UC Riverside

UC Riverside Previously Published Works

Title

R3E⁺ carborane salts of the heavier group 14 elements: E = Ge, Sn, and Pb

Permalink

<https://escholarship.org/uc/item/8z2984bm>

Journal

Organometallics, 29(18)

ISSN

0276-7333

Authors

Wright, JH
Mueck, GW
Tham, FS
[et al.](#)

Publication Date

2010-09-27

DOI

10.1021/om100662r

Peer reviewed

R_3E^+ Carborane Salts of the Heavier Group 14 Elements: E = Ge, Sn, and Pb

James H. Wright II, Gabriel W. Mueck, Fook S. Tham, and Christopher A. Reed*

Department of Chemistry, University of California, Riverside, California 92521-0403

Received July 14, 2010

The synthetic and structural chemistry of catalytically useful trialkylsilylium salts with weakly coordinating carborane anions, $R_3Si(CHB_{11}X_{11})$, has been extended to the heavier group 14 elements. $Et_3Ge(CHB_{11}H_5Br_5)$ was prepared from Et_3GeH and trityl $CHB_{11}H_5Br_6^-$. Its X-ray crystal structure shows ion-like character very similar to its Si congener. The heavier element analogues, $Et_3E(CHB_{11}H_5Br_6)$ (E = Sn, Pb), were prepared by chloride ion abstraction from Et_3SnCl and Et_3PbCl , respectively, using $Et_3Si(CHB_{11}H_5Br_6)$. 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_3E^+ 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 $[Et_3Ge-H-GeEt_3]^+$ can be isolated. It has a distinctive $\nu GeHGe$ IR band at ca. 1740 cm^{-1} analogous to the 1875 cm^{-1} band of the $[Et_3Si-H-Si-Et_3]^+$ 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_3E^+ cations are stabilized in R_3C^+ carbocations by hyperconjugation and can be put in a bottle and characterized by X-ray crystallography when weakly coordinating carboranes, $CHB_{11}R_5X_6^-$ (Figure 1), are used as counterions.¹ On the other hand, three-coordinate trialkylsilylium ions, R_3Si^+ , 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_3Si^+ ion, unless of course the R group is switched to a bulky aryl substituent.³ Nevertheless, “ion-like” trialkylsilyl species $R_3Si^{\delta+}Y^{\delta-}$ are well known with weakly coordinating anions,^{2,4,5} and the closest approach to date uses a fluorinated carborane anion in $Me_3Si(EtCB_{11}F_{11})$.⁶ The sum of the C–Si–C angles in the Me_3Si moiety is 354.4° , only ca. 6°

short of trigonal planarity. Some might call this ionic. While not quite free silylium ions, these ion-like species behave like silylium ions. They are electrophiles *par excellence*, and research emphasis on silylium ions has now shifted from debate over their existence to exploitation of their reactivity.⁷

For reasons of increasing size and metallic character, it is expected that R_3E^+ ions will become progressively less “free” when descending group 14. The closest approach to trialkyl R_3E^+ cations (E = Ge, Sn, Pb) has been made with tri-*n*-butyl- and trimethyl cationic moieties coupled with perfluorinated tetraphenylborate⁸ or permethylated carborane $CB_{11}Me_{12}^-$ 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_3E^+ 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

*To whom correspondence should be addressed. E-mail: chris.reed@ucr.edu.

- (1) Kato, T.; Reed, C. A. *Angew. Chem., Int. Ed.* **2004**, *43*, 2908–2911.
- (2) Reed, C. A. *Acc. Chem. Res.* **1998**, *31*, 325–332.
- (3) Kim, K.-C.; Reed, C. A.; Elliott, D. W.; Mueller, L. J.; Tham, F.; Lin, L.; Lambert, J. B. *Science* **2002**, *297*, 825–827.
- (4) Lambert, J. B.; Kania, L.; Zhang, S. *Chem. Rev.* **1995**, *95*, 1191–1201.
- (5) Mueller, T. *Adv. Organomet. Chem.* **2005**, *53*, 155–215.
- (6) Kuppers, T.; Bernhardt, E.; Eujen, R.; Willner, H.; Lehmann, C. W. *Angew. Chem., Int. Ed.* **2007**, *46*, 6346–6349.

- (7) Reed, C. A. *Acc. Chem. Res.* **2010**, *43*, 121–128.
- (8) Lambert, J. B.; Kuhlmann, B. *J. Chem. Soc., Chem. Commun.* **1992**, 931–932.
- (9) Zharov, I.; King, B. T.; Havlas, Z.; Pardi, A.; Michl, J. *J. Am. Chem. Soc.* **2000**, *122*, 10253–10254.
- (10) Zharov, I.; Weng, T.-C.; Orendt, A. M.; Barich, D. H.; Penner-Hahn, J.; Grant, D. M.; Havlas, Z.; Michl, J. *J. Am. Chem. Soc.* **2004**, *126*, 12033–12046.
- (11) Lee, V. Y.; Sekiguchi, A. *Acc. Chem. Res.* **2007**, *4*, 410–419.
- (12) Lambert, J. B.; Zhao, Y.; Wu, H.; Tse, W. C.; Kuhlmann, B. *J. Am. Chem. Soc.* **1999**, *121*, 5001–5008.

Figure 1. Schematic representation of the icosahedral CB_{11} -based carborane anions used in this work: $\text{CHB}_{11}\text{H}_5\text{Br}_6^-$ (red = H, green = Br) and $\text{CHB}_{11}\text{Cl}_{11}^-$ (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 trialkylgermyl, -stannyl, and -plumbyl cation-like species with halogenated carborane anions in order to make comparisons to their silicon congeners. $\text{R}_3\text{Si}(\text{carborane})$ species are effective new catalysts for the room-temperature polymerization of *cyclo*-hexachlorotriphosphazene in solution¹³ 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 $\text{Et}_3\text{E}(\text{carborane})$ compounds ($\text{E} = \text{Ge}, \text{Sn}, \text{and Pb}$) using halogenated carborane anions (Figure 1). Ethyl substituents on the central element E and the hexabrominated carborane anion $\text{CHB}_{11}\text{H}_5\text{Br}_6^-$ were initially chosen for these studies so that direct structural comparisons could be made to the previously X-ray characterized silyl analogue $\text{Et}_3\text{Si}(\text{CHB}_{11}\text{H}_5\text{Br}_6)$.¹⁵ When coupled with the less basic¹⁶ undecachlorinated carborane anion, $\text{CHB}_{11}\text{Cl}_{11}^-$, the Ge species is vulnerable to formation of the dimeric hydride-bridged $[\text{R}_3\text{Ge}-\text{H}-\text{GeR}_3]^+$ cation in the presence of excess R_3GeH . This unusual μ -hydride is analogous to the $[\text{R}_3\text{Si}-\text{H}-\text{SiR}_3]^+[\text{CHB}_{11}\text{Cl}_{11}]^-$ 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 $\text{R}_3\text{E}(\text{CHB}_{11}\text{H}_5\text{Br}_6)$ for $\text{E} = \text{Ge}, \text{Sn}, \text{and Pb}$. Of the routes available to synthesize ion-like R_3E^+ species for the heavier group 14 elements, electrophilic removal of hydride from R_3EH 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_3SiH , trityl ion readily abstracts hydride from Et_3GeH at room temperature (eq 1) to yield triphenylmethane and the Et_3Ge^+ moiety. A non-donor, weakly basic solvent such as *o*-dichlorobenzene must be used to prevent solvent coordination to the Ge center.

The analogous reactions with Et_3SnH and Et_3PbH are experimentally problematic. Color changes with Et_3SnH suggest complex redox chemistry is occurring rather than hydride abstraction, and the low thermal stability of lead hydrides¹⁸ 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):

All three $\text{Et}_3\text{E}(\text{CHB}_{11}\text{H}_5\text{Br}_6)$ compounds ($\text{E} = \text{Ge}, \text{Sn}, \text{Pb}$) were isolated as colorless solids in reasonable unoptimized yield (45–80%). As shown in the Supporting Information Figure S7, IR spectroscopy identifies the $\nu\text{E}-\text{C}$ peak of the Et_3E^+ moiety at 531, 510, and 451 cm^{-1} for $\text{E} = \text{Ge}, \text{Sn}, \text{and Pb}$, 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 ^1H 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_3Sn^+ cation coupled with the somewhat less coordinating undecachloro carborane anion. This compound was prepared in the same manner as eq 3 using $\text{Et}_3\text{Si}(\text{CHB}_{11}\text{Cl}_{11})$ as the halide-abstracting agent.

X-ray Structures of $\text{Et}_3\text{E}(\text{CHB}_{11}\text{H}_5\text{Br}_6)$ for $\text{E} = \text{Ge}, \text{Sn}, \text{and Pb}$. 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 $\text{Et}_3\text{Ge}(\text{CHB}_{11}\text{H}_5\text{Br}_6)$ is very similar to its Si congener, while that of Sn is very similar to Pb. As shown in Figure 2, $\text{Et}_3\text{Ge}(\text{CHB}_{11}\text{H}_5\text{Br}_6)$ 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

(13) Zhang, Y.; Huynh, K.; Mannes, I.; Reed, C. A. *Chem. Commun.* **2008**, 494–496.

(14) Douvris, C.; Ozerov, O. V. *Science* **2008**, 321, 1188–1190.

(15) Xie, Z.; Manning, J.; Reed, W. R.; Mathur, R.; Boyd, P. D. W.; Benesi, A.; Reed, C. A. *J. Am. Chem. Soc.* **1996**, 118, 2922–2928.

(16) Stoyanov, E. S.; Kim, K.-C.; Reed, C. A. *J. Am. Chem. Soc.* **2006**, 128, 8500–8508.

(17) Hoffmann, S. P.; Kato, T.; Tham, F. S.; Reed, C. A. *Chem. Commun.* **2006**, 767–769.

(18) Becker, W. E.; Cook, S. E. *J. Am. Chem. Soc.* **1960**, 82, 6264–6265.

Figure 2. X-ray structure of $\text{Et}_3\text{Ge}(\text{CHB}_{11}\text{H}_5\text{Br}_6)$ (H atoms omitted for clarity).

Figure 3. X-ray structure of $\text{Et}_3\text{Sn}(\text{CHB}_{11}\text{H}_5\text{Br}_6)$ (H atoms omitted for clarity).

complexes of trialkyl Sn and Ge cations¹⁹ and base-stabilized triaryl tin cations.^{20,21}

Like the Si analogue, the Ge structure is not fully ionic. Nevertheless, the Et_3Ge^+ 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 covalent Ge–Br bond in Ph_3GeBr (2.317 Å)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,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 $\text{Et}_3\text{E}(\text{CHB}_{11}\text{H}_5\text{Br}_6)$ structures (Figures 3,4). Indeed, they are isomorphous and crystallize in the same space group. The sum of the C–E–C angles is very close to 360° in both cases, but this should not be taken as an indication of Et_3E^+ ionicity because it reflects nearly equivalent axial

Figure 4. X-ray structure of $\text{Et}_3\text{Pb}(\text{CHB}_{11}\text{H}_5\text{Br}_6)$ (H atoms omitted for clarity).

interactions from Br atoms of the $\text{CHB}_{11}\text{H}_5\text{Br}_6^-$ anion, giving rise to trigonal-bipyramidal coordination. The axial interactions to the carborane anions are relatively weak and suggest distinctly ion-like structures: $[\text{Et}_3\text{E}^+][\text{CHB}_{11}\text{H}_5\text{Br}_6^-]$. The two axial Sn–Br distances of 2.965 and 3.074 Å are ca. 0.5 Å longer than that in Ph_3SnBr (2.491 Å),²⁴ and the Pb–Br distances of 3.117 and 3.158 Å in $\text{Et}_3\text{Pb}(\text{CHB}_{11}\text{H}_5\text{Br}_6)$ are ca. 0.3 Å longer than in a typical covalent Pb–Br bond such as that in Ph_3PbBr (2.852 Å).²⁵ As expected, these long bonds are nevertheless considerably shorter than the sum of the van der Waals radii (4.02 and 3.87 Å for Sn and Pb, respectively). The Pb-coordinated B–Br bonds of the carborane anion (1.973 and 1.963 Å) are marginally elongated compared to the noncoordinated B–Br bonds (1.943–1.954 Å). This distortion of the anion is not significantly different from that in the Sn structure, where the coordinated B–Br distances are 1.975 and 1.966 Å and the noncoordinated ones are 1.940–1.947 Å.

One additional X-ray structure has been determined in connection to this work, that of $\text{Et}_3\text{Sn}(\text{CHB}_{11}\text{Cl}_{11})$. As expected, when the central atom is a metal, it also forms a carborane anion-bridged polymeric structure with trigonal-bipyramidal coordination at Sn, but there is one difference. The anion bridges through the 7,9 positions rather than the more common 7,12 positions. The reason probably lies in the predominance of crystal-packing forces over site basicity, as seen in the X-ray structure of the carborane acid $\text{H}(\text{CHB}_{11}\text{Cl}_{11})$.²⁶ Although the 12 position is calculated to be more basic than 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 basic¹⁶ and less coordinating¹⁷ 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

(19) Yang, Y.; Panisch, R.; Bolte, M.; Meuller, T. *Organometallics* **2008**, 27, 4847–4853.

(20) Sarazin, Y.; Coles, S. J.; Hughes, D. L.; Hursthouse, M. B.; Bochmann, M. *Eur. J. Inorg. Chem.* **2006**, 3211–3220.

(21) Kašná, B.; Jambor, R.; Dostál, L.; Císařová, I.; Holeček, J.; Štíbr, B. *Organometallics* **2006**, 25, 5139–5144.

(22) Preut, H.; Huber, F. *Acta Crystallogr.* **1979**, B35, 83–86.

(23) Xie, Z.; Bau, R.; Benesi, A.; Reed, C. A. *Organometallics* **1995**, 14, 3933–3941.

(24) Preut, H.; Huber, F. *Acta Crystallogr.* **1979**, B35, 744.

(25) Preut, H.; Huber, F. *Z. Anorg. Allg. Chem.* **1977**, 435, 234.

(26) Stoyanov, E. S.; Hoffmann, S. P.; Juhasz, M.; Reed, C. A. *J. Am. Chem. Soc.* **2006**, 128, 3160–3161.

Figure 5. IR spectra of $[\text{Et}_3\text{SiHGeEt}_3][\text{CHB}_{11}\text{Cl}_{11}]$ (black) and $[\text{Et}_3\text{GeHGeEt}_3][\text{CHB}_{11}\text{Cl}_{11}]$ (blue).

that in Me_3SnCl ²⁷ and 0.50 Å longer than in Ph_3SnCl ,²⁸ 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_3E^+ cations. This contrasts with the data on discrete molecular structures like $\text{Et}_3\text{Si}(\text{carborane})$, where the degree of pyramidalization at Si is an excellent guide to silylium ion character.² Nevertheless, the following reactivity studies confirm that the undecachloro anion is less coordinating than the hexabromo analogue.

Formation of the $[\text{Et}_3\text{Ge}-\text{H}-\text{GeEt}_3]^+$ Cation. When the synthesis of $\text{Et}_3\text{Ge}(\text{CHB}_{11}\text{Cl}_{11})$ is carried out according to eq 1 in the presence of excess Et_3GeH , the germane competes with the carborane anion for coordination to Ge and forms the $[\text{Et}_3\text{Ge}-\text{H}-\text{GeEt}_3]^+$ cation (eq 4):

The reaction is reversible. Indeed, the easiest way to prepare $\text{Et}_3\text{Ge}(\text{CHB}_{11}\text{Cl}_{11})$ is to remove Et_3GeH from the “dimer” product by heating under vacuum. The formation reaction only proceeds with the undecachloro carborane anion; the hexabromo anion is too strongly coordinated. This chemistry exactly parallels that of Si.¹⁷

The μ -hydrido product is readily characterized by IR spectroscopy, where a broad, distinctively shaped peak assigned to $\nu_{\text{as}}\text{GeHGe}$ is observed at ca. 1740 cm^{-1} . This absorption is similar to that observed in the corresponding $[\text{Et}_3\text{Si}-\text{H}-\text{SiEt}_3]^+$ cation at 1875 cm^{-1} (Figure 5) and at generally higher frequencies in related hydride-bridged carbocations.²⁹

The analogous Sn hydride-bridged species does not form when $[\text{Ph}_3\text{C}^+][\text{CHB}_{11}\text{Cl}_{11}]^-$ is treated with excess Et_3SnH (or $n\text{-Bu}_3\text{SnH}$) in *o*-dichlorobenzene. There was no evidence in the IR spectrum for a $\nu_{\text{as}}\text{SnHSn}$ peak expected at ca. 1650 cm^{-1} . The lack of stannane adduct formation may be related to intrinsic Lewis basicity differences or to the higher lattice energy of the low-solubility polymeric $\text{Et}_3\text{Sn}(\text{CHB}_{11}\text{Cl}_{11})$. The low thermal stability of lead hydrides¹⁸

prevented our exploration of the corresponding reaction with Et_3PbH .

Conclusion

The successful synthesis and isolation of $\text{Et}_3\text{E}(\text{carborane})$ species for $\text{E} = \text{Ge}, \text{Sn},$ and Pb adds to the available repertoire of cation-like R_3E^+ Lewis acids of group 14 elements that are coupled with extremely inert carborane counterions. As illustrated by the example of the reaction of $\text{Et}_3\text{Ge}(\text{CHB}_{11}\text{Cl}_{11})$ with Et_3GeH to form the $[\text{Et}_3\text{Ge}-\text{H}-\text{GeEt}_3]^+$ cation, this opens the way to an exploration of their reactivity with weak bases *L* to form higher coordinate cations of the type $[\text{R}_3\text{EL}]^+$. Of further interest is the possibility that these cation-like Lewis acids will allow systematic studies of R_3E^+ cations in important catalytic roles such as the polymerization of phosphazenes¹³ and the activation of C–F bonds.¹⁴

Experimental Section

Reactions were carried out in an inert atmosphere glovebox ($\text{O}_2, \text{H}_2\text{O} < 1\text{ ppm}$). Solvents were dried following literature procedures,³⁰ distilled under Ar, and stored over 4 Å molecular sieves in the glovebox. $[\text{Ph}_3\text{C}][\text{CHB}_{11}\text{H}_5\text{Br}_6]$, $[\text{Ph}_3\text{C}][\text{CHB}_{11}\text{Cl}_{11}]$, $\text{Et}_3\text{Si}(\text{CHB}_{11}\text{H}_5\text{Br}_6)$, and $\text{Et}_3\text{Si}(\text{CHB}_{11}\text{Cl}_{11})$ were prepared by literature methods.³¹ Triethyltin 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.

$\text{Et}_3\text{Ge}(\text{CHB}_{11}\text{H}_5\text{Br}_6)$. In a 12 mL vial equipped with a magnetic stir bar, $[\text{Ph}_3\text{C}][\text{CHB}_{11}\text{H}_5\text{Br}_6]$ (122 mg, 0.142 mmol) was dissolved in dry *o*-dichlorobenzene (1 mL). To this orange solution was added Et_3GeH (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. $^1\text{H NMR}$ ($\text{ODCB-}d_4$, 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 $\text{C}_7\text{H}_{21}\text{B}_{11}\text{Br}_6\text{Ge}$: C, 15.80; H, 3.63. Found: C, 13.69; H, 2.48. FT-IR [ATR]: see Supporting Information.

$[(\text{Et}_3\text{Ge})_2\text{H}][\text{CHB}_{11}\text{Cl}_{11}]$. Et_3GeH (0.5 mL, 3.09 mmol) was added to a stirring suspension of $[\text{Ph}_3\text{C}][\text{CHB}_{11}\text{Cl}_{11}]$ (308.5 mg, 0.403 mmol) in *o*-dichlorobenzene (1 mL). The mixture became clear after a few seconds and was allowed to stir for an additional 10 min. *n*-Hexane was added while stirring to give a white precipitate, which was filtered off (0.23 g, 68%). FT-IR [ATR] spectrum: see Figure 5. Upon heating at 130 °C under vacuum for 3 h, the diagnostic ν_{GeHGe} band at 1740 cm^{-1} disappeared, giving $\text{Et}_3\text{Ge}(\text{CHB}_{11}\text{H}_5\text{Br}_6)$; see Supporting Information Figure S3. Anal. Calcd for $\text{C}_{13}\text{H}_{32}\text{B}_{11}\text{Cl}_{11}\text{Ge}_2$: C, 18.53; H, 3.83. Found: C, 18.71; H, 3.40.

$\text{Et}_3\text{Sn}(\text{CHB}_{11}\text{H}_5\text{Br}_6)$. $\text{Et}_3\text{Si}(\text{CHB}_{11}\text{H}_5\text{Br}_6)$ was prepared from $[\text{Ph}_3\text{C}][\text{CHB}_{11}\text{H}_5\text{Br}_6]$ (135 mg, 0.157 mmol) and excess Et_3SiH in *o*-dichlorobenzene (3 mL). Hexanes (0.5 mL) was added to ensure complete product precipitation. The product was filtered off and resuspended in *o*-dichlorobenzene, and Et_3SnCl (52 mg, 0.21 mmol) was added dropwise. *n*-Hexane (0.5 mL) was carefully layered onto the reaction mixture, and small, colorless X-ray quality crystals of $\text{Et}_3\text{Sn}(\text{CHB}_{11}\text{H}_5\text{Br}_6)$ grew over a week (58 mg, 45%). FT-IR [ATR]: Supporting Information Figure S4. Anal. Calcd for $\text{C}_7\text{H}_{21}\text{B}_{11}\text{Br}_6\text{Sn}$: C, 10.19; H, 2.57. Found: C, 10.16; H, 2.37.

(27) Lefferts, J. L.; Molloy, K. C.; Hossain, M. B.; van der Helm, D.; Zuckerman, J. J. *J. Organomet. Chem.* **1982**, 240, 349.

(28) Tse, J. S.; Lee, F. L.; Gabe, E. J. *Acta Crystallogr.* **1986**, C42, 1876–1878.

(29) Sorensen, T. S. In *Stable Carbocation Chemistry*; Surya Prakash, G. K.; Schleyer, P. v. R., Eds.; Wiley: New York, 1997; Chapter 3.

(30) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*, 2nd ed.; Pergamon Press Ltd.: Sydney, 1980.

(31) See Supporting Information in ref 7.

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 *o*-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 *o*-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 *o*-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.

Acknowledgment. We thank Prof. Evgenii Stoyanov for assistance with IR spectra and NSF for support (CHE-0841428).

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>.