

Tin-Based Organo-Zintl Ions: Alkylation and Alkenylation of Sn_9^{4-}

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Reactions of nine-atom deltahedral clusters (Zintl ions) of tin, Sn_9^{4-} , with alkyl chlorides, RCl ($\text{R} = \text{}^t\text{Bu}$, $\text{}^n\text{Bu}$, $\text{}^s\text{Bu}$), and alkynes ($\text{Me}_3\text{Si}-\text{C}\equiv\text{C}-\text{SiMe}_3$, $\text{Ph}-\text{C}\equiv\text{CH}$) yielded the corresponding alkylated and alkenylated clusters $[\text{Sn}_9-\text{R}]^{3-}$. The triple bonds of the alkynes are hydrogenated to double bonds in the process. These are the first tin-based organo-Zintl ions, that is Zintl ions of tin that were subsequently functionalized with organic groups. They are analogous to the recently reported germanium-based derivatives. The $\text{}^t\text{Bu}$ -, vinyl-, and styrene-functionalized clusters $[\text{Sn}_9-\text{}^t\text{Bu}]^{3-}$, $[\text{Sn}_9-\text{CH}=\text{CH}_2]^{3-}$, and $[\text{Sn}_9-\text{CH}=\text{CH}-\text{Ph}]^{3-}$, respectively, were structurally characterized in the solid state with $[\text{K}(2,2,2\text{-crypt})]^+$ counteranions and in solution by electrospray mass spectrometry. Crystal data: $[\text{K}(2,2,2\text{-crypt})]_3[\text{Sn}_9-\text{}^t\text{Bu}] \cdot 2\text{py}$, triclinic, $P1$, $a = 14.4259(3)$, $b = 16.2725(4)$, and $c = 22.5593(5)$ Å, $\alpha = 86.092(1)$, $\beta = 78.952(1)$, and $\gamma = 65.114(1)^\circ$, $V = 4714.48(7)$ Å³, $Z = 2$; $[\text{K}(2,2,2\text{-crypt})]_3[\text{Sn}_9-\text{CH}=\text{CH}_2] \cdot 2\text{py}$, triclinic, $P-1$, $a = 15.6988(3)$, $b = 17.4195(4)$, and $c = 17.4432(4)$ Å, $\alpha = 86.299(1)$, $\beta = 81.566(1)$, and $\gamma = 85.349(1)^\circ$, $V = 4696.27(18)$ Å³, $Z = 2$; $[\text{K}(2,2,2\text{-crypt})]_3[\text{Sn}_9-\text{CH}=\text{CH}-\text{Ph}] \cdot \text{tol} \cdot 0.75\text{py}$, monoclinic, $C2/c$, $a = 38.5883(9)$, $b = 23.3893(5)$, and $c = 25.0192(5)$ Å, $\beta = 120.269(1)^\circ$, $V = 19502.6(7)$ Å³, $Z = 8$.

Introduction

Although the nine-atom clusters of group 14, also known as deltahedral Zintl ions, have been known for many years, their redox chemistry is only a few years old.¹ Furthermore, most of this chemistry has been carried out only with the germanium clusters Ge_9 . It has been shown that these clusters exist with different charges in ethylenediamine, the typical solvent for such ions, and Ge_9^{4-} , Ge_9^{3-} , and Ge_9^{2-} can be selectively crystallized with different counteranions.^{1,2} This charge flexibility seems to be the reason for the observed extensive redox chemistry of the clusters. Thus, they can oligo- and polymerize by oxidative coupling to form $[\text{Ge}_9-\text{Ge}_9]^{6-}$, $[\text{Ge}_9=\text{Ge}_9=\text{Ge}_9]^{6-}$, $[\text{Ge}_9=\text{Ge}_9=\text{Ge}_9=\text{Ge}_9]^{8-}$, and $\infty\{-(\text{Ge}_9^{2-})-\}$.^{3–14} They can react with main-group organometallic halides and add the corresponding organometallic fragments as exobonded substituents to form $[\text{Ge}_9-\text{L}]^{3-}$ and $[\text{L}-\text{Ge}_9-\text{L}]^{2-}$ where $\text{L} = \text{SnR}_3$, GeR_3 , SbR_2 , BiR_2 , and so forth.^{2,15,16} Each addition to the cluster is a redox process that reduces the overall charge by one. Our more recent work has shown that not only organometallic fragments can be attached to deltahedral clusters but also

organic groups that form direct C–Ge exobonds.^{17–19} This can be achieved via two routes that are referred to as the halide and the alkyne routes and correspond accordingly to reactions with organic halides and alkynes. Whereas the organic fragment of the halide attaches to the cluster as is,¹⁷ the triple bonds in the alkynes undergo hydrogenation to double bonds during the process and add to the cluster as the corresponding alkenyl fragments.^{18,19} We have now extended this work into the corresponding tin clusters, Sn_9^{4-} , and report the synthesis of the alkyl derivative $[\text{Sn}_9-\text{}^t\text{Bu}]^{3-}$ (**1**) made by a reaction with $\text{}^t\text{BuCl}$ and of the alkenyl derivatives $[\text{Sn}_9-\text{CH}=\text{CH}_2]^{3-}$ (**2**) and $[\text{Sn}_9-\text{CH}=\text{CHPh}]^{3-}$ (**3**) made by reactions with $\text{Me}_3\text{SiC}\equiv\text{CSiMe}_3$ and $\text{HC}\equiv\text{CPh}$, respectively.

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It should be pointed out that the nine-atom clusters of silicon, germanium, tin, and lead can participate also in nonredox reactions such as coordination to transition-metal organometallic fragments and centering by transition-metal atoms.^{20–34} Also, clusters of these elements with external organic substituents can be synthesized by a different approach which does not use Zintl ions for the synthesis but rather assembles existing organo-element monomeric fragments into polyatomic aggregates. Three such clusters with Sn–C exobonds are known, namely Sn_8Ar_4 ,³⁵ Sn_9Ar_3 ,³⁶ and $\text{Sn}_{10}\text{Ar}_3^+$,³⁶ and they are all made from organo-Sn(II)-halides by reduction with alkali metals or thermolysis. The Ar-groups, either 2,6-Mes₂C₆H₃ or 2,6-Trip₂C₆H₃, are deliberately chosen to be bulky to protect the tin cores.^{35,36} Although some of these cluster cores may resemble deltahedral Zintl ions, for example the tricapped trigonal prismatic core in Sn_9R_3 resembles the known nine-atom Zintl ions,³⁶ these species are not exactly Zintl ion derivatives because their syntheses do not involve Zintl ions. The three organo-Zintl ions presented here, on the other hand, are such derivatives because they are made from Sn_9^{4-} .

Experimental Section

All operations were carried out under an inert atmosphere or vacuum using standard Schlenk-line or glovebox techniques. Ethylenediamine (Alfa-Aesar, 99%) was distilled over sodium metal and stored in a gastight ampule under nitrogen. Dry pyridine (Acros, 99.5%), ^tBuCl (Acros, 99%), Me₃SiC≡CSiMe₃ (Acros, 99%), and HC≡CPh (Acros, 93%) were used as received, whereas 2,2,2-crypt (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8,8,8]hexacosane, Acros)

was dried under vacuum before use. A precursor with nominal composition K₄Sn₉ was synthesized by heating the stoichiometric mixture of the elements (K: 99+%, Strem; Sn: Alfa-Aesar, rod, 99.999%) at 950 °C for 2 days in sealed niobium containers that were jacketed in evacuated fused-silica ampoules.

Synthesis of [K-(2,2,2-crypt)]₃[Sn₉-^tBu]·2py. K₄Sn₉ (120 mg, 0.098 mmol) and 2,2,2-crypt (220 mg, 0.584 mmol) were dissolved in 3 mL of ethylenediamine in a test tube inside a glovebox. Ethylenediamine solution of ^tBuCl (1.2 mL, 0.13 M, 0.156 mmol) was added dropwise, and the reaction mixture was stirred for a half an hour. The solution was transferred to a Schlenk tube and attached to a Schlenk line outside of the glovebox. The solution was stirred for an additional half an hour before the ethylenediamine was removed under vacuum. The remaining solid material was taken back into the glovebox and redissolved in 2.5 mL of pyridine. Half of this solution was filtered into a test tube and carefully layered with 4 mL of toluene. Blue-purple crystals formed after seven days. There was some tin metal deposition on the walls of the test tube.

Synthesis of [K-(2,2,2-crypt)]₃[Sn₉-CH=CH₂]·2py. K₄Sn₉ (120 mg, 0.098 mmol) and 2,2,2-crypt (226 mg, 0.600 mmol) were dissolved in 3 mL of ethylenediamine in a test tube inside a glovebox. Me₃SiC≡CSiMe₃ (36 mg, 0.211 mmol) was added dropwise, and the reaction mixture was stirred for 16 h. The solution was transferred to a Schlenk tube and attached to a Schlenk line outside of the glovebox. The solution was stirred for an additional half an hour and the ethylenediamine removed under vacuum. The remaining solid material was taken back into the glovebox and redissolved in 2.5 mL of dry pyridine. About 1 mL of this solution was filtered into a test tube and carefully layered with 4 mL of toluene. Long prismatic crystals with purple color formed in a week. They were embedded in some deposited tin metal.

Synthesis of [K-(2,2,2-crypt)]₃[Sn₉-CH=CHPh]·tol·0.75py. K₄Sn₉ (137 mg, 0.112 mmol) and 2,2,2-crypt (229 mg, 0.608 mmol) were dissolved in 3 mL of ethylenediamine in a test tube inside a glovebox. HC≡CPh (32 mg, 0.313 mmol) was added dropwise, and the reaction mixture was stirred for 14 h. The solution was transferred to a Schlenk tube and attached to a Schlenk line outside of the glovebox. The solution was stirred for an additional half an hour before the ethylenediamine was boiled off under vacuum. The remaining solid material was taken back into the glovebox and redissolved using 2.5 mL of dry pyridine, resulting in a deep blue color. Half of this solution was filtered into a test tube and carefully layered with 4 mL of toluene. Long prismatic crystals with a blue color were formed after a week. They were embedded inside deposited tin metal.

Single-crystal X-ray diffraction data sets were collected at 100 K on Bruker APEX-II diffractometers equipped with CCD area detectors using graphite-monochromated Mo K α radiation. The 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 V6.21* package.³⁷ More details about the data collection and structure determinations are given in Table 1. The unit cell of [K-(2,2,2-crypt)]₃[Sn₉-^tBu]·2py has two crystallographically independent [Sn₉-^tBu]³⁻ clusters, one of which is disordered among two very close positions in a 75:25% ratio. Although only the ^tBu substituent of the major fraction is found, the minor fraction is assumed to be substituted as well (25% of a carbon atom amounts to only 1.5 electrons). This, the very low symmetry, and the large unit cell resulted in a number of parameters that exceeded the maximum that could be handled by the *SHELXL*

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Table 1. Selected Data Collection and Refinement Parameters for $[\text{K}-(2,2,2\text{-crypt})]_3[\mathbf{1}] \cdot 2\text{py}$, $[\text{K}-(2,2,2\text{-crypt})]_3[\mathbf{2}] \cdot 2\text{py}$, and $[\text{K}-(2,2,2\text{-crypt})]_3[\mathbf{3}] \cdot \text{tol} \cdot 0.75\text{py}$

compound	$[\text{K-crypt}]_3[\mathbf{1}] \cdot 2\text{py}$	$[\text{K-crypt}]_3[\mathbf{2}] \cdot 2\text{py}$	$[\text{K-crypt}]_3[\mathbf{3}] \cdot \text{tol} \cdot 0.75\text{py}$
formula weight	2530.29	2500.22	2570.58
space group, Z	$P1, 2$	$P\bar{1}, 2$	$C2/c, 8$
<i>a</i> (Å)	14.4259(3)	15.6988(3)	38.5883(9)
<i>b</i> (Å)	16.2725(4)	17.4195(4)	23.3893(5)
<i>c</i> (Å)	22.5593(5)	17.4432(4)	25.0192(5)
α (°)	86.092(1)	86.299(1)	
β (°)	78.952(1)	81.566(1)	120.269(1)
γ (°)	65.114(1)	85.349(1)	
<i>V</i> (Å ³)	4714.48(18)	4696.27(18)	19502.6(7)
radiation, λ (Å)		Mo K α , 0.71073	
ρ_{calc} (g·cm ⁻³)	1.782	1.768	1.751
μ (cm ⁻¹)	2.534	2.543	2.452
R1/wR2 ^a $I \geq 2\sigma(I)$ (%)	3.48/8.78	2.62/6.64	2.85/7.57
R1/wR2 ^a all	4.06/9.10	3.43/7.39	3.35/8.38
data (%)			

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

least-squares program. Instead, the structure refinement was carried out with the *SHELXH* program designed for such an extra large number of parameters, and all of this resulted in a very difficult structure refinement.

Electrospray mass spectrometry was carried out on a Micromass Quattro-LC triple quadrupole mass spectrometer under the following conditions: 100 °C source temperature, 125–175 °C desolvation temperature, 2.80 kV capillary voltage, and a 30–50 V cone voltage. Spectra in negative-ion mode were recorded of the reaction products of the reaction with ^tBuCl in ethylenediamine and of DMF solutions of crystals of $[\text{K}-(2,2,2\text{-crypt})]_3[\text{Sn}_9\text{-CH=CH}_2] \cdot 2\text{py}$ and $[\text{K}-(2,2,2\text{-crypt})]_3[\mathbf{3}] \cdot \text{tol} \cdot 0.75\text{py}$.

Results

The syntheses of $[\text{Sn}_9\text{-}^t\text{Bu}]^{3-}$ (**1**), $[\text{Sn}_9\text{-CH=CH}_2]^{3-}$ (**2**), and $[\text{Sn}_9\text{-CH=CH-Ph}]^{3-}$ (**3**) were carried out similarly by reacting at room temperature ethylenediamine solutions of an intermetallic precursor with nominal composition K_4Sn_9 (made from the elements at elevated temperature) with ethylenediamine solutions of ^tBuCl, $\text{Me}_3\text{SiC}\equiv\text{CSiMe}_3$, and $\text{HC}\equiv\text{CPh}$, respectively. Reactions analogous to the one with ^tBuCl were carried out with the corresponding ⁿBu- and ^sBu-halides where the halogen is at a primary and secondary carbon atom, respectively. According to the electrospray mass spectra of the resulting solutions, Sn_9 -substituted species analogous to **1** formed in both cases. After many failed attempts to crystallize **1** from ethylenediamine solutions, it was successfully crystallized from pyridine. Single crystals of **2** and **3** were later obtained also from pyridine solutions (without attempting crystallization from ethylenediamine) layered with toluene and with the aid of the cation-sequestering agent 2,2,2-crypt (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8,8,8]hexacosane).

The three organo-Zintl ions are structurally very similar (Figure 1). They are all made of very similar nine-atom tin deltahedra with different exobonded organic fragments. The tin cores can be viewed as distorted tricapped trigonal prisms where the trigonal bases of the prisms are made of atoms Sn1–Sn2–Sn3 and Sn4–Sn5–Sn6 (vertical pseudo 3-fold axes in Figure 1) while atoms Sn7, Sn8, and Sn9 are capping

the rectangular faces of the prism. The main distortion is an elongation of one of the three trigonal prismatic edges parallel to the pseudo-3-fold axis. These elongated edges are shown as broken lines in Figure 1 and are between atoms Sn1 and Sn4. They are 3.780(1), 3.6180(4), and 3.7172(4) Å in **1**, **2**, and **3**, respectively, and are much longer than the other two edges made of the pairs Sn2–Sn5 and Sn3–Sn6 with lengths of 3.133(1) and 3.228(1) Å in **1**, 3.1823(4) and 3.2128(4) Å in **2**, and 3.1120(4) and 3.1915(4) in **3**. The exobonded organic group is always bonded to an atom of the elongated edge, atom Sn1 in this case. The Sn–C bond distances of 2.265(7), 2.197(6), and 2.185(5) Å in **1**, **2**, and **3**, respectively, are near the upper limits of observed distances between tin and the sp³ carbon as in **1** (range of 2.04–2.28 Å for more than 8500 distances in the Cambridge Structural Database³⁸) and between tin and sp² carbon as in **2** and **3** (range of 2.07–2.23 Å for 230 distances in the Cambridge Structural Database³⁸). They are very similar, however, to the distances between tin and aromatic carbon in the known organo-tin clusters Sn_8Ar_4 , Sn_9Ar_3 , and $\text{Sn}_{10}\text{Ar}_3^+$, which fall in the range of 2.194–2.280 Å.^{35,36} The C=C double bonds in the vinyl group in **2** and the styrene in **3**, 1.332(9) and 1.361(7) Å, respectively, as well as the remaining C–C distances in the latter are all very typical. The cluster and the phenyl ring in **3** are in the cis position (Figure 1) as observed for all alkenylated germanium Zintl ions (discussed below).^{18,19}

The electrospray mass spectrometry (ES-MS) in negative-ion mode of crystals of $[\text{K}-(2,2,2\text{-crypt})]_3[\mathbf{2}] \cdot 2\text{py}$ and $[\text{K}-(2,2,2\text{-crypt})]_3[\mathbf{3}] \cdot \text{tol} \cdot 0.75\text{py}$ dissolved in DMF (Figure 2) confirmed the presence of the corresponding monoalkenylated tin clusters in solution. The small amount of unreacted Sn_9 clusters visible in the spectrum of $[\text{K}-(2,2,2\text{-crypt})]_3[\text{Sn}_9\text{-CH=CH}_2] \cdot 2\text{py}$ is most likely from solid impurities that often come with the crystals of the compound. The spectra show the organo-Zintl ions **2** and **3** as monoanions, $[\text{Sn}_9\text{-CH=CH}_2]^-$ and $[\text{Sn}_9\text{-CH=CHPh}]^-$, respectively. Such partial oxidation by the electric field of the mass spectrometer is quite typical for polyanions³⁹ and is observed for all germanium-based Zintl ion derivatives.^{1,17–19} Often, polyanions can pair with alkali-metal cations to produce complex monoanions such as $\{(\text{K}^+)[\text{Sn}_9\text{-CH=CH}_2]^{2-}\}^-$ in the spectrum of the styrene– Sn_9 sample (Figure 2). The ES mass spectrum of the reaction mixture of K_4Sn_9 and ^tBuCl in ethylenediamine (before crystallization and without sequestering reagent) shows the presence of both the mono- and di-alkylated species $[\text{Sn}_9\text{-}^t\text{Bu}]^{3-}$ and $[\text{Sn}_9\text{-}^t\text{Bu}]^{2-}$, respectively (Figure 3), observed both as the corresponding monoanions as well as dianions paired with potassium cations. The mass spectra of the analogous reactions with primary and secondary butyl halides showed virtually the same spectra as the one shown in Figure 3, indicating that primary and secondary carbon atoms bond to the clusters equally well.

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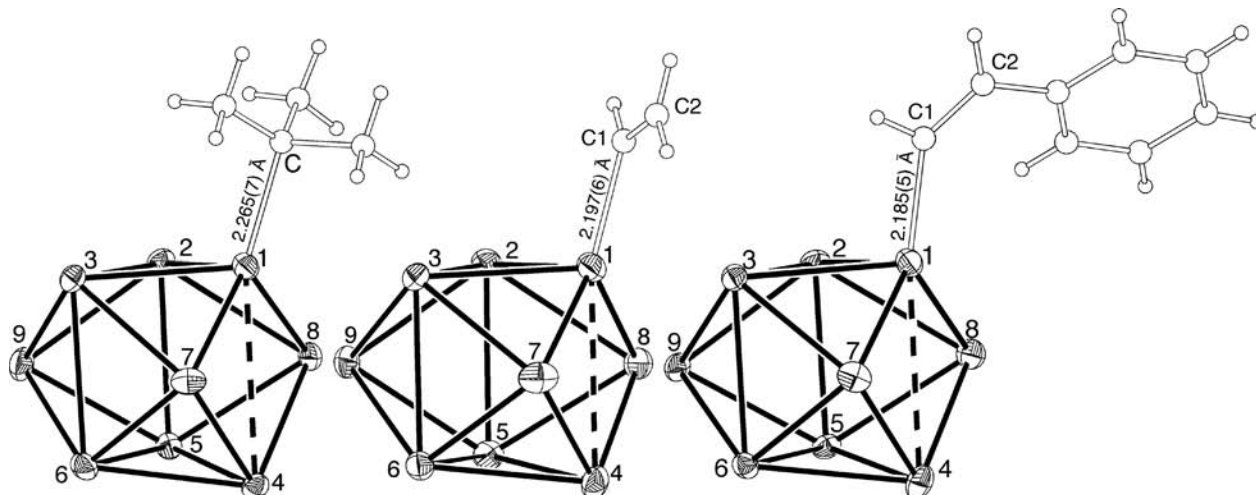


Figure 1. ORTEP drawings (50% thermal ellipsoids for the tin atoms) of the three tin-based organo-Zintl ions $[\text{Sn}_9\text{-}^t\text{Bu}]^{3-}$ (**1**, left), $[\text{Sn}_9\text{-CH=CH}_2]^{3-}$ (**2**, middle), and $[\text{Sn}_9\text{-CH=CH-Ph}]^{3-}$ (**3**, right).

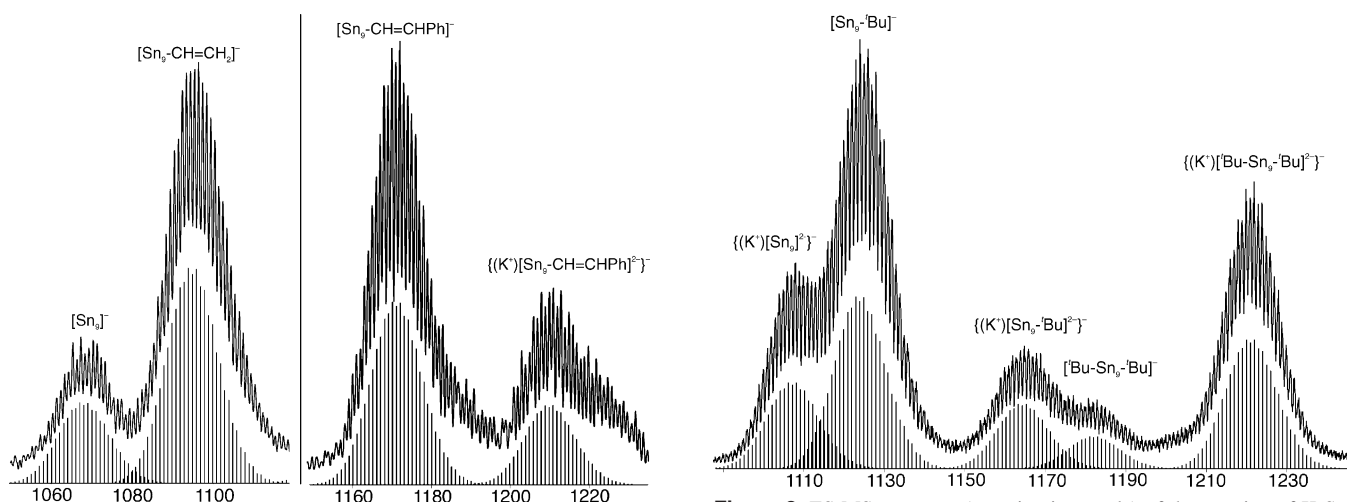


Figure 2. Sections of the ES-MS spectra (negative-ion mode) of crystals of $[\text{K}-(2,2,2\text{-crypt})_3][\mathbf{2}] \cdot 2\text{py}$ (left) and $[\text{K}-(2,2,2\text{-crypt})_3][\mathbf{3}] \cdot \text{tol} \cdot 0.75\text{py}$ (right) dissolved in DMF showing the monovinyl derivative **2** in the former (some unreacted Sn_9 clusters are also present) and the monostyrene substituted **3** in the latter, both as monoanions (the latter is also seen as a dianion paired with potassium cations). The theoretical isotope distributions are shown under the peaks.

Discussion

Overall, the three tin-based organo-Zintl ions are geometrically very similar to the known analogous germanium clusters functionalized with one or two main-group organometallic fragments or organic groups.^{1,17–19} The second external group in the disubstituted germanium species bonds to the second atom of the elongated edge (corresponding to the Sn4 position in the tin clusters). As in substituted germanium clusters, the exobonds in **1–3** are very close to being collinear with and extensions of the elongated edges Sn1–Sn4 with C–Sn1–Sn4 angles of 160.8(2), 164.2(1), and 165.3(1)° for **1**, **2**, and **3**, respectively. The reasons for this, as discussed for germanium clusters, are in the specifics of the electronic structure of the naked nine-atom clusters.¹ Their frontier molecular orbitals involve predominantly the p_z atomic orbitals of the atoms at the triangular bases of the trigonal prism (z along the pseudo 3-fold axis) with the largest contribution coming from the two atoms at the long

Figure 3. ES-MS spectrum (negative-ion mode) of the reaction of K_4Sn_9 with $^t\text{BuCl}$ in ethylenediamine. Present are both mono- and dialkylated clusters $[\text{Sn}_9\text{-}^t\text{Bu}]$ and $[\text{Bu-Sn}_9\text{-}^t\text{Bu}]$ as monoanions as well as their dianions ion-paired with potassium cations (some unreacted Sn_9 clusters are also present). The theoretical isotope distributions are shown under the peaks.

edge of the prism (Sn1 and Sn4 in Figure 1).^{1,40} Thus, redox reactions of addition will naturally involve these frontier orbitals, which, in turn, means that the external substituents will bond to the atoms of the elongated edge, and the exobonds will be aligned along z or very close to it, that is, close to being collinear with the elongated edge.

The bonding within the deltahedral Zintl ions is analogous to that in the well-known cage boranes. The available electrons in both are insufficient for formation of localized 2-center-2-electron bonds between the atoms and are instead delocalized and shared by all atoms. The E_9^{4-} clusters ($\text{E} = \text{Ge}, \text{Sn}, \text{Pb}$) are isostructural and isoelectronic with the *nido*-borane $\text{B}_9\text{H}_9^{4-}$ with 22 cluster-bonding electrons. Each B–H unit in the latter provides two electrons for cluster bonding and so does the E atom in the former, which has four electrons but uses two of them for an external lone pair that

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plays the role of the B–H exobond in the boranes. Like the nine-atom boranes, the naked nine-atom clusters can carry different charges. Thus, the structurally well characterized Si_9^{2-} and the not so well characterized Ge_9^{2-} correspond to the *closo*-borane $\text{B}_9\text{H}_9^{2-}$ and carry 20 cluster bonding electrons.^{41,42} Unlike the boranes, however, the naked clusters are also known with an intermediate charge of $3-$, that is Si_9^{3-} , Ge_9^{3-} , Sn_9^{3-} , and Pb_9^{3-} .^{1,43–46} These clusters carry an odd number of cluster-bonding electrons, 21, and are, therefore, radical anions, $\cdot\text{E}_9^{3-}$. Although Sn_9^{2-} clusters have not been isolated yet, their existence is likely and, together with the known Sn_9^{4-} and Sn_9^{3-} , would complete the tin series.

Each substituent to a cluster decreases its original charge by one without the cluster changing the number of cluster-bonding electrons. This is so because a cluster atom with an exobond uses only one electron for the exobond and, therefore, contributes one electron more for cluster-bonding than a naked atom with a lone pair. Thus, the Sn_9 clusters in all organo-Zintl ions $[\text{Sn}_9\text{--R}]^{3-}$ are still *nido*-clusters with 22 cluster-bonding electrons. Similarly *nido*-clusters are the cores of the observed disubstituted organo-Zintl ions of germanium $[\text{R--Ge}_9\text{--R}]^{2-}$ despite their $2-$ charge.

As in most cases when dealing with novel reactions, the most difficult part is establishing their mechanism or mechanisms. The main problem is that typically, and exactly as in our case, the insufficient number of examples of such reactions at the beginning prevents making meaningful deductions and conclusions concerning the mechanism(s). At the same time, not knowing the mechanism(s) hinders greatly the search for more examples. This is exactly true for the current stage of organo-Zintl chemistry and, therefore, we can offer only some observations, speculations, and a few conclusions about the reactions of nine-atom Sn_9^{4-} ions with alkyl halides and alkynes.

It is very likely that the negatively charged clusters Sn_9^{4-} reduce the organic halide $t\text{BuCl}$ to a chloride anion Cl^- and a $t\text{Bu}$ radical, that is, $\text{Sn}_9^{4-} + t\text{BuCl} \rightarrow \text{Sn}_9^{3-} + t\text{Bu}\cdot + \text{Cl}^-$. A direct $\text{S}_{\text{N}}2$ reaction between Sn_9^{4-} and $t\text{BuCl}$ is ruled out because the tertiary carbon in the $t\text{Bu}$ is protected by the three methyl groups and is inaccessible. The radical can then add to the cluster and form the alkylated species, that is, $\text{Sn}_9^{3-} + t\text{Bu}\cdot \rightarrow [\text{Sn}_9\text{--}t\text{Bu}]^{3-}$. The latter reaction is possible because of the available half-filled HOMO in Sn_9^{3-} positioned predominantly along z .¹

The reactions with alkynes are quite more mysterious at this stage. The reaction of alkynes with alkali metals in amine solvents is well-known and has very different outcomes depending on the position of the triple bond.⁴⁷ Thus, alkynes with terminal triple bonds are reduced to stable anions $\text{RC}\equiv\text{C}^-$ and hydrogen gas, and no further reaction occurs. Alkynes with internal triple bonds, on the other hand, undergo a multistep reaction. They are initially reduced to

radical anions $\text{R}(\text{C}^-)=\text{(C}\cdot\text{)R}$ where the extra electron occupies a low-lying π^* orbital and the C–C bond is no longer triple. This anion is basic enough to abstract a proton from the amine solvent (either liquid ammonia or ethylenediamine) and form $\text{RHC}=\text{(C}\cdot\text{)R}$. Another solvated electron reduces this radical to an anion again, $\text{RHC}=\text{(C}^-\text{)R}$, and a second proton abstraction leads to the final product of $\text{RHC}=\text{CHR}$. The result of such hydrogenation reactions of internal triple bonds by alkali metals in amine solvents is exclusively the *trans* product. The reaction of $\text{PhC}\equiv\text{CH}$ with Sn_9 clusters, on the other hand, produces the *cis*-alkene $[\text{Sn}_9\text{--CH}=\text{CHPh}]^{3-}$. Similarly, *cis* is the alkene of the reaction of Ge_9 clusters with $\text{Fc--C}\equiv\text{CH}$ (Fc is ferrocenyl), $[\text{FcCH}=\text{CH--Ge}_9\text{--CH}=\text{CHFc}]^{2-}$. This difference suggests that different factors play a role in defining the geometry when clusters are involved. It is possible that the negatively charged clusters use the low-lying π^* orbitals of the alkynes to bond to them either by preceding electron transfer or by direct interaction. The step that defines the *cis* geometry most likely involves charge repulsion and therefore *trans* geometry between a lone pair of electrons at the carbon atom bonded to the phenyl group and the negatively charged cluster at the other carbon atom. This will put the Ph group in a *cis* position with respect to the cluster. The reaction with $(\text{Me}_3\text{SiC})_2$ is obviously much more complex because it involves breaking Si–C bonds at some stage and addition of three hydrogen atoms to the triple bond to form $[\text{Sn}_9\text{--CH}=\text{CH}_2]^{3-}$. Clearly, establishing the mechanisms for the reactions with alkynes will be a nontrivial task, but it is our intention to attempt finding out as much as possible about these processes.

Conclusion

We have shown here that the redox reactions of nine-atom Zintl ions are not unique for and limited to germanium clusters but are also feasible for the analogous tin clusters Sn_9 . Moreover, the two types of clusters behave exactly the same and react with alkyl halides to produce alkyl-Zintl ions and with alkynes to produce alkenyl-Zintl ions. The existence of these tin-based organo-Zintl ions suggests that the same or similar species maybe possible for silicon and lead, that is, species like $[\text{Si}_9\text{--R}]^{3-}$, $[\text{R--Si}_9\text{--R}]^{2-}$, $[\text{R--Pb}_9]^{3-}$, and $[\text{R--Pb}_9\text{--R}]^{2-}$ may exist as well. In addition, further chemistry maybe possible with the organic substituents of these organo-Zintl ions, especially when they have secondary organic functional groups such as amines, ketones, multiple bonds, ethers, and so forth. The corresponding organo-Zintl chemistry may produce many new and exciting Zintl-ion-based compounds.

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Supporting Information Available: X-ray crystallographic file in CIF format of the three compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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