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Synthesis and Characterization of Tetrakis(trihalogermyl)methanes. Molecules Containing Sterically Strained Carbon Centers

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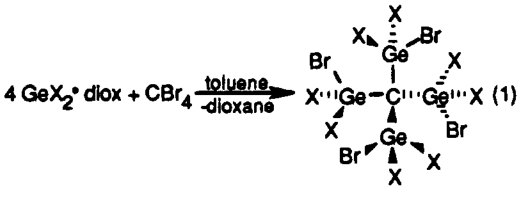
We have recently used tetrasilylmethane, $(H_3Si)_4C$,[1] in the presence of SiH_4 and GeH_4 to grow heteroepitaxial, diamond-structured $Si_{1-x-y}Ge_xC_y$ alloys on (100)Si containing 4−6 at. % C.[2] Encapsulating the C in a diamond-like, tetrahedral environment of Si eliminates strong C−H bonds in the precursor. This novel approach allows the use of low temperature (470 °C) growth conditions in the ultrahigh vacuum chemical vapor deposition (UHV-CVD) reactor which has enabled us to produce metastable, crystalline $Si_{1-x-y}Ge_xC_y$ alloys for bandgap engineering studies and semiconductor applications. These results suggest that molecules containing a central C tetrahedrally bound to Ge might be ideal precursors to the highly sought, metastable $Ge_{1-x}C_x$ alloys. Routes to these materials are of interest because little is known about $Ge_{1-x}C_x$ alloys (stoichiometric GeC is an unknown phase) and current deposition technology (chemical and physical) has not produced pure, crystalline, epitaxial $Ge_{1-x}C_x$ films. Unfortunately, attempts to synthesize the Ge analogue of $(H_3Si)_4C$ by the same method have been unsuccessful. This has led us to search for new routes to these types of molecules. We now report the synthesis of tetrakis(trihalogermyl)methanes, molecules containing a tetrahedral CGe_4 core, and their reductions with $LiAlH_4$.

The germylene complexes, GeX_2·dioxane (X = Cl, Br),[3] undergo complete insertion into the C−Br bonds of CBr_4 to give the tetrakis(trihalogermyl)methane compounds, $(BrCl_2Ge)_4C$ (**1**) and $(Br_3Ge)_4C$ (**2**), in 79% and 94% yields, respectively (eq 1).[4] Dihalogermylenes and their base adducts have been shown previously to be reactive towards C−X bonds and C−C multiple bonds.[5] However, this is the first example of a germylene insertion reaction leading to complete substitution at a single C center.



(**1**, X = Cl; **2**, X = Br)

Compounds **1** and **2** crystallize from toluene as colorless, well-formed, octahedral-shaped crystals. They are air-stable, high melting solids that behave similarly to other highly symmetric compounds containing a tetrahedral core of group IVA elements.[6] This high symmetry leads to exceedingly simple IR spectra for **1** and **2**. The IR spectrum of **1** has an absorption at 701 cm^{-1} which is assigned to υ(Ge−C). A set of absorptions at 447, 421, and 407 cm^{-1} corresponds to υ(Ge−Cl) modes while a related set at 336, 315, and 305 cm^{-1} is due to υ(Ge−Br) modes. The fully brominated **2** shows only two absorptions at 672 cm^{-1} (υ(Ge−C)) and 330 cm^{-1} (υ(Ge−Br)). Both **1** and **2** are volatile in the mass spectrometer and display well-defined isotopic envelopes. However, **1** is susceptible to intermolecular halide scrambling and loss of Cl in the gas phase. This leads to the observation of isotopic envelopes for the series of ions having the composition $CBr_{11-x}Cl_xGe_4$ ($x = 4-11$). These difficulties are eliminated for **2** and its mass spectrum is straightforward with isotopic envelopes observed for M^+, $M^+ - Br$, and $M^+ - GeBr_4$.

In order to determine the bonding parameters of the Ge−C interactions in these highly crowded molecules, an X-ray crystallographic analysis was performed for **2**.[7] However, the high symmetry of the molecule prevents it from ordering the four Ge positions within the crystal lattice. This internal disorder leads to a model of the X-ray data in which the four Ge atoms are distributed among 20 partially occupied sites in a dodecahedral arrangement (Figure 1). The central location of the C atom allows it to refine with full occupancy. In addition, the tight packing of the Br atoms on the outer surface of the molecule fixes their positions capping each face of the dodecahedron. The structure of the related compound $(Me_3Sn)_4C$, has recently been published and shows the same type of symmetry related disorder in the X-ray data.[8]

Although the X-ray data cannot provide the true structure of **2** (i.e. a central C tetrahedrally bound to four $GeBr_3$ moieties), the resulting Ge−C distances have a narrow range (2.006(26)−2.051(29) Å) and should approximate the true Ge−C bond distances. These values are significantly longer than what has been determined through ab initio calculations on the related molecules $(H_3Ge)_4C$ and $(H_3C)_4Ge$.[9] This demonstrates that C can effectively expand its bonding sphere in a sterically demanding Ge environment without fragmenting. Therefore, it may be possible to substitute smaller C atoms into an extended, cubic Ge lattice without creating strain defects.

Preliminary results have demonstrated the reduction of **1** and **2** with $LiAlH_4$ under conditions similar to those used in the

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(1) Schmidbaur, H.; Zech, J. *Eur. J. Solid State Inorg. Chem.* **1992**, *29,* 5.

(2) Todd, M.; Matsunaga, P.; Kouvetakis, J.; Chandrasekhar, D.; Smith, D. J. *Appl. Phys. Lett.* **1995**, *67,* 1247.

(3) (a) Kolesnikov, S. P.; Rogozhin, I. S.; Nefedov, O. M. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1974**, 2297. (b) Herrmann, W.; Denk, M., Eur. Patent 568074.

(4) For **1**: mp 330 °C dec. Anal. Calcd for $CBr_4Cl_8Ge_4$: C, 1.33; Br, 35.3; Cl, 31.3. Found: C, 1.57; Br, 33.3; Cl, 32.8. For **2**: mp 329 °C dec. Anal. Calcd for $CBr_{12}Ge_4$: C, 0.95; Br, 76.0. Found: C, 1.09; Br, 75.8.

(5) For reviews of dihalogermylene chemistry see: Satgè, J; Massol, M.; Rivière, P. *J. Organomet. Chem.* **1973**, 56, 1.

(6) (a) Kaczmarczyk, A.; Millard, M.; Nuss, J. W.; Urry, G. *J. Inorg. Nucl. Chem.* **1964**, *26,* 421. (b) Müller, R.; Müller, W. *Chem. Ber.* **1963**, *96,* 2894. (c) Köbrich, G.; von Nagel, R. *Tetrahedron Lett.* **1970**, 4693.

(7) Crystal data for **2** ($CBr_{12}Ge_4$): colorless blocks, cubic, $Pa\bar{3}$, $a = 12.998$ (2) Å, $V = 2196.0$ (11) $Å^3$, $Z = 4$, $D_{calcd} = 3.821$ $g{\cdot}cm^{-3}$, μ(Mo Kα) = 27.273 mm^{-1}, $T = 298$ K. Of 784 data collected ($3.5° \le 2\theta \le 50°$), 392 were independent and 176 observed ($5\sigma(F_o)$). On the basis of stoichiometry, symmetry operators, and packing constraints, the asymmetric unit consists of $^1/_6$ C, $^2/_3$ Ge, and 2 Br. With Br atoms anisotropic and C and Ge atoms isotropic (to maximize the data to parameter ratio): $R(F) = 8.46\%$ and $R_w(F) = 10.46\%$.

(8) Klinkhammer, K. W.; Kuhner, S.; Regelmann, B.; Weidlein, J. *J. Organomet. Chem.* **1995**, 496, 241.

(9) Toman, J. J.; Frost, A. A.; Topiol, S.; Jacobson, S.; Ratner, M. A. *Theor. Chim. Acta.* **1981**, *58,* 285.

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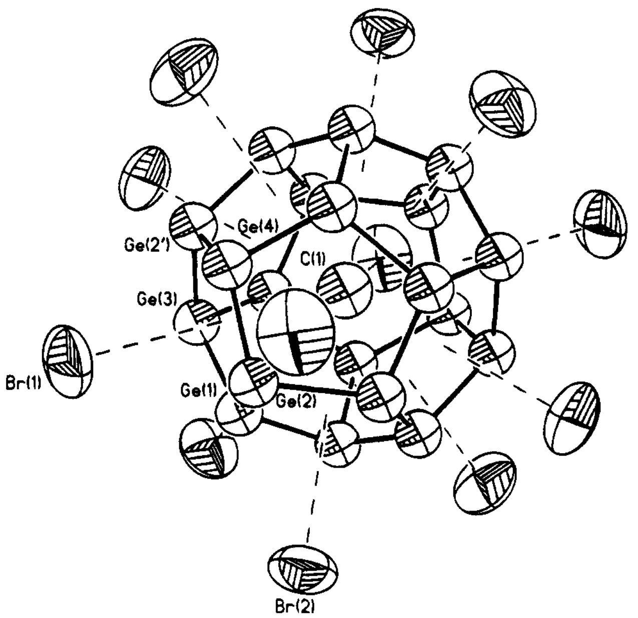
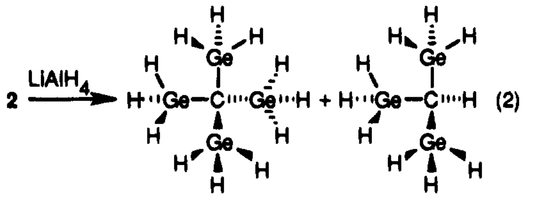


Figure 1. Crystallographic model of the disorder in **2** displaying the dodecahedral arrangement of partially occupied Ge positions. C1 sits at the center of the dodecahedron, and the 12 Br atoms cap each face.

synthesis of $(H_3Si)_4C$.[1] However, only small quantities of $(H_3Ge)_4C$ **3** and $(H_3Ge)_3CH$ **4** (eq 2)[10] have been isolated thus far.



3 **4**

Compounds **3** and **4** were isolated as colorless, low-volatility liquids. Their gas phase IR spectra can be assigned based on comparison with the spectra for $(H_3Ge)_2CH_2$[11] and H_3GeCH_3.[12] Both **3** and **4** show a Ge−H stretching mode at 2075 cm^{-1} and characteristic GeH_3 deformation modes. The spectrum of **4** is distinguished by the presence of weak absorptions for the C−H stretching and bending modes. The most notable feature is the dramatic dependence of the Ge−C stretching vibration on the degree of substitution at the carbon center. For **4** the absorption is at 793 cm^{-1} while for **3** the absorption is at 745 cm^{-1}. This trend continues for $(H_3Ge)_2CH_2$ and H_3GeCH_3 with Ge−C vibrations at 680 and 602 cm^{-1}, respectively. Therefore, eliminating strong C−H bonds from the molecule serves to strengthen the resulting Ge−C interactions.

Table 1. ^1H and ^{13}C NMR[a] Data for Polysubstituted Silyl- and Germylmethanes

compound	^1H, δ	^{13}C, δ	ref
$(H_3Si)_2CH_2$	−0.60 (sept, CH_2) 3.63 (t, SiH_3)	−21.05	14
$(H_3Si)_3CH$	−1.17 (dect, CH) 3.71 (d, SiH_3)	−30.61	14
$(H_3Si)_4C$	3.84 (s, SiH_3)	−38.99	1
$(H_3Ge)_2CH_2$	−0.17 (sept, CH_2) 3.64 (t, GeH_3)	−19.77	11
$(H_3Ge)_3CH$	−0.60 (dect, CH) 3.83 (d, GeH_3)	−28.46	this work
$(H_3Ge)_4C$	4.07 (s, GeH_3)	−37.09	this work

[a] C_6D_6 solution.

The ^1H and ^{13}C NMR spectra for **3** and **4** (Table 1) are consistent with their assigned structures and correlate extremely well with other related silyl- and germylmethanes. The mass spectra of **3** and **4** show isotopic envelopes centered at 308 and 293 amu corresponding to CH_xGe_4 and CH_xGe_3, respectively. Although both molecules appear to lose H atoms readily in the mass spectrometer, the CGe_4 and CGe_3 cores are retained in the gas phase. The isolation of **3** and **4** completes the family of silyl- and germylmethanes, $(H_3M)_{4-x}CH_x$ (M = Si, Ge; x = 0−3).

In conclusion, we have been able to construct molecules containing a central C tetrahedrally encapsulated within a Ge environment. The compounds are quite stable despite the large amount of steric bulk attached to C, suggesting that substitutional C in a Ge cubic lattice can exist without creating strain defects. These halogermylmethanes can be examined as precursors to $Ge_{1-x}C_x$ nanowires or quantum dots through alkali metathesis reactions.[13] Furthermore, their reduction with $LiAlH_4$ leads to the formation of trigermyl- and tetragermylmethane, important precursors for UHV−CVD applications and bandgap engineering studies. Continuing efforts will focus on improving the synthesis of **3** and **4** for further evaluation.

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Supporting Information Available: Text giving experimental and analytical details and tables of crystallographic data, atomic coordinates, bond distances and angles, and anisotropic thermal parameters (14 pages). Ordering information is given on any current masthead page.

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(10) For **3**: vapor pressure: ca. 1 Torr, 20 °C. IR (gas phase): 2075 (vs, GeH str), 888 (w, GeH_3 asym def), 839 (m, GeH_3 sym def), 793 (vs, GeC str), 745 (w), 704 (vw). For **4**: vapor pressure: 15 Torr, 20 °C. IR (gas phase): 3032 (vw, CH str), 2075 (vs, GeH str), 1031 (vw, CH wag), 880 (w, GeH_3 asym def), 837 (m, GeH_3 sym def), 793 (w), 745 (s, GeC str), 704 (w).

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