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Preparation and Properties of 3,4,7,8-Tetragermacycloocta-1,5-diyne and Related Compounds

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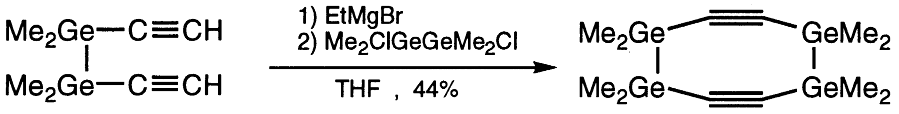
Permethylated 3,4,7,8-tetragermacycloocta-1,5-diyne (**1**) and 3,4-disila-7,8-digermacycloocta-1, 5-diyne (**2**) were prepared. The photoelectron spectra of **1** and **2** were compared with that of their tetrasila-analog **3**. The first ionization potential decreases in the order of **3**, **2**, and **1**. Charge-transfer spectra of **1**-teracyanoethylene (TCNE), **2**-TCNE and 3-TCNE complexes were observed. Only **1** was oligomerized in the presence of TCNE to give its higher homologues. All **1**, **2**, and **3** cycloadded to 2,3-dichloro-5,6-dicyano-1,4-benzoquinone to give the corresponding 1:1 adducts in a [2+6] manner.

A 3,4,7,8-tetrasilacycloocta-1,5-diyne shows characteristic electronic properties which are rationalized by through-bond conjugation among the two in-plane π-orbitals of ethynylenes and the two σ-orbitals of Si-Si bonds.1) To examine the element effect on the σ–π interaction of the disilanylene-ethynylene, the two corresponding germanium analogs, 3,3,4,4,7,7,8,8-octamethyl-3,4,7,8-tetragermacycloocta-1,5-diyne (**1**) and 3,3,4,4,7,7,8,8-octamethyl-3,4-disila-7,8-digermacycloocta-1,5-diyne (**2**) were newly prepared. In this paper, we will describe some physical and chemical properties of **1** and **2**, together with the comparison with those of parent compound, 3,3,4,4,7,7,8,8-octamethyl-3,4,7,8-tetrasilacycloocta-1,5-diyne (**3**).

Tetragermacyclooctadiyne **1** was prepared by the reaction of the di-Grignard reagent derived from 1,2-diethynyl-1,1,2,2-tetramethyldigermane with 1,2-dichlorotetramethyldigermane in THF (44% yield).2) Similarly, disiladigermacyclooctadiyne **2** was prepared by the reaction of the di-Grignard reagent derived from 1,2-diethynyl-1,1,2,2-tetramethyldisilane with 1,2-dichlorotetramethyldigermane in THF (38% yield).3) The structural assignments of **1** and **2** were made on the basis of their spectroscopic data.



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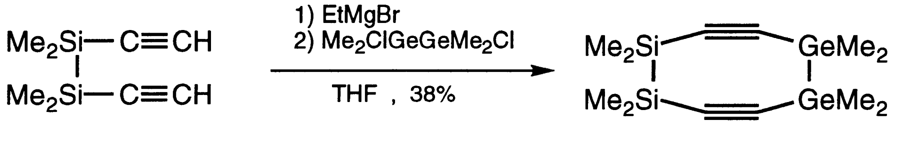

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Table 1. Ionization Potentials, Charge-transfer Energies, and UV Absorption Maxima of **1**, **2**, and **3**

	IP/eV[a)]	E_{CT}/eV[b)]	λ_{max}/nm(ε)[c)]
1	8.00	2.54	238 (17000) 228 (sh 11100)
2	8.15	2.65	244 (18200) 232 (sh 10900)
3	8.18	2.69	251 (18500) 237 (sh 13900)

a) Determined by a photoelectron spectroscopy. b) With TCNE in CH_2Cl_2. c) In c-C_6H_{12}.

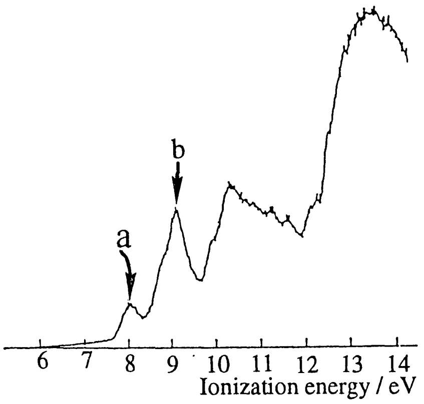


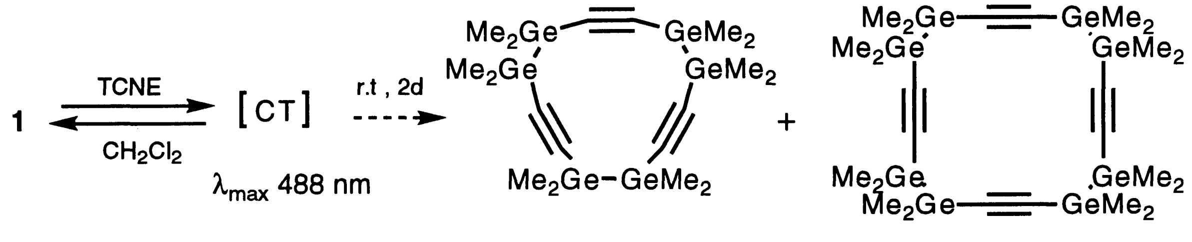
Fig. 1. Photoelecrton spectrum of **1.**

The gas-phase He I photoelectron (PE) spectra of **1**, **2**, and **3** are quite similar in pattern and show two peaks labeled a and b, a around 8 eV and b below 10 eV, well separated from other more intense peaks as shown in Fig. 1 for **1**. The a band of each compound corresponds to the ionization from the HOMO formed mainly by antibonding type interaction between the in-plane π group orbitals of the two ethynylene units and σ group orbitals of the two Ge-Ge units.[1b,c)] The first ionization potentials (IP's) obtained from the PE spectra decrease in the order of **3**, **2**, and **1** as listed in Table 1. The similar trends are recognized for the peaks b, namely the top of the respective peak is at 9.17 (**1**), 9.36 (**2**), and 9.48 (**3**) eV. Thus, HOMO level energy of each compound decreases in the order of **1**, **2**, and **3**. From consideration of the intensities, each peak b is regarded to correspond emissions from several relevant molecular orbitals. The degree of destabilization of the σ-M-M (M=Ge for **1** and Si for **3**) level due to the σ–π through-bond conjugation in **1** and **3** would be conceivable to be similar to each other from comparisons of the first IP's in Table 1 with those of hexamethyldisilane and hexamethyldigermane.[4)] On the other hand, the germanium analogs **1** and **2** show characteristic absorption maxima for these ethynylenes at 238 and 244 nm, respectively, and this indicates the substitution of the Si-Si bond with the Ge-Ge in the molecule causes blue shift of the absorption maximum.[5)] Since generally speaking, the UV absorption at the longest wavelength corresponds to the electronic transition from HOMO to LUMO, the IP values in Table 1 being taken into account, the LUMO level of each compound can be regarded to decrease in the order of **1**, **2**, and **3**.

At present, σ-Si-Si and σ-Ge-Ge bonds are well-known to act as efficient electron donors to form charge-transfer (CT) complexes with electron acceptors such as tetracyanoethylene (TCNE).[6, 7)] **1**, **2**, and **3** (0.1-0.5 M) are colored on mixing with TCNE (0.01-0.02 M) in CH_2Cl_2 to give characteristic intermolecular CT absorptions in the visible region (**1** at 488 nm, **2** at 467 nm, and **3** at 462 nm). The intensities increase with the concentration of both the ethynylene and TCNE. The maxima of the CT spectra are red-shifted in the order of **3**, **2**, and **1** as the IP value of the donor decreases. A linear relationship between the frequencies of CT bands and IP's of respective compounds was observed.

$$E_{CT}(\mathrm{eV}) = 0.801\ \mathrm{IP(PE)} - 3.87\ (r = 0.989)$$

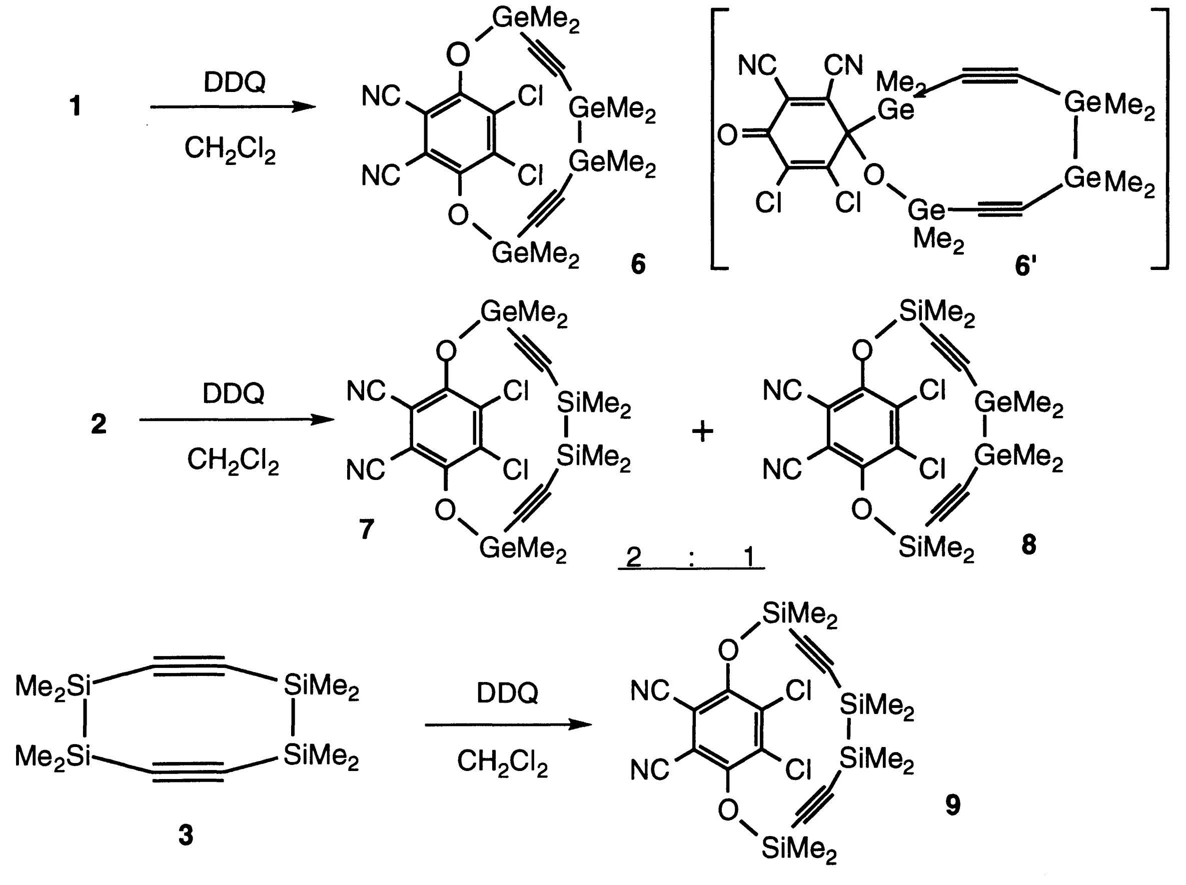
A σ-Ge-Ge bond is more susceptible to electrophiles, and in fact, TCNE is inserted into the σ-Ge-Ge bond of polygermanes to give a 1:1 adduct under mild conditions.[7)] Interestingly, **1** is oligomerized in the presence of TCNE in CH_2Cl_2 at room temperature possibly via the CT complex to give higher homologs **4** and **5** in 20 and 5%, respectively.[8)] However, under the reaction conditions **2** and **3** show only CT bands which are stable



4 20% **5** 5%

prolonged standing at room temperature, and remains unchanged even on irradiation of their CT bands. The electron transfer should be intervened in the oligomerization but the detailed mechanism remains to be clarified.

On mixed with another acceptor, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in CH_2Cl_2, these ethynylenes **1**, **2**, and **3** show also characteristic intermolecular CT absorption maxima even at the longer wavelength, namely, 536, 519 and 516 nm, respectively. However, in contrast to the case of TCNE above, the CH_2Cl_2 solution of **1** and DDQ leads to the formation of [2+6] cycloadduct **6** on standing at ambient temperature as shown in the scheme.[9] Similarly, under similar conditions **2** and **3** with DDQ yield the corresponding bridged adducts **7-9**, respectively.[9] The course of the reaction can be followed by means of ^{1}HNMR, for an example, the Ge-Me signals of **1** in CD_2Cl_2 containing DDQ decreases with concomitant appearance of four signals with equal intensities at δ 0.41, 0.47, 0.95 and 1.00 which are reasonably assigned to those of **6**. Another possible structure **6'** for the cycloadduct is highly improbable since **6'** should give eight kinds of Ge-Me signals in its ^{1}HNMR spectrum. Monitoring by ^{1}HNMR revealed that the cycloaddition of **1** proceeded almost quantitatively, and more smoothly than those of **2** and **3**. Accordingly, **2** forms the cyclo-



adducts **7** and **8** in the 2:1 ratio.

The germanium analogs **1** and **2** show basically similar electronic characteristics of the disilanyleneethynylene **3** as judging from their PE and UV spectra. However, because of the lower IP and the weaker bond strength of the σ-Ge-Ge bond, the germanium analog is more reactive toward electrophiles. Thus, only **1** undergoes oligomerization to give higher homologue in the presence of TCNE, and **1** and **2** undergo more readily the [2+6] cycloaddition with DDQ than sila-analog **3**.

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2) **1**: mp 158-160 °C; ^{1}HNMR ($CDCl_3$) δ 0.47(s, 24H, GeMe); ^{13}CNMR ($CDCl_3$) δ -1.84(GeMe), 116.72 (C=C); Anal. Found: C, 31.53, H, 5.43%. Calcd for $C_{12}H_{24}Ge_4$: C, 31.42, H, 5.27%. MS (rel. intensity) 458(M^+ ^{70}Ge, ^{72}Ge, $^{74}Ge_2$, 33), 443(M^+-Me, ^{70}Ge, ^{72}Ge, $^{74}Ge_2$, 48), 119($GeMe_3^+$, ^{74}Ge, 100).

3) **2**: mp 147-149 °C; ^{1}HNMR ($CDCl_3$) δ 0.23(s, 12H, SiMe), 0.48(s, 12H, GeMe); ^{13}CNMR ($CDCl_3$); δ -2.70 (SiMe), -2.01(GeMe), 117.25(GeC=C), 119.27(SiC=C); Anal. Found: C, 39.10, C, 6.72%. Calcd for $C_{12}H_{24}Ge_2Si_2$: C, 38.98, H, 6.54. MS (rel. intensity) 370(M^+ ^{72}Ge, ^{74}Ge, 40), 355(M^+-Me, ^{72}Ge, ^{74}Ge, 100), 73($SiMe_3$, 94).

4) IP values from PE are reported to be 8.69 eV for hexamethyldisilane[a)] and and 8.57 eV for hexamethyldigermane,[b)] respectively. a) H. Bock and W. Ensslin, *Angew. Chem., Int. Ed. Engl.*, **10**, 404 (1971); b) K. Mochida, S. Masuda, and Y. Harada, *Chem. Lett.*, **1992**, 2281.

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8) **4**: ^{1}HNMR ($CDCl_3$) δ 0.45 (s, 36H, GeMe); ^{13}CNMR ($CDCl_3$); δ -2.16 (GeMe), 111.24 (C=C); MS (rel. intensity) 688 (M^+, ^{70}Ge, $^{72}Ge_2$, $^{74}Ge_3$, 11), 119 ($GeMe_3^+$, ^{74}Ge, 100). **5** :^{1}HNMR ($CDCl_3$) δ 0.47 (s, 48H, GeMe); ^{13}CNMR ($CDCl_3$); δ -1.58(GeMe), 111.84 (C=C); MS (rel. intensity) 916 (M^+, $^{70}Ge_2$, $^{72}Ge_2$, ^{74}Ge, 12), 119 ($GeMe_3^+$, ^{74}Ge, 100).

9) **6**: ^{1}HNMR (CD_2Cl_2) δ 0.41(s, 6H, GeGeMe), 0.47(s, 6H, GeGeMe), 0.95(s, 6H, OGeMe), 1.00(s, 6H, OGeMe); MS (rel. intensity) 686(M^+, $^{72}Ge_2$, $^{74}Ge_2$, 7), 671(M^+-Me, 6), 119($GeMe_3^+$, 100); **7**: ^{1}HNMR (CD_2Cl_2) δ 0.18(s, 6H, SiMe), 0.24(s, 6H, SiMe), 0.96(s, 6H, GeMe), 1.02(s, 6H, GeMe); MS (rel. intensity) 596(M^+, ^{72}Ge, ^{74}Ge, 5), 581(M^+-Me, 7), 119($GeMe_3^+$, ^{74}Ge, 100); **8**: ^{1}HNMR (CD_2Cl_2) δ 0.41(s, 6H, GeMe), 0.47(s, 6H, GeMe), 0.60(s, 6H, SiMe), 0.66 (s, 6H, SiMe); MS (rel. intensity) 596(M^+, ^{72}Ge, ^{74}Ge, 5), 581(M^+-Me, 7), 119($GeMe_3^+$, ^{74}Ge, 100); **9** ^{1}HNMR (CD_2Cl_2) δ 0.16(s, 6H, SiSiMe), 0.22(s, 6H, SiSiMe), 0.60(s, 6H, OSiMe), 0.66(s, 6H, OSiMe); MS (rel. intensity) 506(M^+, 4), 491(M^+-Me, 4), 73 ($SiMe_3^+$, 100).

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