ELSEVIER

Journal of Organometallic Chemistry 568 (1998) 121–125

Journal of Organometallic Chemistry

Chlorinative cleavage of germanium–germanium bonds in permethyloligogermanes initiated by photo-induced electron transfer

Kunio Mochida [a,]*, Hideaki Watanabe [a], Shigeo Murata [b], Mamoru Fujitsuka [c], Osamu Ito [c]

[a] *Department of Chemistry, Faculty of Science, Gakushuin. University, 1-5-1 Mejiro, Toshima-ku, Tokyo 171-8588, Japan*
[b] *National Institute of Materials and Chemical Research, 1-1 Higashi, Tsukuba, Ibaraki 305-0046, Japan*
[c] *Institute for Chemical Reaction Science, Tohoku University, Katahira, Aoba-ku, Sendai 980-8577, Japan*

Received 17 March 1998; received in revised form 18 May 1998

Abstract

Irradiation for permethyloligogermanes, $Me(Me_2Ge)_nMe$ ($n = 2$–5), in CCl_4–CH_3CN in the presence of 9,10-dicyanoanthracene (DCA) afforded the corresponding chlorogermanes and hexachloroethane. Fluorescence of DCA was quenched by the oligogermane with a diffusion-controlled rate. A mechanism of free-radical chlorination involving oligogermane cation radicals and a DCA anion radical is proposed for the germanium–germanium cleavage. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Permethyloligogermanes; 9,10-Dicyanoanthracene; Photo-induced electron transfer

---

1. Introduction

Organometallic compounds containing Group 14 element–Group 14 element and Group 14 element–carbon bonds are excellent electron donors [1]. As electron-rich species, they are subject to cleavage by various organic electrophiles as well as transition metal complexes. Since Group 14 catenates and tetraalkyl Group 14 element compounds have rather low ionization potentials (IPs), electron-transfer (ET) reactions are very important in which the rate is limited by the ability of the Group 14 element compound to transfer an electron to an electron acceptor. While the ET interactions between silicon–silicon σ bonds and certain π acceptors have been amply investigated, there have been few reports on the ET study of germanium–germanium σ bonds [2–7].

We describe herein the studies on chlorinative cleavage of the germanium–germanium σ bonds in permethyloligogermanes initiated by photo-induced ET.

2. Results and discussion

2.1. Chlorinative cleavage of permethyloligogermanes

Permethyloligogermanes, $Me(Me_2Ge)_nMe$ ($n = 2$–5), which have low IPs (7.67–8.58 eV), are excellent electron donors [8,9]. Therefore, donor–acceptor interactions with certain π acceptors are possible for the $Me(Me_2Ge)_nMe$.

Chlorinative cleavage of the $Me(Me_2Ge)_nMe$ ($n = 2$–5) initiated by photo-induced ET in the presence of catalytic amounts (0.1 mol eq.) of several π electron acceptors was examined (Eq. (1)).

$$Me(Me_2Ge)_nMe + \text{Acceptor} \xrightarrow[\substack{CCl_4/CH_3CN \\ 0°C,\ 1\ h}]{h\nu(\lambda > 300\ nm)}$$

$$Me(Me_2Ge)_mCl + Me(Me_2Ge)_{n-m}Cl + (CCl_3)_2 \qquad (1)$$

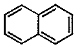
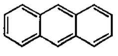
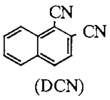
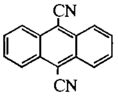
On irradiation for a typical permethyloligogermane, octamethyltrigermane ($Me(Me_2Ge)_3Me$), in carbon tetrachloride (CCl_4, 0.43 ml)-acetonitrile (CH_3CN, 10 ml) in the presence of 9,10-dicyanoanthracene (DCA) (0.1 mol eq.) with a high-pressure Hg arc lamp through a

---

* Corresponding author.

0022-328X/98/$19.00 © 1998 Elsevier Science S.A. All rights reserved.
PII S0022-328X(98)00709-8

Table 1
Chlorinative cleavage of the Ge–Ge bond of $Me(Me_2Ge)_3Me$

Acceptor	E_{red} (V)	Conv. (%)	Products, yield (%)[a]		
			Me_3GeCl	Me_5Ge_2Cl	$(CCl_3)_2$
 (Np)	−2.29	6.0	4.6	5.7	Trace
 (An)	−1.93	35.0	28.6	35.7	11.0
 (DCN)	—[b]	70.0	54.3	67.9	13.0
 (DCA)	−0.89	70.0	65.3	69.3	26.5

[a] GC and NMR yields.
[b] No value.

Pyrex filter at 0°C for 1 h, trimethylchlorogermane (Me_3GeCl, 65.3%) and pentamethylchlorodigermane (Me_5Ge_2Cl, 69.3%) were formed together with hexachloroethane (Cl_3CCCl_3, 26.5%). The use of less than 10 mol% of DCA took longer reaction time. The reaction did not occur without DCA under the same conditions and it is clear that DCA should be excited first by light of wavelength longer than 300 nm.

In mixture with other π acceptors such as naphthalene (Np), anthracene (An), and 1,2-dicyanonaphthalene (DCN) in CCl_4–CH_3CN, $Me(Me_2Ge)_3Me$ also afforded Me_3GeCl (4.6, 28.6 and 54.3%) and Me_5Ge_2Cl (5.7, 35.7, and 67.9%), respectively, together with $(CCl_3)_2$. The radical nature of the intermediate is confirmed by the formation of both chlorogermanes and $(CCl_3)_2$ in the presence of CCl_4.

These results are summarized in Table 1.

From Table 1 it is evident that the conversions of $Me(Me_2Ge)_3Me$ roughly accord with electron affinity of the acceptors [10].

Photolysis of $Me(Me_2Ge)_nMe$ ($n = 2$, 4, 5) in a mixed solvent of CCl_4–CH_3CN in the presence of DCA (0.1 mol eq.) was also carried out. These results of products and selectivity of the chloronative Ge–Ge bonds in oligogermanes are summarized in Table 2.

From Table 2 the conversions of $Me(Me_2Ge)_nMe$ ($n = 2$–5) roughly accord with their IPs, which decrease as the chain length increases [9].

A clear selectivity of chlorinative cleavage between the terminal Ge–Ge bond and the internal Ge–Ge bond could not be observed in $Me(Me_2Ge)_nMe$ ($n = 3$–5); this may be due to the longer Ge–Ge bond length.

2.2. *Quenching experiments of DCA*

In order to confirm the ET from the $Me(Me_2Ge)_nMe$ to the excited state of DCA, we then carried out the quenching experiments of the fluorescence of DCA in CH_3CN with $Me(Me_2Ge)_nMe$. A CH_3CN solution of DCA was excited at 380 nm and the emission band (410–560 nm, $\lambda_{max} = 434$ nm) was quenched with $Me(Me_2Ge)_nMe$ to yield a good linear relationship of the Stern–Volmer plot with a slope of $k_q\tau$. Here, k_q is the fluorescence quenching rate constant, and τ is the fluorescence lifetime of DCA in the absence of quencher. The value of τ was measured to be 12 ns [11].

Table 2
Chlorinative cleavage of the Ge–Ge bond of $\mathrm{Me(Me_2Ge)}_n\mathrm{Me}$ ($n = 2$–5) in $\mathrm{CCl_4}$–$\mathrm{CH_3CN}$

Oligogermane	IPs	Conv. (%)	Products, yield (%)[a]				
			$\mathrm{Me_3GeCl}$	$\mathrm{Me_5Ge_2Cl}$	$\mathrm{Me_7Ge_3Cl}$	$\mathrm{Me_9Ge_4Cl}$	$\mathrm{(CCl_3)_2}$
$\mathrm{Me(Me_2Ge)_2Me}$	8.58	12.0	9.4				Trace
$\mathrm{Me(Me_2Ge)_3Me}$	8.15	70.0	65.3	69.3			26.5
$\mathrm{Me(Me_2Ge)_4Me}$	7.80	75.0	48.8	56.2	52.5		8.0
$\mathrm{Me(Me_2Ge)_5Me}$	7.67	97.0	56.2	38.8	33.0	57.2	7.0

[a] GC and NMR yields.

The values of IPs and k_q of $\mathrm{Me(Me_2Ge)}_n\mathrm{Me}$ ($n = 2$–5) are summarized in Table 3.

The value of k_q of $\mathrm{Me(Me_2Ge)}_n\mathrm{Me}$ increased with decreasing of IPs as shown in Fig. 1 ($r = 0.971$). This is the order of increasing length of the quencher, $\mathrm{Me(Me_2Ge)}_n\mathrm{Me}$ ($n = 2$–5). This indicates the quenching rate is below the diffusion limit.

2.3. Laser flash photolysis

Laser flash photolysis ($\lambda = 354$ nm, pulse width 5 ns, power 18 mJ pulse^{-1}) of the $\mathrm{CH_3CN}$ solution of $\mathrm{Me(Me_2Ge)_4Me}$ with DCA was carried out to obtain information on the reactive intermediates in the ET reaction. Fig. 2 shows the transient absorption spectra obtained after excitation at 100 ns and 1 μs. The broad absorption band extending from 600 to 800 nm is the characteristic band of the anion radical of DCA [12]. The time profile of the absorption band observed at 700 nm is included in Fig. 2. The decay of the anion radical of DCA at 700 nm is almost constant in an acquisition time.

However, failure to detect radical cations of $\mathrm{Me(Me_2Ge)_4Me}$ was partly due to the extremely short lifetime of the radical. The λ_{max}s of the $\mathrm{Me(Me_2Ge)_4Me}$ cation radical generated by pulse radiolysis measurement was at 700 nm. This is close to the observed λ_{max}s of the anion radical of DCA. However, the life-lived time of the $\mathrm{Me(Me_2Ge)_4Me}$ cation radical is estimated to be ca. 40–50 ns [13].

Table 3
DCA fluorescence quenching with $\mathrm{Me(Me_2Ge)}_n\mathrm{Me}$ ($n = 2$–5) in $\mathrm{CH_3CN}$

Oligogermane	IPs (eV)	k_q (10^9 m^{-1} s^{-1})
$\mathrm{Me(Me_2Ge)_2Me}$	8.58	7.4
$\mathrm{Me(Me_2Ge)_3Me}$	8.15	14.3
$\mathrm{Me(Me_2Ge)_4Me}$	7.80	16.9
$\mathrm{Me(Me_2Ge)_5Me}$	7.67	20.1

2.4. Reaction mechanism

At first, ET from $\mathrm{Me(Me_2Ge)}_n\mathrm{Me}$ to the excited singlet state of DCA (DCA*) generates the geminate radical ions composed of the DCA radical anion ($\mathrm{DCA}^{-\bullet}$) and the $\mathrm{Me(Me_2Ge)}_n\mathrm{Me}$ radical cation ($\mathrm{Me(Me_2Ge)}_n\mathrm{Me}^{+\bullet}$). The $\mathrm{Me(Me_2Ge)}_n\mathrm{Me}^{+\bullet}$ undergoes spontaneous scission to $\mathrm{Me(Me_2Ge)}_m^{+}$ and $\mathrm{Me(Me_2Ge)}_{n-m}^{\bullet}$. For example, MINDO UHF calculation of the $\mathrm{Me(Me_2Ge)_3Me}$ cation radical shows that the unpaired electron is nearly localized on the p orbital of a Ge atom of the $\mathrm{Me_5Ge_2}$ moiety, while the charge is localized in the $\mathrm{Me_3Ge}$ moiety in the most stable configuration. This scission is also supported by MS spectra of $\mathrm{Me(Me_2Ge)_3Me}$. $\mathrm{Me(Me_2Ge)}_{n-m}^{\bullet}$ abstracts a chlorine atom from $\mathrm{CCl_4}$ to afford $\mathrm{Me(Me_2Ge)}_{n-m}\mathrm{Cl}$ and $^{\bullet}\mathrm{CCl_3}$. On the other hand, $\mathrm{Me(Me_2Ge)}_m^{+}$ is reduced by $\mathrm{DCA}^{-\bullet}$ to afford $\mathrm{Me(Me_2Ge)}_m^{\bullet}$ together with DCA. $\mathrm{Me(Me_2Ge)}_m^{\bullet}$ thus formed abstracts a chlorine atom from $\mathrm{CCl_4}$ to give $\mathrm{Me(Me_2Ge)}_m\mathrm{Cl}$ and $^{\bullet}\mathrm{CCl_3}$. Finally, $^{\bullet}\mathrm{CCl_3}$ either adds to DCA or dimerizes (Scheme 1).

In contrast to the chlorinative cleavage of the silicon–silicon bonds in permethyloligosilanes ([2]f), that of the germanium–germanium bonds proceeded very smoothly and their selectivity between the terminal Ge–Ge bond and the internal Ge–Ge bond could not be observed.

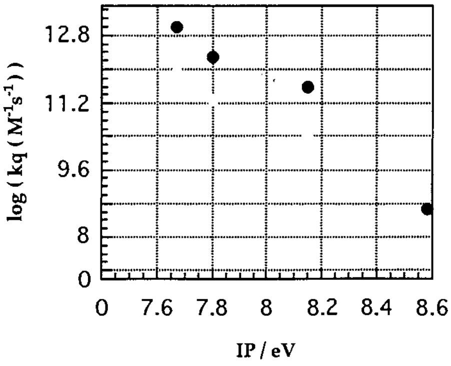


Fig. 1. Correlation between IP of $\mathrm{Me(Me_2Ge)}_n\mathrm{Me}$ ($n = 2$–5) and fluorescence quenching rate constant of DCA–$\mathrm{Me(Me_2Ge)}_n\mathrm{Me}$.

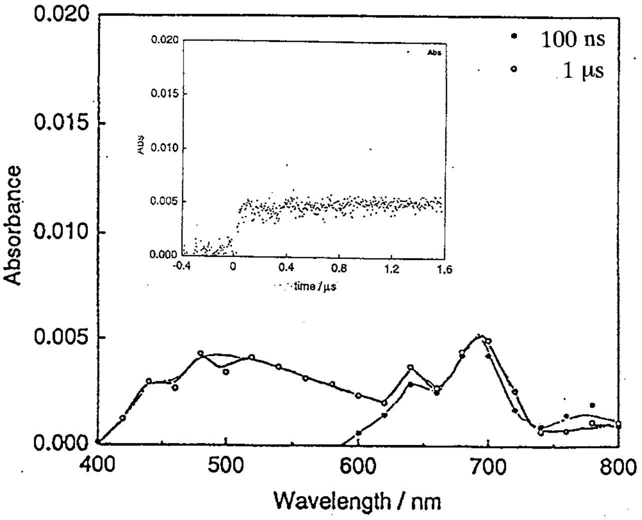


Fig. 2. Transient absorption spectra obtained by 354 nm laser flash photolysis of DCA–Me$(Me_2Ge)_nMe$ in CH_3CN. The insert shows the absorption-time profile at 700 nm.

3. Experimental details

^1H spectra were recorded with a Varian Unity-Inova 400 MHz NMR. The GC-MS spectra were recorded using a JEOL JMS-DX 303 mass spectrometer. The UV-visible spectra were recorded on a Shimadzu UV 2200 spectrometer. The fluorescence spectra were recorded on a Hitachi 850 fluorescence spectrometer. Gas chromatography was done on a Shimadzu GC 8A with 1 m 20% SE30 and 30% Apiezon L columns.

3.1. Materials

Permethyloligogermanes, $Me(Me_2Ge)_nMe$ ($n = 2$–5), Me_3GeCl, Me_5Ge_2Cl, Me_7Ge_3Cl, and Me_9Ge_4Cl were prepared as described ([7]a). 9,10-DCA, Np, An, 1,2-DCN, CCl_4, CH_3CN, and $(CCl_3)_2$ are commercially available.

3.2. Photochemical reactions of permethyloligogermanes, $Me(Me_2Ge)_nMe$ ($n = 2$–5) in the presence of DCA in CCl_4–CH_3CN

As a representative example, the chlorinative cleavage of the Ge–Ge bond of $Me(Me_2Ge)_3Me$ is described. A degassed sealed Pyrex tube containing a mixed solvent of CH_3CN (10 ml)–CCl_4 (4.5 mmol, 0.43 ml) of $Me(Me_2Ge)_3Me$ (0.09 mmol) and DCA (0.009 mmol) was irradiated with a high-pressure Hg arc lamp (450 W) for 1 h at 0°C. NMR, GC, and GC-MS analysis of the resulting mixture showed Me_3GeCl (0.059 mmol, 65.3%), Me_5Ge_2Cl (0.062 mmol, 69.3%), and $(CCl_3)_2$ (0.024 mmol, 26.5%) with internal standard methods.

$$\mathrm{DCA} \xrightarrow{h\nu} \mathrm{DCA}^*$$
$$\mathrm{DCA}^* + \mathrm{Me(Me_2Ge)_nMe} \longrightarrow \mathrm{DCA}^{\bullet-} + \mathrm{Me(Me_2Ge)_nMe}^{\bullet+}$$
$$\mathrm{Me(Me_2Ge)_nMe}^{\bullet+} \longrightarrow \mathrm{Me(Me_2Ge)}_m^{+} + \mathrm{Me(Me_2Ge)}_{n\text{-}m}^{\bullet}$$
$$\mathrm{Me(Me_2Ge)}_{n\text{-}m}^{\bullet} + \mathrm{CCl_4} \longrightarrow \mathrm{Me(Me_2Ge)_{n\text{-}m}Cl} + {}^{\bullet}\mathrm{CCl_3}$$
$$\mathrm{Me(Me_2Ge)}_m^{+} + \mathrm{DCA}^{\bullet-} \longrightarrow \mathrm{Me(Me_2Ge)}_m^{\bullet} + \mathrm{DCA}$$
$$\mathrm{Me(Me_2Ge)}_m^{\bullet} + \mathrm{CCl_4} \longrightarrow \mathrm{Me(Me_2Ge)_mCl} + {}^{\bullet}\mathrm{CCl_3}$$
$${}^{\bullet}\mathrm{CCl_3} \longrightarrow \mathrm{Cl_3C\text{-}CCl_3}$$

Scheme 1.

3.3. Quenching experiment of DCA* with $Me(Me_2Ge)_nMe$ ($n = 2$–5)

Fluorescence spectra were recorded with a Hitachi 850 fluorescence spectrometer, and spectral corrections for emission were made. The emission and excitation band-pass was fixed to 5 nm. Fluorescence quenching was measured by measuring the fluorescence intensity ratio I_o/I at 25°C, where I_o and I are fluorescence intensities in the absence and in the presence of quencher, respectively. Since the fluorescence spectrum did not change upon quenching, I_o/I was replaced by the intensity ratio at the wavelength of maximum intensity. The samples were not deoxygenated.

3.4. Time-resolved optical absorption

The sample was placed in a quartz cell with an optical length of 5 mm and degassed by four freeze–pump–thaw cycles. The concentrations of $Me(Me_2Ge)_4Me$ were ca. 10^{-3} M. The solution was excited by a Nd:YAG laser (Quanta-Ray GCR-130, 6 ns, fwhm) used for the probe beam, which was detected with a Si-PIN photodiode (Hamamatsu, C5331-SPL) after passing through the quartz cell and a monochromator (Ritsu, MC-10N). The output from the Si-PIN photodiode was recorded with a digitizing oscilloscope (HP 54510B, 300 MHz). The details of the laser photolysis apparatus have been published elsewhere ([7]b).

Acknowledgements

The authors thank Mitsubishi Material Co., Ltd., for the gift of germanium tetrachloride.

References

[1] J.K. Kochi, Organometallic Mechanisms and Catalysis, Academic Press, New York, 1978.

[2] ET reaction of Si–Si with TCNE: (a) V.F. Traven, R. West, J. Am. Chem. Soc. 95 (1973) 6824. (b) H. Sakurai, M. Kira, T. Uchida, J. Am. Chem. Soc. 95 (1973) 6826. (c) M. Kira, K. Sakamoto, H. Sakurai, J. Am. Chem. Soc. 105 (1983) 7469; H.

Sakurai, K. Sakamoto, M. Kira, Chem. Lett. (1984) 1213; M. Kira, K. Takeuchi, H. Sakurai, in: M. Kobayashi (Ed.), Studies in Organic Chemistry, Vol. 31, Elsevier, Amsterdam 1987, p. 407; M. Kira, K. Takeuchi, C. Kabuto, H. Sakurai, Chem. Lett. (1988) 353. (d) Y. Nakadaira, N. Komatsu, H. Sakurai, Chem. Lett. (1985) 1781; H. Watanabe, M. Kato, E. Tabei, H. Kawabara, N. Hirai, T. Sato, Y. Nagai, J. Chem. Soc., Chem. Commun. (1986) 1662. (e) S. Kyushin, Y. Ehara, Y. Nakadaira, M. Ohashi, J. Chem. Soc., Chem. Commun. (1989) 279; Y. Nakadaira, A. Sekiguchi, Y. Funada, H. Sakurai, Chem. Lett. (1991) 327; Y. Nakadaira, S. Otani, S. Kyushin, M. Ohashi, H. Sakurai, Y. Funada, K. Sakamoto, A. Sekiguchi, Chem. Lett. (1991) 601. (f) Y. Nakadaira, S. Kyushin, M. Ohashi, Yuki Gosei Kagaku Kyokaishi 48 (1990) 331 and references cited therein. (g) K. Mizuno, Y. Otsuji, Top. Curr. Chem. 169 (1994) 301; K. Mizuno, Y. Otsuji, Yuki Gosei Kagaku Kyokaishi 47 (1989) 916 and references cited therein.

[3] ET reaction of Sn–Sn with TCNE: (a) P.J. Krusic, H. Stoklosa, L.E. Manzer, P. Meakin, J. Am. Chem. Soc. 97 (1975) 667. (b) J.A.B. Cornwell, P.G. Harrison, J.A. Richards, J. Organomet. Chem. 67 (1974) C43.

[4] ET reaction of Si–C with ArCN: (a) Y. Nakadaira, S. Kyushin, M. Ohashi, Yuki Gosei Kagaku Kyokaishi 48 (1990) 331 and references cited therein. (b) K. Mizuno, Y. Otsuji, Top. Curr. Chem. 169 (1994) 301; K. Mizuno, Y. Otsuji, Yuki Gosei Kagaku Kyokaishi 47 (1989) 916 and references cited therein. (c) U.C. Yoon, P.S. Mariano, Acc. Chem. Res. 25 (1992) 233.

[5] ET reaction of Sn–C with TCNE: S. Fukuzumi, K. Mochida, J.K. Kochi, J. Am. Chem. Soc. 101 (1979) 5961; S. Fukuzumi, C.L. Wong, J.K. Kochi, J. Am. Chem. Soc. 102 (1980) 2928.

[6] ET reaction of Si–C and Si–Si with C_{60}: T. Akasaka, W. Ando, K. Kobayashi, S. Nagase, J. Am. Chem. Soc. 115 (1993) 1605; T. Akasaka, W. Ando, K. Kobayashi, S. Nagase, J. Am. Chem. Soc. 115 (1993) 10366.

[7] ET reaction of Ge–Ge with TCNE and C_{60}: (a) K. Mochida, C. Hodota, R. Hata, S. Fukuzumi, Organometallics 12 (1993) 586; K. Mochida, R. Hata, C. Hodota, S. Fukuzumi, M. Kako, Y. Nakadaira, Chem. Lett. (1995) 245. (b) A. Watanabe, O. Ito, K. Mochida, Organometallics 14 (1995) 4281; O. Ito, Y. Sasaki, A. Watanabe, K. Mochida, Bull. Chem. Soc. Jpn. 69 (1996) 2167; K. Mochida, M. Akazawa, M. Fujitsuka, A. Watanabe, O. Ito, Bull. Chem. Soc. Jpn. 70 (1997) 2249.

[8] K. Mochida, S.D. Worley, J.K. Kochi, Bull. Chem. Soc. Jpn. 58 (1985) 3389.

[9] K. Mochida, S. Masuda, Y. Harada, Chem. Lett. (1992) 2281.

[10] P. Kebarle, S. Chowdhury, Chem. Rev. 87 (1987) 513.

[11] S. Murata, unpublished results.

[12] H.F. Davis, B.B. Lohray, K.R. Gopodas, C.V. Kumar, P.K. Das, M.V. George, J. Org. Chem. 50 (1985) 3685.

[13] K. Mochida, R. Hata, H. Chiba, S. Seki, Y. Yoshida, S. Tagawa, to be published.