Synthesis and Properties of a Strained Germacycle Having a Ge−Ge Bond, 3,4-Benzo-1,1,2,2-tetraethyl-1,2-digermacyclobut-3-ene

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A new strained germacycle, 3,4-benzo-1,1,2,2-tetraethyl-1,2-digermacyclobut-3-ene (**1**), was prepared by treatment of 1,2-bis(chlorodiethylgermyl)benzene with sodium in toluene. At ambient temperature, **1** was gradually oxidized in air to give 3,4-benzo-1,3-digerma-2-oxacyclopent-4-ene (**2**), and in the presence of sulfur, **1** was converted to 3,4-benzo-1,3-digerma-2-thiacyclopent-4-ene (**3**), quantitatively under similar thermal conditions. The digermacyclobutene **1** was thermally labile and readily underwent ring-opening polymerization in toluene to give the corresponding polymer **4** ($M_n = 4.4 \times 10^5$, $M_w = 7.4 \times 10^5$, $M_w/M_n = 1.7$). On thermolysis at 160 °C for 20 h, **1** gave two products, 4,5-benzo-1,2,3-trigermacyclopent-4-ene (**5**) and 3,4:6,7-dibenzo-1,2,5-trigermacyclohepta-3,6-diene (**6**), in reasonable yields. On the other hand, the thermolysis of **1** in the presence of phenylacetylene gave 2,3-benzo-1,4-digerma-5-phenyl-cyclohexa-2,5-diene (**7**), quantitatively. Further, **1** was thermolyzed in CCl_4 to give two chlorinated products, 1,2-bis(chlorodiethylgermyl)benzene (**9**) and 1-(chlorodiethylgermyl)-2-(diethyl(trichloromethyl)germyl)benzene (**10**), in reasonable yields. The reaction mechanisms for the polymerization and the thermolysis are discussed.

Introduction

In recent years, the chemical and physical properties of the Si−Si bond have been extensively studied and are subjects of current interest in view of the potential applications of organosilicon compounds to advanced materials.[1] However, much less interest has been paid to the chemistry of the Ge−Ge bond.

A Si−Si bond and its higher analog Ge−Ge σ bonds are formally similar to a C−C σ bond but are well-known to be much more reactive than the latter under various reaction conditions.[2] Although the group 14 dimetalloid σ bond is reactive as the corresponding C−C π bond,[3] the peralkylated simple σ bond of this type is still inert under conventional reaction conditions including in the presence of oxygen, moisture, or some transition metal complex at ambient temperature, except when powerful halogenating or oxidizing agents are used.[4] Therefore, to study the fundamental reactivities of the dimetalloid bond, it is essential to activate the σ bond to some degree by ring strain[5] and/or electronic effects[6] such as fluorine substitution[6a,b] or σ−π conjugation.[6c−g] In fact, a strained simple ring having a Si−Si bond, such as a 1,2-disilacyclobutene,[5c−e] has been shown to be an informative ring system

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(6) (a) Fluorine substitution: Tamao, K.; Hayashi, T.; Kumada, M. *J. Organomet. Chem.* **1976**, *114*, C19. (b) Tamao, K.; Okazaki, S.; Kumada, M. *J. Organomet. Chem.* **1978**, *146*, 87. (c) σ−π Conjugation: Sakurai, H.; Nakadaira, Y.; Hosomi, H.; Eriyama, Y.; Kabuto, C. *J. Am. Chem. Soc.* **1983**, *105*, 3359. (d) Morokuma, K. In *Organosilicon and Bioorganosilicon Chemistry*; Sakurai, H., Ed.; Horwood Limited: Chichester, U.K., 1985; Chapter 4. (e) Gleiter, R.; Schafer, W.; Sakurai, H. *J. Am. Chem. Soc.* **1985**, *107*, 3046. (f) Komoriya, H.; Kako, M.; Nakadaira, Y.; Mochida, K.; Kubota, M.; Kobayashi, T. *Chem. Lett.* **1994**, 1439. (g) Komoriya, H.; Kako, M.; Nakadaira, Y.; Mochida, K.; Kubota, M.; Kobayashi, T. *J. Organomet. Chem.* **1995**, *499*, 123.

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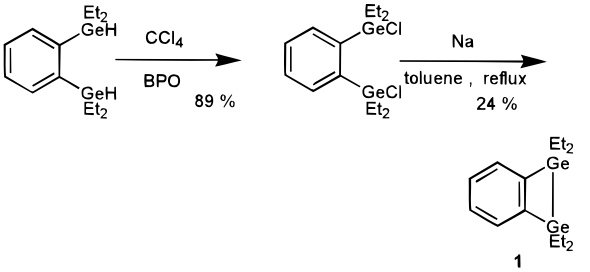
whereby to examine the chemical nature of a Si–Si σ bond. Our current interest in the properties of the Ge–Ge bond[6f–g] prompted us to prepare a readily accessible strained digermacycle, benzo-1,2-digermacyclobutene.[7] Along with the preparation of the digermacyclic system, we report some of its characteristics chemical properties.

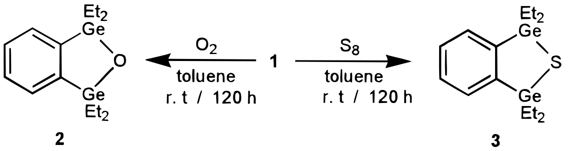
Results and Discussion

Preparation, Oxidation, and Sulfurization of 1. The benzo-1,2-digermacyclobutene 3,4-benzo-1,1,2,2-tetraethyl-1,2-digermacyclobut-3-ene (**1**) was prepared by a similar reported method for the preparation of a benzo-1,2-disilacyclobutene.[5o,p] Thus, 1,2-bis(diethylgermyl)benzene was prepared by the reaction of the Grignard reagent derived from *o*-dibromobenzene with chlorodiethylgermane *in situ* in THF. After chlorination of the 1,2-bis(diethyl)germylbenzene with carbon tetrachloride in the presence of a catalytic amount of benzoyl peroxide, the resulting 1,2-bis(chlorodiethylgermyl)benzene was cyclized by sodium in boiling toluene to give **1** in 24% yield (eq 1).



(1)

Benzodigermacyclobutene **1** is highly reactive but can purified by rapid chromatography with a short silica-gel column and by simple distillation (Kugelrohr) under reduced pressure. From consideration of the reaction conditions described in the literature,[5o,p] **1** seems to be less reactive than a silicon analog, 3,4-benzo-1,1,2,2-tetramethyl-1,2-disilacyclobutene, but more reactive than the tetraethyl silicon analog. Thus, **1** in toluene is gradually oxidized in air at room temperature to give 4,5-benzo-1,3-digerma-2-oxacyclopent-4-ene (**2**) in quantitative yields (eq 2).[7g] Under similar conditions, sulfur is also inserted into the Ge–Ge bond of **1** to give 4,5-benzo-1,3-digerma-2-thiacyclopent-4-ene (**3**) in high yields (eq 2).[7g,8]



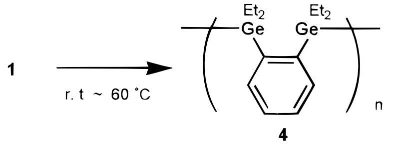
(2)

Table 1. Polymerization of 1

solvent	concn (mol/L)	temp (°C)	time (h)	polymer yield (%)	molecular weight		
					M_n[a]	M_w[a]	M_w/M_n[a]
none	neat	rt	16	97	*b*	*b*	*b*
toluene	0.6	rt	16	90	4.4×10^5	7.4×10^5	1.7
toluene	0.2	rt	16	10	3.5×10^5	5.6×10^5	1.6
toluene	0.2	60	16	28	1.9×10^5	3.0×10^5	1.7
hexane	0.2	rt	16	10	2.7×10^5	4.3×10^5	1.6
hexane	0.2	60	16	24	7.1×10^3	1.8×10^4	2.6
toluene[c]	0.2	rt	16	38	9.2×10^4	2.0×10^5	2.2

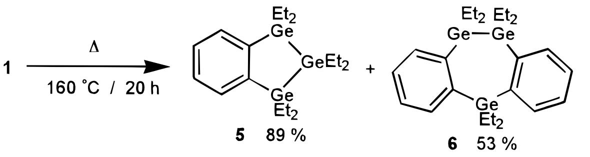
[a] Determined by gel permeation chromatography (GPC), THF solvent, polystyrene standard. [b] Insoluble in THF. [c] Containing $AlCl_3$ (3 mol %) as a Lewis catalyst.

Polymerization of 1. 1 is thermally labile and undergoes polymerization quite rapidly to yield insoluble solids in THF and other common organic solvents as shown in Table 1. Thus, **1** in toluene (0.6 mol/L) was evacuated and sealed in a glass tube, and then this was allowed to stand for 16 h at room temperature. Under these conditions **1** underwent ring-opening polymerization to give poly[*o*-(tetraethyldigermanylene)-phenylene] (**4**) in 90% yield (eq 3). In GPC analysis, **4** gave one peak with $M_n = 4.4 \times 10^5$ and $M_w = 7.4 \times 10^5$ ($M_w/M_n = 1.7$) based on the polystyrene standard. In addition, it should be noted the molecular weight distribution of the polymer prepared is in a rather narrow range (Table 1). The ^1H and ^{13}C NMR spectra of polymer **4** are quite similar to those of **1** and in accord with the structure shown as **4**. The polymerization of **1** proceeds similarly in less polar hexane as shown in Table 1. In the polymerization, the yield and molecular weight of **4** strongly depends on the concentration of **1** employed. Further, the effect of the reaction temperature is generally not significant as shown in Table 1, but polymerization at a higher temperature caused a small increase in the polymer yield and a small decrease in the molecular weight. These results seems to be similar to those reported for the tetramethyl silicon analog.[5o] The effect of a Lewis acid catalyst such as $AlCl_3$ on polymerization is not so significant as in the case of the silicon analog; namely, it similarly decreased the molecular weight to some extent and increased the polymer yield only to a lesser extent.[5o]



(3)

Thermolysis of 1. Thermolysis of **1**, carried out in an evacuated sealed tube at 160 °C for 20 h, gave rather unexpected products, 4,5-benzo-1,1,2,2,3,3-hexaethyl-1,2,3-trigermacyclopent-4-ene (**5**) and 3,4:6,7-dibenzo-1,1,2,2,5,5-hexaethyl-1,2,5-trigermacyclohepta-3,6-diene (**6**), in 89 and 53% yields, respectively (eq 4). The structures of both products **5** and **6** are fully consistent with their ^1H and ^{13}C NMR spectra together with mass spectrometric analysis. Thus, the ^{13}C NMR spectrum of **5** showed four peaks at 3.58, 7.78, 10.16, and 12.47



(4)

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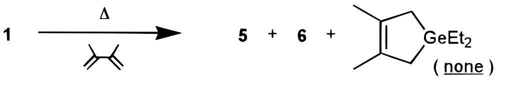
(7) For the preparation of sufficient amounts of the appropriate germacyle to study chemical properties of a Ge–Ge bond, a pertinent synthetic method for a simple 1,2-digermacyclobutene and -cyclobutane has not been reported so far. (a) 1,2-Digermacyclobutene: Billeb, G.; Neuman, W. P.; Steinfoff, S. *Tetrahedron Lett.* **1988**, *29*, 5245. (b) Espenbetov, A. A.; Struchkov, Yu. T.; Kolesnikov, S. P.; Nefedov, O. M. *J. Organomet. Chem.* **1984**, *275*, 33. (c) Nefedov, O. M.; Egorov, A. M.; Gal'minas, A. M.; Kolesnikov, S. P.; Krebs, A.; Berndt, J. *J. Organomet. Chem.* **1986**, *301*, C21. (d) Ando, W.; Tsumuraya, T. *J. Chem. Soc., Chem. Commun.* **1989**, 770. (e) Billeb, G.; Brauer, H.; Neumann, W. P.; Weisbeck, M. *Organometallics* **1992**, *11*, 2069. (f) 1,2-Digermacyclobutane: Ohgaki, H.; Kabe, Y.; Ando, W. *Organometallics* **1995**, *14*, 2139. (g) 1,2-Digermacyclopentane: Mazerolles, P.; Lesbre, M.; Joanny, M. *J. Organomet. Chem.* **1969**, *16*, 227. We thank a reviewer for supplying this reference.

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

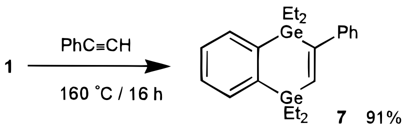
ppm in roughly 1:2:2:1 ratio which are indicative of two kinds of ethyl groups on the Ge atoms in a 2:1 ratio. In addition, there are three peaks at 127.14, 133.72, and 151.35 ppm attributable to those of the symmetrically substituted phenylene carbons. Along with the chemical shifts and the number of the ^{13}C NMR signals above, the benzo-1,2,3-trigermacyclopentene structure for the product **5** is also in accord with the molecular ion peak at *m*/*z* 468 in the mass spectrum coupled with the molecular symmetry. Similarly, the ^{13}C NMR spectrum of **6** consists of two types of resonance signals, namely, the higher field signals at 7.09, 8.94, 8.97, and 9.92 ppm in approximately 2:1:1:2 ratio, which are ascribable to carbons of two kinds of ethyl groups on the Ge atoms, and the lower field signals at 126.90, 127.36, 133.92, 134.51, 146.76, and 148.02 ppm, which are assignable to unsymmetrically substituted phenylene carbons. Thus, in addition to the chemical shifts and the number of the ^{13}C NMR signals, the molecular ion peak at *m*/*z* 544 in the mass spectrum is certainly consistent with structure **6**.

At first glance at the structures of **5** and **6**, diethylgermylene may conceivably be evolved during the thermolysis and to undergo insertion into the activated Ge−Ge bond of **1**.[9] Then, **1** was thermolyzed in the presence of a germylene trap, namely, either 2,3-dimethyl-1,3-butadiene[10] or dimethylphenylsilane[11] under similar conditions in a sealed tube. In either case, the expected germylene trapped product, namely, 1,1-diethyl-3,4-dimethyl-1-germacyclopent-3-ene or (diethylgermyl)dimethylphenylsilane, was not detected in the thermolysate but **5** and **6** were formed in similar yields as in the case of the thermolysis in the absence of the trapping agent (eqs 5 and 6). On the other hand, the thermolysis of **1** in the presence of phenylacetylene at 160 °C for 16 h yielded 2,3-benzo-1,4-digerma-5-phenylcyclohexa-2,5-diene (**7**) in 91% yield (eq 7).[5c,d] The structure of **7** is fully compatible with its spectroscopic properties, such as ^{1}H, ^{13}C NMR, and mass spectral data. In this case, none of **5** and **6** was detected in the thermolysate. Next, to trap another possible reactive intermediate, such as a germyl diradical **8** (Scheme 1),[12] **1** was thermolyzed in CCl_4 at 160 °C for 16 h to give two chlorinated products, 1,2-bis(chlorodiethylgermyl)benzene (**9**) and 1-(chlorodiethylgermyl)-2-((trichloromethyl)diethylgermyl)benzene (**10**) in 48 and 48% yields, respectively (eq 10).[13] The former **9** is the precursor of **1** as mentioned above (eq 1), and the structure of the latter **10** is fully compatible with its ^{1}H and ^{13}C NMR spectra along with mass spectrometric data. In addition to the carbon signals due to two kinds of ethyl groups on the Ge atoms, the ^{13}C NMR spectrum of **10** shows the signal at 96.70 ppm assignable to trichloromethyl carbon together with six signals at lower field, 128.73, 128.78, 134.64, 137.37, 139.87, and 143.36 ppm, arising from the unsymmetrically substituted phenylene carbons. The presence of a trichloromethyl group in **10** implies that the intervening germyl radical intermediate should be highly reactive.

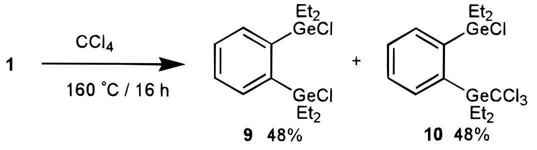


(5)

(6)

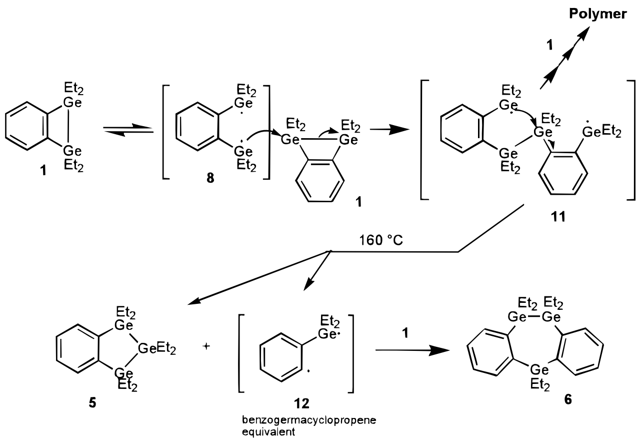


(7)



(8)

Scheme 1



Mechanistic Considerations. While at ambient temperature **1** undergoes ring-opening polymerization to give polymer **4** with high molecular weight, the thermolysis of **1** at higher temperature affords benzo-1,2,3-trigermacyclopentene **5** and dibenzo-1,2,5-trigermacycloheptadiene **6**, respectively, in reasonable yields. This can be rationalized as shown in Scheme 1. Since the Ge−Ge bond concerned is highly strained and the resultant germyl radical may be stabilized by the phenylene π-system to some extent, the homolytic scission of the activated Ge−Ge bond should occur readily to yield a bis(germyl) diradical **8**, which should revert to **1** again without difficulty by intramolecular

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[9] (a) Castel, A.; Escudié, J.; Riviere, P.; Satgé, J.; Bochkarev, M. N.; Maiorova, L. P.; Razuvaev, G. A. *J. Organomet. Chem.* **1981**, *210*, 37. (b) Mochida, K.; Kikkawa, H.; Nakadaira, Y. *Chem. Lett.* **1988**, 1089. (c) Mochida, K.; Kikkawa, H.; Nakadaira, Y. *J. Organomet. Chem.* **1991**, *412*, 9. Under certain reaction conditions, free dimethylgermylene reacts with some kinds of alkynes to yield the corresponding 1,2,3-trigermacyclopent-4-ene. However, from some experimental evidence, the trigermacyclopentene is suggested to be not the product from the corresponding 1,2-digermacyclobutene but rather arises from the reaction of the cyclotrigermane intermediate with the alkyne, whereas the silicon analog, a 1,2,3-trisilacyclopentene, is formed by insertion of a silylene into a 1,2-disilacyclobutene.[7e]

[10] Schriever, M.; Neuman, W. P. *J. Am. Chem. Soc.* **1983**, *105*, 897.

[11] Baines, K. M.; Cooke, J. A.; Vittal, J. J. *J. Chem. Soc., Chem. Commun.* **1992**, 1484.

[12] In thermolytic reactions of a silicon analog 3,4-benzo-1,1,2,2-tetraethyldisilacyclobutene, the corresponding *o*-quinodisilane has been postulated as an important reaction intermediate.[5p−r] However, in contrast, on consideration of germanium being the higher group 14 element and of a germyl radical being less reactive than a silyl radical, the reaction intermediate should be represented more adequately by diradical structure **8** rather than the corresponding *o*-quinodigermane.

[13] (a) Sakurai, H.; Mochida, K. *J. Chem. Soc., Chem. Commun.* **1971**, 1581. (b) Sakurai, H.; Mochida, K.; Hosomi, A.; Mita, F. *J. Organomet. Chem.* **1972**, *38*, 275. (c) Sakurai, H.; Mochida, K. *J. Organomet. Chem.* **1972**, *42*, 339. (d) Sakurai, H. In *Free Radical*; Kochi, J., Ed.; Wiley Interscience: New York, 1973; Vol. 2, p 741. (e) Coates, D. A.; Tedder, J. M. *J. Chem. Soc., Perkin Trans. 2* **1979**, 1568.

bond formation. The intervening diradical **8** should be trapped readily by means of phenylacetylene and carbon tetrachloride to yield **7**,[14] **9**, and **10**, respectively. Further, one of the germyl radical centers attacks intermolecularly on the activated Ge–Ge bond of a second molecule to bring about ring opening and to generate a dimeric germyl diradical **11** as shown by arrows in Scheme 1. One of the radical centers of the key intermediate **11** adds subsequently to the Ge–Ge bond of the other benzo-1,2-digermacyclobutene **1** to give a similar diradical with higher molecular weight as shown in the scheme. Repetition of the ring opening followed by radical addition eventually leads to polymer **4**.

On the other hand, it is noted the germyl radical center of **11** is well situated for intramolecular attack on one of the Ge atoms as depicted by arrows in the scheme. Thus, at higher temperature, such as at 160 °C, the intramolecular process would prevail to afford **5** with extrusion of a diradical **12**, which is conceivably a benzogermacyclopropene equivalent.[15] **12** should be highly reactive and finally insert into the reactive Ge–Ge bond of **1** to yield **6**.

Interestingly, on the thermolysis at 250 °C in a sealed degassed tube, a silicon analog, 3,4-benzo-1,1,2,2-tetraethyl-1,2-disilacyclobutene, has been reported to yield 4,5-benzo-1,1,2,2,3,3-hexaethyl-1,1,2,3-trisilacyclopentene and 2,3:5,6-dibenzo-1,1,4,4-tetraethyl-1,4-disilacyclohexadiene.[5q] The former corresponds to the silicon analog of **5**, but the latter does not. Formation of the dibenzo-1,4-disilacyclohexadiene was explained by dimerization of the benzosilacyclopropene. In the thermolysis of **1**, **12** may be too reactive to survive long enough to undergo dimerization.

Experimental Section

General Methods. All reactions were carried out under an atmosphere of argon excepting polymerization and thermolytic reactions, which were carried out in a degassed sealed glass tube. THF and toluene were dried by refluxing over sodium benzophenone ketyl and distilled just before use. Carbon tetrachloride was refluxed over CaH_2 and distilled before use. NMR spectra were obtained on Varian Unity plus 300 and 500 MHz spectrometers. GCMS spectra were measured on Shimadzu QP-1000 and Hitachi M-2500 spectrometers. Molecular weights of polymers were determined with a Tosoh-CCPD gel permeation chromatograph using THF as the eluent and relative to the polystyrene standard.

Materials. *o*-Dibromobenzene, phenylacetylene, 2,3-dimethyl-1,3-butadiene, and dimethylphenylsilane were commercially available. Chlorodiethylgermane was prepared as reported in the literature.[18]

Preparation of 1,2-Bis(diethylgermyl)benzene. To a mixture of magnesium (9.5 g, 0.390 mol), chlorodiethylgermane (65.0 g, 0.390 mol), and THF (270 mL) was added *o*-dibromobenzene (38.2 g, 0.162 mol) in THF (80 mL) over a period of 3 h at room temperature. After reflux for 18 h, the mixture was hydrolyzed with water whereupon hexane (200 mL) was added. The organic layer was separated, washed with water, and dried over Na_2SO_4. After the solvent was evaporated, the residue was distilled under reduced pressure to give 1,2-bis(diethylgermyl)benzene (29.9 g, 0.088 mol, 54% yield): bp 97 °C/0.15 mmHg; ^1H NMR ($CDCl_3$) δ 1.02–1.16 (m, 20H, EtGe), 4.51 (br s, 2H, HGe), 7.26–7.46 (m, 4H, phenylene ring protons); ^{13}C NMR ($CDCl_3$) δ 5.93, 10.09 (EtGe), 127.67, 134.77, 145.50 (phenylene ring carbons); MS *m*/*z* (relative intensity) 340 (M^+, ^{74}Ge, ^{72}Ge, 2), 311 ($M^+ - Et$, ^{74}Ge, ^{72}Ge, 100); HRMS calcd for $C_{14}H_{26}{}^{74}Ge_2$ 342.0458, found 342.0465. Anal. Calcd for $C_{14}H_{26}Ge$: C, 49.52; H, 7.72. Found: C, 49.55; H, 7.53.

Preparation of 1,2-Bis(chlorodiethylgermyl)benzene. A solution of 1,2-bis(diethylgermyl)benzene (25.0 g, 73.6 mmol) in CCl_4 (130 mL) containing a catalytic amount of benzoyl peroxide (178 mg, 0.74 mmol) was heated to reflux for 5 h. The solvent was evaporated, and the residue was distilled under reduced pressure to give 1,2-bis(chlorodiethylgermyl)benzene (26.9 g, 65.9 mmol, 89% yield): bp 135 °C/0.2 mmHg; ^1H NMR ($CDCl_3$) δ 1.02–1.22 (m, 20H, EtGe), 7.31–7.79 (m, 4H, phenylene ring protons); ^{13}C NMR ($CDCl_3$) δ 8.25, 14.14 (EtGe), 129.02, 135.25, 142.40 (phenylene ring carbons); MS *m*/*z* (relative intensity) 379 ($M^+ - Et$, ^{74}Ge, ^{72}Ge, 100); HRMS calcd for $C_{12}H_{19}{}^{74}Ge_2Cl_2$ ($M^+ - Et$) 380.9287, found 380.9273. Anal. Calcd for $C_{14}H_{24}Ge_2Cl_2$: C, 41.17; H, 5.92. Found: C, 41.02; H, 5.95.

Preparation of 3,4-Benzo-1,1,2,2-tetraethyl-1,2-digermacyclobut-3-ene (1). A solution of 1,2-bis(chlorodiethylgermyl)benzene (5.0 g, 12.2 mmol) in toluene (40 mL) was slowly added to sodium (0.7 g, 30.0 mmol) in refluxing toluene (80 mL). After the mixture continued to reflux for 16 h, the resulting salt was filtered off. The filtrate was concentrated under reduced pressure at below 30 °C, and the residue was diluted with hexane. The crude solution thus obtained was chromatographed rapidly on a silica gel short column with hexane to remove the germoxane. After evaporation of the solvent, the residue was Kugelrohr-distilled (115–120 °C/0.1 mmHg) to afford **1** (1.0 g, 2.96 mmol, 24% yield). Pure **1** was diluted with hexane (<2%) and stored below −20 °C in Ar. Under these conditions, **1** was stable for several months. **1**: ^1H NMR ($CDCl_3$) δ 1.06–1.31 (m, 20H, EtGe), 7.28–7.56 (m, 4H, phenylene ring protons); ^{13}C NMR ($CDCl_3$) δ 8.52, 10.54 (EtGe), 128.00, 132.70, 158.65 (phenylene ring carbons); MS (20 eV) *m*/*z* (relative intensity) 338 (M^+, ^{74}Ge, ^{72}Ge, 32), 309 ($M^+ - Et$, ^{74}Ge, ^{72}Ge, 100); HRMS calcd for $C_{14}H_{24}{}^{74}Ge_2$ 340.0302, found 340.0313. Anal. Calcd for $C_{14}H_{24}Ge_2$: C, 49.82; H, 7.17. Found: C, 49.74; H, 7.19.

Oxidation of 1. A solution of **1** (100 mg, 0.296 mmol) in toluene (3 mL) was stirred for 120 h in air. GC and GCMS analysis showed that **2** was produced quantitatively. **2**: ^1H NMR ($CDCl_3$) δ 1.03–1.19 (m, 20H, EtGe), 7.33–7.53 (m, 4H, phenylene ring protons); ^{13}C NMR ($CDCl_3$) δ 7.89, 10.32 (EtGe), 128.58, 131.88, 146.92 (phenylene ring carbons); MS *m*/*z* (relative intensity) 354 (M^+, ^{74}Ge, ^{72}Ge, 0.2), 325 ($M^+ - Et$, ^{74}Ge, ^{72}Ge, 100); HRMS calcd for $C_{12}H_{19}{}^{74}Ge_2O$ ($M^+ - Et$) 326.9860, found 326.9864. Anal. Calcd for $C_{14}H_{24}Ge_2O$: C, 47.57; H, 6.84. Found: C, 47.80; H, 7.09.

Sulfurization of 1. A mixture of **1** (100 mg, 0.296 mmol), sulfur (19 mg, 0.592 mmol), and toluene (3 mL) was stirred

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[14] Benzo-1,4-digermacyclohexadiene **7** may be possibly formed by way of a 4 + 2 cycloaddition reaction.

[15] Silacyclopropenes[16] are thermally stable at ambient temperature; however only a few germacyclopropenes are known so far.[17] This may be indicative that a germacyclopropene is far less stable than a silacyclopropene.

[16] (a) Conlin, R. T.; Gaspar, P. P. *J. Am. Chem. Soc.* **1976**, *98*, 3715. (b) Seyferth, D.; Annarelli, D. C.; Vick, S. C. *J. Am. Chem. Soc.* **1976**, *98*, 6382. (c) Ishikawa, M.; Fuchikami, T.; Kumada, M. *J. Am. Chem. Soc.* **1977**, *99*, 245. (d) Sakurai, H.; Kamiyama, Y.; Nakadaira, Y. *J. Am. Chem. Soc.* **1977**, *99*, 3879.

[17] (a) Krebs, A.; Berndt, J. *Tetrahedron Lett.* **1988**, *24*, 4083. (b) Egorov, M. P.; Kolesnikov, S. P.; Struchkov, Yu. T.; Antipin, M. Yu.; Sereda, S. V.; Nefedov, O. M. *J. Organomet. Chem.* **1985**, *290*, C27.

[18] (a) Lesbre, M.; Satgé, J. *Comput. Rend.* **1961**, *252*, 1976. (b) Satgé, J. *Am. Chem. (Paris)* **1961**, *6*, 519.

[19] The ^{13}C NMR chemical shift of the vinyl carbon in **7** is known to be remarkably low.[20] In fact, the silicon analog of **7** has been reported to show the vinylic carbon signal at 161.1 ppm.[5p] In conformity with these results, 3,3,7,7-tetraethyl-1-phenyl-3,7-digermacycloheptene, obtained from the cycloaddition of 1,1,2,2-tetramethyl-1,2-digermacyclopentane[7g] with phenylacetylene in the presence of a palladium catalyst, shows the corresponding ^{13}C NMR signal at 163.46 ppm.[21] In this case, the vinylic carbon signal is unambiguously assigned.

[20] Sakurai, H.; Tobita, H.; Nakadaira, Y. *Chem. Lett.* **1982**, 1251.

[21] Komoriya, H.; Kako, M.; Nakadaira, Y. Unpublished results.

for 120 h at room temperature in Ar. The resulting solution was evaporated, followed by purification with silica gel TLC to give **3** (103 mg, 0.28 mmol, 94% yield). Similarly, at reflux temperature the sulfurization was complete in 1 h (95% yield). **3**: ^{1}H NMR ($CDCl_3$) δ 1.05−1.27 (m, 20H, EtGe), 7.35−7.53 (m, 4H, phenylene ring protons); ^{13}C NMR ($CDCl_3$) δ 8.74, 11.95 (EtGe), 128.28, 131.73, 146.90 (phenylene ring carbons); MS *m*/*z* (relative intensity) 370 (M^+, ^{74}Ge, ^{72}Ge, 2), 341 (M^+ − Et, ^{74}Ge, ^{72}Ge, 100); HRMS calcd for $C_{14}H_{24}{}^{74}Ge_2S$ 372.0022, found 372.0023. Anal. Calcd for $C_{14}H_{24}Ge_2S$: C, 45.50; H, 6.55. Found: C, 45.71; H, 6.78.

Polymerization of 1. A solution of **1** (100 mg, 0.296 mmol) in toluene (0.5 mL) was evacuated and sealed in a glass tube, and this was allowed to stand for 16 h. The resulting mixture was reprecipitated from hexane to give a white solid polymer (90 mg, 90% yield): ^{1}H NMR (C_6D_6) δ 1.07−1.24 (EtGe), 7.14−7.65 (phenylene ring protons); ^{13}C NMR (C_6D_6) δ 8.21, 10.59 (EtGe), 128.85, 132.23, 147.74 (phenylene ring carbons); $M_n = 4.4 \times 10^5$, $M_w = 7.4 \times 10^5$, $M_w/M_n = 1.7$ (GPC, THF, polystyrene standard). Anal. Calcd for $C_{14}H_{24}Ge_2$: C, 49.82; H, 7.17. Found: C, 49.65; H, 7.17.

Thermolysis of 1. A degassed sealed tube containing **1** (446 mg, 1.32 mmol) was heated at 160 °C for 20 h. The tube was cooled and opened. The contents was chromatographed on silica gel with hexane to afford **5** (184 mg, 0.393 mmol, 89% yield) and **6** (127 mg, 0.233 mmol, 53% yield). The yields of both products **5** and **6** are calculated on the basis of the stoichiometry expressed by Scheme 1. **5**: ^{1}H NMR ($CDCl_3$) δ 1.02−1.20 (m, 30H, EtGe), 7.24−7.56 (m, 4H, phenylene ring protons); ^{13}C NMR ($CDCl_3$) δ 3.58, 7.78, 10.16, 12.47 (EtGe), 127.14, 133.72, 151.35 (phenylene ring carbons); MS *m*/*z* (relative intensity) 468 (M^+, ^{74}Ge, $^{72}Ge_2$, 8), 439 (M^+ − Et, ^{74}Ge, $^{72}Ge_2$, 42); HRMS calcd for $C_{18}H_{34}{}^{74}Ge{}^{72}Ge_2$ 468.0314, found 468.0318. Anal. Calcd for $C_{18}H_{34}Ge_3$: C, 46.17; H, 7.32. Found: C, 46.41; H, 7.57. **6**: ^{1}H NMR ($CDCl_3$) δ 0.91−1.29 (m, 30H, EtGe), 7.23−7.55 (m, 8H, phenylene ring protons); ^{13}C NMR ($CDCl_3$) δ 7.09, 8.94, 8.97, 9.92 (EtGe), 126.90, 127.36, 133.92, 134.51, 146.76, 148.02 (phenylene ring carbons); MS (20 eV) *m*/*z* (relative intensity) 544 (M^+, ^{74}Ge, $^{72}Ge_2$, 5), 515 (M^+ − Et, ^{74}Ge, $^{72}Ge_2$, 82); HRMS calcd for $C_{22}H_{33}{}^{74}Ge{}^{72}Ge_2$ (M^+ − Et) 515.0236, found 515.0234. Anal. Calcd for $C_{24}H_{38}Ge_3$: C, 52.96; H, 7.04. Found: C, 52.89; H, 7.31.

Thermolysis of 1 in the Presence of Phenylacetylene. A degassed sealed tube containing **1** (150 mg, 0.444 mmol) and phenylacetylene (136 mg, 1.33 mmol) was heated at 160 °C for 16 h. The contents were chromatographed on silica gel TLC with hexane to give **7** (178 mg, 0.405 mmol, 91% yield): ^{1}H NMR ($CDCl_3$) δ 0.87−1.13 (m, 20H, EtGe), 6.95 (s, 1H, HC═C), 7.20−7.52 (m, 9H, aromatic protons); ^{13}C NMR ($CDCl_3$) δ 7.41, 7.93, 9.08, 9.19 (EtGe), 126.07, 126.45, 127.59, 127.71, 128.26, 133.25, 133.29, 145.27, 145.83, 147.24 (aromatic carbons), 142.90 (H*C*═C), 160.38 (*C*═CH);[19] MS *m*/*z* (relative intensity) 411 (M^+ − Et, ^{74}Ge, ^{72}Ge, 83); HRMS calcd for $C_{20}H_{25}{}^{74}Ge_2$ (M^+ − Et) 413.0380, found 413.0368. Anal. Calcd for $C_{22}H_{30}Ge_2$: C, 60.10; H, 6.88. Found: C, 60.31; H, 7.01.

Thermolysis of 1 in the Presence of 2,3-Dimethyl-1,3-butadiene. A degassed sealed tube containing **1** (100 mg, 0.296 mmol), 2,3-dimethyl-1,3-butadiene (486 mg, 5.92 mmol), and benzene (5 mL) was heated at 160 °C for 20 h. GC and GCMS analysis of the resulting mixture showed **5** (80%) and **6** (58%) were produced.

Thermolysis of 1 in the Presence of Dimethylphenylsilane. A degassed sealed tube containing **1** (100 mg, 0.296 mmol) and dimethylphenylsilane (807 mg, 5.92 mmol) was heated at 160 °C for 20 h. GC and GCMS analysis of the resulting mixture showed **5** (98%) and **6** (50%) were produced.

Thermolysis of 1 in CCl_4. A degassed sealed tube containing **1** (200 mg, 0.592 mmol) and CCl_4 (3 mL) was heated at 160 °C for 16 h. The reaction mixture was analyzed by GC and GCMS as being **9** (48%) and **10** (48%). Pure **10** was isolated by preparative GC. **10**: ^{1}H NMR ($CDCl_3$) δ 1.03−1.62 (m, 20H, EtGe), 7.28−8.05 (m, 4H, phenylene ring protons); ^{13}C NMR ($CDCl_3$) δ 8.19, 9.02, 9.53, 13.34 (EtGe), 96.70 (CCl_3), 128.73, 128.78, 134.64, 137.37, 139.87, 143.36 (phenylene ring carbons); MS *m.z* (relative intensity) 461 (M^+ − Et, ^{74}Ge, ^{72}Ge, 0.8), 373 (M^+ − CCl_3, ^{74}Ge, ^{72}Ge, 100). Anal. Calcd for $C_{15}H_{24}Ge_2Cl_4$: C, 36.67; H, 4.92. Found: C, 36.73; H, 4.78.

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