Electronic properties, polymerization, and cycloaddition of 3,4,7,8-tetragermacycloocta-1,5-diyne and related compounds ☆

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Abstract

Permethylated 3,4,7,8-tetragermacycloocta-1,5-diyne (1) and 3,4-disila-7,8-digermacycloocta-1,5-diyne (2) were prepared. The photo-electron spectra of 1 and 2 were compared with that of their tetrasila analogue 3. The first ionization energy decreases in the order 3 > 2 > 1. Charge-transfer spectra of 1–tetracyanoethylene (TCNE), 2–TCNE and 3–TCNE complexes were observed. In CH_2Cl_2 containing TCNE 1 underwent oligomerization to give its higher homologues, and in CH_3CN containing a catalytic amount of TCNE both 1 and 2 were polymerized to give the corresponding polymers almost quantitatively, whereas the sila analogue 3 was stable under these conditions. All compounds 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.

Keywords: Germanium; Charge transfer; Group 14; Photoelectron spectroscopy; Main Group metals; Silicon

1. Introduction

3,4,7,8-Tetrasilacycloocta-1,5-diynes show character-istic 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 [2–4]. However, in rigid cyclic diacetylenes with a saturated carbon bridging units, such as 1,5-cyclooc-tadiyne, it has been demonstrated that the transannular interaction of the two triple bonds via through bonds should not be so significant by comparison of photo-electron (PE) spectra of related diacetylenes [5]. In addition, recently a 3,4,7,8-tetrasilacycloocta-1,5-diyne has been shown to act as a precursor of polydisilanyle-neethynylene [6]. Partly to examine the element effect on the σ–π interaction of the disilanyleneethynylene and also to explore new types of germanium-containing

polymers [7], two corresponding germanium analogue, 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 pre-pared. In this paper, we describe the electronic proper-ties, polymerization and cycloaddition of 1 and 2, to-gether with a comparison with those of the parent compound, 3,3,4,4,7,7,8,8-octamethyl-3,4,7,8-tetrasila-cycloocta-1,5-diyne (3) [1].

2. Results and discussion

2.1. Preparation of octamethyl-3,4,7,8-tetragerma-cycloocta-1,5-diyne (1) and octamethyl-3,4-disila-7,8-digermacycloocta-1,5-diyne (2)

First, 1,2-diethynyl-1,1,2,2-tetramethyldigermane was prepared by the reaction of 1,2-dichlorotetramethyldi-germane with 2 mol of ethynyl Grignard reagent in THF. The diethynyldigermane obtained was converted into the di-Grignard reagent and was reacted with the 1,2-dichlorodigermane in THF to give the tetragermacy-

Table 1

Orbital energies (E_j) calculated for 1, 2 and 3 using the MNDO method

j (MO No.)	$-E_j$ (eV)		
	1	2	3
44 (HOMO)	8.912	8.996	9.139
43	9.567	9.723	9.886
42	10.573	10.588	10.596
41	10.632	10.670	10.698
40	10.716	10.754	10.777
39	11.418	11.444	11.464

[a] Calculated for comparison [4,9].

Table 2

Ionization energies (IE), charge-transfer energies (E_{CT}) and UV absorption maxima (λ_{max}) of 1, 2 and 3

Compound	IE (eV) [a]	E_{CT} (eV) [b]	λ_{max} (nm) (ε) [c]
1	8.00, 9.17	2.54	238 (17000)
			228 (sh 11100)
2	8.15, 9.36	2.65	244 (18200)
			232 (sh 10900)
3	8.18 [d], 9.48 [d]	2.69	251 (18500) [d]
			237 (sh 13900)

[a] Determined by PE spectroscopy.
[b] With TCNE in CH_2Cl_2.
[c] In cyclohexane.
[d] Measured for comparison under the same conditions as for 1 and 2 [4].

clooctadiyne 1 (44% yield) (Eq. 1). Similarly, the disi-ladigermacyclooctadiyne 2 was prepared by the reaction of the di-Grignard reagent derived from 1,2-diethynyl-1,1,2,2-tetramethyldisilane with 1,2-dichlorotetrameth-yldigermane in THF (38% yield) (Eq. 2). The structural assignments of 1 and 2 were made on the basis of their spectroscopic data.

2.2. Photoelectron and UV spectra and orbital sequence

The molecular orbital sequence and energies have been predicted for 1, 2 and 3 by MNDO calculations [8,9]. According to the calculations, the orderings of the orbitals are the same among these cyclic diynes, and the calculated orbital energies of the six HOMOs are given in Table 1. The calculated orbital sequence for 1 will be taken into account in drawing an orbital energy in the discussion afterwards (Fig. 2).

The gas-phase He I PE spectra of 1 and 2 are shown in Fig. 1 and the ionization energy (IE) values of the ethynylenes including 3 obtained from the PE spectra are summarized in Table 2. The PE spectra of 1, 2 and 3 are similar in pattern, as predicted by the MNDO calculations and show two bands labelled a and b, with a around 8 eV and b around 9.5 eV, well separated from the following more intense bands, as shown in Fig. 1. Taking into account the observed IE values and MNDO results, a symmetry-adapted orbital interaction diagram was drawn for 1 as shown in Fig. 2. This

diagram reveals that a strong $\sigma-\pi$ interaction between the in-plane π group orbitals and the σ group orbitals of the cyclic diethynylene should be due to the small energy separation of the orbitals concerned, as indicated in the case of 3. Thus, the a band of each compound corresponds to the ionization from the HOMO formed mainly by an 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 (Fig. 2) [3,4]. The first IEs obtained from the PE spectra decrease in the order of 3 > 2 > 1, as listed in Table 2. Similar trends are found for peaks b, namely the top of the respective peak is at 9.17 (1), 9.36 (2) and 9.48 (3) eV (Table 2). Thus, the HOMO level energy of each compound decreases in the order 1 > 2 > 3, in accordance with the MNDO predictions (Table 1). From consideration of the intensities, each b band is regarded as corresponding to emissions from several relevant molecular orbitals as shown in Fig. 2.

Although the periodic numbers of the two elements germanium and silicon in the Periodic Table are different, i.e. the former is higher than the latter, the degrees of destabilization of the σ-M–M (M = Ge for 1 and Si for 3) levels due to the $\sigma-\pi$ through-bond conjugation in 1 and 3 are concluded to be similar to each other from comparison of the first IEs in Table 2 with those
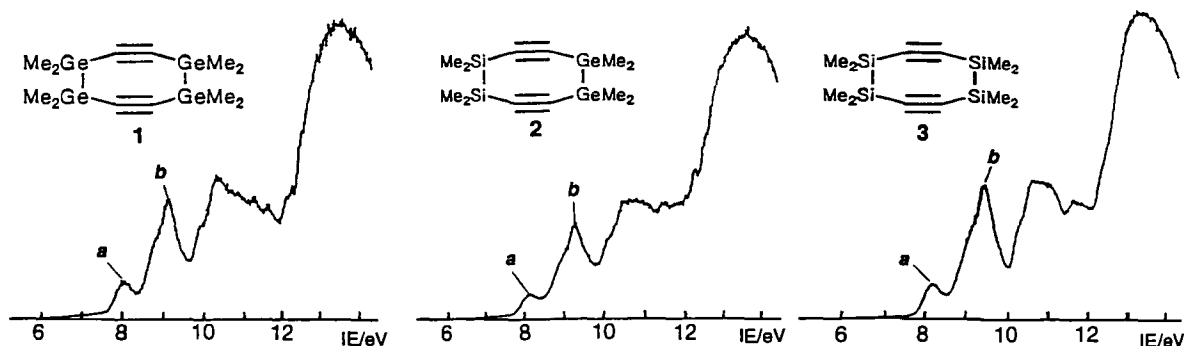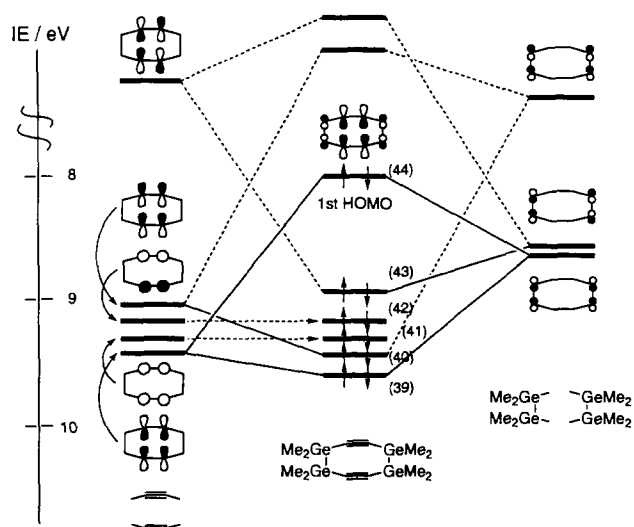

Fig. 1. Photoelectron spectra of 1, 2 and 3.

Fig. 2. Schematic diagram of basis group orbital interaction diagram for 1. The MOs are arranged with reference to *IE* values obtained from the PE spectrum.

of hexamethyldisilane (*IE* 8.69 eV) and hexamethyldigermane (*IE* 8.57 eV) [13,14]. It is worth noting that the first *IE* of 2 is closer to that of 3 than 1.

On the other hand, the germanium analogue 1 and 2 show characteristic UV absorption maxima for these ethynylenes at 238 and 244 nm, respectively, and this indicates that substitution of the Si–Si bond with the Ge–Ge bond in the molecule causes a blue shift of the absorption maximum [15]. Since, in general, the UV absorption at the longest wavelength corresponds to the electronic transition from HOMO to LUMO, the *IE* values in Table 2 being taken into account, the LUMO level of each compound can be considered to decrease in the order 1 > 2 > 3.

2.3. Charge-transfer spectra and polymerization

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) [18,19]. Compounds 1, 2 and 3 (0.1–0.5 M) become coloured 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 increasing 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 *IE* value of the donor decreases (Table 2). A linear relationship between the frequencies of CT bands and the *IE*s of the respective compounds is observed according to the equation

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

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 [14]. Unlike the polygermane, 1 turns out to be oligomerized in the presence of TCNE in CH_2Cl_2 at room temperature, possibly via a CT complex, to give higher homologues 4 and 5 in 20 and 5% yield, respectively (Eq. 3). The ^1H NMR spectrum of 4 reveals only one Ge–Me signal as a singlet at 0.45 ppm, and in the ^{13}C NMR spectrum only two resonances appear at −2.16 and 111.24 ppm, which are attributable to Ge–Me and ethynylene carbon atoms, respectively. In addition, it shows an MS peak at *m/z* 688, which is in accord with structure 4. The ^1H and ^{13}C NMR spectra of 5 are similar to those of 4, but 5 shows an MS peak at *m/z* 916, demonstrating it to be a dimer of 1. Interestingly, in the more polar solvent CH_3CN containing of a catalytic amount of TCNE, 1 and 2 undergo ring-opening polymerization to give 6 and 7, respectively, in almost quantitative yields (Eqs. 4 and 5). However, under the reaction conditions 3 show only the CT maximum which is stable on prolonged standing at room temperature, and remains unchanged even on irradiation of the CT band. These two polymers, 6 and 7, show similar ^1H and ^{13}C NMR spectra to those of starting diynes 1 and 2, respectively. In GPC analysis, both give one peak with $M_n = 5.0 \times 10^3$ ($M_w/M_n = 1.4$) and 4.4×10^3 ($M_w/M_n = 1.3$), respectively, based on a polystyrene standard. All the above data indicate that 6 and 7 should be a digermanyleneethynylene unit-containing polymer and an alternating digermanyleneethynylene and disilanyleneethynylene unit-containing polymer, respectively. Although some polymers containing the disilyleneethynylene unit have been synthesized [6], 6 and 7 constitute the first two examples of polymers containing the digermanyleneethynylene unit [20].

The mechanism of the oligomerization and polymerization of 1 is not clear but a possible reaction pathway is depicted in Scheme 1. Thus, the first step probably involves electron transfer from 1 to TCNE to form a radical ion pair, such as $1^{+\cdot}\cdot[TCNE]^{-\cdot}$. Then, since 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) readily inserts into the Ge–Ge bonds of these cyclic ethynylenes (see Eq. 6), the dimerization of $1^{+\cdot}$ with 1 should proceed with cleavage of the Ge–Ge bonds of both molecules involved, and this gives $5'^{+\cdot}$ as a key intermediate. The chemical behaviour of $5'^{+\cdot}$ is rationalized in terms of an open-chain structure in which the one-electron Ge–Ge bond dissociates to yield the cationic and radical ends [21]. Back electron transfer to $5'^{+\cdot}$ from the TCNE radical anion forms the Ge–Ge bond again to yield 5. On the other hand, the intramolecular cyclization affords 4 accompanied by elimination of a bisgermylethynylene unit, possibly followed by back electron transfer from the TCNE radical anion.

In more polar CH_3CN, $5'^{+\cdot}$ reacts more readily with another molecule of **1** similarly and consecutively to give polymer **6**. The TCNE-catalysed polymerization of **2** in CH_3CN occurs more slowly but it is conceivable that it proceeds by a similar mechanism to that above.

2.4. Cycloaddition

On mixing with another acceptor, DDQ in CH_2Cl_2, the ethynylenes **1**, **2** and **3** also show characteristic intermolecular CT absorption maxima even at longer wavelengths, namely 536, 519 and 516 nm, respectively. However, in contrast to the case with TCNE above, a CH_2Cl_2 solution of **1** and DDQ leads to the formation of the [2 + 6] cycloadduct **8** on standing at ambient temperature (Eq. 6). Similarly, under similar conditions **2** and **3** with DDQ yield the corresponding bridged adducts **9–11**. The course of the reaction can be followed by means of ^1H NMR spectroscopy. For example, the Ge–Me signals of **1** in CD_2Cl_2 containing DDQ decrease with the 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 **8**. Another possible structure, **8′**, for the cycloadduct is highly improbable since it should give eight kinds of Ge–Me signals in its ^1H NMR spectrum. Monitoring by ^1H NMR reveals that the cycloaddition of **1** proceeds almost quantitatively, and more smoothly than those of **2** and **3**. Accordingly, **2** forms the cycloadducts **9** and **10** in a 2:1 ratio. However, simple linear 1,2-di-ethynyltetramethyldigermane and 1,2-diethynyltetra-methyldisilane do not undergo the addition reaction with DDQ in CH_2Cl_2.

Recently, on irradiation in the presence of hexameth-yldisilane and hexamethyldigermane in chloroform,
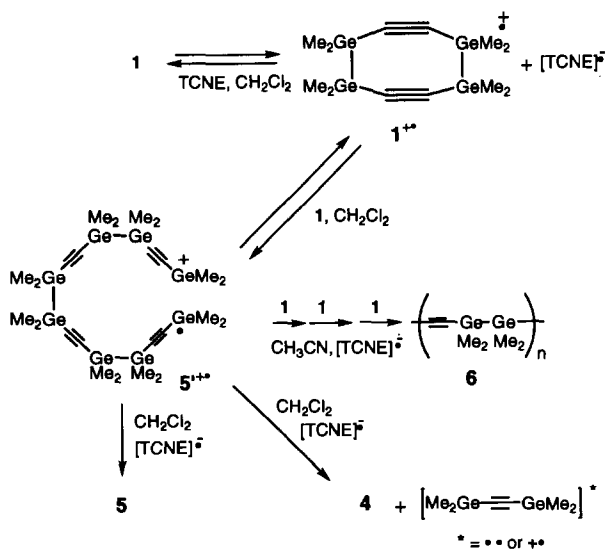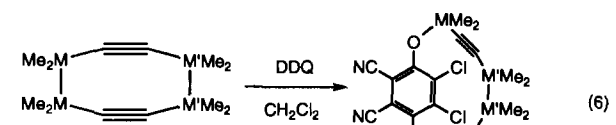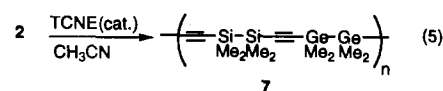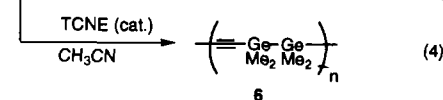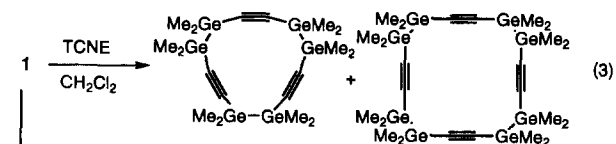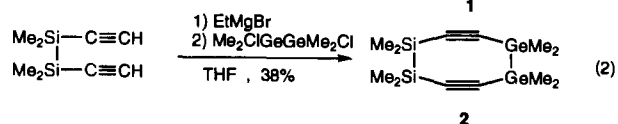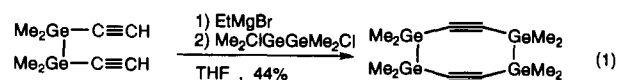
Scheme 1.

some quinones were reported to give the corresponding mono- and di-metallated hydroquinones by way of triplet radical ion pairs generated by electron transfer [22,23]. However, the cycloaddition mechanism of the cyclic diethynylenes and DDQ is not yet clear but is conceived to proceed via these electron donor–acceptor pairs from considerations of the appearance of the characteristic CT absorption band and the relative reactivity among these diynes. The cycloaddition above constitutes another example showing the insertion of a quinone unit into Si–Si and Ge–Ge bonds without transition metal catalysts [24,25].

3. Conclusion

The germanium analogues **1** and **2** show basically similar electronic characteristics to the disilanyle-neethynylene **3** as judged from their PE and UV spectra. However, because of the lower IE and the weaker bond strength of the σ-Ge–Ge bond, the germanium analogue is more reactive toward electrophiles. Thus, in CH_2Cl_2 containing TCNE, **1** undergoes oligomerization to give its higher homologues **4** and **5**, and in CH_3CN containing a catalytic amount of TCNE, both **1** and **2** are polymerized to give the corresponding polymers, **6** and

Form 1.

7, almost quantitatively, whereas the sila analogue **3** is stable under these conditions. All compounds **1, 2** and **3** cycloadd to DDQ to give the corresponding 1 : 1 adducts in a [2 + 6] manner.

4. Experimental section

All reactions were carried out under an atmosphere of argon. THF was dried over sodium metal under reflux and distilled just before use. Acetonitrile, hexane and methylene chloride were refluxed over CaH_2 and distilled before use. NMR spectra were obtained on a JEOL Alpha-400 spectrometer at ambient temperature. UV spectra were recorded on Hitachi U-3300 spectrometer. GC–mass and mass spectra were measured on Shimazu 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 are relative to a polystyrene standard. The gas-phase He I photoelectron spectra of the ethynylenes were measured with the instrument described previously [26,27]. The sample inlet and target chamber systems were heated at 121°C during measurements. Molecular orbital calculations were performed using the MOPAC program (version 6.01) [11].

4.1. Materials

Tetracyanoethylene (TCNE) and dicyanodichlorobenzoquinoe (DDQ) were commercially available.

4.2. Preparation of 1,2-diethynyl-1,1,2,2-tetramethyldigermane

In a 200 ml two-necked flask fitted with a stirrer, reflux condenser and dropping funnel were placed a solution of ethynylmagnesium bromide in THF (0.5 M, 100 ml). To this was added a solution of 1,1,2,2-tetramethyl-1,2-dichlorodigermane (6.3 g, 22.7 mmol) in THF (20 ml) with cooling in an ice–water bath. After the mixture had been hydrolysed with water, diethyl ether (200 ml) was added. The organic layer was separated, washed with water and dried over Na_2SO_4. After distilling off the solvent, the residue was distilled under reduced pressure to give 1,1,2,2-tetramethyl-1,2-diethynyldigermane (5.0 g, 86% yield): b.p. 68°C/20 mmHg; ^{1}H NMR (CDCl$_3$), δ 0.52 (s, 12H, GeMe), 2.35 (s, 2H, CH); ^{13}C NMR (CDCl$_3$) δ –2.28 (GeMe), 87.63 (CGeMe), 93.87 (CH); MS (relative intensity, %), 254 (M$^+$– Me, ^{72}Ge, ^{74}Ge, 4), 119 (GeMe$_3^+$, ^{74}Ge, 100); Anal. Found: C, 37.80; H, 5.69%. Calc. for $C_8H_{14}Ge_2$: C, 37.63; H, 5.53%.

4.3. Preparation of octamethyl-3,4,7,8-tetragermacycloocta-1,5-diyne (1)

In a 50 ml two-necked flask fitted with a stirrer, a reflux condenser and a dropping funnel were placed magnesium (0.52 g, 21.5 mmol) and THF (5 ml). To this was added a solution of ethyl bromide (2.56 g, 23.5 mmol) in THF (15 ml) over a period of 45 min at room temperature. After stirring for 1 h, the ethylmagnesium bromide thus produced was added to a solution of 1,2-diethynyl-1,1,2,2-tetramethyldigermane (2.5 g, 9.8 mmol) in THF (10 ml) over a period of 30 min at room temperature, and the reaction mixture was stirred for 1 h to give the di-Grignard reagent. In another 200 ml three-necked flask fitted with a stirrer, a reflux condenser and two dropping funnels were placed THF (90 ml). In one dropping funnel was placed a THF solution of the di-Grignard reagent and in the other was placed 1,2-dichlorotetramethyldigermane (2.7 g, 9.8 mmol) in THF (30 ml). These two solutions were dropped slowly into the flask over a period of 5 h at room temperature. After stirring for 15 h, the mixture was hydrolysed with dilute hydrochloric acid, then diethyl ether (200 ml) was added. The organic layer was separated, washed with water and dried over Na_2SO_4. After evaporation of the solvent, the residue was sublimed at 110–120°C (0.15 mmHg) to give **1** (1.98 g, 4.3 mmol, 44% yield): m.p. 158–160°C; ^{1}H NMR (CDCl$_3$), δ 0.47 (s, 24H, GeMe); ^{13}C NMR (CDCl$_3$), δ –1.84 (GeMe), 116.72 (C≡C); Anal. Found: C, 31.53; H, 5.43%. Calc. for $C_{12}H_{24}Ge_4$: C, 31.42; H, 5.27%. MS (relative 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).

4.4. Preparation of octamethyl-3,4-disila-7,8-digermacycloocta-1,5-diyne (2)

This compound was prepared as above using 1,2-diethynyl-1,1,2,2-tetramethyldisilane instead of 1,2-diethynyl-1,1,2,2-tetramethyldigermane [28]. This yielded **2** (2.8 g, 7.6 mmol, 38% yield): m.p. 147–149°C; ^{1}H NMR (CDCl$_3$), δ 0.23 (s, 12H, SiMe), 0.48 (s, 12H, GeMe); ^{13}C NMR (CDCl$_3$), δ –2.70 (SiMe), –2.01 (GeMe), 117.25 (GeC≡C), 119.27 (SiC≡C); Anal. Found: C, 39.10; H, 6.72%. Calc. for $C_{12}H_{24}Ge_2Si_2$: C, 38.98; H, 6.54%. MS (relative intensity, %), 370 (M$^+$ ^{72}Ge, ^{74}Ge, 40), 355 (M$^+$– Me, ^{72}Ge, ^{74}Ge, 100), 73 (SiMe$_3$, 94).

4.5. Charge-transfer spectra

First TCNE (25 mg, 0.2 mmol) was dissolved in CH_2Cl_2 (10 ml) by stirring with a supersonic cleaner. Compound **1** (about 50 mg) was added to the TCNE solution (1 ml) and the characteristic CT absorption of the resultant coloured solution was recorded on the UV

spectrophotometer. CT spectra of **2** and **3** were measured in the same manner.

4.6. Oligomerization of 1

A mixture of **1** (300 mg, 0.65 mmol), TCNE (168 mg, 1.30 mmol) and CH_2Cl_2 (15 ml) was stirred for 2 days at room temperature. To the mixture was added hexane (30 ml) and the precipitate that formed was removed by filtration. The filtrate was concentrated and was chromatographed by preparative TLC (silica gel; benzene–hexane, 1 : 1) to give a white solid (76.4 mg). The solid was composed of **4** and **5** (4 : 1), as determined by NMR spectroscopic and HPLC methods. Recrystallization from hexane gave pure **4**. Compound **5** was isolated pure by means of HPLC. **4**: ^{1}H NMR ($CDCl_3$), δ 0.45 (s, 36H, GeMe); ^{13}C NMR ($CDCl_3$), δ −2.16 (GeMe), 111.24 (C≡C); MS (relative intensity, %), 688 (M$^+$, ^{70}Ge, ^{72}Ge$_2$, ^{74}Ge$_3$, 11), 119 (GeMe$_3^+$, ^{74}Ge, 100); HRMS, m/z calc. for $C_{18}H_{36}^{74}Ge_3^{72}Ge_2^{70}Ge$, 687.8136; found, m/z 687.8094. **5**: ^{1}H NMR ($CDCl_3$), δ 0.47 (s, 48H, GeMe); ^{13}C NMR ($CDCl_3$), δ −1.58 (GeMe), 111.84 (C≡C); MS (relative intensity, %), 916 (M$^+$, ^{70}Ge$_2$, ^{72}Ge$_2$, ^{74}Ge, 12), 119 (GeMe$_3^+$, ^{74}Ge, 100); HRMS, m/z calc. for $C_{24}H_{48}^{74}Ge_4^{72}Ge_3^{70}Ge$, 917.7508; found, m/z 917.7490.

4.7. Polymerization of 1

In a 30 ml flask fitted with a stirrer and a reflux condenser were placed **1** (200 mg, 0.44 mmol), TCNE (5 mg, 0.04 mmol) and CH_3CN (10 ml) and the mixture was stirred at 50°C. After 2 h, polymer **6** was obtained as a white precipitate, which was separated by filtration and washed with CH_3CN. This gave **6** as a white powder (190 mg): ^{1}H NMR ($CDCl_3$), δ 0.46 (s, GeMe); ^{13}C NMR ($CDCl_3$), δ −1.77 (GeMe), 111.89 (C≡C); $M_w = 7.1 \times 10^3$, $M_n = 5.0 \times 10^3$ ($M_w/M_n = 1.4$).

4.8. Polymerization of 2

Compound **2** (200 mg, 0.54 mmol) was treated with TCNE in CH_3CN in the same way as above to give polymer **7** (186 mg): ^{1}H NMR ($CDCl_3$), δ 0.22 and 0.47 (both singlets, equal intensity, SiMe and GeMe); ^{13}C NMR ($CDCl_3$), δ −2.96 (SiMe), −1.93 (GeMe), 112.38 (GeC≡C), 114.43 (SiC≡C); $M_w = 5.8 \times 10^3$, $M_n = 4.4 \times 10^3$ ($M_w/M_n = 1.3$).

4.9. Cycloaddition of 1 with DDQ

In a 5 mm NMR sample tube were placed **1** (10 mg, 0.022 mmol), DDQ (9.9 mg, 0.044 mmol) and CD_2Cl_2 (0.5 ml) and the solution was degassed and sealed. The progress of the cycloaddition was monitored periodi-

cally by ^{1}H NMR spectroscopy. After 6 h, the reaction was completed to form **8** quantitatively. Compound **8** was sensitive to moisture and failed to be isolated pure. **8**: ^{1}H NMR (CD_2Cl_2), δ 0.41 (s, 6H, GeGeMe), 0.47 (s, 6H, GeGeMe), 0.95 (s, 6H, OGeMe), 1.00 (s, 6H, OGeMe); ^{13}C NMR ($CDCl_3$), δ −2.56 (GeGeMe), −2.49 (GeGeMe), 4.31 (OGeMe), 4.76 (OGeMe), 106.03 (CN), 106.59 (=CCN), 114.08 (GeGeC≡), 116.65 (OGeC≡), 133.73 (=CCl), 153.71 (=CO); MS (relative intensity, %), 686 (M$^+$, ^{72}Ge$_2$, ^{74}Ge$_2$, 7), 671 (M$^+$ − Me, 6), 119 (GeMe$_3^+$, 100); HRMS, m/z calc. for $C_{20}H_{24}O_2N_2Cl_2^{74}Ge_4$, 689.8062; found, m/z 689.8087.

4.10. Cycloaddition of 2 with DDQ

Compound **2** was treated with DDQ in CD_2Cl_2 in the same way and the cycloaddition was monitored by NMR spectroscopy. The reaction took about 2 days to be completed at ambient temperature and gave two kinds of cycloadducts, **9** and **10** in a 2 : 1 ratio, quantitatively. Both products were too sensitive to moisture to be isolated. **9**: ^{1}H NMR (CD_2Cl_2), δ 0.18 (s, 6H, SiMe), 0.24 (s, 6H, SiMe), 0.96 (s, 6H, GeMe), 1.02 (s, 6H, GeMe); ^{13}C NMR ($CDCl_3$), δ −3.70 (SiSiMe), −3.68 (SiSiMe), 4.38 (OGeMe), 4.82 (OGeMe), 107.08 (=CCN), 108.35 (CN), 116.57 (OGeC≡), 114.55 (SiSiC≡), 134.20 (=CCl), 154.20 (=CO); MS (relative intensity, %) 596 (M$^+$, ^{72}Ge, ^{74}Ge, 5), 581 (M$^+$ − Me, 7), 119 (GeMe$_3^+$, ^{74}Ge, 100); HRMS, m/z calc. for $C_{20}H_{24}O_2N_2Cl_2Si_2$, 597.9177; found, m/z 597.9178. **10**: ^{1}H NMR (CD_2Cl_2), δ 0.41 (s, 6H, GeMe), 0.47 (s, 6H, GeMe), 0.60 (s, 6H, SiMe), 0.66 (s, 6H, SiMe); ^{13}C NMR ($CDCl_3$), δ −2.49 (GeGeMe), −2.44 (GeGeMe), 1.85 (OSiMe), 2.30, 107.56 (CN), 110.63 (=CCN), 113.70 (GeGeC≡), 117.93 (OSiC≡), 133.87 (=CCl), 151.55 (=CO); MS (relative intensity, %), 596 (M$^+$, ^{72}Ge, ^{74}Ge, 5), 581 (M$^+$ − Me, 7), 119 (GeMe$_3^+$, ^{74}Ge, 100); HRMS, m/z calc. for $C_{20}H_{24}O_2N_2Cl_2Si_2$, 597.9177; found, m/z 597.9178.

4.11. Cycloaddition of 3 with DDQ

Compound **3** was treated with DDQ in CD_2Cl_2 in the same way and the cycloaddition was monitored by NMR spectroscopy. The reaction took about 2 days to be completed at ambient temperature and gave tthe cycloadduct **11**, quantitatively. The product was too sensitive to moisture to be isolated. **11**: ^{1}H NMR (CD_2Cl_2), δ 0.16 (s, 6H, SiSiMe), 0.22 (s, 6H, SiSiMe), 0.60 (s, 6H, OSiMe), 0.66 (s, 6H, OSiMe); ^{13}C NMR ($CDCl_3$), δ −3.72 (SiSiMe), −3.69 (SiSiMe), −1.76 (OSiMe), −2.25 (OSiMe), 107.50 (=CCN), 109.31 (CN), 113.63 (SiSiC≡), 117.21 (OSiC≡), 133.92 (=CCl), 151.57 (=CO); MS (relative intensity, %) 506 (M$^+$, 4), 491 (M$^+$ − Me, 4), 73 (SiMe$_3^+$, 100); HRMS,

m/z calc. for $C_{20}H_{24}O_2N_2Cl_2Si_4$, 506.0292; found, m/z 506.0280.

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References and notes

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