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### Preliminary communication

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## 4,8-Dichloroocta-t-butyltetracyclo[3.3.0.0<sup>2,7</sup>.0<sup>3,6</sup>]octagermane

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### Abstract

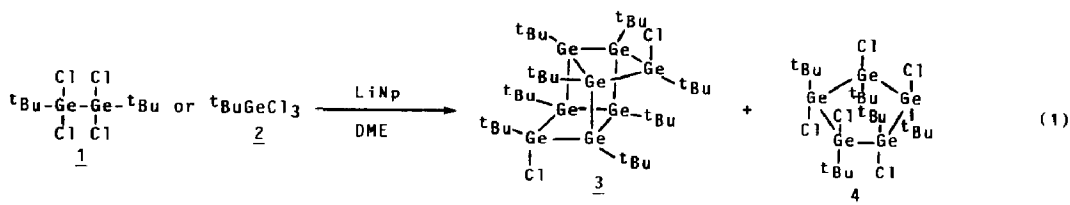
A polyhedral germane, 4,8-dichloroocta-t-butyltetracyclo[3.3.0.0<sup>2,7</sup>.0<sup>3,6</sup>]octagermane, was prepared by reductive reactions of either 1,2-di-t-butyl-1,1,2,2-tetrachlorodigermane or t-butyltrichlorogermane with lithium naphthalenide. The structure of the new compound was determined by X-ray crystallographic analysis as well as by NMR spectra.

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Polyhedral compounds consisting of a framework of group 4B atoms other than carbon attract much interest. The bicyclo[1.1.0]tetrasilane [1] and bicyclo[2.2.0]hexasilane [2] bicyclic silicon systems were prepared by both Masamune et al. and Nagai et al. via reductive coupling of chlorosilanes containing bulky groups. The synthesis of octasilacubane has also been reported [3].

Very recently, we have reported hexagermaprismane, tetracyclo[2.2.0.0<sup>2,6</sup>.0<sup>3,5</sup>]-1,2,3,4,5,6-hexagermane, as the first polyhedral germanium compound prepared by condensation of bis(trimethylsilyl)methyltrichlorogermane with lithium [4]. Hexagermaprismane shows very specific physical and chemical properties resulting from its highly rigid structure. As part of our studies on polyhedral germanes, we also tried reductive coupling of 1,2-di-t-butyl-1,1,2,2-tetrachlorodigermane (1) with t-butyltrichlorogermane (2), which gave 4,8-dichloroocta-t-butyltetracyclo[3.3.0.0<sup>2,7</sup>.0<sup>3,6</sup>]octagermane (3) which is a new type of polyhedral germanium compound. We now report the characterization of 3 by NMR spectroscopy, and its crystal structure.

During the course of our investigations, Kabe and Masamune reported the reductive coupling of 1,2-di-t-butyl-1,1,2,2-tetrachlorodisilane to tricyclo[2.2.0.0<sup>2,5</sup>]-hexasilane and tetracyclo[3.3.0.0<sup>2,7</sup>.0<sup>3,6</sup>]octasilane derivatives [5]. When the present work was almost completed, we learned that Weidenbruch et al. obtained 4,8-dibromoocta-t-butyltetracyclo[3.3.0.0<sup>2,7</sup>.0<sup>3,6</sup>]octagermane by reductive coupling of 1,1,2,2-tetrabromo-1,2-di-t-butylidigermane [6].



Scheme 1.

### Experimental

Compound 1 was added to 4 equiv. of lithium naphthalenide (LiNp) in dimethoxyethane (DME) at  $-70^\circ\text{C}$ . The mixture was stirred for one hour and additionally for 12 h at room temperature. After removal of naphthalene and polymeric substances, the products were separated by preparative HPLC (JAI gel column) equipped with a recycling system. t-butyltrichlorogermane gave similar results. By the usual work-up tetracyclooctagermane (3) (10% from 1) formed together with a small amount of penta-t-butylpentachlorocyclopentagermane (4) and an unidentified reactive yellow substance. The structure of 3 was determined by X-ray crystallographic analysis as well as by NMR spectra\*.

In the mass spectrum of 3, the  $M^+$  cluster (FD) was observed in the range 1096–1122, in excellent agreement with the calculated formula  $\text{C}_{32}\text{H}_{72}\text{Cl}_2\text{Ge}_8$  which indicated the molecule to consist of a skeleton of eight t-BuGe units (Fig. 1). X-ray structural determination confirmed unequivocally the molecular structure of 3 as

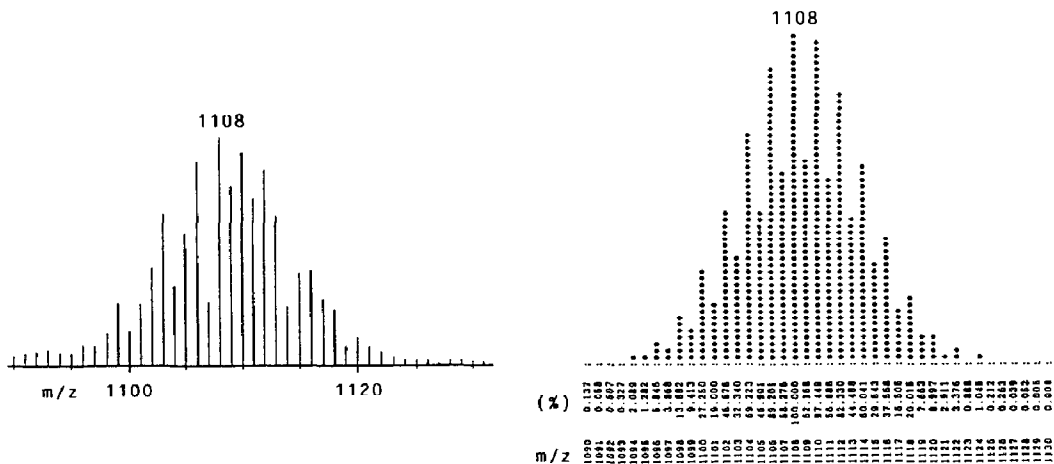


Fig. 1. Observed and calculated mass spectra (FD) of 3.

\* **Compound 3:** M.p.  $> 360^\circ\text{C}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.37 (s, 18H), 1.40 (s, 18H), 1.45 (s, 18H), 1.48 (s, 18H);  $^{13}\text{C}$  NMR (75.5 MHz,  $\text{CDCl}_3$ ):  $\delta$  29.3, 32.6, 33.0, 34.2, 35.6, 37.6, 37.9, 38.2; mass spectrum (FD): 1096–1122 ( $M^+$ ); UV (hexane): 225 nm ( $1.01 \times 10^5$ ). **Compound 4:** M.p.  $176\text{--}177^\circ\text{C}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.43 (s, 9H), 1.44 (s, 18H), 1.45 (s, 18H);  $^{13}\text{C}$  NMR (75.5 MHz,  $\text{CDCl}_3$ ):  $\delta$  28.7, 29.0, 29.1, 39.2, 40.7, 41.6; mass spectrum (FD): 816–834 ( $M^+$ ).

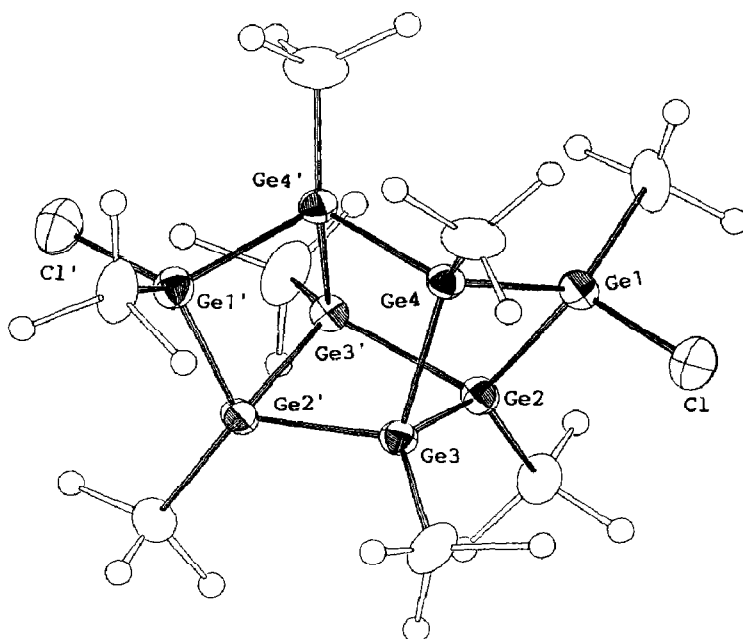


Fig. 2. ORTEP drawing of **3**. Selected bond lengths (Å) and bond angles (°): Ge(1)–Ge(2) 2.442, Ge(1)–Ge(4) 2.470, Ge(2)–Ge(3) 2.473, Ge(3)–Ge(4) 2.537, Ge(2)–Ge(3′) 2.481, Ge(4)–Ge(4′) 2.466,  $\sigma(\text{Ge–Ge})$  0.006. Ge(2)–Ge(1)–Ge(4) 86.3, Ge(1)–Ge(2)–Ge(3) 89.5, Ge(1)–Ge(2)–Ge(3′) 104.1, Ge(3)–Ge(2)–Ge(3′) 82.5, Ge(2)–Ge(3)–Ge(4) 84.3, Ge(2)–Ge(3)–Ge(2′) 91.5, Ge(4)–Ge(3)–Ge(2′) 104.0, Ge(1)–Ge(4)–Ge(3) 87.5, Ge(1)–Ge(4)–Ge(4′) 103.6, Ge(3)–Ge(4)–Ge(4′) 94.3,  $\sigma(\text{Ge–Ge–Ge})$  0.2.

shown in Fig. 2\*. The skeleton of **3** is constructed by three square four-membered rings and two five-membered rings.

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra (Fig. 3) exhibit only four signals assigned to *t*-butyl groups due to the  $C_2$  symmetry of the molecule. In the  $^{13}\text{C}$  NMR spectrum, one *t*-butyl group (29.3 ppm for the methyl C and 35.6 ppm for the quaternary C) can be seen besides the three other sets (32.6, 33.0, 34.2 ppm for the methyl C and 37.6, 37.9, 38.2 ppm for the quaternary C). Since the latter sets are largely deshielded, it is most likely that these three *t*-butyl groups bind to the germanium atoms of the fused four-membered rings. The origin of deshielding can be explained by the increased *s*-character of the C–Ge bonds. As a result, signals for *t*-butyl protons attached to

\* Crystal data of **3**. Molecular formula  $\text{C}_{32}\text{H}_{72}\text{Cl}_2\text{Ge}_8$ , mol. wt. 1108.7, monoclinic, space group *Cc*, *a* 20.385(5), *b* 11.037(3), *c* 20.772(4) Å,  $\beta$  100.28(3)°, *V* 4710.8(14) Å<sup>3</sup>, *Z* = 4, *D<sub>c</sub>* 1.56 g/cm<sup>3</sup>,  $\mu(\text{Mo–K}\alpha)$  51.00 cm<sup>−1</sup>. The positions of heavy atoms (Ge and Cl) and central carbon atoms of *t*-butyl groups were satisfactorily refined, but temperature factors of a few methyl carbons result in abnormal anisotropic features, implying some disorder. Among attempted refinement either for the possible space group (*Cc* or *C2/c*), the latter was judged to be correct. Thus the molecule has crystallographic two-fold axis symmetry. The *R* value was 0.10 for 1672 reflections with  $F_0 > 3\sigma(F_0)$  and  $\sin \theta/\lambda < 0.50$ . No refinement of hydrogen atoms was made. A rather low level of accuracy is due to a problems with crystal formation.

Further details of atomic coordinates, thermal parameters, bond lengths, bond angles, and list of  $F_0 - F_c$  are available as supplementary materials (18 pages).

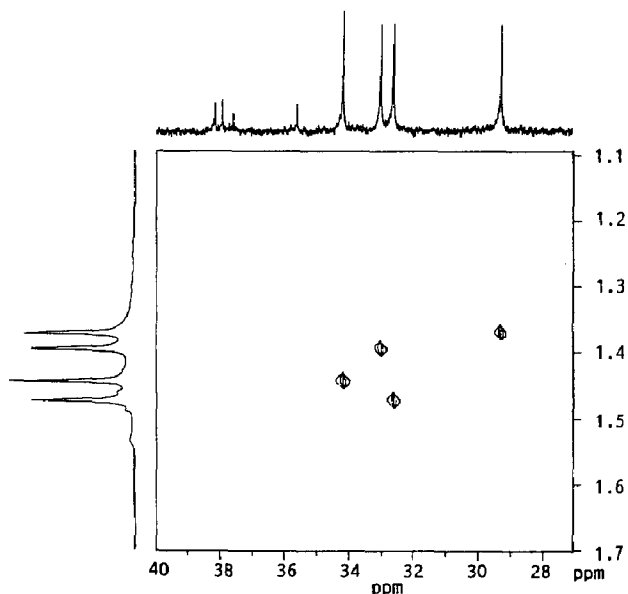


Fig. 3.  $^1\text{H}$ - $^{13}\text{C}$  COSY plot of **3** in  $\text{CDCl}_3$ .

these germanium atoms appear at relatively lower field (1.40, 1.45, and 1.48 ppm) than the other (1.37 ppm). The  $^1\text{H}$ - $^{13}\text{C}$  COSY plot supports the analysis. The skeleton of **3** is very similar to that of a polyhedral silicon compound reported recently by Masamune's group [5].

Related work is in progress.

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