × 0.15
radiatn	Cu Kα
μ, mm^{-1}	3.0
$2\theta_{max}$, deg	128
no. of data	5462
no. of data in refinement	4321
no. of parameters	527
R (R_w)	0.078 (0.064)
w	$1/\sigma(F_o)$
final ρ, e $Å^{-3}$	−0.4–0.3
S	3.0
$(\Delta/\sigma)_{max}$	0.42

X-ray Crystal Analysis of 2. Crystals suitable for X-ray analysis were obtained from hexane. A single crystal with dimensions of 0.4 × 0.3 × 0.15 mm was used for the X-ray measurement. The crystal has monoclinic space group $P2_1/a$ with cell dimensions a = 31.873 (6) Å, b = 8.899 (2) Å, c = 11.773 (2) Å, β = 99.82 (2)°, V = 3290.3 $Å^3$, and D_{calcd} = 1.32 g cm^{-3} (Z = 4). The intensities of 5462 independent reflections ($2\theta \leq 128°$) were measured on a Rigaku automated four-circle diffractometer AFC-5R in the $2\theta/\omega$ scan mode using Cu Kα radiation with a graphite monochromator. A total of 4321 reflections with $F_o \geq 2\sigma(F_o)$ were used for the analysis. No correction was made for absorption. The crystal and experimental data are summarized in Table III. The structure was solved by direct method with MULTAN 78. In the refinement performed by successive Fourier and block-diagonal-matrix least-squares anisotropic thermal parameters were used for the non-hydrogen atoms and isotropic thermal factors were used for the hydrogen atoms of which the positions were determined from calculations. The final *R* factor was 0.078. The molecular structure with an atomic labeling scheme, the bond lengths, and the selected bond angles are shown in Figure 1, Table I, and Table II, respectively. Atomic coordinates for the non-hydrogen atoms are given in Table IV.

Photolysis of 2 with 2,3-Dimethyl-1,3-butadiene. A solution of 2 (65.3 mg, 0.1 mmol), 2,3-dimethyl-1,3-butadiene (411 mg, 5 mmol), and cyclohexane (6 mL) was irradiated with a low-pressure mercury lamp for 5 h at room temperature. Separation of the reaction mixture by preparative TLC (silica gel, benzene/hexane = 1/3) gave 11 (42%) and 3 (18%).

All spectral data obtained for 11[19] and 3 were identical with those of authentic samples.

Pyrolysis of 2 with 2,3-Dimethyl-1,3-butadiene under Flowing Nitrogen. The pyrolysis apparatus consisted of a 28 cm × 1 cm Pyrex tube packed with Pyrex chips. The upper end of the tube was equipped with a rubber cap for syringe introduction of the sample and a nitrogen inlet. The pyrolysis tube was maintained at 500 °C, and the nitrogen flow was ca. 10

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[19] Rivière, P.; Castel, A.; Satgé, J. *J. Organomet. Chem.* 1982, *232*, 123.

Table IV. Fractional Atomic Coordinates ($\times 10^4$) and Thermal Parameters ($Å^2$) for 2 (Esd's in Parentheses)

atom	x	y	z	B_{eq}, $Å^2$
Ge(1)	1518.1 (3)	2997.9 (12)	1965.0 (8)	3.90
Ge(2)	881.3 (3)	2309.2 (12)	2627.8 (8)	3.87
S	1089 (1)	1126 (3)	1114 (2)	4.35
C(1)	2101 (2)	2459 (10)	2823 (7)	3.48
C(2)	2345 (2)	3712 (10)	3271 (7)	3.67
C(3)	2754 (2)	3416 (11)	3909 (7)	4.33
C(4)	2908 (2)	1992 (11)	4056 (7)	4.53
C(5)	2660 (3)	808 (11)	3640 (8)	4.91
C(6)	2242 (3)	1033 (11)	3014 (8)	4.68
C(2′)	2221 (3)	5273 (12)	3132 (9)	5.89
C(4′)	3368 (3)	1707 (14)	4682 (10)	7.04
C(6′)	1999 (3)	−332 (13)	2606 (12)	8.80
C(7)	1555 (2)	4620 (9)	872 (6)	2.90
C(8)	1802 (3)	4391 (11)	3 (7)	4.09
C(9)	1891 (3)	5565 (12)	−674 (7)	4.68
C(10)	1733 (3)	6998 (12)	−547 (7)	4.70
C(11)	1469 (2)	7188 (11)	248 (7)	3.92
C(12)	1380 (2)	6020 (10)	946 (6)	3.41
C(8′)	1970 (3)	2843 (13)	−238 (7)	5.35
C(10′)	1849 (3)	8310 (15)	−1241 (9)	7.31
C(12′)	1091 (3)	6373 (11)	1828 (7)	4.23
C(13)	354 (2)	3474 (9)	2350 (6)	2.99
C(14)	33 (2)	3403 (10)	1339 (7)	3.55
C(15)	−318 (3)	4320 (11)	1298 (7)	4.07
C(16)	−382 (2)	5322 (11)	2120 (7)	4.04
C(17)	−62 (3)	5394 (10)	3106 (7)	3.85
C(18)	300 (2)	4501 (10)	3195 (7)	3.27
C(14′)	50 (3)	2310 (12)	388 (7)	5.13
C(16′)	−776 (3)	6267 (13)	2032 (9)	6.13
C(18′)	631 (3)	4701 (11)	4284 (7)	4.37
C(19)	875 (2)	971 (10)	3933 (8)	3.81
C(20)	1162 (3)	1197 (10)	5048 (8)	4.17
C(21)	1099 (3)	311 (11)	5971 (8)	4.63
C(22)	781 (3)	−723 (11)	5930 (9)	5.29
C(23)	516 (3)	−937 (11)	4850 (9)	5.50
C(24)	565 (3)	−96 (10)	3895 (8)	4.45
C(20′)	1525 (3)	2273 (12)	5194 (7)	5.05
C(22′)	724 (3)	−1654 (14)	6926 (10)	7.82
C(24′)	265 (3)	−453 (12)	2763 (9)	5.86

mL/min. The sample was introduced drop by drop using a syringe. The pyrolysates were trapped in a receiver cooled by dry ice–MeOH. A solution of **2** (65.3 mg, 0.1 mmol), 2,3-dimethyl-1,3-butadiene (411 mg, 5 mmol), and benzene (4 mL) was pyrolyzed at 500 °C under flowing nitrogen. Separation of the reaction mixture by preparative TLC (silica gel, benzene/hexane = 1/3) gave **11** (25%) and **3** (30%).

Photolysis of 7 with 2,3-Dimethyl-1,3-butadiene. A solution of **7** (70 mg, 0.1 mmol), 2,3-dimethyl-1,3-butadiene (411 mg, 5 mmol), and cyclohexane (10 mL) was irradiated with a low-pressure mercury lamp for 4 h at room temperature. Separation of the reaction mixture by preparative TLC (silica gel, benzene/hexane = 1/3) gave **11** (36%).

Pyrolysis of 7 with 2,3-Dimethyl-1,3-butadiene under Flowing Nitrogen. The pyrolysis was carried out by the same procedure used for the pyrolysis of **2**. A solution of **7** (70 mg, 0.1 mmol), 2,3-dimethyl-1,3-butadiene (411 mg, 5 mmol), and benzene (5 mL) was pyrolyzed at 470 °C under flowing nitrogen. Separation of the reaction mixture by preparative TLC (silica gel, benzene/hexane = 1/3) gave **11** (10%), **14** (19%), and unreacted **7** (49%). For **14**: mp 219–220 °C; ^1H NMR ($CDCl_3$) δ 2.27 (s, 12 H), 2.53 (s, 24 H), 6.83 (s, 8 H); MS, *m/e* (relative intensity) 780 (30, M^+), 661 (100, M^+ − Mes), 431 (37, Mes_3Ge), 320 (63, Mes_2Ge), 193 (74, MesGe). Anal. Calcd for $C_{36}H_{46}Se_2Ge_2$: C, 55.44; H, 5.68. Found: C, 55.43; H, 5.69.

Reaction of 2 with Pyridine *N*-Oxide. A solution of **2** (65.3 mg, 0.1 mmol), pyridine *N*-oxide (120 mg, 1.26 mmol), and benzene (5 mL) was heated to reflux for 6 h. **15** was isolated in 60% yield by preparative TLC (silica gel, benzene/hexane = 1/3). For **15**: mp 220–222 °C; ^1H NMR ($CDCl_3$) δ 2.25 (s, 12 H), 2.43 (s, 24 H), 6.90 (s, 8 H); MS, *m/e* (relative intensity) 670 (7, M^+), 551 (70, M^+ − Mes), 431 (100, Mes_3Ge), 344 (91, $Mes_2Ge{=}S$), 328 (33, $Mes_2Ge{=}O$), 312 (27, Mes_2Ge). Anal. Calcd for $C_{36}H_{44}OSGe_2$: C, 64.53; H, 6.61. Found: C, 64.23; H, 6.60.

Reaction 2 with Sulfur. A mixture of **2** (65.3 mg, 0.1 mmol), sulfur (256 mg, 8 mmol), and toluene (5 mL) was heated to reflux for 20 h. **3** was isolated by preparative TLC (silica gel, benzene/hexane = 1/3) in 46% yield.

Reaction of 2 with Selenium. A mixture of **2** (32.6 mg, 0.05 mmol), selenium (79 mg, 1 mmol), and toluene (3 mL) was heated to reflux for 36 h. **16** was isolated by preparative TLC (silica gel, benzene/hexane = 1/3) in 28% yield. For **16**: mp 218–219 °C; ^1H NMR ($CDCl_3$) δ 2.30 (s, 12 H), 2.60 (s, 24 H), 7.00 (s, 8 H); MS, *m/e* (relative intensity) 732 (3, M^+), 613 (58, M^+ − Mes), 431 (15, Mes_3Ge), 390 (16, $Mes_2Ge{=}Se$), 344 (65, $Mes_2Ge{=}S$), 312 (23, Mes_2Ge), 193 (29, MesGe), 105 (100). Anal. Calcd for $C_{36}H_{44}SSeGe_2$: C, 58.99; H, 6.05. Found: C, 58.96; H, 6.08.

Reaction of 7 with Pyridine *N*-Oxide. A solution of **7** (42.3 mg, 0.06 mmol), pyridine *N*-oxide (90.3 mg, 0.95 mmol), and benzene (3 mL) was heated to reflux for 3 h. Separation of the reaction mixture by TLC (silica gel, benzene/hexane = 1/3) gave **17** (34%) and **14** (38%). For **17**: mp 205–207 °C; ^1H NMR ($CDCl_3$) δ 2.27 (s, 12 H), 2.42 (s, 24 H), 6.83 (s, 8 H); MS, *m/e* (relative intensity) 716 (9, M^+), 597 (36, M^+ − Mes), 478 (32, M^+ − 2Mes), 431 (28, Mes_3Ge), 390 (27, $Mes_2Ge{=}Se$), 328 (39, $Mes_2Ge{=}O$), 312 (63, Mes_2Ge), 238 (100). Anal. Calcd for $C_{36}H_{44}OSeGe_2$: C, 60.31; H, 6.18. Found: C, 60.20; H, 6.31.

Reaction of 7 with Sulfur. A mixture of **7** (70 mg, 0.1 mmol), sulfur (256 mg, 8 mmol), and toluene (5 mL) was heated to reflux for 17.5 h. **16** was isolated by preparative TLC (silica gel, benzene/hexane = 1/3) in 58% yield.

Reaction of 7 with Selenium. A mixture of **7** (70 mg, 0.1 mmol), selenium (79 mg, 1 mmol), and xylene (5 mL) was heated to reflux for 20 h. **14** was isolated by preparative TLC (silica gel, benzene/hexane = 1/3) in 47% yield.

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Supplementary Material Available: Tables of bond angles, anisotropic thermal factors, and H-atom parameters for **2** (3 pages); a listing of structure factors (27 pages). Ordering information is given on any current masthead page.