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**R$_3$E$^+$ Carborane Salts of the Heavier Group 14 Elements:**

E = Ge, Sn, and Pb

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The synthetic and structural chemistry of catalytically useful trialkylsilyl salts with weakly coordinating carborane anions, R$_3$Si(CHB$_{11}$X$_6$), has been extended to the heavier group 14 elements. Et$_3$Ge(CHB$_{11}$H$_5$Br$_6$) was prepared from Et$_3$GeH and trityl CHB$_{11}$H$_5$Br$_6$. Its X-ray crystal structure shows ion-like character very similar to its Si congener. The heavier element analogues, Et$_3$E(CHB$_{11}$H$_5$Br$_6$) (E = Sn, Pb), were prepared by chloride ion abstraction from Et$_3$SnCl and Et$_3$PbCl, respectively, using Et$_3$Si(CHB$_{11}$H$_5$Br$_6$). Their crystal structures differ from those of the four-coordinate lighter elements by adopting five-coordinate trigonal-bipyramidal stereochemistries, reflecting the periodic table transition of these elements from semi-metals to metals. The carborane anions are weak, bridging, axial ligands connecting trigonal Et$_3$E$^+$ cation-like moieties in polymeric chain structures. When the less coordinating CHB$_{11}$Cl$_{11}$- anion is used, excess germane competes with the carborane anion for coordination to Ge and a salt of the new hydride-bridged cation [Et$_3$Ge–H–GeEt$_3$]$^+$ can be isolated. It has a distinctive νGeHGe IR band at ca. 1740 cm$^{-1}$ analogous to the 1875 cm$^{-1}$ band of the [Et$_3$Si–H–Si–Et$_3$]$^+$ cation. Comparable chemistry is not observed for the Sn and Pb congeners.

**Introduction**

Of all group-related elements in the periodic table, those of group 14 have perhaps the greatest opportunity to show diverse behavior. C is a nonmetal, Si and Ge are semi-metals, and Sn and Pb are metals. Trigonal-planar trialkyl R$_3$E$^+$ cations are stabilized in R$_4$C$^-$ carboxylates by hyperconjugation and can be put in a bottle and characterized by X-ray crystallography when weakly coordinating carboranes, CHB$_{11}$R$_3$X$_6$ (Figure 1), are used as counterions.1 On the other hand, three-coordinate trialkylsilyl ions, R$_3$Si$^+$, are unknown in condensed phases because hyperconjugative stabilization is weaker and silicon is both larger and more electropositive than carbon.2 It is difficult to prevent coordination of a solvent molecule to Si, and there is no anion sufficiently weakly coordinating to yield a truly free R$_3$Si$^+$ ion, unless of course the R group is switched to a bulky aryl substituent.3 Nevertheless, “ion-like” trialkylsilyl species R$_3$SiH$^+$Y$^-$ are well known with weakly coordinating anions,2,4,5 and the closest approach to date uses a fluorinated tetraphenylborate8 or permethylated carborane CHB$_{11}$Me$_2$ anions.9,10 The solid-state structures with permethylated carborane anions have been deduced from X-ray, EXAFS, and DFT calculations to favor five-coordination via significant coordination of methyl groups from the alkane-like anion. The tendency of these heavier R$_3$E$^+$ cations to behave as metals and expand their coordination number overrides any vestige of nonmetallic sp$^2$ behavior. It is hard to imagine the existence of a three-coordinate trialkyl cation with Ge, Sn, or Pb in a condensed phase, although free, or nearly free, cations have been well established with trialkylsilyl11 and bulky aryl12 substituents. However, these

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The carborane anions used in this work: CHB\(_{11}\)H\(_5\)Br\(_6\) (red = H, green = Br) and CHB\(_{11}\)Cl\(_{11}\) (red, green = Cl).

Figure 1. Schematic representation of the icosahedral CB\(_{11}\)-based carborane anions used in this work: CHB\(_{11}\)H\(_5\)Br\(_6\) (red = H, green = Br) and CHB\(_{11}\)Cl\(_{11}\) (red, green = Cl).

substituents are less useful than simple alkyls for reactivity and catalytic studies.

We have become interested in developing the systematic chemistry of trialkygermyl, -stannyl, and -plumbyl cation-like species with halogenated carborane anions in order to make comparisons to their silicon congeners. R\(_3\)Si(carborane) species are effective new catalysts for the room-temperature polymerization of cyclo-hexachlorotriphosphazene in solution\(^{13}\) and the hydrodefluorination of fluorocarbons.\(^{14}\) In the latter case, carborane anions are the only anions sufficiently inert to survive the extremely electrophilic conditions.

Herein, we report the synthesis, isolation, and X-ray crystal structures of the heavier group 14 element Et\(_3\)E(carborane) compounds (E = Ge, Sn, and Pb) using halogenated carborane anions (Figure 1). Ethyl substituents on the central element E and the hexabrominated carborane anion CHB\(_{11}\)-H\(_5\)Br\(_6\) were initially chosen for these studies so that direct structural comparisons could be made to the previously X-ray characterized silyl analogue Et\(_3\)Si(CHB\(_{11}\)H\(_5\)Br\(_6\)).\(^{15}\) When coupled with the less basic\(^{16}\) undecachloro carborane anion, CHB\(_{11}\)Cl\(_{11}\), the Ge species is vulnerable to formation of the dimeric hydride-bridged [R\(_3\)Ge-H-GeR\(_3\)]\(^{-}\) cation in the presence of excess R\(_3\)GeH. This unusual μ-hydride is analogous to the [R\(_3\)Si-H-SiR\(_3\)]\(^{-}\)CHB\(_{11}\)Cl\(_{11}\) salts that were discovered when silyl cation formation is performed in the presence of excess silane and the very weakest coordinating anions.\(^{17}\) Attempts to prepare the corresponding hydride-bridged cations with Sn failed.

Results and Discussion

Synthesis of R\(_3\)E(CHB\(_{11}\)H\(_5\)Br\(_6\)) for E = Ge, Sn, and Pb. Of the routes available to synthesize ion-like R\(_3\)E\(^+\) species for the heavier group 14 elements, electrophilic removal of hydride from R\(_3\)EH using an analogous lighter element cation (eq 1) is one of the most reliable. This method exploits the generally decreasing E-H bond strength going down the group. Thus, as it does with Et\(_3\)SiH, trityl ion readily abstracts hydride from Et\(_3\)GeH at room temperature (eq 1) to yield triphenylmethane and the Et\(_3\)Ge\(^+\) moiety. A non-donor, weakly basic solvent such as o-dichlorobenzene must be used to prevent solvent coordination to the Ge center.

\[
\text{Et}_3\text{GeH} + \text{[Ph}_3\text{C}^+][\text{CHB}_{11}\text{H}_5\text{Br}_6^-] \rightarrow \text{Ph}_3\text{CH} + \text{Et}_3\text{Ge}(\text{CHB}_{11}\text{H}_5\text{Br}_6) \quad (1)
\]

The analogous reactions with Et\(_3\)SnH and Et\(_3\)PbH are experimentally problematic. Color changes with Et\(_3\)SnH suggest complex redox chemistry is occurring rather than hydride abstraction, and the low thermal stability of lead hydrides\(^{18}\) makes room-temperature reactions impossible. Instead, the preferred method is to use a silyl carborane as a chloride rather than hydride acceptor (eqs 2 and 3):

\[
\begin{align*}
\text{Et}_3\text{SnCl} + \text{Et}_3\text{Si}(\text{CHB}_{11}\text{H}_5\text{Br}_6) & \rightarrow \text{Et}_3\text{SiCl} + \text{Et}_3\text{Sn}(\text{CHB}_{11}\text{H}_5\text{Br}_6) \quad (2) \\
\text{Et}_3\text{PbCl} + \text{Et}_3\text{Si}(\text{CHB}_{11}\text{H}_5\text{Br}_6) & \rightarrow \text{Et}_3\text{PbCl} + \text{Et}_3\text{Si}(\text{CHB}_{11}\text{H}_5\text{Br}_6) \quad (3)
\end{align*}
\]

All three Et\(_3\)E(CHB\(_{11}\)H\(_5\)Br\(_6\)) compounds (E = Ge, Sn, Pb) were isolated as colorless solids in reasonable unoptimized yield (45–80%). As shown in the Supporting Information Figure S7, IR spectroscopy identifies the νE=C moiety at 351, 510, and 451 cm\(^{-1}\) for E = Ge, Sn, and Pb, respectively. The corresponding peak for νSiC is 570 cm\(^{-1}\). Only the germyl carborane had sufficient solubility in non-donor solvents for characterization by NMR spectroscopy, and the H results in o-dichlorobenzene are as expected. Ge does not have a suitable NMR nucleus to explore the relationship between downfield chemical shift and the degree of germylum ion character that was so useful in Si chemistry. Thus, crystals for X-ray analysis were sought in each case and were typically grown directly from reaction mixtures by layering o-dichlorobenzene solutions with hexanes. Also included is a fourth structure: that of the Et\(_3\)Sn\(^+\) cation coupled with the somewhat less coordinating undecachloro carborane anion. This compound was prepared in the same manner as eq 3 using Et\(_3\)Si(CHB\(_{11}\)Cl\(_{11}\)) as the halide-abstracting agent.

X-ray Structures of Et\(_3\)E(CHB\(_{11}\)H\(_5\)Br\(_6\)) for E = Ge, Sn, and Pb. True to the trend in the periodic table that makes the covalent radius of Ge relatively close to Si (filling of the 3d orbitals) and the radius of Sn relatively close to that of Pb (filling of the 4f orbitals, i.e., the lanthanide contraction), the structure of Et\(_3\)Ge(CHB\(_{11}\)H\(_5\)Br\(_6\)) is very similar to its Si congener, while that of Sn is very similar to Pb. As shown in Figure 2, Et\(_3\)Ge(CHB\(_{11}\)H\(_5\)Br\(_6\)) has a flattened tetrahedral, four-coordinate geometry and is molecularly discrete. On the other hand, the Sn and Pb analogues have five-coordinate trigonal-bipyramidal structures with bridging carborane anions, giving rise to polymeric structures. This explains their relative solubilities. Only the molecularly discrete Si and Ge derivatives have significant solubility in chlorocarbon solvents. The five-coordinate structures of the heavier elements have stereochemistries that are related to bis-alkene

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complexes of trialkyl Sn and Ge cations\textsuperscript{19} and base-stabilized triaryl tin cations.\textsuperscript{20,21}

Like the Si analogue, the Ge structure is not fully ionic. Nevertheless, the Et\textsubscript{3}Ge\textsuperscript{2-} moiety is clearly only weakly coordinated to the carborane anion and shows a close approach toward trigonal planarity. The coordinated B–Br bond (1.994 Å) of the anion is detectably elongated relative to the range of uncoordinated B–Br bonds (1.937–1.955 Å). The sum of the C–Ge–C angles is 351.9°, ca. 8° shy of planarity. The Ge–Br distance of 2.535(2) Å is ca. 0.21 Å longer than the Ge–Br bond length in Ph\textsubscript{3}GeBr (2.317 Å)\textsuperscript{22} but very much shorter than the sum of the van der Waals radii (3.85 Å). The average Ge–C bond length is 1.943 Å. In the corresponding Si compound,\textsuperscript{23} the sum of the C–Si–C angles is 349.0° and the Si–Br bond lengthening is ca. 0.23 Å. The close parallel between Si and Ge is striking.

There is also a close parallel between Sn and Pb in their polymeric Et\textsubscript{3}E(CHB\textsubscript{11}H\textsubscript{5}Br\textsubscript{6})\textsubscript{2-} structures (Figures 3,4). Indeed, the predominance of crystal-packing forces over site basicity, as seen in the X-ray structure of the carborane acid H(CHB\textsubscript{11}Cl\textsubscript{11}), where the 12 position is calculated to be more basic than the 7–11 positions. The reason probably lies in the undecachloro carborane anion is less basic\textsuperscript{16} and less coordinating\textsuperscript{17} than the hexabromo analogue at Sn, but there is one difference. The anion bridges through the 7,11 positions, the difference is small and the solid-state structure of the acid shows protonation via Cl atoms in the 7–11 positions.

The undecachloro carborane anion is less basic\textsuperscript{16} and less coordinating\textsuperscript{17} than the hexabromo analogue, so a somewhat more ionic complex might be expected. The average Sn–C bond length of 2.136(2) Å in the undecachloro compound is nominally shorter than that in the hexabromo complex (2.140(2) Å), but this is barely statistically significant. The average axial Sn–Cl distance of 2.991 Å is 0.45 Å longer than

\textsuperscript{22} Preut, H.; Huber, F. \textit{Acta Crystallogr.} \textbf{1979}, \textit{B35}, 83–86.

\textsuperscript{24} Preut, H.; Huber, F. \textit{Acta Crystallogr.} \textbf{1979}, \textit{B35}, 744.
that in Me$_3$SnCl$^-$ and 0.50 Å longer than in Ph$_3$SnCl$^-$ but on a percentage basis, these extensions are not particularly different from those in the hexabromo structure. Overall, these data indicate that in this particular structural motif it is difficult to use X-ray structural data to measure relative binding tendencies of carborane anions to R$_2$E$^+$ cations. This contrasts with the data on discrete molecular structures like Et$_3$Si(carborane), where the degree of pyramidalization at Si is an excellent guide to silylium ion character.

**Formation of the [Et$_3$GeH−H−GeEt$_3$]$^{+}$ Cation.** When the synthesis of Et$_3$Ge(CHB$_{11}$Cl$_{11}$)$_2$ is carried out according to eq 1 in the presence of excess Et$_3$GeH, the germane competes with the carborane anion for coordination to Ge and forms the [Et$_3$GeH−H−GeEt$_3$]$^{+}$ cation (eq 4):

\[
\text{Et}_3\text{Ge}([\text{CHB}_{11}\text{Cl}_{11}]) + \text{Et}_3\text{GeH} \rightarrow [\text{Et}_3\text{GeH}−\text{H}−\text{GeEt}_3]^+ [\text{CHB}_{11}\text{Cl}_{11}^-]
\]

The reaction is reversible. Indeed, the easiest way to prepare Et$_3$Ge(CHB$_{11}$Cl$_{11}$)$_2$ is to remove Et$_3$GeH from the “dimer” product by heating under vacuum. The formation reaction only proceeds with the undecachloro carborane anion; the hexabromo anion is less coordinating than the hexabromo analogue.

**Experimental Section**

Reactions were carried out in an inert atmosphere glovebox (O$_2$, H$_2$O < 1 ppm). Solvents were dried following literature procedures, distilled under Ar, and stored over 4 A molecular sieves in the glovebox. [Ph$_3$C][CHB$_{11}$H$_5$Br$_6$], [Ph$_3$C][CHB$_{11}$Cl$_{11}$], Et$_3$Si(CHB$_{11}$H$_5$Br$_6$)$_2$, and Et$_3$Si(CHB$_{11}$Cl$_{11}$)$_2$ were prepared by literature methods. Triethylin chloride (98%) was purchased from Strem, triethylgermane (98%) from Aldrich, and triethyllead chloride from Pfaltz and Bauer and used as received.

**Caution:** Trialkyl derivatives of group 14 elements are highly toxic and should be handled with great care.

Et$_3$Ge(CHB$_{11}$H$_5$Br$_6$)$_2$. In a 12 mL vial equipped with a magnetic stir bar, [Ph$_3$C][CHB$_{11}$H$_5$Br$_6$] (122 mg, 0.142 mmol) was dissolved in dry o-dichlorobenzene (1 mL). To this orange solution was added Et$_3$GeH (0.1 mL, 0.6 mmol) with stirring. The solution turned clear within seconds. Within 10 min, a white precipitate had formed and hexane was added to facilitate additional crystallization. The product was filtered off and collected on a medium frit (89 mg, 81%). Single crystals were grown by careful layering of the reaction mixture with n-hexane.

$^1$H NMR (ODCB-$d_2$, 300 MHz, 25 °C): 2.71 (s, CH carborane), 1.75–1.67 (q, CH$_2$), 1.16–1.10 ppm (t, CH$_3$). Anal. Calcd for C$_{25}$H$_{47}$Br$_6$Et$_3$Ge: C, 13.41; H, 2.84. Found: C, 13.40; H, 2.84.

Et$_3$Ge(CHB$_{11}$Cl$_{11}$)$_2$. The successful synthesis and isolation of Et$_3$E(carborane) species for E = Ge, Sn, and Pb adds to the available repertory of cation-like R$_2$E$^+$ Lewis acids of group 14 elements that are coupled with extremely inert carborane counterions. As illustrated by the example of the reaction of Et$_3$Ge(CHB$_{11}$Cl$_{11}$)$_2$ with Et$_3$GeH to form the [Et$_3$GeH−H−GeEt$_3$]$^{+}$ cation, this opens the way to an exploration of their reactivity with weak bases to form higher coordinate cations of the type [R$_2$EJ+]$^+$.

Of further interest is the possibility that these cation-like Lewis acids will allow systematic studies of R$_2$E$^+$ cations in important catalytic roles such as the polymerization of phosphazenes and the activation of C–F bonds.

**Conclusion**

The successful synthesis and isolation of Et$_3$E(carborane) species for E = Ge, Sn, and Pb adds to the available repertory of cation-like R$_2$E$^+$ Lewis acids of group 14 elements that are coupled with extremely inert carborane counterions. As illustrated by the example of the reaction of Et$_3$Ge(CHB$_{11}$Cl$_{11}$)$_2$ with Et$_3$GeH to form the [Et$_3$GeH−H−GeEt$_3$]$^{+}$ cation, this opens the way to an exploration of their reactivity with weak bases to form higher coordinate cations of the type [R$_2$EJ+]$^+$.

Of further interest is the possibility that these cation-like Lewis acids will allow systematic studies of R$_2$E$^+$ cations in important catalytic roles such as the polymerization of phosphazenes and the activation of C–F bonds.

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Et₃Pb(CHB₁₁H₅Br₆). This was prepared in the same manner as Et₃Sn(CHB₁₁H₅Br₆) using Et₃PbCl (40.6 mg, 0.123 mmol) and Et₃Si(CHB₁₁H₅Br₆) (91.0 mg, 0.124 mmol) in 0-dichlorobenzene (3 mL) and stirring for 24 h. X-ray quality crystals were grown by careful layering of n-hexane (78.2 mg, 70%). FT-IR [ATR]: Supporting Information Figure S5. Anal. Calcd for [Et₃Pb][CHB₁₁H₅Br₆]: C, 9.20; H, 2.32. Found: C, 9.52; H, 2.56.

Et₃Sn(CHB₁₁Cl₁₁)-C₆H₄Cl₂. Et₃Si(CHB₁₁Cl₁₁) was prepared from [Ph₃C][CHB₁₁Cl₁₁] (53.4 mg, 0.07 mmol) and Et₃SiH in 0-dichlorobenzene (3 mL), adding n-hexane (0.5 mL) after 10 min to precipitate the product. Longer stirring times sometimes led to the formation of waxy solids. Et₃Si(CHB₁₁Cl₁₁) was filtered off (11.7 mg, 0.018 mmol) and resuspended in 0-dichlorobenzene. Three drops of Et₃SnCl was added and the reaction mixture stirred for 24 h. Crystals of an o-dichlorobenzene solvate suitable for X-ray analysis were grown by careful layering of the reaction mixture with n-hexane (5.3 mg, 40%). Anal. Calcd for Et₃Sn(CB₁₁Cl₁₁): C, 11.51; H, 2.21. Found: C, 10.98; H, 2.10. FT-IR [ATR]: Supporting Information Figure S6.

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Supporting Information Available: IR and NMR spectra and X-ray data. This material is available free of charge via the Internet at http://pubs.acs.org.