

## Heteroatomic Deltahedral Zintl Ions of Group 14 and their Alkenylation

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Reported is the synthesis of  $\text{Ge}_{9-x}\text{Sn}_x$  heteroatomic deltahedral Zintl ions and their alkenylation by reactions with alkynes. The nine-atom clusters are made either by extraction from mixed Ge/Sn precursors with nominal composition  $\text{K}_4\text{Ge}_{9-x}\text{Sn}_x$  or by dissolution of mixtures of the corresponding binary precursors  $\text{K}_4\text{Ge}_9$  and  $\text{K}_4\text{Sn}_9$  in solvents with high dielectric constants such as DMF, DMSO, and acetonitrile. Reactions of the heteroatomic clusters with alkynes such as  $\text{Me}_3\text{SiC}\equiv\text{CSiMe}_3$ ,  $\text{HC}\equiv\text{CCpr}$  (Cpr=cyclopropyl), and  $\text{HC}\equiv\text{CPh}$  in ethylenediamine resulted in the following structurally characterized compounds with alkenylated heteroatomic clusters:  $[\text{K}-(2,2,2\text{-crypt})]_3[\text{Ge}_8\text{Sn}_1\text{-CH}=\text{CH}_2]\cdot\text{en}\cdot\text{tol}$  (**1**), triclinic,  $P\bar{1}$ ,  $a = 13.9220(3)$  Å,  $b = 14.9788(3)$  Å, and  $c = 21.5892(5)$  Å,  $\alpha = 94.2580(10)^\circ$ ,  $\beta = 98.5210(10)^\circ$ , and  $\gamma = 98.4890(10)^\circ$ ,  $V = 4382.31(16)$  Å<sup>3</sup>,  $Z = 2$ ;  $[\text{K}-(2,2,2\text{-crypt})]_4[\text{Ge}_2\text{Sn}_7(\text{CH}=\text{CH}_2)_2]\cdot\text{en}$  (**2**), monoclinic,  $P2_1/c$ ,  $a = 48.1883(15)$  Å,  $b = 12.1551(4)$  Å, and  $c = 21.4824(7)$  Å,  $\beta = 90.052(2)^\circ$ ,  $V = 12583.0(7)$  Å<sup>3</sup>,  $Z = 4$ ;  $[\text{K}-(2,2,2\text{-crypt})]_3[\text{Ge}_8\text{Sn}_1\text{-CH}=\text{CHCpr}]\cdot\text{en}$  (**3**), monoclinic,  $P2_1/c$ ,  $a = 17.9132(9)$  Å,  $b = 22.7967(11)$  Å, and  $c = 21.6922(12)$  Å,  $\beta = 98.409(2)^\circ$ ,  $V = 8763.0(8)$  Å<sup>3</sup>,  $Z = 4$ ;  $[\text{K}-(2,2,2\text{-crypt})]_3[\text{Ge}_2\text{Sn}_7\text{-CH}=\text{CHPh}]\cdot 2\text{en}$  (**4**), monoclinic,  $P2_1/n$ ,  $a = 13.2583(5)$  Å,  $b = 47.0565(17)$  Å, and  $c = 15.9978(6)$  Å,  $\beta = 111.536(2)^\circ$ ,  $V = 9284.1(6)$  Å<sup>3</sup>,  $Z = 4$ . The potassium counterions of the divinyl-substituted cluster in **2** were exchanged for tetrapropylammonium cations, and the resulting compound was also crystallized and structurally characterized:  $[\text{Pr}_4\text{N}]_4[\text{Ge}_2\text{Sn}_7(\text{CH}=\text{CH}_2)_2]_2$  (**5**), triclinic,  $P\bar{1}$ ,  $a = 11.6757(8)$  Å,  $b = 18.8150(16)$  Å, and  $c = 21.0608(17)$  Å,  $\alpha = 112.327(3)^\circ$ ,  $\beta = 91.550(3)^\circ$ , and  $\gamma = 91.892(3)^\circ$ ,  $V = 4273.5(6)$  Å<sup>3</sup>,  $Z = 2$ . All clusters were also characterized in solution by electrospray mass spectrometry.

### Introduction

Although Zintl ions were introduced between the late 1890s and early 1930s,<sup>1</sup> they were not structurally characterized until many years later.<sup>2</sup> Moreover, the connection between them and the Zintl phases was not recognized until the late 1990s when the well-known deltahedral Zintl ions  $\text{Ge}_9^{4-}$  were also found in the Zintl phases  $\text{Cs}_4\text{Ge}_9$  and  $\text{Rb}_4\text{Ge}_9$ .<sup>3</sup> Since then, these group 14 deltahedral clusters

$\text{E}_9^{n-}$  ( $\text{E} = \text{Si}, \text{Ge}, \text{Sn}, \text{Pb}$ ) have been at the forefront of a rapidly developing and exciting new chemistry.<sup>4</sup> Notable milestones in their chemistry are the oxidative coupling of  $\text{Ge}_9^{4-}$  to oligomers and infinite chains,<sup>5–10</sup> the capping of the clusters by transition-metal organometallic fragments, i.e., the addition of a tenth vertex,<sup>11</sup> the insertion of a

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transition-metal atom at the center of the cluster, which is sometimes combined with capping and oligomerization,<sup>12</sup> the addition of main-group organometallic fragments as exobonded substituents,<sup>6a,9c,13,15</sup> and the functionalization of the clusters with various organic residues by reactions with organic halides and alkynes.<sup>14,15</sup> This latter development of attaching organic fragments directly to the clusters has opened up a new field, namely, organo-Zintl chemistry, that is potentially fertile for further synthetic explorations.

Despite all of these advancements in the chemistry of homoatomic Zintl ions, primarily Ge- and Sn-based, very little attention has been paid to heteroatomic species. At the same time, it is well-known that, theoretically, the electrical and optical properties of heteroatomic and metal-doped semiconductors can be tailored by varying the composition.<sup>16</sup> The band gap of germanium, for instance, can be adjusted by the incorporation of tin into its structure: this narrows it to direct-band-gap levels of under 0.7 eV at a rate of approximately 12 meV per atomic percent of tin.<sup>16</sup> However, the solubility of these elements in each other is extremely low under equilibrium conditions. Therefore, the growth of 3D heterostructures is severely limited, and the resulting heteroatomic systems are typically viewed either as impurities in the lattice or as polycrystalline/amorphous solid mixtures. Annealing of the supersaturated solutions usually leads to segregated regions of the pure elements.<sup>17</sup> Ion implantation, on the other hand, is often accompanied by radiation damage.<sup>17</sup> At the same time, in spite of the obvious connection to heteroatomic clusters as potential “building blocks” for bulk, perhaps metastable, heteroatomic materials, only a few such clusters have been structurally characterized so far. The few examples are [Sn<sub>2</sub>Bi<sub>2</sub>]<sup>2-</sup>,<sup>18</sup> [Pb<sub>2</sub>Sb<sub>2</sub>]<sup>2-</sup>,<sup>19</sup> [InBi<sub>3</sub>]<sup>2-</sup>,<sup>20</sup> [GaBi<sub>3</sub>]<sup>2-</sup>,<sup>20</sup> [In<sub>4</sub>Bi<sub>5</sub>]<sup>3-</sup>,<sup>20</sup> [TlSn<sub>9</sub>]<sup>3-</sup>,<sup>21</sup> [TlSn<sub>8</sub>]<sup>3-</sup>,<sup>21</sup> and [Ti<sub>2</sub>Te<sub>2</sub>]<sup>2-</sup>.<sup>22</sup> Interestingly, none of these involves elements of the same group, although Rudolph and co-workers have studied the systems Ge<sub>9-x</sub>Sn<sub>x</sub> and Sn<sub>9-x</sub>Pb<sub>x</sub> in solutions by <sup>119</sup>Sn and <sup>207</sup>Pb NMR.<sup>23</sup> Of particular interest is the eventual

use of such clusters for the synthesis of hybrid nanoobjects combining a metal and a semiconductor or two different semiconductors where the ratio of the two elements could be varied by design. Of similar interest would be achieving bulk metastable heteroatomic phases in analogy with the recently reported synthesis of metastable bulk elemental germanium with the clathrate I structure made from homoatomic Ge<sub>9</sub> clusters.<sup>24</sup> All of these perspectives prompted us to explore for possible ways to synthesize heteroatomic clusters, specifically Ge<sub>9-x</sub>Sn<sub>x</sub>, and to investigate their reactivity and how it compares to the corresponding homoatomic species. Herein we describe the synthesis of mixed nine-atom clusters Ge<sub>9-x</sub>Sn<sub>x</sub> both from tertiary precursors with nominal compositions K<sub>4</sub>Ge<sub>9-x</sub>Sn<sub>x</sub> and from mixtures of binary precursors with compositions K<sub>4</sub>Ge<sub>9</sub> and K<sub>4</sub>Sn<sub>9</sub>. Subsequently, some of these heteroatomic deltahedral clusters were alkenylated by reactions with alkynes to produce the first structurally characterized heteroatomic organo-Zintl ions in [K(2,2,2-crypt)]<sub>3</sub>[GeSn<sub>8</sub>-HC=CH<sub>2</sub>] $\cdot$ tol $\cdot$ en (1), [K-(2,2,2-crypt)]<sub>4</sub>[Ge<sub>2</sub>Sn<sub>7</sub>(CH=CH<sub>2</sub>)<sub>2</sub>] $\cdot$ en (2), [K-(2,2,2-crypt)]<sub>3</sub>[GeSn<sub>8</sub>-CH=CHCpr] $\cdot$ en (3), [K-(2,2,2-crypt)]<sub>3</sub>[Ge<sub>2</sub>Sn<sub>7</sub>-CH=CH-Ph] $\cdot$ 2en (4), and the cation-exchanged product [Pr<sub>4</sub>N]<sub>4</sub>[Ge<sub>2</sub>Sn<sub>7</sub>(CH=CH<sub>2</sub>)<sub>2</sub>] (5). This work also highlights the importance of electrospray mass spectrometry (ES-MS) for the characterization of such compounds.

## Experimental Section

All manipulations were carried out under nitrogen using standard Schlenk-line and glovebox techniques as described in detail elsewhere.<sup>14</sup> Ethylenediamine (Alfa-Aesar, 99%) was distilled over sodium metal and stored in a gastight ampule under nitrogen in the glovebox. Dried toluene was stored over molecular sieves in the glovebox. Pyridine (anhydrous, Acros, 99.0%), dimethylformamide (DMF; anhydrous, Acros, 99.8%), dimethyl sulfoxide (DMSO; anhydrous, Aldrich, 99.8%), bis(trimethylsilyl)acetylene (Me<sub>3</sub>-SiC $\equiv$ CSiMe<sub>3</sub>, Acros, 99%), cyclopropylacetylene (HC $\equiv$ CCpr, with Cpr = cyclopropyl; Acros, 99%), and phenylacetylene (HC $\equiv$ CPh, with Ph = phenyl; Acros, 99%) were used as received. Tetrapropylammonium bromide (Pr<sub>4</sub>NBr; Acros, 98%) and 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo-[8.8.8]hexacosane (2,2,2-crypt; Acros, 98%) were used as received after careful drying under vacuum. Precursors with nominal compositions K<sub>4</sub>Ge<sub>9-x</sub>Sn<sub>x</sub> for x = 0, 1, 4.5, 6, 8, and 9 were synthesized by heating of the corresponding mixture of the elements (K, +99%, Strem; Ge, 99.999%, Alfa-Aesar; Sn, 99.999%, Alfa-Aesar) at 950 °C for 2 days in sealed niobium containers that were jacketed in evacuated fused-silica ampules.

**Mass Spectrometry.** ES-MS spectra in negative-ion mode were recorded on a Micromass Quattro-LC triple-quadrupole mass spectrometer (100 °C source temperature, 125 °C desolvation temperature, 2.5 kV capillary voltage, and 30–55 V cone voltage).<sup>14</sup> The samples were introduced by direct infusion with a Harvard syringe pump at 10  $\mu$ L/min. The samples were taken from compounds 1–5 before setting them aside for crystallization.

**Synthesis of Heteroatomic Zintl Ions Ge<sub>9-x</sub>Sn<sub>x</sub> from Tertiary Precursors.** A total of 3 mL of solvent (ethylenediamine, pyridine, DMF, acetonitrile, or DMSO) was added to 0.1 mmol of K<sub>4</sub>Ge<sub>9-x</sub>Sn<sub>x</sub> via a syringe, and the resulting solution was stirred

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for 30 min at room temperature. The reaction mixture was then centrifuged for 15–30 min and then filtered through a glass fiber filter pipet. In the case of pyridine, acetonitrile, and DMSO as the solvent of choice, about 1–2 equiv of sequestering agent, either 2,2,2-crypt or 18-crown-6, was added to improve the solubility of the precursor. Aliquots of the filtered reaction solution were then taken up in a gastight syringe, and the solutions were characterized by ES-MS. Observed ions in all solvents (negative-ion mode,  $m/z$ ):  $\text{Ge}_9^-$  (654),  $\text{Ge}_8\text{Sn}^-$  (700),  $\text{Ge}_7\text{Sn}_2^-$  (747),  $\text{Ge}_6\text{Sn}_3^-$  (793),  $\text{Ge}_5\text{Sn}_4^-$  (838),  $\text{Ge}_4\text{Sn}_5^-$  (884),  $\text{Ge}_3\text{Sn}_6^-$  (930),  $\text{Ge}_2\text{Sn}_7^-$  (977),  $\text{GeSn}_8^-$  (1023), and  $\text{Sn}_9^-$  (1069).

**Synthesis of Heteroatomic Zintl Ions  $\text{Ge}_{9-x}\text{Sn}_x$  from Binary Precursors.** A total of 1.5–2 mL of solvent via a syringe was added to 0.1 mmol of  $\text{K}_4\text{Ge}_9$  and 0.1 mmol of  $\text{K}_4\text{Sn}_9$  in two separate test tubes, and the resulting solution was stirred for 10–15 min at room temperature, resulting in a dark-red color. The two solutions were then combined and stirred for 30 min at room temperature. The solutions were then centrifuged for 15–30 min and filtered through a glass fiber filter pipet. Again, sequestering agents were added when pyridine, acetonitrile, and DMSO were used as solvents. Aliquots of the filtered reaction solution were then taken up in a gastight syringe, and the solutions were then characterized by ES-MS. Observed ions in ethylenediamine and pyridine solutions (negative-ion mode,  $m/z$ ):  $\text{Ge}_9^-$  (654),  $\text{KGe}_9^-$  (693),  $\text{Sn}_9^-$  (1069),  $\text{KSn}_9^-$  (1108). Observed ions in DMF, acetonitrile, and DMSO solutions (negative-ion mode,  $m/z$ ):  $\text{Ge}_9^-$  (654),  $\text{Ge}_8\text{Sn}^-$  (700),  $\text{Ge}_7\text{Sn}_2^-$  (747),  $\text{Ge}_6\text{Sn}_3^-$  (793),  $\text{Ge}_5\text{Sn}_4^-$  (838),  $\text{Ge}_4\text{Sn}_5^-$  (884),  $\text{Ge}_3\text{Sn}_6^-$  (930),  $\text{Ge}_2\text{Sn}_7^-$  (977),  $\text{GeSn}_8^-$  (1023), and  $\text{Sn}_9^-$  (1069).

**General Synthetic Procedures for Compounds 1–4.** Approximately 3–4 mL of ethylenediamine was added via a syringe to 0.1 mmol of a precursor with nominal composition  $\text{K}_4\text{Ge}_{4.5}\text{Sn}_{4.5}$  or  $\text{K}_4\text{Ge}_6\text{Sn}_3$  in a test tube, and the resulting solution was stirred for 30–45 min at room temperature, resulting in an intense deep-red solution. A 2–4-fold excess of the alkyne ( $\text{Me}_3\text{SiC}\equiv\text{CSiMe}_3$ ,  $\text{CprC}\equiv\text{CH}$ , or  $\text{PhC}\equiv\text{CH}$ ) was then syringed dropwise, and stirring was continued for 12–24 h at room temperature. The initial oily red-brown mixture changed to a dark-brown solution upon completion. It was then centrifuged for 15 min and filtered via a glass fiber pipet. Aliquots of this solution were used for ES-MS and crystallization by layering with a solution of 2,2,2-crypt (0.293 mmol) dissolved in 8 mL of toluene. In addition, compound 2 was also synthesized by reacting a DMF solution of a mixture of the binary precursors  $\text{K}_4\text{Ge}_9$  and  $\text{K}_4\text{Sn}_9$  with  $\text{Me}_3\text{SiC}\equiv\text{CSiMe}_3$ . Thus, 0.1 mmol of  $\text{K}_4\text{Ge}_9$  and 0.1 mmol of  $\text{K}_4\text{Sn}_9$  were stirred in 3 mL of DMF for 30 min at room temperature. All volatiles were then removed in vacuo (i.e., the reaction solution was transferred from a test tube to a Schlenk tube in the glovebox and then to a Schlenk line; all of the DMF solvent was removed under vacuum; the Schlenk tube with the resulting brown-red precipitate was then brought back into the glovebox for further reaction). The resulting brown-red precipitate was redissolved in 3 mL of ethylenediamine, to which 0.4 mmol of  $\text{Me}_3\text{SiC}\equiv\text{CSiMe}_3$  was slowly added. Standard workup and crystallization procedures followed, and compound 2 was crystallized from the solution.

**Synthesis of Compound 5.** A total of 0.1 mmol of  $\text{K}_4\text{Ge}_{4.5}\text{Sn}_{4.5}$  or  $\text{K}_4\text{Ge}_6\text{Sn}_3$  was dissolved in 3–4 mL of ethylenediamine (a red solution) at room temperature, reacted with 0.4 mmol of  $\text{Me}_3\text{SiC}\equiv\text{CSiMe}_3$  (a dark-brown solution upon completion), and the solution was centrifuged for 15–30 min, followed by filtration through a glass fiber filter pipet. Separately, 0.376 mmol of  $\text{Pr}_4\text{NBr}$  was dissolved in 8 mL of toluene (sonication for 1 h increases the solubility significantly), and this solution was layered on top of the ethylenediamine solution of divinyl-functionalized clusters. Small yellow-red blocks crystallized in very low yields after a few weeks.

**ES-MS Results ( $m/z$ ).** All samples were taken from the reaction mixtures prior to crystallization of the corresponding

compounds. Compounds 1, 2, and 5:  $\text{Ge}_9\text{R}^-$  (680),  $\text{Ge}_8\text{Sn}^-$  (699),  $\text{Ge}_9\text{R}_2^-$  (707),  $\text{KGe}_9\text{R}^-$  (719),  $\text{Ge}_8\text{SnR}^-$  (726),  $\text{KGe}_9\text{R}_2^-$  (746),  $\text{Ge}_8\text{SnR}_2^-$  (753),  $\text{KGe}_8\text{SnR}^-$  (765),  $\text{Ge}_7\text{Sn}_2\text{R}^-$  (772),  $\text{KGe}_8\text{SnR}_2^-$  (792),  $\text{Ge}_7\text{Sn}_2\text{R}_2^-$  (799),  $\text{KGe}_7\text{Sn}_2\text{R}^-$  (811),  $\text{Ge}_6\text{Sn}_3\text{R}^-$  (818),  $\text{KGe}_7\text{Sn}_2\text{R}_2^-$  (838),  $\text{Ge}_6\text{Sn}_3\text{R}_2^-$  (845),  $\text{KGe}_6\text{Sn}_3\text{R}^-$  (857),  $\text{Ge}_5\text{Sn}_4\text{R}^-$  (864),  $\text{KGe}_6\text{Sn}_3\text{R}_2^-$  (884),  $\text{Ge}_5\text{Sn}_4\text{R}_2^-$  (891),  $\text{KGe}_5\text{Sn}_4\text{R}^-$  (903),  $\text{Ge}_4\text{Sn}_5\text{R}^-$  (910),  $\text{KGe}_5\text{Sn}_4\text{R}_2^-$  (930),  $\text{Ge}_4\text{Sn}_5\text{R}_2^-$  (937),  $\text{KGe}_4\text{Sn}_5\text{R}^-$  (949),  $\text{Ge}_3\text{Sn}_6\text{R}^-$  (956),  $\text{KGe}_4\text{Sn}_5\text{R}_2^-$  (976),  $\text{Ge}_3\text{Sn}_6\text{R}_2^-$  (983),  $\text{KGe}_3\text{Sn}_6\text{R}^-$  (995),  $\text{Ge}_2\text{Sn}_7\text{R}^-$  (1002),  $\text{KGe}_3\text{Sn}_6\text{R}_2^-$  (1022),  $\text{Ge}_2\text{Sn}_7\text{R}_2^-$  (1029),  $\text{KGe}_2\text{Sn}_7\text{R}^-$  (1041),  $\text{GeSn}_8\text{R}^-$  (1048),  $\text{KGe}_2\text{Sn}_7\text{R}_2^-$  (1068),  $\text{GeSn}_8\text{R}_2^-$  (1075),  $\text{KGeSn}_8\text{R}^-$  (1087),  $\text{Sn}_9\text{R}^-$  (1094),  $\text{KGeSn}_8\text{R}_2^-$  (1114),  $\text{Sn}_9\text{R}_2^-$  (1121), where R is  $-\text{CH}=\text{CH}_2$ . Compound 3:  $\text{Ge}_9\text{R}^-$  (720),  $\text{KGe}_8\text{Sn}^-$  (738),  $\text{KGe}_9\text{R}^-$  (759),  $\text{Ge}_8\text{SnR}^-$  (766),  $\text{Ge}_9\text{R}_2^-$  (787),  $\text{KGe}_8\text{SnR}^-$  (805),  $\text{Ge}_7\text{Sn}_2\text{R}^-$  (812),  $\text{Ge}_8\text{SnR}_2^-$  (833),  $\text{KGe}_7\text{Sn}_2\text{R}^-$  (851),  $\text{Ge}_6\text{Sn}_3\text{R}^-$  (858),  $\text{Ge}_7\text{Sn}_2\text{R}_2^-$  (879),  $\text{KGe}_6\text{Sn}_3\text{R}^-$  (897),  $\text{Ge}_5\text{Sn}_4\text{R}^-$  (904),  $\text{Ge}_6\text{Sn}_3\text{R}_2^-$  (925),  $\text{KGe}_5\text{Sn}_4\text{R}^-$  (943),  $\text{Ge}_4\text{Sn}_5\text{R}^-$  (952),  $\text{Ge}_5\text{Sn}_4\text{R}_2^-$  (973),  $\text{KGe}_4\text{Sn}_5\text{R}^-$  (991),  $\text{Ge}_3\text{Sn}_6\text{R}^-$  (998),  $\text{Ge}_4\text{Sn}_5\text{R}_2^-$  (1019),  $\text{KGe}_3\text{Sn}_6\text{R}^-$  (1037),  $\text{Ge}_2\text{Sn}_7\text{R}^-$  (1044),  $\text{Ge}_3\text{Sn}_6\text{R}_2^-$  (1065),  $\text{KGe}_2\text{Sn}_7\text{R}^-$  (1083),  $\text{GeSn}_8\text{R}^-$  (1090),  $\text{KGe}_3\text{Sn}_6\text{R}_2^-$  (1104),  $\text{Ge}_2\text{Sn}_7\text{R}_2^-$  (1111),  $\text{KGe}_2\text{Sn}_7\text{R}^-$  (1129),  $\text{Sn}_9\text{R}^-$  (1136),  $\text{KGe}_2\text{Sn}_7\text{R}_2^-$  (1150),  $\text{GeSn}_8\text{R}_2^-$  (1157), where R is  $-\text{CH}=\text{CHCpr}$ . Compound 4:  $\text{Ge}_9\text{R}^-$  (756),  $\text{KGe}_9\text{R}^-$  (795),  $\text{Ge}_8\text{SnR}^-$  (802),  $\text{KGe}_8\text{SnR}^-$  (841),  $\text{Ge}_7\text{Sn}_2\text{R}^-$  (848),  $\text{KGe}_7\text{Sn}_2\text{R}^-$  (889),  $\text{Ge}_6\text{Sn}_3\text{R}^-$  (894),  $\text{Ge}_5\text{Sn}_4\text{R}^-$  (940),  $\text{Ge}_4\text{Sn}_5\text{R}^-$  (986),  $\text{Ge}_3\text{Sn}_6\text{R}^-$  (1032),  $\text{Ge}_2\text{Sn}_7\text{R}^-$  (1078),  $\text{GeSn}_8\text{R}^-$  (1124),  $\text{Sn}_9\text{R}^-$  (1170), where R is  $-\text{CH}=\text{CHPh}$ .

**Structure Determination.** X-ray diffraction data sets of single crystals of compounds 1–5 were collected at 100 K on a Bruker D8 APEX-II or a Bruker X8 APEX-II diffractometer equipped with CCD area detectors using graphite-monochromated Mo  $\text{K}\alpha$  radiation. The single crystals were selected under Paratone-N oil, mounted on Mitegen micromount loops, and positioned in the cold stream of the diffractometer. The structures were solved by direct methods and refined on  $F^2$  using the *SHELXTL*, version 6.21, package.<sup>25</sup> Further details of the data collections and refinements are listed in Table 1. Compounds 1 and 5 contain two crystallographically different but otherwise identical clusters.

## Results and Discussion

From our experience with homoatomic germanium and tin clusters and from the reported results in the literature, we noticed that while the  $\text{Ge}_9$  and  $\text{Sn}_9$  clusters preserve their nine-atom nuclearity in most reactions, this is not the case with lead clusters, which end up both with higher and lower nuclearity, often centered or capped. Some examples are  $[\text{Ni}@\text{Pb}_{10}]^{2-}$ ,<sup>26</sup>  $[\text{Pt}@\text{Pb}_{12}]^{2-}$ ,<sup>27</sup>  $[\text{Pb}_5\text{Mo}_2(\text{CO})_6]^{4-}$ ,<sup>28</sup>  $\text{Pb}_{10}^{2-}$ ,<sup>29</sup> and  $\text{Pb}_5^{2-}$ ,<sup>30</sup> although deviations from nine-atom nuclearity or multiples of it are also  $\text{Ge}_5^{2-}$ ,<sup>31</sup>  $\text{Sn}_5^{2-}$ ,<sup>30,32</sup>  $[\text{Ni}_2\text{Sn}_{17}]^{4-}$ ,<sup>33</sup>  $[\text{Pt}_2\text{Sn}_{17}]^{4-}$ ,<sup>34</sup> and the nondeltahedral  $[\text{Co}@\text{Ge}_{10}]^{3-12c}$  and

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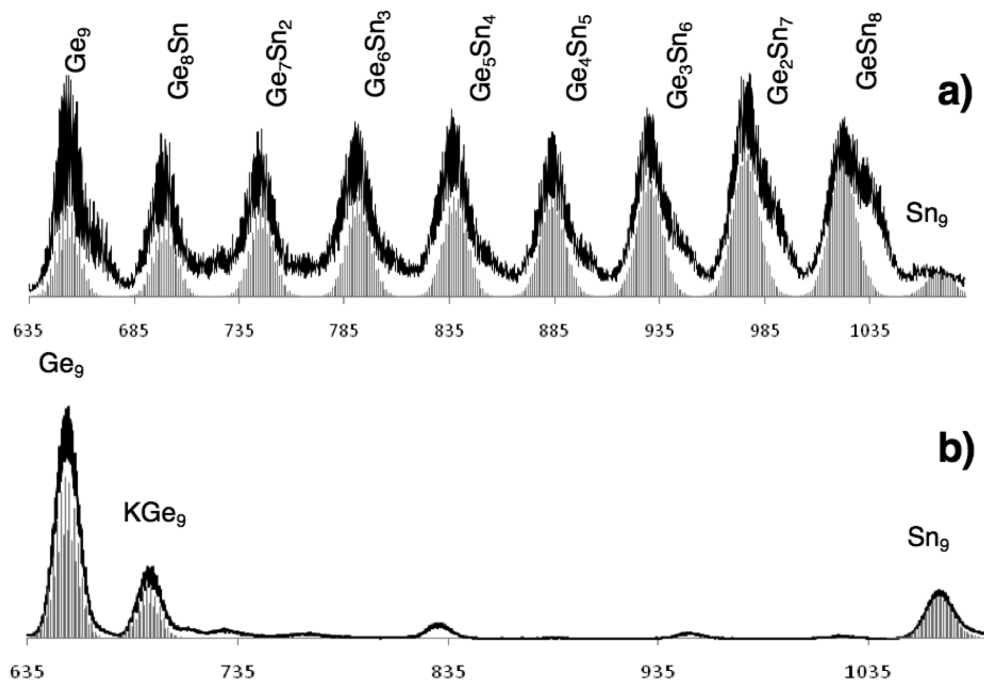
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Table 1. Selected Data Collection and Refinement Parameters for Compounds 1–5

	1	2	3	4	5
fw	2402.9	3783.01	2395.08	2445.11	2805.61
space group, <i>Z</i>	<i>P</i> $\bar{1}$ , 2	<i>P</i> $2_1/c$ , 4	<i>P</i> $2_1/c$ , 4	<i>P</i> $2_1/n$ , 4	<i>P</i> $\bar{1}$ , 2
<i>a</i> (Å)	13.9220(3)	48.1883(15)	17.9132(9)	13.2583(5)	11.6757(8)
<i>b</i> (Å)	14.9788(3)	12.1551(4)	22.7967(11)	47.0565(17)	18.8150(16)
<i>c</i> (Å)	21.5892(5)	21.4824(7)	21.6922(12)	15.9978(6)	21.0608(17)
$\alpha$ (deg)	94.2580(10)	90	90	90	112.327(3)
$\beta$ (deg)	98.5210(10)	90.052(2)	98.409(2)	111.536(2)	91.550(3)
$\gamma$ (deg)	98.4890(10)	90	90	90	91.892(3)
<i>V</i> (Å <sup>3</sup> )	4382.31(16)	12583.0(7)	8763.0(8)	9284.1(6)	4273.5(6)
radiation, $\lambda$ (Å)			Mo K $\alpha$ , 0.710 73		
$\rho_{\text{calcd}}$ (g·cm <sup>-3</sup> )	1.820	1.997	1.815	1.750	2.180
$\mu$ (mm <sup>-1</sup> )	2.781	3.855	2.781	2.684	5.422
R1/wR2 <sup>a</sup> [ <i>I</i> $\geq$ 2 $\sigma$ ( <i>I</i> )]	0.0398, 0.0904	0.0421, 0.1136	0.0432, 0.0933	0.0737, 0.1840	0.0454, 0.1188
R1/wR2 <sup>a</sup> , all data	0.0561, 0.0984	0.0532, 0.1197	0.0495, 0.1249	0.0896, 0.1958	0.0602, 0.1327

$$^a \text{R1} = [\sum ||F_o| - |F_c||] / \sum |F_o|; \text{wR2} = \{[\sum w[(F_o)^2 - (F_c)^2]^2] / [\sum w(F_o^2)^2]\}^{1/2}; w = [\sigma^2(F_o)^2 + (AP)^2 + BP]^{-1}, \text{ where } P = [(F_o)^2 + 2(F_c)^2] / 3.$$



**Figure 1.** ES-MS spectra (negative-ion mode) of (a) solutions of  $\text{K}_4\text{Ge}_9$  and  $\text{K}_4\text{Sn}_9$  dissolved together in DMF, DMSO, or acetonitrile. (b) ES-MS spectra of the same precursors dissolved together in ethylenediamine or pyridine. Solutions of tertiary precursors with nominal composition  $\text{K}_4\text{Ge}_{9-x}\text{Sn}_x$  in any of the solvents show spectra as in part a. The theoretical isotope distributions are shown under the peaks.

$[\text{Fe}@\text{Ge}_{10}]^{3-}$ .<sup>12d</sup> Because it is unlikely that the lead clusters are reassembled atom by atom from the well-known  $\text{Pb}_9$  clusters, the next logical assumption is that perhaps they interact directly with each other and exchange atoms and/or fragments during such rendezvous. This different behavior of the different clusters, i.e.,  $\text{Pb}_9$  versus  $\text{Ge}_9$  and  $\text{Sn}_9$ , is in all likelihood based on the combined properties of the element forming the clusters such as its electronegativity, atomic size, inert-pair effects, etc., and the solvent in which they are dissolved such as the dielectric constant, polarity, molecule dimensions, coordinating capability, etc.

In order to test the effect of the solvent on cluster interactions and atom exchange, we carried out ES-MS studies of solutions made of tertiary  $\text{K-Ge-Sn}$  precursors and solutions of mixed binary  $\text{K-Ge}$  and  $\text{K-Sn}$  precursors in different solvents. Independent of the solvent, the spectra of the solutions of the tertiary  $\text{K-Ge-Sn}$  precursors showed all possible clusters  $\text{Ge}_{9-x}\text{Sn}_x$ , with  $x$  being an integer from 0 to 9 (Figure 1a). These results are similar to those reported by

Rudolph and co-workers, who similarly dissolved tertiary precursors in ethylenediamine.<sup>23</sup> However, when a mixture of the binary precursors  $\text{K}_4\text{Ge}_9$  and  $\text{K}_4\text{Sn}_9$  is dissolved in ethylenediamine or pyridine, the spectra show only the homoatomic clusters  $\text{Ge}_9$  and  $\text{Sn}_9$  (Figure 1b). Yet, when the same mixture of binary precursors is dissolved in DMF, DMSO, or acetonitrile, the spectra show the same collection of heteroatomic clusters as that in solutions of the tertiary precursors  $\text{K-Ge-Sn}$ ; i.e., all possible  $\text{Ge}_{9-x}\text{Sn}_x$  are seen (Figure 1a).

This different behavior in the different solvents suggests that the homoatomic clusters interact somehow and exchange atoms in DMSO, DMF, and acetonitrile but not in ethylenediamine and pyridine. One of the major differences between these groups of solvents is in their dielectric constants and, therefore, in their ability to screen charged species such as the anionic clusters. Thus, DMSO, DMF, and acetonitrile have very high dielectric constants of  $\epsilon = 47.24$ , 38.25, and 36.64, respectively, and provide a medium with

lower dielectric permeability that perhaps allows for the ionic clusters to “see” each other. The dielectric constants of ethylenediamine and pyridine, on the other hand, are much lower,  $\epsilon = 13.82$  and  $13.26$ , respectively, and may prevent such interactions between the clusters. Besides the differences in the dielectric constants, it is also plausible that the better coordinating ability of pyridine and the chelating capabilities of ethylenediamine may prevent atom exchange. The different behavior of the  $\text{Pb}_9$  clusters in ethylenediamine may be due to their larger size and, therefore, larger surface for charge distribution.<sup>26–29,34</sup> The resulting more diffuse negative charge may, in turn, permit cluster–cluster interactions even in ethylenediamine despite the solvent’s lower dielectric constant.

The tertiary precursors  $\text{K}_4\text{Ge}_{9-x}\text{Sn}_x$ , on the other hand, provide heteroatomic clusters in all five solvents. While this result was expected for the solvents with high dielectric constants, i.e., DMSO, DMF, and acetonitrile, it was somewhat unexpected for the extractions in ethylenediamine and pyridine, i.e., the solvents with low dielectric constants. The tertiary precursors, as already mentioned, are made by simply mixing the elements and heating them together at high temperatures. This naturally raised the question of whether the tertiary precursors already contain heteroatomic clusters  $\text{Ge}_{9-x}\text{Sn}_x$  that are then simply extracted into solutions or, perhaps, the precursors are intimate mixtures of very small domains of the binary  $\text{K}_4\text{Ge}_9$  and  $\text{K}_4\text{Sn}_9$ , and the heteroatomic clusters form somehow at the solid–liquid interface upon extraction because of their proximity. Unfortunately, all of our attempts for structural characterization of the tertiary precursors were unsuccessful. It is well-known that the simple binary phases diffract very poorly,<sup>35</sup> and this, as it turned out, is greatly exacerbated for the tertiary precursors. All that can be seen by powder X-ray diffraction are a couple of very broad peaks at low angles and nothing else. All single crystals that were selected diffracted extremely poorly or were not single at all. Several attempts to carry out diffraction with synchrotron radiation proved futile as well. Thus, at this stage it is unclear how the mixed-atom clusters form upon extraction from the tertiary precursors. Nonetheless, it is important that we have access to such heteroatomic clusters even in solvents with low dielectric constants, specifically in ethylenediamine, which is the typical solvent for carrying out reactions with deltahedral Zintl ions.

A number of phases with heteroatomic clusters were crystallized from such solutions of tertiary precursors, and single-crystal X-ray diffraction data sets were collected for many of them. However, as can be expected, all nine cluster positions were with mixed Ge/Sn occupancy, and this made the refinement of the structures unsatisfactory and, thus, unsuitable for publication.<sup>36</sup> Nonetheless, the partial refinements clearly showed the presence of heteroatomic nine-atom clusters, while the number of cation positions (all well refined) indicated the cluster charges. Some of the compounds, as it turned out, are isostructural with known compounds with homoatomic clusters. For example, three compounds with the general stoichiometry  $[\text{K}-(2,2,2\text{-crypt})]_6[\text{Ge}_{9-x}\text{Sn}_x][\text{Ge}_{9-y}\text{Sn}_y] \cdot 2.5\text{en}$  but with three different sets of

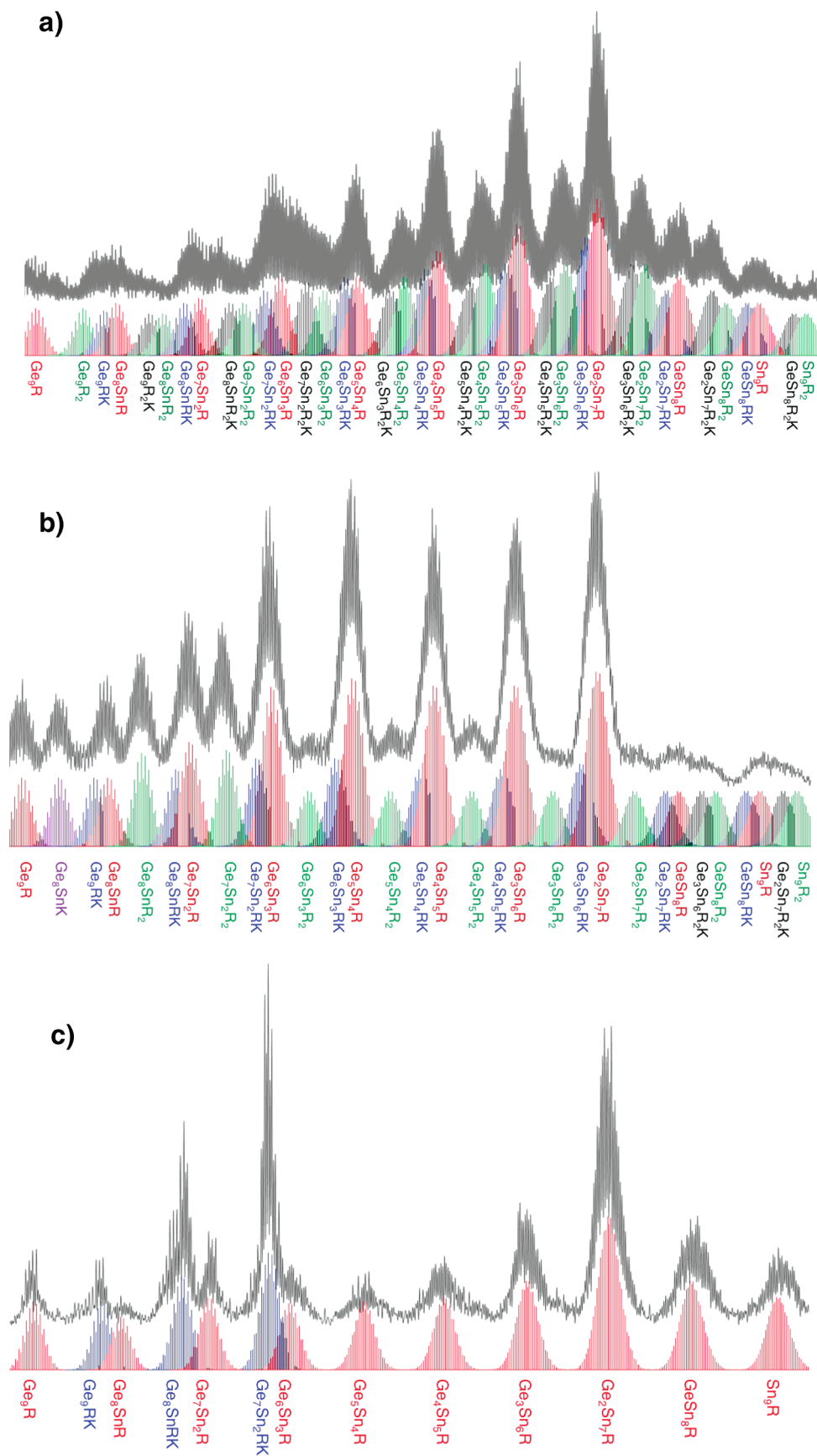
$x$  and  $y$  (and different lattice parameters) that were crystallized from three different mixtures are isostructural with the known  $[\text{K}-(2,2,2\text{-crypt})]_6[\text{Ge}_9]_2 \cdot 2.5\text{en}$ .<sup>36</sup> On the other hand, another three compounds,  $[\text{Na}-(2,2,2\text{-crypt})]_3[\text{Ge}_{9-x}\text{Sn}_x]$ ,  $[\text{Rb}-(2,2,2\text{-crypt})]_6[\text{Ge}_{9-x}\text{Sn}_x][\text{Ge}_{9-y}\text{Sn}_y] \cdot 3\text{en} \cdot \text{tol}$ , and  $\text{Rb}_4[\text{Ge}_{9-x}\text{Sn}_x] \cdot 2\text{en}$ , exhibit new overall structures.<sup>36</sup> Notice that the clusters in the last compound are of 4– oxidation state,  $[\text{Ge}_{9-x}\text{Sn}_x]^{4-}$ , while the others are with 3– charge,  $[\text{Ge}_{9-x}\text{Sn}_x]^{3-}$ .

With these heteroatomic clusters at hand and with the knowledge of the reactivity of the analogous homoatomic species  $\text{Ge}_9$  and  $\text{Sn}_9$  toward alkyl halides,<sup>14a–c,15</sup> and alkynes,<sup>14a,d,e</sup> we were interested in the reactivity of the heteroatomic species toward the same substrates and how it compares to the homoatomic ones. Furthermore, we hoped and expected that the functionalized clusters may have full homoatomic positional occupancies that would lead to better crystal structure determinations. Thus, using the same reaction procedures as those for the homoatomic clusters,<sup>14</sup> we carried out reactions of  $\text{Ge}_{9-x}\text{Sn}_x$  clusters with alkyl halides and alkynes. Unfortunately, our attempts with halides have been unsuccessful to this date, with all reactions resulting in cluster decomposition. It should be pointed out that the reactions of even the homoatomic clusters with alkyl halides, especially primary and secondary halides,<sup>14a–c</sup> are often accompanied by some partial decomposition and are not as clean as the analogous reactions with alkynes.<sup>14a,d,e</sup> Overall, they are very sensitive to the specific conditions (the concentration of the clusters, the rate of addition of the halide and in what form, etc.), and often it takes quite some time to find the proper parameters. Furthermore, it is possible that the mixed-atom clusters are more reactive because of the uneven distribution of charges and, in the presence of strong electrophiles, are more readily oxidized to either the corresponding elements or some other product without intact clusters. Fortunately, however, the reactions with alkynes proceeded smoothly and produced the corresponding alkenylated heteroatomic clusters. Thus, the reactions of  $\text{Ge}_{9-x}\text{Sn}_x$  clusters with  $\text{Me}_3\text{SiC}\equiv\text{CSiMe}_3$ ,  $\text{HC}\equiv\text{CCpr}$ , and  $\text{HC}\equiv\text{CPh}$  are accompanied by a change of color from deep red to dark brown in about 24 h, and on the basis of the experiences with homoatomic clusters, this typically indicates the end point of the reaction. ES-MS spectra of the resulting solutions (prior to crystallization of compounds **1–5**) confirmed the existence of a range of mono- and dialkenylated heterometallic clusters  $\text{Ge}_{9-x}\text{Sn}_x\text{R}$  and  $\text{RGe}_{9-x}\text{Sn}_x\text{R}$ , where R is  $-\text{CH}=\text{CH}_2$ ,  $-\text{CH}=\text{CHCpr}$ , or  $-\text{CH}=\text{CHPh}$  (Figure 2). The fact that compound **2** can be synthesized both from dissolved tertiary precursor in ethylenediamine and from a mixture of the binary precursors  $\text{K}_4\text{Ge}_9$  and  $\text{K}_4\text{Sn}_9$  first dissolved in DMF in order to form the mixed-atom clusters and then transferred to ethylenediamine confirms that the source of the heteroatomic clusters does not matter; i.e., the clusters have the same reactivity and charges in both cases. This indicates also that, once the clusters are formed, they remain intact, allowing for further exploration.

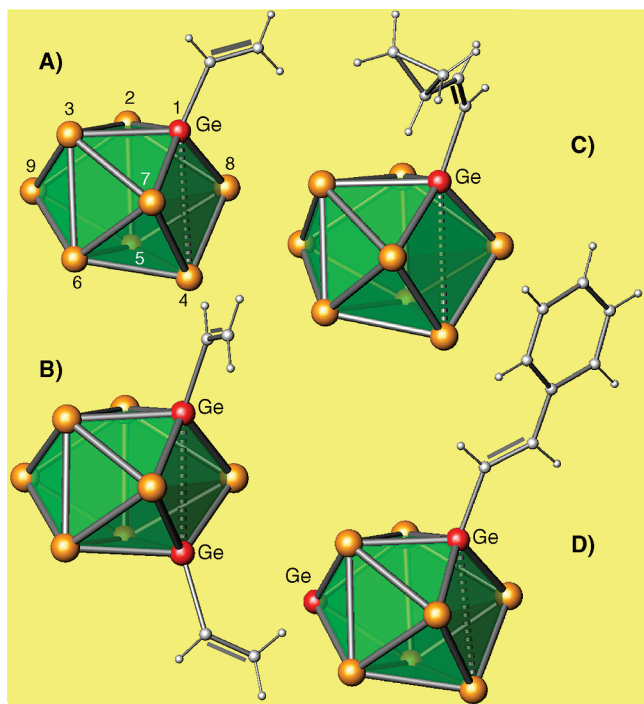
Despite the series of alkenylated clusters with various Ge/Sn ratios produced by these reactions with alkynes, only a single representative was crystallized from each reaction solution upon layering with toluene. The clusters in all of the crystallized compounds, **1–5**, exhibit the usual distorted tricapped trigonal-prismatic shape (Figure 3; the two triangular bases of the trigonal prism are made of atoms 1–2–3

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**Figure 2.** ES-MS spectra (negative-ion mode) of ethylenediamine solutions of the reactions of  $Ge_{9-x}Sn_x$  clusters with (a)  $Me_3SiC\equiv CSiMe_3$ , (b)  $HC\equiv CCpr$ , and (c)  $HC\equiv CPh$ . Shown are also the theoretical isotope distributions for  $KGe_{9-x}Sn_x$  (purple),  $Ge_{9-x}Sn_xR$  (red),  $KGe_{9-x}Sn_xR$  (blue),  $Ge_{9-x}Sn_xR_2$  (green), and  $KGe_{9-x}Sn_xR_2$  (black), where R stands for  $-CH=CH_2$  in part a,  $-HC=CHCpr$  in part b, and  $-HC=CHPh$  in part c.



**Figure 3.** Alkenylated heteroatomic clusters: (A)  $[\text{GeSn}_8\text{-HC=CH}_2]^{3-}$  in **1**; (B)  $[\text{Ge}_2\text{Sn}_7(\text{HC=CH}_2)_2]^{2-}$  in **2** and **5**; (C)  $[\text{GeSn}_8\text{-HC=CHCPr}]^{3-}$  in **3**; (D)  $[\text{Ge}_2\text{Sn}_7\text{-HC=CHPh}]^{3-}$  in **4**. The numbering scheme is shown in part A only (Ge, red; Sn, gold).

and 4–5–6, while the capping atoms are 7–8–9). As in the homoatomic examples, the organic groups are bonded to the atoms forming one of the trigonal-prismatic edges parallel to the pseudo-3-fold axis (edge 1–4, Figure 3A), and this edge is substantially longer than the other two in the prism, which is typical for all known homoatomic examples.<sup>4–14</sup> Thus, Ge1–Sn4 in **1**, **3**, and **4** is within 3.5–3.8 Å, while the pairs Sn2–Sn5 and Sn3–Sn6 are shorter than 3.2 Å. Similarly, Ge1–Ge4 in **2** and **5** is around 3.25 Å, while the purely tin edges are close to 3.0 Å.

Interestingly, although not entirely unexpected, the organic substituents in all clusters are bonded to germanium and none to the tin atoms. There are two reasons for expecting such a bonding pattern. First, the dissociation energy of the Ge–C bond,  $255 \text{ kJ}\cdot\text{mol}^{-1}$ , is quite a bit higher than that of the Sn–C bond,  $193 \text{ kJ}\cdot\text{mol}^{-1}$ .<sup>37</sup> Second, our studies of the reactivity of  $\text{Sn}_9$  clusters toward alkynes have shown that alkylation of these clusters is much more difficult compared to that of  $\text{Ge}_9$  and does not seem to proceed beyond monosubstitution, i.e.,  $[\text{Sn}_9\text{R}]^{3-}$ .<sup>14b</sup> The Ge–C distances are within the range 1.94–2.02 Å and are similar to those in functionalized homoatomic germanium clusters.<sup>14a,d,e</sup> At the same time, they are much shorter than the Sn–C distances in the known alkenylated tin clusters, 2.197(6) Å in  $[\text{Sn}_9\text{HC=CH}_2]^{3-}$  and 2.185(5) Å in  $[\text{Sn}_9\text{HC=CHPh}]^{3-}$ .<sup>14b</sup> In addition, according to the Cambridge Structure Database, they are well within the range of typical Ge– $\text{C}_{\text{sp}^2}$  distances of 1.91–2.04 Å and well outside the typical Sn– $\text{C}_{\text{sp}^2}$  range of 2.07–2.23 Å.<sup>38</sup> All of this provides additional evidence that the alkenyl groups are attached to germanium and not the tin atoms of the clusters.

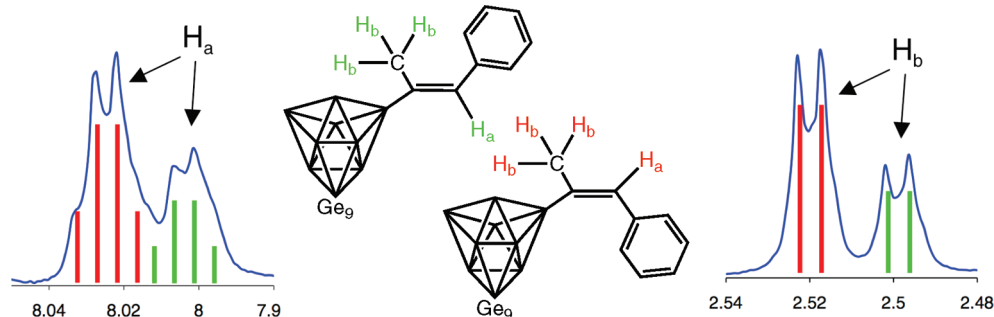
Further proof for the identities of the atoms within the clusters and for the absence of mixed occupancies are the well-differentiated distances around the germanium and tin atoms in the clusters and the absence of abnormal thermal displacement parameters. The latter (Figure S1 in Supporting Information) are very well behaved and either very close to spherical or slightly elongated tangentially to the cluster surface. Had there been sites with mixed Ge/Sn occupancies, their thermal ellipsoids are expected to be elongated radially to the cluster's curvature because of the different bonds to the surrounding atoms when the position is occupied by germanium or tin. The distances at a particular atom in the cluster are also very informative about the identity of the atom. This is especially important for the naked germanium atom that caps the trigonal prism at position 9 in the cluster of compound **4** (Figure 3d). In all other clusters, the germanium atoms are exobonded and, therefore, at the ends of the elongated edges of these clusters, i.e., at positions 1 and 4. Starting with the exobonded germanium atoms in **1–5**, their distances to the surrounding tin atoms are in the range 2.7–2.8 Å. They are noticeably shorter than the corresponding Sn–Sn distances at exobonded tin atoms in functionalized homoatomic  $\text{Sn}_9$  clusters, which are in the range 2.91–2.94 Å,<sup>14b</sup> and are much longer than the Ge–Ge distances at exobonded germanium atoms in substituted  $\text{Ge}_9$  clusters, which are in the range 2.52–2.58 Å.<sup>14a,c–e</sup> Typically, distances around naked atoms are slightly longer than those with exobonds, mainly because of the lone pair of electrons at the former and those associated with its higher negative charge. This is exactly the case with position 9 of the clusters in **4**, where the distances are in the range 2.78–2.85 Å. This range corresponds clearly to Ge–Sn distances when compared to the much longer Sn–Sn distances of ca. 2.95 Å at the Sn9 position in substituted tin-only clusters<sup>14b</sup> and to the similarly shorter Ge–Ge distances of ca. 2.62 Å at the same position in substituted germanium-only clusters.<sup>14a,c–e</sup>

Compared to the other compounds, the cluster in **4** is clearly different in having a germanium vertex without an exobond. It is not clear whether this is some special case or simply just that this compound happened to crystallize from a mixture of many species. In other words, it might be due to the crystallization specifics in each solution; for example, clusters with naked germanium atoms simply might not be able to crystallize. What is also puzzling is why only clusters with no more than two germanium atoms crystallize from the solutions that, according to ES-MS, clearly contain substituted clusters with the whole gamut of Ge/Sn ratios. Numerous attempts to isolate germanium-rich species were made but failed. One such series of attempts was to work with germanium-rich tertiary precursors, i.e., precursors with nominal composition of up to  $\text{K}_4\text{Ge}_8\text{Sn}$ , but these resulted in the same substituted clusters crystallized in the same compounds. In another approach, the binary precursors  $\text{K}_4\text{Ge}_9$  and  $\text{K}_4\text{Sn}_9$  were mixed in DMF in ratios of up to 10:1, and because the reaction with alkynes needs a protic solvent, the solid material was transferred in ethylenediamine after DMF was pumped off. Nonetheless, after the reactions were carried out with the corresponding alkynes, the crystalline phases were the same. Again, all of this might simply be due to the crystallization capability (packing, charges, solvent inclusion, etc.) of these mixed Ge/Sn clusters.

(37) Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M. *Advanced Inorganic Chemistry*, 6th ed.; Wiley-Interscience: New York, 1999; p 259.

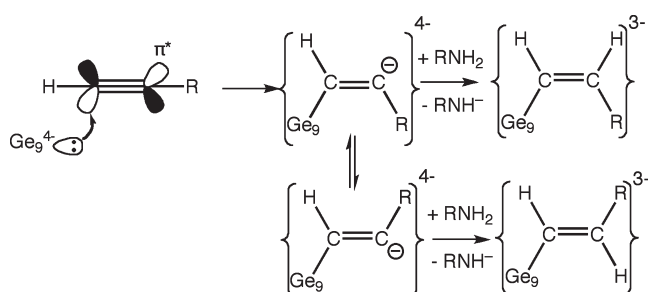
(38) Allen, F. H. *Acta Crystallogr., Sect. B* **2002**, *58*, 380.





**Figure 4.**  $^1\text{H}$  NMR spectrum of the reaction between  $\text{Ge}_9^{4-}$  and  $\text{MeC}\equiv\text{CPh}$  showing the products of both anti (red) and syn (green) addition of the cluster and a proton to the triple bond. The  $\text{H}_a$  proton (at the  $\text{sp}^2$  carbon atom) is coupled to the three methyl protons and shows a quartet (left), while the latter show doublets (right). The full spectrum is available in the Supporting Information of ref <sup>14a</sup>.  $^1\text{H}$  NMR data (pyridine- $d_5$ ):  $\delta$  2.50 (d,  $J = 2$  Hz,  $\text{trans}$ - $[\text{Ge}_9(\text{C}(\text{CH}_3)=\text{CHPh})]^{3-}$ ), 2.52 (d,  $J = 2$  Hz,  $\text{cis}$ - $[\text{Ge}_9(\text{C}(\text{CH}_3)=\text{CHPh})_2]^{2-}$ ), 8.004 (q,  $J = 2$  Hz,  $\text{trans}$ - $[\text{Ge}_9(\text{C}(\text{CH}_3)=\text{CHPh})]^{3-}$ ), 8.025 (q,  $J = 2$  Hz,  $\text{cis}$ - $[\text{Ge}_9(\text{C}(\text{CH}_3)=\text{CHPh})_2]^{2-}$ ).

### Scheme 1



One more interesting feature of the cluster in compound **4** is the stereochemistry of the substituent. While the cluster and the organic substituent at the double bonds in all reported cases of alkenylated  $\text{Ge}_9$  and  $\text{Sn}_9$  clusters<sup>14</sup> and in the mixed Ge/Sn species  $[\text{Sn}_8\text{Ge}-\text{CH}=\text{CHCpr}]^{3-}$  of compound **3** are in cis geometry, the phenyl group and the cluster are trans to each other in compound **4**. In other words, instead of the typically observed anti addition of the cluster and a proton across the triple bond, the addition in **4** is syn. Despite being the first example of different stereochemistry, however, this case was not unexpected and was actually welcomed as a confirmation of the proposed reaction mechanism.<sup>14a</sup> We have shown before that alkenylation of  $\text{Ge}_9$  clusters by a reaction with alkynes is a nucleophilic addition of the clusters to the triple bond.<sup>14</sup> In such additions, a filled and outward-protruding molecular orbital of a strong anionic nucleophile, the clusters in our case, attacks the empty  $\pi^*$  orbitals of the triple bond and supplies a pair of electrons to it. This results in the “breaking” of one of the  $\pi$  bonds between the carbon atoms and the formation of a bond between one of them and the nucleophile. The second carbon atom ends up carrying the negative charge (Scheme 1) as a lone pair of electrons. The more stable configuration of this electron pair is trans to the cluster, which leaves the organic substituent in a cis geometry with respect to the cluster. The quick anti protonation of the anionic carbon atom by protons from the ethylenediamine solvent defines the final geometry of the species. However, if the anion is externally stabilized by the organic substituent, it may have enough time and a lower barrier to rearrange before the protonation to occur as a syn addition (Scheme 1). Such an addition has been shown to partially occur in reactions involving the anionic nucleophiles  $\text{R}_3\text{Sn}^-$  when one of the alkyne substituents is an aryl or an alkoxy group that can stabilize the vinyl anion by

either  $\pi$  conjugation and/or electron withdrawing.<sup>39–42</sup> Thus, the reaction of  $\text{Et}_3\text{Sn}^-$  with methylphenylacetylene results in the nucleophile being exclusively bonded to the methyl side of the triple bond and the products from the anti and syn additions in a ratio of 4:1.<sup>41</sup> The reaction of the clusters with  $\text{HC}\equiv\text{CPh}$  most likely produced the cis isomer in higher yield, but for one reason or another, only the minor trans anion produced crystals. This is corroborated by previous  $^1\text{H}$  NMR studies of a very similar reaction between homoatomic  $\text{Ge}_9^{4-}$  clusters and  $\text{MeC}\equiv\text{CPh}$ , which have shown clearly both *cis*- and *trans*- $\text{Ge}_9(\text{Me})\text{C}=\text{CHPh}$  in the solution (Figure 4), although, in that case, only the cis isomer was crystallized.<sup>14a</sup> This outcome is very similar to the aforementioned reaction between  $\text{Et}_3\text{Sn}^-$  and the same alkyne.<sup>41</sup> In both cases, the nucleophile is bonded to the methyl end of the molecule and the two stereoisomers are present. Thus, the *trans*- $[\text{Sn}_7\text{Ge}_2\text{CH}=\text{CHPh}]^{3-}$  species represent the previously missing structurally characterized isomer. In a way, its existence proves once again that these reactions are nucleophilic additions of the clusters to triple bonds.

The exchange of potassium for tetrapropylammonium counteranions was carried out for the dianions  $[\text{Ge}_2\text{Sn}_7(\text{CH}=\text{CH}_2)_2]^{2-}$ . It confirmed that this is possible not only with homoatomic but also heteroatomic clusters. Furthermore, it provided further proof for the overall stoichiometry of the cluster and the positions of the tin and germanium atoms. The structure determination of the crystallized compound  $[\text{Pr}_4\text{N}]_4[\text{Ge}_2\text{Sn}_7(\text{CH}=\text{CH}_2)_2]_2$  showed that the anions are virtually identical with those in  $[\text{K}-(2,2,2\text{-crypt})]_4[\text{Ge}_2\text{Sn}_7(\text{CH}=\text{CH}_2)_2]_2 \cdot \text{en}$  (both compounds have two crystallographically different clusters each). The atom distribution and distances in the clusters are exactly the same, and the only small differences are in the rotations of the substituents around the Ge–C bonds. It has been shown before for homoatomic clusters that such cation exchange with large “greasy” cations, for example, tetraoctylammonium, makes the compounds soluble in many common solvents, which are typically much less polar than ethylenediamine.<sup>14c</sup> This would eventually make further

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modification of the organic side arms possible by reactions that are possible only in such solvents.

### Conclusions

Heteroatomic clusters  $[\text{Ge}_{9-x}\text{Sn}_x]^{4-}$  for  $x = 0-9$  can be made either by extraction from tertiary precursors with nominal composition  $\text{K}_4\text{Ge}_{9-x}\text{Sn}_x$  or by dissolution of mixtures of binary precursors  $\text{K}_4\text{Ge}_9$  and  $\text{K}_4\text{Sn}_9$  in solvents with high dielectric constants such as DMF, DMSO, and acetonitrile. ES-MS exhibits the whole gamut of species independent of the starting stoichiometries, and partial structure determinations from single-crystal X-ray diffraction show Ge/Sn mixing at all nine cluster positions. The clusters react with alkynes in the same way as the corresponding homoatomic species  $\text{Ge}_9^{4-}$  and  $\text{Sn}_9^{4-}$  to form mono- and dialkenylated products. According to ES-MS, all possible compositions  $\text{Ge}_{9-x}\text{Sn}_x$  are functionalized by such reactions. Among these, only four species were crystallized and structurally characterized, namely,  $[\text{GeSn}_8\text{-HC=CH}_2]^{3-}$ ,  $[\text{Ge}_2\text{Sn}_7(\text{HC=CH}_2)_2]^{2-}$ ,  $[\text{GeSn}_8\text{-HC=CHCpr}]^{3-}$ , and  $[\text{Ge}_2\text{Sn}_7\text{-HC=CHPh}]^{3-}$ . The potassium counteranions of the divinyl-substituted species were exchanged with tetrapropylammonium cations, and the new compound  $[\text{Pr}_4\text{N}]_4[\text{Ge}_2\text{Sn}_7(\text{HC=CH}_2)_2]_2$  was crystallized and also structurally characterized. The organic

substituents in all clusters are bonded to germanium atoms, but one of the two germanium atoms in  $[\text{Ge}_2\text{Sn}_7\text{-HC=CHPh}]^{3-}$  is without an exobond. Another first-of-a-kind structural feature in the latter species is that the cluster and phenyl group are trans to each other, while in all other cases, for both homo- and heteroatomic clusters, the organic substituent is always cis to the cluster.

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**Supporting Information Available:** Table with selected distances of the clusters in **1-5** compared to similarly functionalized homoatomic clusters, ORTEP drawings of the clusters, and X-ray crystallographic files in CIF format (five structures). This material is available free of charge via the Internet at <http://pubs.acs.org>.