gional NMR Facility (Grant No. CHE-79-16324). We also thank Andrea Owyeung for the illustrations.

Supplementary Material Available: Tables of positional and thermal parameters and complete interatomic distances and angles for **3**–**6**, **8**, **10**, and **11** (62 pages); tables of observed and calculated structure factors (81 pages). Ordering information is given on any current masthead page. Tables of crystallographic data for the compounds **4**,[3] Tl[**5**]$\cdot{}^2/_3C_7H_8$,[7] Tl[**6**],[8] **8**$\cdot{}^1/_2C_6H_6$,[4] $[(PPh_3)_2N]$[**10**],[5] and Na[**11**][6] were supplied with the now-published initial preliminary communications pertaining to these structures.

Molecular Structures and Reactivities of Digermiranes and Azadigermiridines

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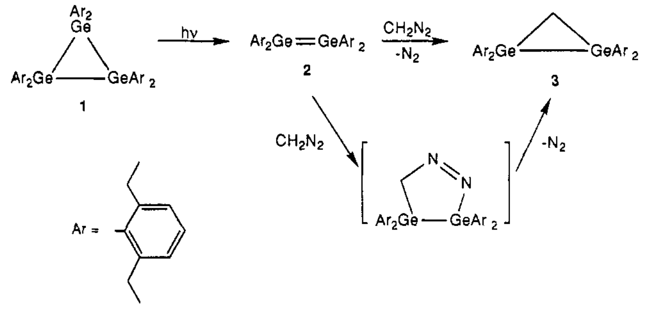
Received December 19, 1989

Reaction of tetrakis(2,6-diethylphenyl)digermene (**2**) with diazomethane produces 1,1,2,2-tetrakis(2,6-diethylphenyl)digermirane (**3**). The photolysis of **3** with a high-pressure mercury lamp yields germene **13** and germylene **14**. The digermirane **3** reacts with pyridine *N*-oxide, sulfur, and selenium to yield the insertion products of O, S, and Se into the germanium–germanium bond. 2,2,3,3-Tetrakis(2,6-diethylphenyl)-1-phenylazadigermiridine (**5**) is also prepared by the reaction of **2** with phenyl azide. The structures of the digermirane **3** and the azadigermiridine **5** have been determined by X-ray crystal analyses. Both **3** and **5** have relatively short germanium–germanium bond distances of 2.379 (1) Å and nearly planar arrangements of C_{Ar}, C_{Ar}, and Ge atoms around each germanium.

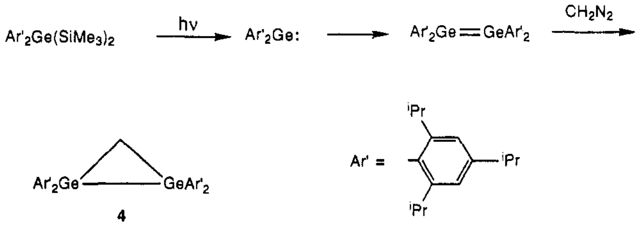
Introduction

In recent years the chemistry of metal group 14 three-membered heterocycles has progressed rapidly, owing to the synthesis of a variety of small-ring systems involving group 14 elements.[2-10] Especially, the synthesis of small-ring systems involving a germanium–germanium bond has received considerable attention because of interest in the reactivity of the reactive germanium–germanium bonds in the ring.[7-10] Recently, we prepared thia- and selenadigermiranes by the reactions of digermene with sulfur and selenium, demonstrating that this method was useful for the preparation of three-membered cyclogermanes containing a germanium–germanium bond.[6a,8] Masamune prepared three-membered Ge–Ge ring compounds from the cycloaddition reaction of the Ge═Ge double bond, but the chemical reactivities are not well-known.[10a] In this paper we report the first synthesis of digermiranes and azadigermiridines from the reactions of digermenes with diazomethane and phenyl azide, including the crystal structures of a digermirane and an azadigermiridine and some of the chemical properties of these.[9,10a]

Scheme I



Scheme II



Results and Discussion

Preparation of Digermiranes and Azadigermiridines. Irradiation of a cyclohexane solution of hexakis(2,6-diethylphenyl)cyclotrigermane (**1**)[7b,c] at room temperature with a low-pressure mercury lamp afforded tetrakis(2,6-diethylphenyl)digermene (**2**) in good yields, as

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

(2) Baudler, M. *Pure Appl. Chem.* **1980**, *52*, 755.

(3) Krebs, A.; Berndt, J. *Tetrahedron Lett.* **1983**, *24*, 4083.

(4) Andrianarison, M.; Coulet, C.; Declercq, J.-P.; Dubourg, A.; Escudie, J.; Ranaivonjatovo, H.; Satge, J. *Organometallics* **1988**, *7*, 545.

(5) Cowley, A. H.; Hall, S. W.; Nunn, C. W.; Power, J. M. *J. Chem. Soc., Chem. Commun.* **1988**, 753.

(6) (a) Ando, W.; Tsumuraya, T. *Tetrahedron Lett.* **1986**, *27*, 3251. (b) Tsumuraya, T.; Sato, S.; Ando, W. *Organometallics* **1989**, *8*, 161. (c) Ando, W.; Tsumuraya, T. *Organometallics* **1989**, *8*, 1467.

(7) (a) Masamune, S.; Hanzawa, Y.; Williams, D. J. *J. Am. Chem. Soc.* **1982**, *104*, 6136. (b) Snow, J. T.; Murakami, S.; Masamune, S.; Williams, D. J. *Tetrahedron Lett.* **1984**, *25*, 4191. (c) Ando, W.; Tsumuraya, T. *J. Chem. Soc., Chem. Commun.* **1987**, 1514. (d) Weidenbruch, M.; Grimm, F.-T.; Herrndorf, M.; Schafer, A.; Peters, K.; Schnering, G. *J. Organomet. Chem.* **1988**, *341*, 335.

(8) Tsumuraya, T.; Sato, S.; Ando, W. *Organometallics* **1988**, *7*, 2015.

(9) For a preliminary report on the preparation of digermirane and an azadigermiridine, see: Ando, W.; Tsumuraya, T. *Organometallics* **1988**, *7*, 1882.

(10) (a) Very recently, Masamune et al. reported the preparation of a digermirane and an azadigermiridine; see: Batcheller, S. A.; Masamune, S. *Tetrahedron Lett.* **1988**, *29*, 3383. (b) Masamune, S.; Batcheller, S. A.; Park, J.; Davis, W. M.; Yamashita, O.; Ohta, Y.; Kabe, Y. *J. Am. Chem. Soc.* **1989**, *111*, 1888.

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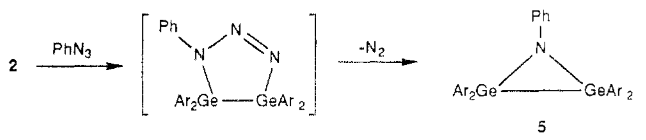
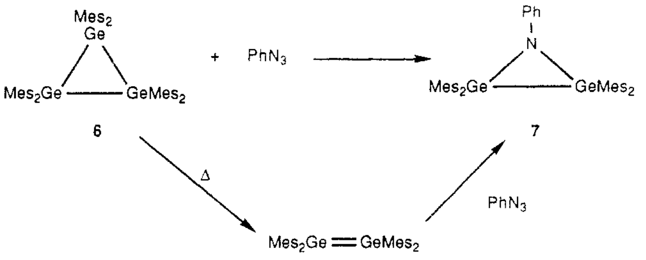
Scheme III



Scheme IV



reported previously by Masamune et al.[7b,11] A cyclohexane solution of **2** (prepared from 0.5 mmol of **1**) was transferred to an ethereal solution of diazomethane (ca. 5 mmol, dried by KOH and degassed) under argon at -78 °C. After addition was completed, the resulting mixture was warmed to room temperature. During the reaction, dinitrogen was evolved and the solution became pale yellow. Crystallization of the residue from hexane afforded 1,1,2,2-tetrakis(2,6-diethylphenyl)digermirane (**3**) as colorless crystals in 72% yield (based on the cyclotrigermane **1** used) (Scheme I). The structure of **3** was confirmed by ^{1}H NMR, ^{13}C NMR, and mass spectroscopic analyses and also by an X-ray diffraction study. In the ^{13}C NMR spectrum of **3** the characteristic three-membered-ring carbon was observed at δ 7.0 ppm and the coupling constant $^1J_{C-H}$ (144 Hz) is larger than that of the normal sp^3 carbon ($^1J_{C-H} \approx$ 130 Hz). Digermirane **3** is fairly stable toward air and moisture, but when heated to its melting point of 196–197 °C, **3** decomposes to an unidentified product. The formation of **3** can be rationalized in terms of a dipolar addition of diazomethane to **2** followed by loss of N_2 (Scheme I).

Similarly, tetrakis(2,4,6-triisopropylphenyl)digermene,[12] which was generated by the photolysis of the bis(trimethylsilyl)germane,[13] reacted with diazomethane to yield the corresponding digermirane (**4**) in 6% yield (based on the bis(trimethylsilyl)germane) (Scheme II).

Wishing to have the analogous nitrogen-containing digermirane, we next tried the reaction of digermenes with phenyl azide. When a cyclohexane solution of digermene **2** was transferred to a hexane solution of phenyl azide at -78 °C, and the mixture was warmed to room temperature, colorless crystals identified as 2,2,3,3-tetrakis(2,6-diethylphenyl)-1-phenylazadigermiridine (**5**) was obtained in 68% yield (Scheme III). Azadigermiridine **5** is remarkably stable toward atmospheric oxygen and moisture and does not decompose even when heated to its melting point of 217–219 °C.

In the ^{1}H and ^{13}C NMR spectra of **5** only one set of signals attributed to the 2,6-diethylphenyl group is observed. This suggests that in solution the inversion barrier at the nitrogen is very low or that the geometry at nitrogen is planar. In the solid state compound **5** has a planar arrangement at nitrogen, as shown later.

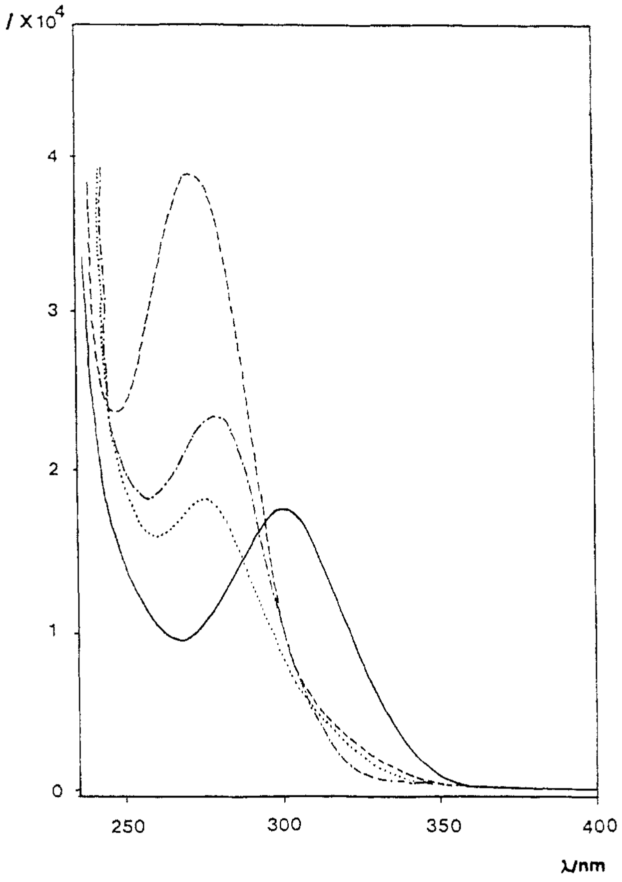
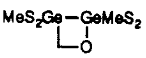
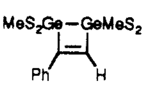
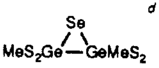
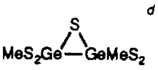


Figure 1. UV spectra of digermiranes in cyclohexane: (—) **3**; (- - -) **5**; (–·–) 2,2,3,3-tetramesitylthiadigermirane; (···) 2,2,3,3-tetramesitylselenadigermirane.

Table I. Electronic Absorption Maxima and Oxidation Potentials of Three- and Four-Membered Cyclogermanes

compd	λ_{max}, nm (log ϵ)	E_{pa},[a] V vs SCE
 [b]		1.91
 [c]	269 (4.35)	1.45
 [c]	250 (4.57)	1.34
 [d]	274 (4.27)	1.34
 [d]	278 (4.37)	1.27
5	270 (4.60)	0.90
1[e]	272 (4.67), 309 (sh)	0.80
6[f]	268 (4.69), 310 (sh)	0.72
3	300 (4.24)	0.72

[a] The first anodic peak potential. [b] See ref 6b. [c] See ref 14. [d] See ref 8. [e] See ref 7b. [f] See ref 7c.

When a benzene solution of hexamesitylcyclotrigermane (**6**; 0.3 mmol)[7c] and phenyl azide (3 mmol) was heated to reflux for 10 h, 2,2,3,3-tetramesityl-1-phenylazadigermiridine (**7**) (Mes = mesityl = 2,4,6-trimethylphenyl) was obtained as a colorless crystalline solid in 59% yield (Scheme IV). Azadigermiridine **7** is evidently derived from tetramesityldigermene, generated by the

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

(12) Very recently, Masamune et al. reported the preparation of the same digermene by a reductive coupling reaction of the corresponding dichlorogermane; see: Park, J.; Batcheller, S. A.; Masamune, S. *J. Organomet. Chem.* **1989**, *367*, 39.

(13) (a) Ando, W.; Itoh, H.; Tsumuraya, T.; Yoshida, H. *Organometallics* **1987**, *7*, 1880. (b) Ando, W.; Itoh, H.; Tsumuraya, T. *Organometallics* **1989**, *8*, 2759.

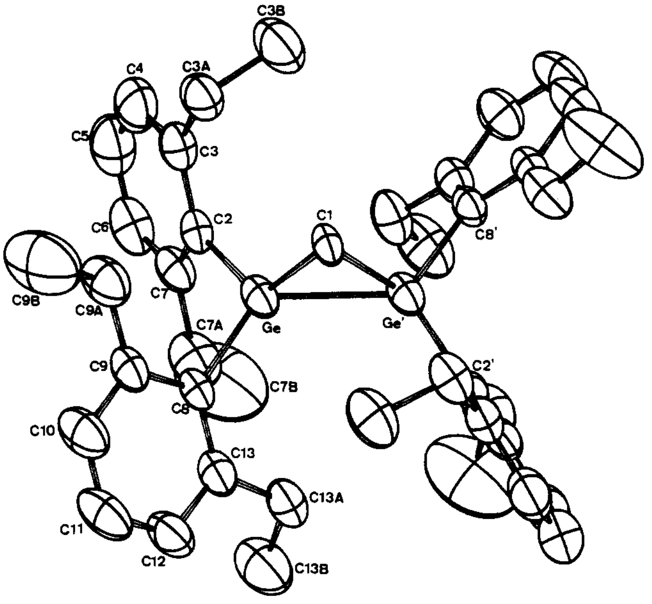

Figure 2. Molecular conformation and atomic labeling of 3.

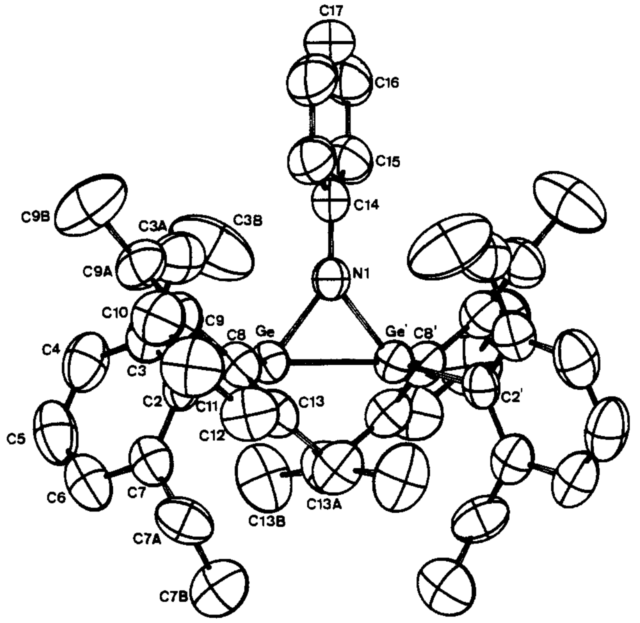

Figure 3. Molecular conformation and atomic labeling of 5.

thermolysis of cyclotrigermane **6**.[14]

UV Spectra and Oxidation Potentials of Digermiranes. Digermiranes and their heterocyclic analogues show characteristic absorption maxima at 270–300 nm. The electronic spectra of digermirane **3**, azadigermiridine **5**, 2,2,3,3-tetramesitylthiadigermirane, and 2,2,3,3-tetramesitylselenadigermirane are shown in Figure 1, and their absorption maxima and oxidation potentials[15] are summarized in Table I, together with those of some other three- and four-membered cyclogermanes. Bathochromic shifts were observed for three-membered cyclogermanes compared to four-membered cyclogermanes, and the anodic peak potentials were lowered with a decrease in ring size. Since aryldisilanes Ar–Si–Si show absorptions in the region from 230 to 240 nm attributed to charge-transfer interaction between the Si–Si σ bond and the π^* orbitals of the aromatic ring, the absorptions observed at 250–300 nm for three- and four-membered cyclogermanes are ascribed to similar charge-transfer interaction between Ge–Ge σ bond and π^* orbitals of the aromatic ring.[16] The low oxidation potentials observed for three-membered cyclogermanes are not characteristic of three-membered rings because 3-(2-adamantyl)-2,2-dimesitylthiagermirane[6b] has an oxidation potential of 1.91 V (vs SCE). The existence of the Ge–Ge bond is essential for decreasing the oxidation potentials. Therefore, the first anodic wave may correspond to the first one-electron removal from the Ge–Ge bond of the four- and three-membered cyclogermanes.

Table II. Bond Lengths (Å) for 3, with Estimated Standard Deviations in Parentheses

Ge–C(1)	1.970 (1)	Ge–C(8)	1.975 (4)
Ge–C(2)	1.984 (3)	Ge–Ge'	2.379 (1)

Table III. Bond Angles (deg) for 3, with Estimated Standard Deviations in Parentheses

C(1)–Ge–C(2)	122.7 (1)	C(8)–Ge–Ge'	121.2 (1)
C(1)–Ge–C(8)	110.3 (1)	Ge–C(8)–C(9)	116.9 (2)
C(2)–Ge–C(8)	112.6 (1)	Ge–C(8)–C(13)	123.4 (2)
Ge–C(2)–C(3)	121.8 (3)	Ge–C(1)–Ge'	74.3 (1)
Ge–C(2)–C(7)	117.7 (2)	C(2)–Ge–Ge'	123.1 (1)
C(1)–Ge–Ge'	52.9 (1)		

Table IV. Bond Lengths (Å) for 5, with Estimated Standard Deviations in Parentheses

Ge–N(1)	1.876 (1)	Ge–C(8)	1.986 (4)
Ge–C(2)	1.971 (4)	Ge–Ge'	2.379 (1)

Table V. Bond Angles (deg) for 5, with Estimated Standard Deviations in Parentheses

N(1)–Ge–C(2)	120.0 (2)	N(1)–Ge–Ge'	50.6 (1)
N(1)–Ge–C(8)	113.7 (2)	C(8)–Ge–Ge'	127.2 (1)
C(2)–Ge–C(8)	109.9 (2)	Ge–C(8)–C(9)	116.6 (2)
Ge–N(1)–C(14)	140.6 (4)	Ge–C(8)–C(13)	121.2 (2)
Ge–C(2)–C(3)	124.8 (2)	Ge–N(1)–Ge'	78.7 (2)
Ge–C(2)–C(7)	117.1 (2)	C(2)–Ge–Ge'	121.1 (1)

Crystal Structure of Digermirane 3 and Azadigermiridine 5. The structures of the digermirane **3** and azadigermiridine **5** were confirmed by an X-ray diffraction study. The molecular structures with atomic labeling schemes are shown in Figures 2 and 3, respectively.

The crystal structure of **3** possesses a crystallographic 2-fold axis bisecting the digermirane ring. The bond lengths in the three-membered ring are 2.379 (1) Å for the Ge–Ge bond and 1.970 (1) Å for the Ge–C bonds. The endocyclic bond angles of Ge and C are 52.9 (1) and 74.3 (0)°, respectively. The four aryl substituents are each twisted about the C_{Ar}–Ge bond in the same direction, forming dihedral angles of 63.4 (2) and 68.2 (2)° with the central digermirane ring. The independent Ge–C_{Ar} bond lengths are 1.984 (3) and 1.975 (4) Å, respectively. Other bond lengths and angles for **3** are listed in Tables II and III.

The crystal structure of **5** also possesses crystallographic 2-fold rotation symmetry with N1, C14, and C17 on this axis. In this molecule the $NC_{Ph}Ge_2$ skeleton is completely planar. However, this planar geometry at nitrogen is not surprising because planarity about nitrogen is also observed in trisilylamines and disilylamines, although the reasons for this planarity have been debated inconclusively.[17] The bond lengths in the three-membered ring

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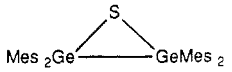
(14) Ando, W.; Tsumuraya, T. *J. Chem. Soc., Chem. Commun.* **1989**, 770.

(15) For oxidation potentials of cyclopolysilanes, see: Watanabe, H.; Yoshizumi, K.; Muraoka, T.; Kato, M.; Nagai, Y.; Sato, T. *Chem. Lett.* **1985**, 1683.

(16) Sakurai, H. *J. Organomet. Chem.* **1980**, *200*, 261. For a contrasting assignment, see: Shizuka, H.; Oguchi, H.; Ishikawa, M.; Kumada, M. *J. Chem. Soc., Faraday Trans. 1* **1984**, *80*, 383.

are 2.379 (1) Å for the Ge–Ge bond and 1.876 (1) Å for the Ge–N bonds. The endocyclic bond angles of Ge and N are 50.6 (1) and 78.7 (2)°, respectively. The four aryl substituents on germanium are each twisted about the C_{Ar}–Ge bond, forming dihedral angles of 63.2 (1) and 63.0 (2)° with the central azadigermiridine ring. The phenyl ring attached to nitrogen is twisted about the N–Ge bond, forming a dihedral angle of 82.8 (2)° with the central azadigermiridine ring. The independent Ge–C_{Ar} bond lengths are 1.971 (4) and 1.986 (4) Å, respectively. Other bond lengths and angles for **5** are listed in Tables IV and V.

It is worth noting that both compounds **3** and **5** have relatively short Ge–Ge bond distances of 2.379 (1) Å, which are shorter than the normal bond length of 2.44 Å. The short Ge–Ge bond distance is not characteristic of three-membered rings, because hexakis(2,6-dimethylphenyl)cyclotrigermane[7a] and hexa-*tert*-butylcyclotrigermane[7d] have longer than normal bond lengths of 2.537–2.563 Å. Another structural feature of **3** is the nearly planar arrangements of the bonded carbon and germanium atoms around each germanium. The sums of the bond angles of C_{Ar}–Ge–Ge′, C_{Ar}–Ge–Ge′, and C_{Ar}–Ge–C_{Ar}′ around each germanium atom for compounds **3** and **5** are 356.9 and 358.2°, respectively. Recently, we reported similar structural features for thiadigermirane **8**, a relatively short Ge–Ge bond distance of 2.376 (2) Å and a nearly planar arrangement of C_{Ar}, C_{Ar}, and Ge atoms around each germanium.[8]



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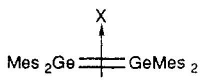
The above results can be interpreted in terms of Dewar's model of metal–olefin bonding.[18] Cremer and Kraka have used this method to describe the continuum between three-membered rings and π complexes in the three-membered monosubstituted hydrocarbons C–C–X.[19] They predict that π-complex character is increased if the electron-acceptor ability of X toward an ethylene unit is increased. Very recently, Grev et al. reported a theoretical investigation of three-membered rings containing two silicon atoms, Si–Si–X, and similar results were obtained for these systems.[20] Therefore, this method may apply to three-membered rings containing two germanium atoms, Ge–Ge–X. In the case of **3** and **5**, the Ge═Ge bond should be a better donor of π-electron density to the substituent X (X = CH_2, NPh) and a better acceptor of electron density through back-donation. On the other hand, carbon and nitrogen are more electronegative than germanium and should act as a better electron acceptors of electron density but poor donors. All these facts suggest that **3** and **5** have some of the character of π-complex **9**. Similar structural features were observed in the three-membered heterocycles Si–Si–X (X = O, S, CH_2)[21] and the thiaphosphagermirane system P–S–Ge.[4] Contributions from π complexes are postulated in these systems.



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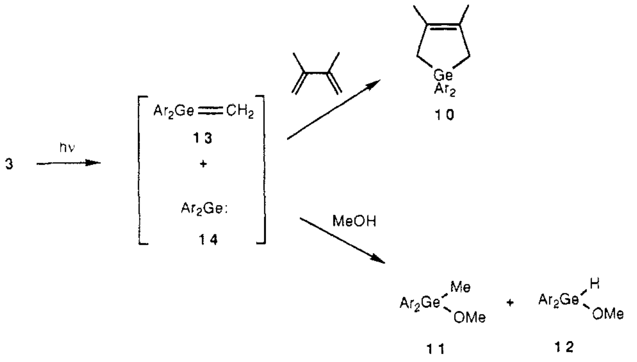
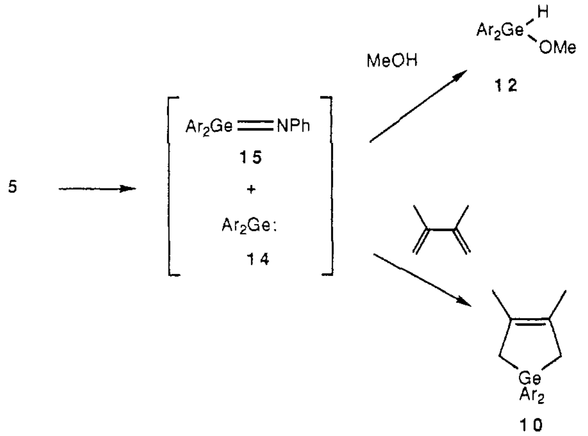
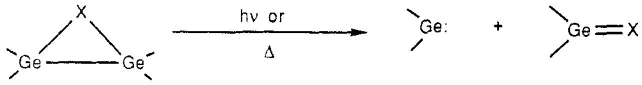
Scheme V



Scheme VI



Scheme VII



Photolysis of 3 and 5. Irradiation of a benzene solution of **3** (0.072 mmol) in the presence of an excess of 2,3-dimethyl-1,3-butadiene (5 mmol) with a high-pressure mercury lamp through a Pyrex filter for 2.5 h provided germacyclopent-3-ene **10** in 50% yield as well as unidentified polymeric products. Using a large excess of methanol as a trapping reagent led to the formation of two products, quantitative yields of methoxymethylgermane **11** and methoxygermane **12**. These results clearly indicate that digermirane **3** is fragmented into the corresponding germene **13** and germylene **14** as shown in Scheme V. While the germylene **14** reacted efficiently with the butadiene and methanol, the germene **13** did not react with the butadiene and underwent polymerization. Photolysis of azadigermiridine **5** with 2,3-dimethyl-1,3-butadiene or methanol produced only products from germylene **14** in good yield. Although germanimine **15** was not trapped by butadiene or methanol, it is quite reasonable to assume that germanimine **15** and germylene **14** are generated in the photodecomposition of **5** as in the case of digermirane, thiadigermirane, and selenadigermirane (Scheme VI).[8]

Digermirane systems Ge—Ge—X (X = CH_2, NPh, S, and Se) are revealed to be decomposed into germylenes

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(17) (a) Hedberg, K. *J. Am. Chem. Soc.* **1955**, *77*, 6491. (b) Beagleg, B.; Conrad, A. R. *Trans. Faraday Soc.* **1970**, *66*, 2740. (c) Ebswotth, E. A.; Murray, E. K.; Rankin, D. W. H.; Robertson, H. E. *J. Chem. Soc., Dalton Trans.* **1984**, 563. (d) Glidewell, C.; Rankin, D. W. H.; Robiette, A. G.; Sheldrick, G. M. *J. Mol. Struct.* **1969**, *4*, 215. (e) Glidewell, C.; Rankin, D. W. H.; Robiette, A. G.; Sheldrick, G. M. *J. Mol. Struct.* **1970**, *6*, 231. (f) Gundersen, G.; Rankin, D. W. H.; Robertson, H. E. *J. Chem. Soc., Dalton Trans.* **1985**, 191.

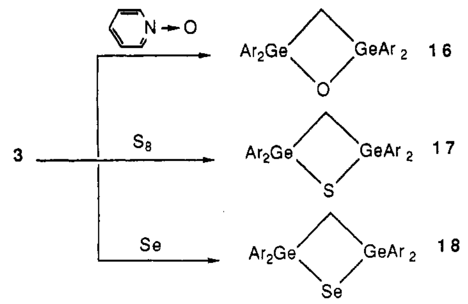
(18) (a) Dewar, M. J. S. *Bull. Soc. Chim. Fr.* **1951**, *18*, C71. (b) Chatt., J.; Duncanson, L. A. *J. Chem. Soc.* **1953**, 2939.

(19) Cremer, D.; Kraka, E. *J. Am. Chem. Soc.* **1985**, *107*, 3800.

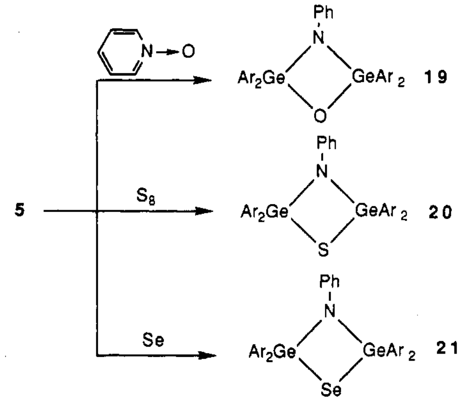
(20) Grev, R. S.; Schaefer, H. F. *J. Am. Chem. Soc.* **1987**, *109*, 6577.

(21) (a) Masamune, S.; Murakami, S.; Tobita, H.; Williams, D. J. *J. Am. Chem. Soc.* **1983**, *105*, 7776. (b) West, R.; De Young, D. J.; Haller, K. J. *J. Am. Chem. Soc.* **1985**, *107*, 4942. (c) Yokelson, H.; Millivolte, A. J.; Gillette, G. R.; West, R. *J. Am. Chem. Soc.* **1987**, *109*, 6865.

Scheme VIII



Scheme IX



and unsaturated Ge species Ge=X, indicating that digermiranes Ge—Ge—X may be conveniently used as precursors of bulky-group-substituted germylenes and unsaturated Ge compounds (Scheme VII).

Reactions of 3 and 5 with Pyridine *N*-Oxide, Sulfur, and Selenium. Ring-Expansion Reactions. Although digermirane 3 is inert toward atmospheric oxygen, it is readily oxidized by pyridine *N*-oxide to yield 1,2,4-oxadigermetane 16 in quantitative yield. In contrast, oxadigermetane 16 could not be isolated from the reaction of 3 with *m*-chloroperbenzoic acid, probably due to the decomposition of 16 under acidic conditions. Elemental sulfur and selenium also reacted with 3 to give the ring-expansion products 17 and 18 in 87% and 94% yields, respectively (Scheme VIII). Unlike 1,2,4-oxa- and 1,2,4-thiadigermetanes, which have been reported earlier,[22] compounds 16 and 17 do not decompose even when heated to their melting points. This unusual thermal stability is probably induced by the bulky groups on germanium.

Similarly, azadigermiridine 5 reacted with pyridine *N*-oxide, sulfur, and selenium to yield the four-membered-ring products 19, 20, and 21 in 58%, 12%, and 81% yields, respectively (Scheme IX). These results indicate that the Ge–Ge bonds of 3 and 5 are more reactive than the normal Ge–Ge bond because of the ring strain. The above method is useful for the preparation of digermetanes containing heteroatoms.

Experimental Section

General Procedure. All reactions were carried out under an atmosphere of dry argon. The ^1H and ^{13}C NMR spectra were recorded on JEOL PMX 60 SI, JEOL FX-90Q, JEOL FX-100, and Bruker AM-500 spectrometers. UV–vis spectra were recorded on a JASCO Ubest 50 spectrometer. Mass spectra were obtained on Hitachi RMU-6M and JEOL JMX-DX 300 mass spectrometers. Cyclic voltammograms were obtained in 0.1 M $^nBu_4NClO_4/CH_2Cl_2$ solution (vs SCE; scan rate 200 mV/s; Hokuto Denko Ltd. potentiostat/galvanostat, Model HA-301). Preparative HPLC separations were carried out on a LC-08 apparatus (Japan Analytical Industries Co., Ltd.) with a JAIGEL-1H column (20 mm i.d. × 600 mm × 2). All melting points were uncorrected.

Materials. Cyclotrigermanes 1 and 6 were prepared by reductive coupling of the corresponding dichlorogermanes with Mg and $MgBr_2$ in THF as shown in ref 7c. Bis(2,4,6-triisopropylphenyl)bis(trimethylsilyl)germane was prepared by the method described in ref 13b. A Diazomethane solution in ether[23] and phenyl azide[24] were prepared according to literature procedures. Pyridine *N*-oxide, elemental sulfur, and selenium were purchased from Wako Pure Chemical Industries, Ltd., and were used as received. 2,3-Dimethyl-1,3-butadiene was purchased from Aldrich Chemical Co., Inc., and used as received. Cyclohexane, benzene, toluene, and xylene used in syntheses and reactions were all distilled from calcium hydride before use. Hexane and pentane were dried over lithium aluminum hydride and then distilled. Methanol was dried over CaO and distilled before use.

Preparation of 1,1,2,2-Tetrakis(2,6-diethylphenyl)digermirane (3). A suspension of hexakis(2,6-diethylphenyl)cyclotrigermane (1; 508 mg, 0.5 mmol) in 10 mL of cyclohexane placed in a quartz tube was irradiated at room temperature with a low-pressure mercury lamp (spiral, 125-W output) for 6 h. During this photolysis all of 1 dissolved and the solution became intensely yellow. This yellow solution of tetrakis(2,6-diethylphenyl)digermene was added to an ethereal solution of diazomethane at −78 °C. After addition was completed, the mixture was warmed to room temperature. During this procedure, nitrogen gas was evolved and the solution became pale yellow. After evaporation of the solvent, hexane was added to afford colorless crystals in 3 in 72% yield: mp 196–197 °C dec; ^1H NMR (500 MHz, $CDCl_3$) δ 0.85 (t, J = 7.5 Hz, 24 H), 1.39 (s, 2 H), 2.73 (dq, J = 7.5, 15.0 Hz, 8 H), 2.98 (dq, J = 7.5, 15.0 Hz, 8 H), 6.96 (d, J = 7.6 Hz, 8 H), 7.17 (t, J = 7.6 Hz, 4 H); ^{13}C NMR (25 MHz, $CDCl_3$) δ 7.0 (t), 15.3 (q), 30.1 (t), 125.4 (d), 128.8 (d), 138.8 (s), 149.8 (s); MS *m/e* (relative intensity) 692 (3, M^+), 559 (8, M^+ − Ar), 354 (13, $Ar_2Ge{=}CH_2$), 340 (100, Ar_2Ge), 207 (43, ArGe); UV (hexane) λ_{max} 300 nm (log ϵ = 4.24). Anal. Calcd for $C_{41}H_{54}Ge_2$: C, 71.15; H, 7.86. Found: C, 71.06; H, 7.90.

Preparation of 1,1,2,2-Tetrakis(2,4,6-triisopropylphenyl)digermirane (4). A pentane (20 mL) solution of bis(2,4,6-triisopropylphenyl)bis(trimethylsilyl)germane (625 mg, 1 mmol) placed in a quartz tube was irradiated at room temperature with a low-pressure mercury lamp (spiral, 125-W output) for 23 h, giving a yellow solution of tetrakis(2,4,6-triisopropylphenyl)digermene. This yellow solution of the digermene was added to an ethereal solution of diazomethane at −78 °C. After addition was completed, the mixture was warmed to room temperature. During this reaction, nitrogen gas was evolved and the solution became pale yellow. After evaporation, the mixture was separated by preparative HPLC and preparative TLC (silica gel, hexane) to give colorless crystals of digermirane 4 in 6% yield: mp 202–203 °C; ^1H NMR (60 MHz, $CDCl_3$) δ 0.10 (d, J = 7 Hz, 6 H), 1.45 (d, J = 7 Hz, 6 H), 1.55 (d, J = 7 Hz, 12 H), 1.0–1.5 (m, 50 H), 2.5–4.0 (m, 12 H), 6.80 (s, 4 H), 6.87 (s, 4 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 5.55 (t), 23.71 (q), 24.27 (q), 24.54 (q), 24.59 (q), 24.60 (q), 24.62 (q), 24.68 (q), 25.20 (q), 25.62 (q), 25.81 (q), 25.87 (q), 26.33 (q), 31.45 (d), 34.68 (d), 34.84 (d), 35.60 (d), 36.46 (d), 37.42 (d), 121.81 (d), 122.03 (d), 122.62 (d), 123.24 (d), 134.92 (s), 137.86 (s), 149.63 (d), 150.12 (s), 154.15 (s), 154.89 (s), 155.34 (s), 155.62 (s); MS *m/e* (relative intensity) 972 (26, M^+), 929 (10, $M^+ - {}^iPr$), 769 (9, M^+ − Ar′), 494 (23, $Ar'_2Ge{=}CH_2$), 480 (100, Ar'_2Ge). Anal. Calcd for $C_{61}H_{94}Ge_2$: C, 75.33; H, 9.74. Found: C, 75.77; H, 9.94.

Preparation of 2,2,3,3-Tetrakis(2,6-diethylphenyl)-1-phenylazadigermiridine (5). A cyclohexane (30 mL) solution of digermene 2, prepared by the photolysis of cyclotrigermane 1 (1.02 g, 1 mmol), was added to a hexane (10 mL) solution of phenyl azide (357 mg, 3 mmol) at −78 °C. After addition was completed, the mixture was warmed to room temperature. During

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(22) Barrau, J.; Hamida, B.; Agrebi, A.; Satge, J. *Organometallics* **1987**, *6*, 659.

(23) de Goer, T. J.; Backer, H. J. *Organic Syntheses*; Wiley: New York, 1963; Collect. Vol. IV, p 250.

(24) Lindsay, R. O.; Allen, C. F. H. *Organic Syntheses*; Wiley: New York, 1955; Collect. Vol. III, p 710.

this procedure nitrogen gas was evolved and the solution turned pale yellow. After evaporation, hexane was added to give colorless crystals of azadigermiridine **5** in 68% yield: mp 217–219 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.71 (br t, J = 7.4 Hz, 24 H), 2.58 (br dq, J = 7.4, 14.8 Hz, 8 H), 2.73 (dq, J = 7.4, 14.8 Hz, 8 H), 6.68 (d, J = 7.8 Hz, 2 H), 6.76 (t, J = 7.8 Hz, 1 H), 7.00 (d, J = 7.6 Hz, 8 H), 7.05 (t, J = 7.8 Hz, 2 H), 7.22 (t, J = 7.6 Hz, 4 H); ^{13}C NMR (25 MHz, $CDCl_3$) δ 15.0 (q), 30.4 (t), 119.3 (d), 123.8 (d), 125.6 (d), 128.1 (d), 129.2 (d), 141.9 (s), 148.4 (s), 153.0 (s); MS *m/e* (relative intensity) 769 (2, M^+), 678 (11, $M^+ - NPh$), 636 (2, $M^+ - Ar$), 473 (9, Ar_3Ge), 431 (24, $Ar_2Ge{=}NPh$), 340 (100, Ar_2Ge), 207 (59, ArGe); UV (hexane) λ_{max} 270 nm (log ϵ = 4.60). Anal. Calcd for $C_{46}H_{57}NGe_2$: C, 71.83; H, 7.47; N, 1.82. Found: C, 71.65; H, 7.45; N, 1.81.

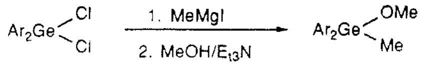
Preparation of 2,2,3,3-Tetrakis(2,4,6-trimethylphenyl)-1-phenylazadigermiridine (7). A mixture of hexamesitylcyclotrigermane (**6**; 280 mg, 0.3 mmol), phenyl azide (357 mg, 3 mmol), and benzene (5 mL) was heated to reflux for 10 h. After evaporation, hexane was added to give colorless crystals of azadigermiridine **7** in 59% yield: mp 263–265 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.14 (s, 24 H), 2.23 (s, 12 H), 6.69 (d, J = 8.0 Hz, 1 H), 6.73 (s, 8 H), 7.07 (t, J = 8.0 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.05 (q), 23.54 (q), 119.14 (d), 124.28 (d), 128.45 (d), 128.50 (d), 138.46 (s), 138.49 (s), 142.51 (d), 154.00 (s). Anal. Calcd for $C_{42}H_{49}NGe_2$: C, 70.75; H, 6.93; N, 1.96. Found: C, 70.68; H, 7.07; N, 1.90.

X-ray Crystal Analysis of 3 and 5. Crystals of dimensions 0.4 × 0.3 × 0.2 mm for **3** and 0.4 × 0.3 × 0.2 mm for **5**, obtained from hexane, were used for the X-ray analysis. Lattice constants were determined by a least-squares fit of angular settings of 20 reflections within the range $30 < 2\theta < 50°$. Intensity data were obtained on a Rigaku AFC-5R diffractometer equipped with graphite-monochromatized Cu Kα radiation and using the θ–2θ scan technique ($2\theta < 128°$). During data collection three standards, measured before every 200 reflections, indicated no systematic variation of intensity with time. Of 2937 and 3350 independent reflections measured, only 2715 and 2965 for **3** and **5**, respectively, were considered as observed on the basis of the criterion $F_o > 2\sigma(F_o)$. All intensities were corrected for Lorentz and polarization effects but not for absorption. Crystal data for **3**: $C_{41}H_{51}Ge_2$; mol wt 692.2; monoclinic; $C2/c$; a = 23.001 (4) Å, b = 9.397 (1) Å, c = 19.226 (1) Å, β = 120.50 (1)°; V = 3580.6 Å^3; Z = 4; ρ = 1.29 g cm^{-3}; μ(Cu Kα) = 25 cm^{-1}; $F(000)$ = 1452; T = 297 K. Crystal data for **5**: $C_{46}H_{57}NGe_2$; mol wt 762.9; monoclinic; $A2/a$; a = 14.788 (3) Å, c = 17.301 (4) Å, β = 93.06 (2)°; V = 4013.9 Å^3; Z = 4; ρ = 1.27 g cm^{-3}; μ(Cu Kα) = 23 cm^{-1}; $F(000)$ = 1616; T = 297 K. Both structures of **3** and **5** were solved by MULTAN 84[25] and refined by block-diagonal least-squares methods. Positions of the hydrogen atoms were estimated from standard geometry. The final refinements with anisotropic temperature factors for the non-hydrogen atoms and isotropic temperature factors for the hydrogen atoms lowered the R values to 0.053 (R_w = 0.048 ($w = 1/\sigma^2(F_o)$) and 0.047 (R_w = 0.045 ($w = 1/\sigma^2(F_o)$) for **3** and **5**, respectively. The goodness of fit values were 2.39 and 2.10, and maximum and minimum heights in the final difference Fourier syntheses were +0.3, −0.2 and +0.2, −0.2 e Å^{-3} for **3** and **5**, respectively. The maximum and average shifts in the final cycles of refinements were 0.32, 0.06 and 0.28, 0.05 of the corresponding standard deviations for **3** and **5**, respectively. The molecular structures with atomic labeling schemes, the bond lengths and angles involving germanium atoms, and atomic coordinates for the non-hydrogen atoms are given in Figure 2 and Tables II, III, and VI for **3** and Figure 3 and Tables IV, V, and VII for **5**.

Photolysis of 3 with 2,3-Dimethyl-1,3-butadiene. A benzene (5 mL) solution of digermirane **3** (50 mg, 0.072 mmol) and 2,3-dimethyl-1,3-butadiene (411 mg, 5 mmol) was irradiated with a high-pressure mercury lamp for 2.5 h. Separation of the reaction mixture by preparative TLC (silica gel, 1/3 benzene/hexane) gave the germacyclopent-3-ene **10** in 50% yield. All spectral data obtained for **10** were identical with those of an authentic sample.[11]

Photolysis of 3 with Methanol. A mixture of **3** (50 mg, 0.072 mmol), methanol (32 mg, 1 mmol), and benzene (1 mL) was irradiated with a high-pressure mercury lamp for 3 h. Separation of the mixture by preparative HPLC gave quantitative yields of **11** and **12**. Physical and spectral data for **11**: colorless oil; ^{1}H NMR (60 MHz, $CDCl_3$) δ 1.00 (t, J = 7 Hz, 12 H), 1.02 (s, 3 H), 2.75 (q, J = 7 Hz, 8 H), 3.40 (s, 3 H), 6.9–7.4 (m, 6 H); high-resolution MS calcd for $C_{21}H_{29}OGe$ ($M^+ - Me$) *m/e* 371.1428, found *m/e* 371.1441.

Compound **11** was prepared independently by the reaction of dichlorobis(2,6-diethylphenyl)germane with methylmagnesium iodide followed by treatment with methanol and triethylamine:



$$Ar_2GeCl_2 \xrightarrow[\text{2. MeOH/Et}_3\text{N}]{\text{1. MeMgI}} Ar_2Ge(OMe)Me$$

11

An ethereal solution of methylmagnesium iodide (3.3 mmol) was

Table VI. Fractional Atomic Coordinates (×10^4) and Thermal Parameters (Å^2) for 3, with Estimated Standard Deviations in Parentheses

atom	x	y	z	B_{eq}[a]
Ge	598.5 (3)	2416 (1)	2911.1 (3)	3.52
C(1)	0 (0)	744 (7)	2500 (0)	3.0
C(2)	1205 (2)	2973 (5)	2505 (3)	3.3
C(3)	1376 (2)	2004 (6)	2062 (3)	4.2
C(3A)	1144 (3)	508 (6)	1874 (3)	4.7
C(3B)	539 (3)	325 (7)	1025 (3)	6.6
C(4)	1788 (2)	2549 (7)	1770 (3)	5.9
C(5)	2012 (3)	3897 (7)	1905 (3)	6.3
C(6)	1838 (3)	4805 (6)	2324 (3)	5.4
C(7)	1421 (2)	4352 (5)	2612 (3)	4.0
C(7A)	1236 (3)	5415 (6)	3065 (4)	5.8
C(7B)	1073 (5)	6826 (9)	2750 (5)	14.1
C(8)	1048 (2)	2507 (6)	4100 (2)	3.2
C(9)	1567 (2)	1538 (5)	4535 (3)	3.7
C(9A)	1782 (3)	495 (6)	4120 (3)	5.3
C(9B)	2259 (4)	−630 (8)	4589 (4)	10.8
C(10)	1887 (3)	1511 (6)	5378 (3)	5.3
C(11)	1695 (3)	2415 (7)	5778 (3)	5.8
C(12)	1184 (3)	3361 (6)	5356 (3)	5.0
C(13)	854 (2)	3449 (6)	4510 (3)	3.9
C(13A)	309 (2)	4543 (6)	4112 (3)	5.1
C(13B)	529 (3)	6051 (7)	4427 (4)	7.2

[a] $B_{eq} = {}^4/_3(\beta_{11}/a^{*2} + \beta_{22}/b^{*2} + \beta_{33}/c^{*2})$.

Table VII. Fractional Atomic Coordinates (×10^4) and Thermal Parameters (Å^2) for 5, with Estimated Standard Deviations in Parentheses

atom	x	y	z	B_{eq}[a]
Ge	7960.0 (3)	2323.4 (3)	5585.3 (3)	3.86
N(1)	7500 (0)	3247 (3)	5000 (0)	4.3
C(2)	7449 (3)	2044 (3)	6584 (2)	4.1
C(3)	6932 (3)	2603 (3)	7015 (2)	5.2
C(3A)	6674 (4)	3490 (3)	6737 (3)	7.0
C(3B)	5725 (5)	3602 (5)	6526 (4)	11.9
C(4)	6623 (4)	2338 (4)	7719 (3)	6.5
C(5)	6824 (4)	1550 (4)	8011 (3)	7.1
C(6)	7319 (3)	997 (3)	7595 (3)	6.2
C(7)	7628 (3)	1226 (3)	6885 (2)	4.9
C(7A)	8140 (3)	562 (3)	6462 (3)	6.2
C(7B)	7579 (4)	−188 (4)	6183 (3)	7.6
C(8)	9304 (3)	2294 (3)	5694 (2)	4.4
C(9)	9718 (3)	2843 (3)	6249 (3)	5.0
C(9A)	9182 (3)	3417 (3)	6740 (3)	6.1
C(9B)	9680 (4)	4087 (4)	7192 (4)	10.6
C(10)	10668 (3)	2822 (3)	6337 (3)	6.8
C(11)	11159 (3)	2274 (4)	5909 (3)	7.7
C(12)	10745 (3)	1746 (3)	5368 (3)	6.5
C(13)	9804 (3)	1747 (3)	5243 (3)	4.8
C(13A)	9380 (3)	1144 (3)	4655 (3)	5.9
C(13B)	9844 (4)	1031 (4)	3921 (3)	8.4
C(14)	7500 (0)	4127 (4)	5000 (0)	4.7
C(15)	8314 (4)	4576 (3)	5068 (3)	6.3
C(16)	8302 (5)	5471 (3)	5061 (3)	8.6
C(17)	7500 (0)	5891 (5)	5000 (0)	9.8

[a] $B_{eq} = {}^4/_3(\beta_{11}/a^{*2} + \beta_{22}/b^{*2} + \beta_{33}/c^{*2})$.

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(25) Main, P.; Germain, G.; Woolfson, M. M. MULTAN 84: A System for Computer Programs for the Automatic Data; University of York, York, England, and University of Louvain, Louvain, Belgium, 1984.

added to an ethereal solution of dichlorobis(2,6-diethylphenyl)germane (1.23, g, 3 mmol) at room temperature. After addition was completed, the mixture was warmed to reflux overnight. The mixture was hydrolyzed with dilute hydrochloric acid and extracted with ether. The organic layer was dried by $MgSO_4$ and concentrated in vacuo. To the residue was added hexane (20 mL), methanol (0.5 mL), and triethylamine (0.5 mL), and the mixture was stirred overnight. Separation of the mixture by preparative HPLC gave 11 in 6% yield.

All spectral data obtained for 12 were identical with those of an authentic sample.[11]

Photolysis of 5 with 2,3-Dimethyl-1,3-butadiene. A solution of **5** (50 mg, 0.065 mmol), 2,3-dimethyl-1,3-butadiene (411 mg, 5 mmol), and benzene (5 mL) was irradiated with a high-pressure mercury lamp for 2 h. Separation of the reaction mixture by preparative TLC (silica gel, 1/3 benzene/hexane) gave the germacyclopent-3-ene **10** in 70% yield.

All spectral data obtained for **10** were identical with those of an authentic sample.[11]

Photolysis of 5 with Methanol. A mixture of **5** (50 mg, 0.065 mmol), methanol (32 mg, 1 mmol), and benzene (0.5 mmol) was irradiated with a high-pressure mercury lamp for 6 h. Analysis of the photolysate by GLC and ^1H NMR methods indicated that a 79% yield of **12**.

Reaction of 3 with Pyridine *N*-Oxide. A solution of **3** (50 mg, 0.072 mmol), pyridine *N*-oxide (95 mg, 1 mmol), and benzene (5 mL) was heated to reflux for 5 h. After evaporation, pyridine and pyridine *N*-oxide were removed in vacuo. **16** was isolated in quantitative yield as colorless crystals: mp 194–195 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 0.89 (t, J = 7.5 Hz, 24 H), 2.69 (s, 2 H), 2.85 (q, J = 7.5 Hz, 16 H), 6.97 (d, J = 7.6 Hz, 8 H), 7.21 (t, J = 7.6 Hz, 4 H); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 15.7 (q), 28.4 (t), 32.9 (t), 126.1 (d), 129.4 (d), 139.6 (s), 149.0 (s); MS *m/e* (relative intensity) 708 (13, M^+), 678 (11, $M^+ - CH_2 - O$), 575 (13, $M^+ - Ar$), 442 (15, $M^+ - 2Ar$), 356 (27, $Ar_2Ge{=}CH_2$), 340 (100, Ar_2Ge). Anal. Calcd for $C_{41}H_{54}OGe_2$: C, 69.55; H, 7.69. Found: C, 69.49; H, 7.70.

Reaction of 3 with Sulfur. A mixture of **3** (50 mg, 0.072 mmol), sulfur (179 mg, 0.7 mmol), and benzene (5 mL) was heated to reflux for 27 h. **17** was isolated by preparative TLC (silica gel, 1/3 benzene/hexane) in 87% yield: colorless crystals; mp 121–123 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 0.92 (t, J = 7.5 Hz, 24 H), 2.79 (dq, J = 7.5, 15.0 Hz, 12 H), 2.87 (dq, J = 7.5, 15.0 Hz, 12 H), 2.93 (s, 2 H), 6.98 (d, J = 7.6 Hz, 8 H), 7.22 (t, J = 7.6 Hz, 4 H); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 15.5 (q), 28.8 (t), 37.7 (t), 126.2 (d), 129.2 (d), 140.9 (s), 148.4 (s); MS *m/e* (relative intensity) 724 (1, M^+), 591 (100, $M^+ - Ar$), 372 (13, $Ar_2Ge{=}S$), 354 (26, $Ar_2Ge{=}CH_2$), 340 (52, Ar_2Ge). Anal. Calcd for $C_{41}H_{54}SGe_2$: C, 68.01; H, 7.52. Found: C, 67.56; H, 7.65.

Reaction of 3 with Selenium. A mixture of **3** (50 mg, 0.072 mmol), selenium (79 mg, 1 mmol), and toluene (5 mL) was heated to reflux for 11 h. Separation of the reaction mixture by preparative TLC (silica gel, 1/3 benzene/hexane) gave **18** in 94% yield: colorless crystals; mp 128–129 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 0.92 (t, J = 7.4 Hz, 24 H), 2.78 (dq, J = 7.4, 14.8 Hz, 8 H), 2.87 (dq, J = 7.4, 14.8 Hz, 8 H), 3.27 (s, 2 H), 6.98 (d, J = 7.6 Hz, 8 H), 7.22 (t, J = 7.6 Hz, 4 H); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 15.5 (q), 28.9 (t), 40.8 (t), 126.2 (d), 129.2 (d), 140.4 (s), 148.2 (s); MS *m/e* (relative intensity) 770 (15, M^+), 637 (100, $M^+ - Ar$), 418 (15, $Ar_2Ge{=}Se$), 354 (41, $Ar_2Ge{=}CH_2$), 340 (73, Ar_2Ge). Anal. Calcd for $C_{41}H_{54}SeGe_2$: C, 63.86; H, 7.05. Found: C, 63.68; H, 7.16.

Reaction of 5 with Pyridine *N*-Oxide. A solution of **5** (76.8 mg, 0.1 mmol), pyridine *N*-oxide (95 mg, 1 mmol), and benzene (5 mL) was heated to reflux for 32 h. Separation of the reaction mixture by preparative TLC (silica gel, 1/3 benzene/hexane) gave **19** in 58% yield: colorless crystals; mp 287–290 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 0.76 (br t, J = 7.2 Hz, 24 H), 2.57 (br dq, J = 7.2, 14.4 Hz, 8 H), 2.77 (br dq, J = 7.2, 14.4 Hz, 8 H), 6.65 (d, J = 7.3 Hz, 2 H), 6.77 (t, J = 7.3 Hz, 1 H), 7.01 (d, J = 7.6 Hz, 8 H), 7.03 (t, J = 7.3 Hz, 2 H), 7.26 (t, J = 7.6 Hz, 4 H); MS *m/e* (relative intensity) 785 (2, M^+), 694 (72, $M^+ - NPh$), 561 (100, $M^+ - NPh - Ar$), 431 (15, $Ar_2Ge{=}NPh$), 356 (12, $Ar_2Ge{=}O$), 340 (53, Ar_2Ge). Anal. Calcd for $C_{46}H_{57}NOGe_2$: C, 70.36; H, 7.31; N, 1.78. Found: C, 70.36; H, 7.41; N, 1.69.

Reaction of 5 with Sulfur. A mixture of **5** (63.5 mg, 0.085 mmol), sulfur (128 mg, 0.5 mmol), and toluene (3 mL) was heated to reflux for 36 h. **20** was isolated by preparative TLC (silica gel, 1/3 benzene/hexane) in 12% yield: colorless crystals; mp 217–218 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 0.78 (t, J = 7.4 Hz, 24 H), 2.57 (dq, J = 7.4, 14.8 Hz, 8 H), 2.81 (br dq, J = 7.4, 14.8 Hz, 8 H), 6.67 (d, J = 7.3 Hz, 2 H), 6.80 (t, J = 7.3 Hz, 1 H), 6.97 (t, J = 7.3 Hz, 2 H), 7.03 (d, J = 7.7 Hz, 8 H), 7.27 (t, J = 7.7 Hz, 8 H); MS *m/e* (relative intensity) 801 (11, M^+), 710 (100, $M^+ - NPh$), 668 (67, $M^+ - Ar$). Anal. Calcd for $C_{46}H_{57}NSGe_2$: C, 68.96; H, 7.17; N, 1.75. Found: C, 68.88; H, 7.22; N, 1.67.

Reaction of 5 with Selenium. A mixture of **5** (76.8 mg, 0.1 mmol), selenium (79 mg, 1 mmol), and xylene (5 mL) was heated to reflux for 11 h. Separation of the reaction mixture by preparative TLC (silica gel, 1/3 benzene/hexane) gave **21** in 81% yield: colorless crystals; mp 201–203 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 0.78 (t, J = 7.4 Hz, 24 H), 2.58 (dq, J = 7.4, 14.8 Hz, 8 H), 2.84 (br dq, J = 7.4, 14.8 Hz, 8 H), 6.66 (d, J = 7.7 Hz, 2 H), 6.80 (t, J = 7.7 Hz, 1 H), 6.95 (t, J = 7.7 Hz, 2 H), 7.02 (d, J = 7.6 Hz, 8 H), 7.26 (t, J = 7.6 Hz, 4 H); MS *m/e* (relative intensity) 847 (2, M^+), 756 (25, $M^+ - NPh$), 431 (100, $Ar_2Ge{=}NPh$), 418 (51, $Ar_2Ge{=}Se$). Anal. Calcd for $C_{46}H_{57}NSeGe_2$: C, 65.14; H, 6.77; N, 1.65. Found: C, 65.01; H, 6.84; N, 1.65.

Acknowledgment. This research was partly supported by a Grant-in-Aid for Scientific Research (No. 63106003) from the Ministry of Education, Science, and Culture of Japan.

Supplementary Material Available: Tables of bond distances and angles, anisotropic thermal factors, and H atom parameters for **3** and **5** (6 pages); listings of structure factors for **3** and **5** (25 pages). Ordering information is given on any current masthead page.