Tetraphenyldiphosphine Disulfide, $(C_6H_5)_2P(S)P(S)(C_6H_5)_2$. Tetraphenyldiphosphine, from the initial preparation, was added to 25 ml of toluene containing sufficient sulfur for complete reaction. The mixture was heated to 100–105° with stirring, under an inert atmosphere for 6 hr. The hot toluene solution was then filtered and evaporated. This reaction resulted in essentially 100% conversion based on the initial quantity of tetraphenyldiphosphine. The white crystals obtained from this reaction were recrystallized from chloroform–methanol and vacuum dried. The infrared spectrum[2,3] was identical with that reported for tetraphenyldiphosphine disulfide. The mass spectrum was consistent, exhibiting a peak at 434, attributable to the parent ion $[(C_6H_5)_2P(S)P(S)(C_6H_5)_2$, mol wt 434].

Diphenylphosphinic Anhydride, $(C_6H_5)_2P(O)OP(O)(C_6H_5)_2$. Tetraphenyldiphosphine, 0.22 g (0.6 mmol) from the initial preparation, was added to 15 ml of toluene containing a small amount of diphenylchlorophosphine (0.05 g). Dry oxygen in excess was introduced into the solution at room temperature, and the reaction continued until oxygen take-up ceased. The toluene solution was then filtered through decolorizing charcoal, concentrated by evaporation under vacuum, and allowed to stand at room temperature. The crystals which formed on standing were washed repeatedly with dry, cold heptane or ether and dried under vacuum at room temperature. The material was then recrystallized several times from toluene. In this preparation as in those above, the presence of moisture led to the formation of diphenylphosphinic acid, which was removed by washing with 1% aqueous potassium hydroxide as described previously.

Diphenylphosphinic anhydride melted at 144–145°, lit.[10] 142–143°. Its infrared spectrum contained a band at 1236 cm^{-1} assigned to the $P{=}O$[21] stretching frequency and a band at 960 cm^{-1} assigned to the $P{-}O{-}P$[22] linkage.

Mass spectral data showed a parent ion peak corresponding to a mass of 418 $[(C_6H_5)_2P(O)OP(O)(C_6H_5)_2$; mol wt 418], and a fragmentation pattern consistent with that of diphenylphosphinic anhydride.

Anal. Calcd for $C_{24}H_{20}O_3P_2$: C, 68.90; H, 4.82; P, 14.81; O, 11.47. Found: C, 68.65; H, 4.66; P, 14.71; O, 11.96.

This reaction results in virtually complete conversion of the tetraphenyldiphosphine, forming a mixture containing more than 95% anhydride and less than 5% tetraphenyldiphosphine dioxide.

Diphenylphosphinic anhydride was produced in an identical manner using tetraphenyldiphosphine monoxide instead of the tetraphenyldiphosphine as starting material.

Diphenylphosphinic anhydride was also produced by adding oxygen directly to the cooled reaction mixture from the initial tetraphenyldiphosphine preparation, without first actually isolating the tetraphenyldiphosphine. Isolation and purification of the product were carried out as described previously. Yields based on calcium carbide consumed were about 40%.

In all of the procedures described, product yields were approximately 40%. These yields could be substantially improved by complete recovery of product retained on the inorganic salts and carbon.

Acknowledgment. Partial support of the investigation from the FMC Corporation, Princeton, N. J., and their assistance with the analytical work, is gratefully acknowledged.

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The Preparation and Characterization of 1-Germa-, 1-Stanna-, and 1-Plumba-2,3-dicarba-*closo*-dodecaborane(11)

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Abstract: Treatment of (3)-1,2-$B_9C_2H_{11}{}^{2-}$ with carbenoid germanium, tin, and lead reagents leads to the formation of icosahedral tricarbaborane analogs, $MC_2B_9H_{11}$ (M = Ge, Sn, Pb). The characterization of these new carbametallic boranes gives no evidence for substituents pendent from the metal. Facile removal of the metal is effected by treatment with methanolic KOH.

Extension of the known isoelectronic series of the icosahedral species $(B_{12}H_{12})^{2-}$, $(B_{11}CH_{12})^{-}$, and $B_{10}C_2H_{12}$ yields the unknown tricarbaborane $[B_9C_3H_{12}]^+$. The latter cation, owing to the characteristic electronegativity of neutral polyhedral carboranes,[1] would probably be acidic or perhaps even exist as the neutral $B_9C_3H_{11}$ molecule.

Results and Discussion

We have isolated carbametallic boranes[2] analogous to $B_9C_3H_{11}$ in that a carbon atom is replaced by another main group IV element, $MC_2B_9H_{11}$ (M = Ge, Sn, Pb). These carbametallic boranes, 1-germa-, 1-stanna-, and 1-plumba-2,3-dicarba-*closo*-dodecaborane(11), are formed from carbenoid reagents according to

$$\text{(3)-1,2-}B_9C_2H_{11}{}^{2-} + MX_2 \longrightarrow MB_9C_2H_{11} + 2X^- \quad (1)$$
$$(M = Ge, Sn, Pb)$$

The formation of $MC_2B_9H_{11}$ species by using $:MCl_2$ reagents to insert a metal atom into the vacant icosahedral position of the (3)-1,2-$B_9C_2H_{11}{}^{2-}$ ion[3] renders the reaction similar to that described by Hawthorne and Wegner[4] for the insertion of RB with $RBCl_2$ reagents. Todd, *et al.*,[5] describe another parallel in the formation of $B_{10}H_{10}CHP$ by treatment of $(B_{10}H_{10}CH)^{3-}$ with

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(1) For a discussion of polyhedral boranes and carboranes, see (a) E. L. Muetterties and W. H. Knoth, "Polyhedral Boranes," Marcel Dekker, New York, N. Y., 1968; (b) M. F. Hawthorne in "Chemistry of Boron and its Compounds," E. L. Muetterties, Ed., John Wiley and Sons, New York, N. Y., 1967.

(2) R. L. Voorhees and R. W. Rudolph, *J. Amer. Chem. Soc.*, **91**, 2173 (1969).

(3) M. F. Hawthorne, D. C. Young, P. M. Garret, D. A. Owen, S. G. Schwerin, F. N. Tebbe, and P. A. Wegner, *ibid.*, **90**, 862 (1968).

(4) M. F. Hawthorne and P. A. Wegner, *ibid.*, **90**, 896 (1968).

(5) L. J. Todd, L. J. Little, and H. T. Silverstein, *Inorg. Chem.*, **8**, 1698 (1969).

Table I. Infrared Spectra of $MC_2B_9H_{11}$ Species (M = Ge, Sn, Pb)

Compound	Vibrational frequencies, cm^{-1} ν(CH)	ν(BH)	δ(CH)	δ(BH)	Cage motions	ν(MC)
$GeC_2B_9H_{11}$	3052	2553	1227, 1217, 1092	1048, 1015, 994, 967, 942, 903, 863	765, 737, 721, 700, 674, 619, 562	277
$SnC_2B_9H_{11}$	3041	2597, 2560, 2515	1234, 1086	1043, 1022, 1000, 962, 946, 915, 893, 871, 858, 840	762, 739, 723, 703, 673, 611, 557, 478	
$PbC_2B_9H_{11}$	3043	2580, 2544, 2499, 2465	1236, 1080	1022, 1001, 964, 946, 894, 868, 843	765, 745, 722, 706, 680, 665, 604, 556	

PCl_3. Just as the latter yields a "bare" P atom, metal atom insertion results in a bare icosahedral site as depicted in Figure 1. The Ge and Sn compounds are colorless sublimable solids (80 and 140° *in vacuo*, respectively), monomeric in benzene. Since the Pb homolog is less soluble in benzene, comparable molecular weight data are not available. The Pb derivative is yellow and sublimes at 250° *in vacuo*.

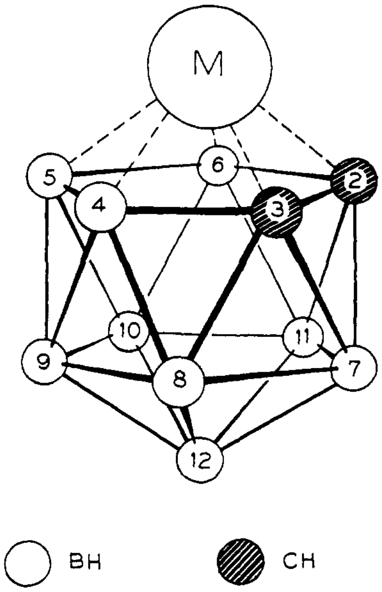

Figure 1. Proposed structure and numbering convention for $MC_2B_9H_{11}$ compounds (M = Ge, Sn, Pb). For $PbC_2B_9H_{11}$ the Pb atom may be "slipped" toward B atoms 4, 5, and 6.

The stability of the icosahedron containing these group IV metals is reflected in their mass spectra. All of the homologs show the expected parent ion peak ($^{76}Ge^{12}C_2{}^{11}B_9{}^1H_{11}$ = 210; $^{124}Sn^{12}C_2{}^{11}B_9{}^1H_{11}$ = 258; $^{208}Pb^{12}C_3{}^{11}B_9{}^1H_{13}$ = 356[6]). However, the total ion intensity distribution varies considerably with the metal. Thus, with the Ge congener *ca.* 90% of the total ion intensity was observed in the envelopes resulting from the parent ion and from the successive removal of B and/or C atoms from the parent; less than 10% of the total intensity was observed in the Ge^+ region. For the Sn derivative the total ion intensity was equally distributed between Sn^+ peaks and the parent ($SnC_2B_9H_{11}$) plus the fragments due to C and/or B loss. By contrast, the Pb homolog[6] displayed a relatively weak parent (*ca.* 5% of total intensity); the remainder of the spectrum consisted mainly of $B_9C_2H_{11}$ fragmentation (*ca.* 30% of total intensity) and Pb^+ ions (*ca.* 65% of total intensity). These patterns in ion intensity distribution point to decreasing stability in the parent icosahedral molecule in the order of $GeC_2B_9H_{11}$ > $SnC_2B_9H_{11}$ > $PbC_2B_9H_{11}$. Moreover, $GeC_2B_9H_{11}$ was the only member of the series giving readily discernible peaks due to the doubly charged parent ion. The mass spectral results lead us to speculate that thermal isomerization without destruction of the icosahedron, will occur readily for $GeC_2B_9H_{11}$.

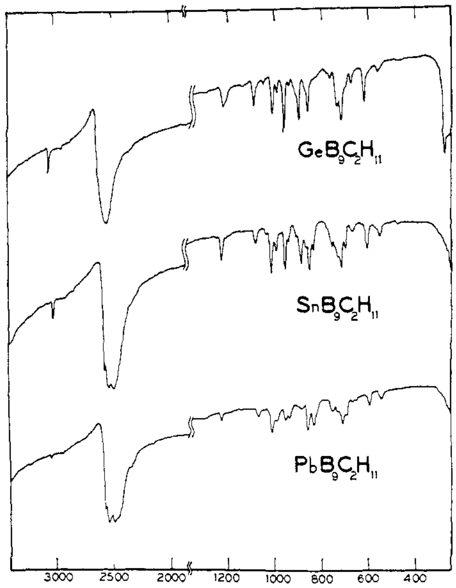

Figure 2. The infrared spectra (KBr disk) of $MC_2B_9H_{11}$ compounds (M = Ge, Sn, Pb).

The infrared spectra of the three species are very similar. They all display well separated frequencies near 3050, 2600–2450, and 1230 cm^{-1} characteristic of the ν(CH), ν(BH), and δ(CH) motions, for *o*-carborane moieties,[7] respectively, but absorptions were noticeably absent from the region characteristic of M–H (M = Ge, Sn, Pb) stretching motions (2100–1700 cm^{-1}).[8] The spectra are displayed in Figure 2 and the frequencies tabulated in Table I along with tentative assignments.

The ^1H nmr spectral data for the three $MC_2B_9H_{11}$ species are given in Table II. The data derived from $GeC_2(CH_3)B_9H_{10}$ and $GeC_2(CH_3)_2B_9H_9$ bear a striking similarity to those of the C-methyl and C,C′-dimethyl derivatives of *o*-carborane (Table II).

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[6] $PbC_2B_9H_{10}(CH_3)$ was used for the mass spectral characterization because of its greater volatility.

[7] H. Schroeder, T. L. Heying, and J. R. Reiner, *Inorg. Chem.*, **2**, 1092 (1963); R. P. Alexander and J. Schroeder, *ibid.*, **2**, 1107 (1963).

[8] J. W. Straley, C. H. Tindal, and J. H. Nielsen, *Phys. Rev.*, **62**, 161 (1942); G. R. Wilkinson and M. K. Wilson, *J. Chem. Phys.*, **25**, 784 (1956).

Table II. ^{1}H Nmr Data for $MC_2B_9H_{11}$ Species

Compound	Chemical shift, ppm[a]		Solvent
$GeC_2B_9H_{11}$	−3.34 (CH)		CD_3CN
$SnC_2B_9H_{11}$	−2.70 (CH)		CD_3CN
$PbC_2B_9H_{11}$	−2.70 (CH)		CD_3CN
$GeC_2B_9H_{11}$	−1.90 (CH)		C_6D_6
$GeC_2(CH_3)B_9H_{10}$	−2.47 (CH, 1),	−1.33 (CCH_3, 3)	C_6D_6
$GeC_2(CH_3)_2B_9H_9$		−1.52 (CCH_3)	C_6D_6
o-$C_2B_{10}H_{12}$	−2.42 (CH)		C_6D_6
o-$C_2(CH_3)B_{10}H_{11}$	−2.48 (CH, 1),	−1.32 (CCH_3, 3)	C_6D_6
o-$C_2(CH_3)_2B_{10}H_{10}$		−1.39 (CCH_3)	C_6D_6

[a] All chemical shifts were determined relative to the internal standard tetramethylsilane; assignments and relative intensities are given in parentheses.

The ^{11}B nmr spectra are shown in Figure 3. Based on the proposed structure for these carbametallic boranes (Figure 1), six boron environments in the intensity ratios 2:2:2:1:1:1 might be observed in the ^{11}B nmr. Characteristic of diamagnetic carbametallic boranes with the metal centered over the pentagonal face of the $B_9C_2H_{11}$ moiety,[9] the spectra of $GeC_2B_9H_{11}$ and $SnC_2B_9H_{11}$ lack resolution at 32.1 MHz. However, the spectrum of $PbC_2B_9H_{11}$ (Figure 3) displays a low-field doublet (9.4 ppm, intensity 1) separated from the other resonance signals (21.1–38.3 ppm, intensity 8). Thus, the spectrum is similar to those of the diamagnetic d^8 bis-(π-(3)-1,2-dicarbollyl) metalates reported by Warren and Hawthorne.[10] The latter transition metal complexes have been shown by Wing[11] to have suffered a slip distortion from the symmetrical sandwich structure. Although the Pb atom is not sandwiched between two carborane moieties in $PbC_2B_9H_{11}$, based on the ^{11}B nmr spectrum, the Pb atom may be "slipped" from an "icosahedral" position toward boron atoms 4, 5, and 6 (Figure 1). The unique boron resonance (9.4 ppm, Figure 3) also displays a small low-field shoulder which by shape analysis and area estimation (including the unresolved portions of the shoulder under the doublet and to its high-field side) gave an area of *ca.* 20% of the total and a $J_{^{207}\text{Pb}\text{B}} = 175$ Hz. We know of no other observation of ^{207}Pb–B spin–spin coupling.

X-Ray structural investigations of these novel carbametallic boranes have thus far been frustrated by their pronounced tendency to form disordered lattices upon crystallization.

The chemical characterization of these species is rather rudimentary. All three homologs undergo facile degradation in methanolic KOH to selectively remove the metal atom and regenerate the $B_9C_2H_{12}^-$ ion. The ease of metal atom removal is probably related to the facility of "front-side" attack on the bare metal and to its relatively electropositive nature. For instance, the blockage of frontal attack by exopolyhedral substituents has been demonstrated to preclude removal of the substituted boron from the icosahedron by base degradation.[4] Also, even though the P atom in phosphacarboranes is exposed, it is very difficult to remove by base degradation, the more electropositive B atom being preferentially removed from the phosphacarborane icosahedron.[5]

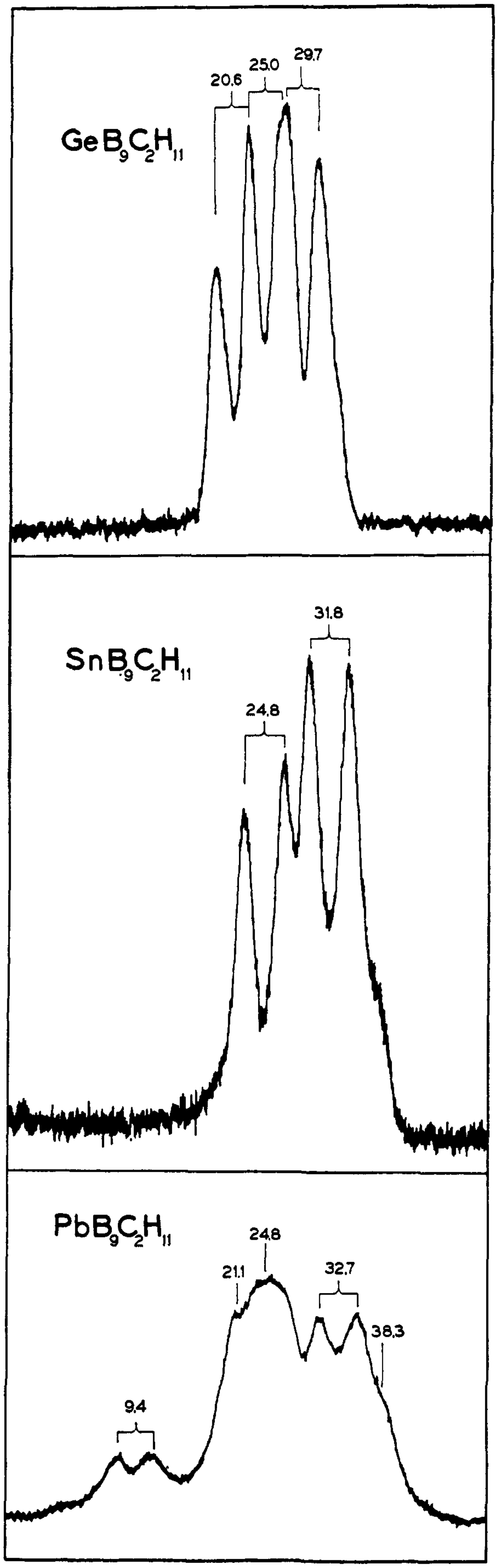

Figure 3. The ^{11}B nmr spectra of $MC_2B_9H_{11}$ compounds (M = Ge, Sn, Pb). Chemical shifts are reported relative to the external standard $B(OMe)_3$.

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(9) M. F. Hawthorne, D. C. Young, T. D. Andrews, D. V. Howe, R. L. Pilling, A. D. Pitts, M. Reintjes, L. F. Warren, Jr., and P. A. Wegner, *J. Amer. Chem. Soc.*, **90**, 879 (1968).

(10) L. F. Warren, Jr., and M. F. Hawthorne, *ibid.*, **90**, 4823 (1968).

(11) R. M. Wing, *ibid.*, **90**, 4828 (1968).

We have also observed recovery of Sn in the form of $SnCl_2$ when $SnC_2B_9H_{11}$ is treated with HCl in benzene. Hydrogen chloride appears to be a strong enough "base" to effect degradation according to

$$SnC_2B_9H_{11} + 2HCl \longrightarrow SnCl_2 + B_9C_2H_{13} \qquad (2)$$

Chemical and structural studies of these tricarbaborane analogs are continuing.

Experimental Section

Materials. Solvents were dried and stored over Linde Type 4A molecular sieves before use. Sodium hydride, as a 59% dispersion, was obtained from Metal Hydrides, Inc. Germanium iodide was obtained from Rocky Mountain Research Chemicals, Inc. All other chemicals were reagent grade and were used without further purification. Literature procedures were used for the preparation of 1,2-dicarba-*closo*-dodecaborane,[12,13] its derivatives, and their corresponding (3)-1,2-dicarbadodecahydroundecaborate(−1) salts.[12]

Infrared spectra were obtained as KBr disks with a Beckman IR-20 instrument. Proton nmr spectra were determined with a Varian A-60 spectrometer. The ^{11}B nmr spectra were determined at 32.1 MHz with a Varian HA-100 instrument. Mass spectra were taken with a Varian CH-5 mass spectrometer. Elemental analyses were made by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y., and Huffman Laboratories, Wheatridge, Colo.

1-Stanna-2,3-dicarba-*closo*-dodecaborane(11). In a 100-ml three-necked flask, equipped with a condenser, nitrogen inlet, and magnetic stirrer, which had been flushed with nitrogen for 1 hr, were placed 1.0 g (5.16 mmol) of the trimethylammonium salt of $B_9C_2H_{12}^-$, 50 ml of benzene, and 5.7 mmol of NaH (0.47 g of 59% dispersion which had been washed twice with hexane). The mixture was brought to reflux and flushed with nitrogen until trimethylamine could no longer be detected in the exhaust stream (usually *ca.* 4 hr). Anhydrous $SnCl_2$ (1.07 g, 5.7 mmol) was then added. After 24 hr of reflux under nitrogen, the mixture was placed in a Soxhlet thimble and extracted with benzene for 24 hr. Evaporation of the extract gave the crude product (in *ca.* 75% yield) which could be purified further by recrystallization from dry benzene or sublimation *in vacuo* at 140° to give 0.84 (3.45 mmol) of the product. The compound discolored at 210° and blackened at 265° (sealed tube).

Anal. Calcd for $B_9C_2SnH_{11}$: B, 38.75; C, 9.56; H, 4.42; Sn, 47.27; mol wt, 251.1. Found: B, 38.35; C, 10.40; H, 4.53; Sn, 48.51; mol wt (isopiestic in benzene), 251 ± 10.

1-Germa-2,3-dicarba-*closo*-dodecaborane(11). The procedure for $GeC_2B_9H_{11}$ is similar to that for $SnC_2B_9H_{11}$ but employs 1.83 g (5.6 mmol) of anhydrous GeI_2. The product is quite soluble in benzene and can be extracted in 2 hr. The benzene is removed with a rotary evaporator, and 0.35 g (1.7 mmol) of the pure product is obtained by sublimation at 80° *in vacuo*. The compound was observed to soften at 342° and blacken at 352° in a sealed tube.

Anal. Calcd for $B_9C_2GeH_{11}$: B, 47.44; C, 11.71; H, 5.41; Ge, 35.43; mol wt, 205.0. Found: B, 47.12; C, 11.94; H, 5.50; Ge, 35.67; mol wt (isopiestic in benzene), 209 ± 10.

1-Plumba-2,3-dicarba-*closo*-dodecaborane(11). For the preparation of $PbC_2B_9H_{11}$, anhydrous $Pb(CH_3COO)_2$ (1.68 g, 5.17 mmol) was prepared by the azeotropic removal (in benzene) of the water from $Pb(CH_3COO)_2 \cdot 2H_2O$. The general procedure used for $SnC_2B_9H_{11}$ applies.

Extraction of the yellow product with benzene gave 0.63 g (1.86 mmol) of $PbC_2B_9H_{11}$. A somewhat higher yield and a purer product was obtained by preparing the C-methyl derivative starting with trimethylammonium (3)-1-methyl-1,2-dicarbadodecahydroundecaborate. Sublimation occurs at 250° *in vacuo*. $PbC_2B_9H_{11}$ was observed to blacken at 250° in a sealed tube.

Anal. Calcd for $B_9C_3PbH_{13}$: B, 27.49; C, 10.18; H, 3.70; Pb, 58.61. Found: B, 27.02; C, 10.39; H, 4.38; Pb, 57.64.

Methanolic KOH Degradation of $MC_2B_9H_{11}$ Species. Typically 0.5–1.0 mmol of the $MC_2B_9H_{11}$ compound was added to 75 ml of 1.5 *M* methanolic KOH and the mixture allowed to reflux for 24 hr. The $B_9C_2H_{12}^-$ ion was recovered as the tetramethylammonium salt, dried *in vacuo*, weighed, and identified by its ir and nmr spectra. The exact method of recovery of $Me_4NB_9C_2H_{12}$ depended on the metal removed in the degradation. In the case of Ge, after 24 hr at reflux, the solution was made slightly acidic with 10% HCl, and heated to drive off MeOH; Me_4NCl was added to precipitate $Me_4NB_9C_2H_{12}$ (95% recovery). For Sn, after 24 hr reflux, H_2O (100 ml) was added (in acidic solution $SnO_2 \cdot xH_2O$ precipitates), the methanol driven off by heating, and Me_4NCl added to bring down the $B_9C_2H_{12}^-$ ion (93% recovery with no tin in the precipitate as shown by X-ray fluorescence).

In the case of Pb, neutralization was effected with 30% H_2SO_4; the precipitated $PbSO_4$ was recovered by filtration, washed, and dried (100% recovery). The $B_9C_2H_{12}^-$ ion was readily recovered after addition of Me_4NCl to filtrate and heating to drive off the methanol (98% recovery).

The Reaction of HCl and $SnC_2(CH_3)_2B_9H_9$. Hydrogen chloride was bubbled (120 bubbles/min) through a solution of $SnC_2(CH_3)_2B_9H_9$ (50 mg, 0.18 mmol) in 60 ml of benzene for 15 min. The white precipitate was recovered, dried, weighed (17 mg, 0.09 mmol, 50% recovery), and identified as $SnCl_2$ by its characteristic X-ray powder photograph and melting point (observed, 245–248°; reported, 246°).

Acknowledgment. The authors gratefully acknowledge the use of the University of Colorado facilities for the determination of the ^{11}B nmr spectra and mass spectra.

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[12] M. F. Hawthorne, T. D. Andrews, P. M. Garret, F. P. Olsen, M. Reintjes, F. N. Tebbe, L. F. Watten, P. A. Wegner, D. C. Young, R. P. Alexander, R. W. Blundon, H. A. Schroeder, and T. L. Heying, *Inorg. Syn.*, **10**, 91 (1967).

[13] C. H. Kutal, D. A. Owen, L. J. Todd, R. C. Stafford, and N. R. Fetter, *ibid.*, **11**, 19 (1968).