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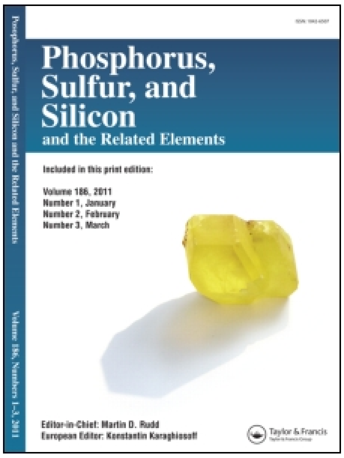

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Cage Compounds of Si and Ge: Synthesis and Structures

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CAGE COMPOUNDS OF SI AND GE: SYNTHESIS AND STRUCTURES

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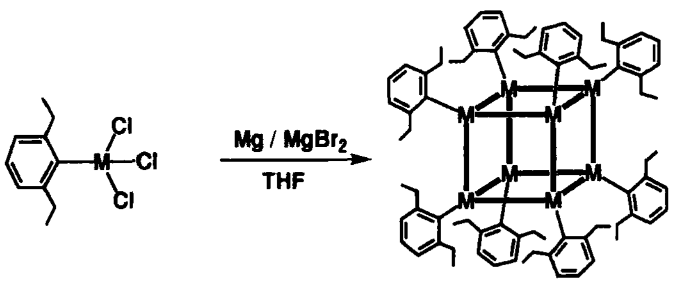
Syntheses, characterization, and reactions of octasilacubane Si_8R_8 (R = 2,6-diethylphenyl), octagermacubane Ge_8R_8 (R = 2,6-diethylphenyl), hexasilaprismane Si_6R_6 (R = 2,6-diisopropylphenyl), and hexagermaprismane Ge_6R_6 (R = 2,6-diisopropylphenyl) are reported.

INTRODUCTION

Synthesis of cage compounds of Si and Ge is one of the greatest synthetic challenge in the small ring system of higher row group 14 elements.[1] Herein, our recent results on the chemistry of the cage-cluster compounds of Si and Ge will be reported.

RESULTS AND DISCUSSION

Trihalogenosilanes and trihalogenogermanes bearing appropriate substituents can serve as precursors to cage compounds of Si and Ge by reductive coupling reactions. Octasilacubane (**1a**) and octagermacubane (**1b**) were synthesized by dechlorinative coupling reactions of (2,6-diethylphenyl)trichlorosilane and (2,6-diethylphenyl)trichloro-

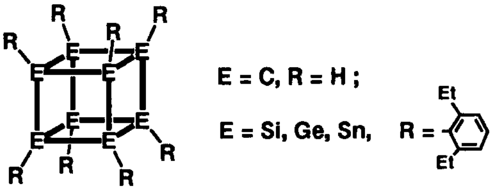


1a: M = Si; 1b: M = Ge

germane with Mg/MgBr2 reagent in THF.[2] The crystal structures of these cubanes show that the 2,6-diethylphenyl groups lie in alternatively with dihedral angles of ca. 90°. As a result, the cubic skeleton of **1a** and **1b** is efficiently protected by the eight 2,6-diethylphenyl groups. The structural parameters of the cubanes determined by X-ray diffractions together with C_8H_8[3] are given in Table I. The E-E-E bond angles for the all cubanes range from 89 - 91°, thus the skeletons are made up of the almost perfect cubic arrangement of group 14 elements. The E-E bond lengths of R_8E_8 (2.399 Å for Si, 2.490 Å for Ge, and 2.854 Å for Sn[4]) are apparently longer than the normal values. These values are in close agreement with those of the calculated for E_8H_8 (2.382 Å for Si, 2.527 Å for Ge, and 2.887 Å for Sn).[5]

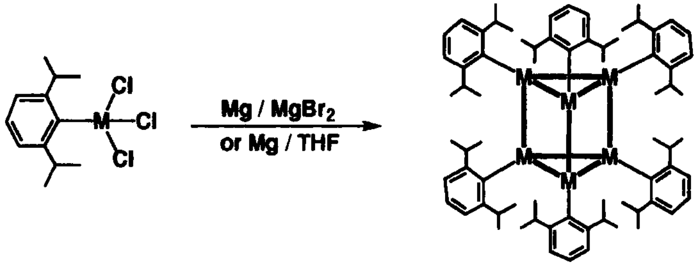
TABLE I

Structural parameters of cubane composed of group 14 element.



	C_8H_8	Si_8R_8	Ge_8R_8	Sn_8R_8
E-E (Å)				
X-ray	1.551 (av.) (1.549-1.553)	2.399 (av.) (2.384-2.411)	2.490 (av.) (2.478-2.503)	2.854 (av.) (2.839-2.864)
calculated	1.559	2.382	2.527	2.887
normal	1.54	2.34	2.40	2.78
E-Car (Å)	1.06 (av.)	1.911 (av.)	1.982 (av.)	2.193 (av.)
E-E-E (deg)	89.3-90.5	88.9-91.1	88.9-91.1	89.1-91.1

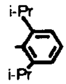
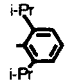
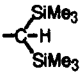
Hexasilaprismane (**2a**) and hexagermaprismane (**2b**) were prepared by the dechlorinative coupling reactions of (2,6-diisopropylphenyl)trichlorosilane and (2,6-diisopropylphenyl)trichlorogermane in THF, respectively.[6] The structural parameters of prismanes (C, Si, Ge) together with calculated values are shown in Table II. The calculations of C and Si prismanes predict shortening of the bond length of the three-membered unit (*a*) relative to that of four-membered unit (*b*). Indeed, unsubstituted prismane[7] and the derivative C_6Me_6[8] are in accordance with this prediction. However,

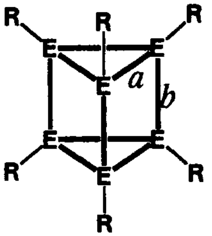


2a: M = Si; **2b**: M = Ge

owing to steric repulsions the skeleton of Si$_6$R$_6$ (**2a**: R = 2,6-i-Pr$_2$C$_6$H$_3$) (a = 2.374 - 2.387 Å, b = 2.365 - 2.389 Å) is slightly distorted from an ideal triangular prism geometry. Both bond a and bond b in **2a** are longer than those of calculated for Si$_6$H$_6$ (a = 2.359 Å, b =2.375 Å).[9] In contrast, bond a is distinctly longer than bond b in Ge$_6$R$_6$ **2b** (R = 2,6-i-Pr$_2$C$_6$H$_3$, a = 2.503 Å, b = 2.468 Å). Due to the bulky substituents, both bond a and bond b in Ge$_6$R$_6$ (R = CH(SiMe$_3$)$_2$, a = 2.580 Å, b = 2.522 Å) are longer than those in **2b**, but bond a is appreciably longer than bond b as found in **2b**.[10]

TABLE II
Structural parameters of prismane composed of group 14 element.

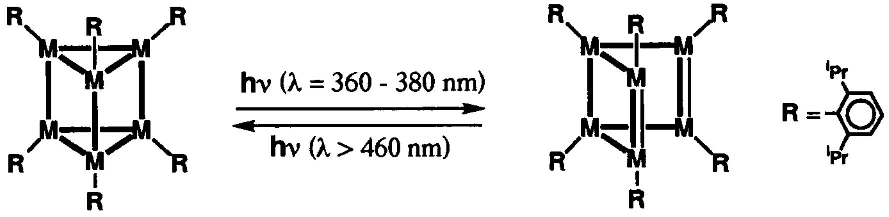
E	R	a (Å)	b (Å)	Method
C	H	1.507	1.549	Calcd.
		1.500	1.585	ED
	Me	1.540	1.551	ED
Si	H	2.359	2.375	Calcd.
		2.380 (2.374-2.387)	2.373 (2.365-2.389)	XRD
Ge	H	2.502	2.507	Calcd.
		2.503 (2.497-2.507)	2.468 (2.465-2.475)	XRD
		2.580 (2.578-2.584)	2.522 (2.516-2.526)	XRD



ED: electron diffraction

XRD: X-ray diffraction

Hexasilaprismane **2a** is photosensitive. Upon irradiation with a light of wavelength of 360 - 380 nm in solution (3-MP or 2-MeTHF) at -50 °C or in a glass matrix at 77 K, new absorption bands appeared at 335 nm, 455 nm, and 500 nm assignable to the absorption bands of hexasila-Dewar benzene **3a**. Excitation of these bands with a light of wavelength longer than 460 nm resulted in the immediate regeneration of **2a**. Hexasila-Dewar benzene **3a** is a thermally labile molecule and is readily reverted to **2a**. The half-life is $t_{1/2} = 0.52$ min at 0 °C in 3-MP (first-order rate constant, $k = 2.21 \times 10^{-2}\ s^{-1}$). The activation energy (Ea) to produce hexasilaprismane **2a** is only 13.7 kcal/mol. The small Ea value is consistent with the high reactivity of Si=Si double bonds. Hexagermaprismane **2b** also afforded the hexagerma-Dewar benzene **3b** with absorption bands at 342 nm, 446 nm, and 560 nm.



2a: M = Si; **2b**: M = Ge

3a: M = Si; **3b**: M = Ge

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