band $\nu_8 + \nu_9$ seen near 550 cm^{-1}. If the other vibration involved in the "hot" band series is one of the PCN bending modes which are the lowest frequency fundamentals, a simple Boltzmann distribution does not account for the intensity of the observed series. For example, using ν_9 as the vibration which is excited, the population of the $v = 1$ level should be 48% of the ground state population and $v = 2$ less than 25%. It is possible, when the Boltzmann factor is on the order of unity, the intensity of such a $\nu_k + (\nu_l - \nu_l')$ "hot" band is of the same order as that of the fundamental if the degree of coupling between the two vibrations is great enough.[15] A similar effect has been observed for silacyclopentane by Durig and Willis.[16]

Although some evidence of the $2 \leftarrow 1$ transition of ν_9 was seen, the "hot" band transitions of ν_8 are apparently not very different in frequency from the $1 \leftarrow 0$ transition and are evident as a slight broadening of the main Q branch to the high-frequency side.

We have included the results of both normal-coordinate treatments to emphasize the danger of using normal-coordinate analysis to aid in the assignment of vibrational spectra. Both force fields reproduced the observed spectrum adequately, but we were forced to reject the assignment which gave the "cleaner" potential energy distribution in favor of one which we feel is more nearly correct.

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References and Notes

(1) Taken in part from the Ph.D. thesis of A. J. Zozulin which is to be submitted to the Department of Chemistry in partial fulfillment of the Ph.D. degree.

(2) P. L. Lee, K. Cohn, and R. H. Schwendeman, *Inorg. Chem.*, **11**, 1917 (1972).

(3) R. W. Rudolph, R. C. Taylor, and R. W. Parry, *J. Am. Chem. Soc.*, **88**, 3729 (1966).

(4) (a) F. A. Miller, S. G. Frankis, and O. Sala, *Spectrochim. Acta*, **21**, 775 (1965); (b) J. R. Durig, A. W. Cox, Jr., and Y. S. Li, *Inorg. Chem.*, **13**, 2303 (1974).

(5) G. G. Flaskerud, K. E. Pullen, and J. M. Shreeve, *Inorg. Chem.*, **8**, 728 (1969).

(6) J. G. Morse, K. Cohn, R. W. Rudolph, and R. W. Parry, *Inorg. Synth.* **10**, 147 (1967).

(7) D. F. Shriver, "The Manipulation of Air-Sensitive Compounds", McGraw-Hill, New York, N.Y. 1969, p 91.

(8) The funds to purchase the Digilab FTS-15 B interferometer were given by the National Science Foundation by Grant MPS-75-06926.

(9) F. A. Miller and B. M. Harney, *Appl. Spectrosc.*, **24**, 291 (1970).

(10) M. L. Dewaulle and M. F. Francois, *J. Chim. Phys. Phys.-Chim. Biol.*, **46**, 87 (1949).

(11) J. R. Durig, A. W. Cox, Jr., and Y. S. Li, *Inorg. Chem.*, **13**, 2302 (1974).

(12) M. K. Wilson and S. R. Polo, *J. Chem. Phys.*, **20**, 1716 (1952).

(13) R. W. Rudolph and R. W. Parry, *Inorg. Chem.*, **4**, 1339 (1965).

(14) A Muller, O. Glemser, and E. Niecke, *Z. Naturforsch. B*, **21**, 732 (1966).

(15) G. Herzberg, "Molecular Spectra and Molecular Structure II. Infrared and Raman Spectra of Polyatomic Molecules", Van Nostrand-Reinhold, New York, N.Y. 1945, p 267.

(16) J. R. Durig and J. N. Willis, Jr., *J. Mol. Spectrosc.*, **32**, 320 (1969).

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Small Metallocarboranes of Tin and Lead

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The polyhedral cage compounds $SnC_2B_4H_6$, $PbC_2B_4H_6$, $Sn(CH_3)_2C_2B_4H_4$, and $Pb(CH_3)_2C_2B_4H_4$ have been prepared by reactions of $SnCl_2$ and $PbBr_2$ with the $C_2B_4H_7^-$ and *C,C'*-$(CH_3)_2C_2B_4H_5^-$ ions in tetrahydrofuran. From their ^{11}B and ^1H NMR, IR, and mass spectra, these species were characterized as pentagonal-bipyramidal systems with the metal atom occupying an apex location and presumably directing an unshared electron pair outward from the polyhedron. The corresponding reactions employing GeI_2 gave highly unstable germacarboranes which were not isolated. Reactions of the $C_2B_5H_7^{2-}$ ion with $SnCl_2$, $PbBr_2$, and GeI_2 gave neutral 2,4-$C_2B_5H_7$ but no isolable heterocarborane products. The gas-phase reaction of $Sn(CH_3)_2C_2B_4H_4$ with $(\eta^5\text{-}C_5H_5)Co(CO)_2$ gave 1,2,3-$(\eta^5\text{-}C_5H_5)Co(CH_3)_2C_2B_4H_4$ and $(\eta^5\text{-}C_5H_5)CoSn(CH_3)_2C_2B_4H_4$, a cage system containing tin and cobalt in the same polyhedron.

Introduction

Polyhedral carboranes containing an atom of germanium, tin, or lead (but not silicon) as an integral member of the cage have been known since Rudolph and co-workers[1] prepared $MC_2B_9H_{11}$ (M = Ge, Sn, Pb) and Todd et al.[2] synthesized $CH_3GeCB_{10}H_{11}$. More recent work has produced $(CO)_5M\text{–}GeCB_{10}H_{11}^-$ species[3] in which an $M(CO)_5$ ligand (M = Cr, Mo, W) is σ bonded to a germacarborane cage, as well as the germaphospha- and germaarsacarboranes[4] $GePCB_9H_{10}$ and $GeAsCB_9H_{10}$. In addition, the 11-vertex *nido*-metalloboranes $(CH_3)_2GeB_{10}H_{12}$ and $(CH_3)_2SnB_{10}H_{12}$ have been reported by Loffredo and Norman.[5] Except for the latter two 11-atom cages, all of the above species are 12-vertex systems analogous to the prototype icosahedral carborane, $C_2B_{10}H_{12}$.

Other than bridged species such as μ-$(CH_3)_3MC_2B_4H_7$ (M = Si, Ge, Sn, Pb)[6] and μ-$(CH_3)_3M(CH_3)_2C_2B_4H_5$ (M = Si, Ge)[7] in which the metal is joined to the cage via a B–M–B three-center bond but is not fully a part of the cage framework, no examples of sub-icosahedral carboranes containing group 4 heteroatoms have been reported.[8] Indeed, the only small carboranes containing main-group heteroatoms of *any* type are the $CH_3MC_2B_4H_6$ species (M = Ga, In).[9] During earlier studies in this laboratory,[6] we explored the possibility that the group 4 bridged compounds μ-$GeH_3C_2B_4H_7$, μ-$(CH_3)_3SnC_2B_4H_7$, and μ-$(CH_3)_3PbC_2B_4H_7$ and/or various silicon analogues of these could be converted to closed polyhedral heterocarboranes of the formula $MC_2B_4H_6$. These efforts were encouraged by the finding[10] that the bridged species μ-$[(\eta^5\text{-}C_5H_5)Fe(CO)_2]C_2B_4H_7$ is indeed converted to the *closo*-metallocarboranes $(\eta^5\text{-}C_5H_5)Fe^{II}C_2B_4H_7$ and $(\eta^5\text{-}C_5H_5)Fe^{III}C_2B_4H_6$ by ultraviolet irradiation; however, no such cage closure has been achieved with the group 4 compounds.

Since, on the other hand, the insertion of transition metal ions into small metallocarboranes such as $C_2B_4H_8$, $C_2B_3H_5$, and $C_2B_5H_7$ has generated a versatile and rich chemistry,[11] it appeared likely that this latter work could usefully be extended to some of the main-group elements. In this paper we describe the synthesis of some lower homologues of the $MC_2B_{n-2}H_n$ series as well as a novel cage system which incorporates both main-group and transition metals.

Table I. 32.1-MHz ^{11}B FTNMR Data

Compd	Solvent	δ, ppm[a] (*J*, Hz)	Rel area
$SnC_2B_4H_6$ (I)	$CDCl_3$	+0.1 (165), −6.2 (180)	3:1
$PbC_2B_4H_6$ (II)	Acetone-d_6	+35.5 (151), +19.7 (132), −6.7 (166)	1:2:1
$Sn(CH_3)_2C_2B_4H_4$ (III)	$CDCl_3$	+17.6 (144), −1.6 (168)	3:1
$Pb(CH_3)_2C_2B_4H_4$ (IV)	Acetone-d_6	+33.3 (130), +20.1 (140), +1.0 (180)	1:2:1
$(C_5H_5)CoSn(CH_3)_2C_2B_4H_4$ (V)	$CDCl_3$	−9.0 (130), −36.3 (170)	3:1

[a] Chemical shifts relative to $BF_3 \cdot O(C_2H_5)_2$ *with positive sign indicating shift to lower field (less shielding)*; this new convention, reversing the previous practice for ^{11}B NMR, was agreed to in plenary session at the Third International Meeting on Boron Chemistry in Munich and Ettal, West Germany, July 1976.

Table II. 100-MHz ^{1}H FTNMR Data

Compd	Solvent	δ, ppm[a] (rel area)	Assignment
I	$CDCl_3$	+6.3 (2), +3.8 (1), +2.5 (3)	CH, BH, BH
II	CD_2Cl_2	+6.55 (2), +5.15 (1), +3.85 (2), +2.19 (1)	CH, BH, BH, BH
III	$CDCl_3$	+4.17 (1), +4.03 (3), +2.41 (6)	BH, BH, CH_3
IV	CD_2Cl_2	+4.71 (1), +3.88 (2), +2.88 (1), +2.50 (6)	BH, BH, BH, CH_3
V	$CDCl_3$	+5.36 (5), +2.22 (3), +2.16 (3)	C_5H_5, CH_3, CH_3

[a] Chemical shifts relative to $(CH_3)_4Si$ with positive sign indicating shift to lower field. BH chemical shifts were obtained from ^{11}B-decoupled spectra.

Reactions of $SnCl_2$, $PbBr_2$, and GeI_2 with $C_2B_5H_7^{2-}$. In attempting to insert group 4 atoms into small carborane frameworks, we followed approaches similar to those which had been successful with transition metal reagents,[10-13] utilizing the $C_2B_5H_7^{2-}$ dianion, the $C_2B_4H_7^-$ monoanion, and the *C*,*C'*-dimethyl derivative of the latter species.

Reduction of *closo*-2,4-$C_2B_5H_7$ with sodium naphthalide in tetrahydrofuran (THF) generates the $C_2B_5H_7^{2-}$ dianion,[10,12] which on treatment with $SnCl_2$ yields primarily the neutral carborane; traces of species corresponding to $SnC_2B_4H_6$ and $SnC_2B_5H_7$ were detected mass spectroscopically but were not isolated (see eq 1). Analogous experiments using $PbBr_2$ and GeI_2 similarly failed to give isolable metallocarboranes, but the formation of 2,4-$C_2B_5H_7$ in each case is of interest since it provides direct evidence of the existence of the $C_2B_5H_7^{2-}$ species. As with most of the $C_2B_{n-2}H_n^{2-}$ anions derived by reduction of polyhedral carboranes (the exception[14] being $C_2B_9H_{11}^{2-}$), the $C_2B_5H_7^{2-}$ dianion has never actually been characterized although metallocarboranes formally incorporating it have been reported, e.g., $(CO)_3FeC_2B_5H_7$[10] and $(\eta^5\text{-}C_5H_5)CoC_2B_5H_7$.[12]

$$2,4\text{-}C_2B_5H_7 \xrightarrow[C_{10}H_8]{Na} C_2B_5H_7^{2-} \xrightarrow{SnCl_2} \underset{11\%}{C_2B_5H_7} + Sn^0 + NaCl + \text{traces of stannacarboranes} \quad (1)$$

The oxidation of $C_2B_5H_7^{2-}$ ion to $C_2B_5H_7$ by $SnCl_2$ is analogous to the reaction of 1,7-$C_2B_9H_{11}^{2-}$ ion with $SnCl_2$ in benzene to give 2,3-$C_2B_9H_{11}$ and tin metal.[1c] However, the same 1,7-$C_2B_9H_{11}^{2-}$ anion reacts with GeI_2 to form a stable germacarborane, 3,1,7-$GeC_2B_9H_{11}$,[1c] in contrast to the treatment of $C_2B_5H_7^{2-}$ with GeI_2 described above.

Reactions of $SnCl_2$, $PbBr_2$, and GeI_2 with $C_2B_4H_7^-$ and *C*,*C'*-$(CH_3)_2C_2B_4H_5^-$. The anions produced by deprotonation of 2,3-$C_2B_4H_8$ and its dimethyl derivative proved much more amenable to insertion of tin and lead than was the $C_2B_5H_7^{2-}$ species, but again no germacarboranes were isolated. Addition of $SnCl_2$ or $PbBr_2$ to a THF solution of $NaC_2B_4H_7$ produced respectively off-white solid $SnC_2B_4H_6$ (I) and light yellow solid $PbC_2B_4H_6$ (II) in low yields.

$$2,3\text{-}C_2B_4H_8 \xrightarrow[THF]{NaH} Na^+C_2B_4H_7^- \xrightarrow[-NaX]{MX_2} MC_2B_4H_6 + C_2B_4H_8$$

$$MX_2 = SnCl_2, PbBr_2$$

Table III. High-Resolution Mass Measurements[a]

Compd	Formula	Mass	
		Calcd	Obsd
I	$^{122}Sn^{12}C_2{}^{11}B_3{}^{10}B^1H_6{}^{+\,b}$	194.9912	194.9916
II	$^{208}Pb^{12}C_2{}^{11}B_4{}^1H_7{}^+$	283.0686	283.0686
III	$^{120}Sn^{12}C_4{}^{11}B_4{}^1H_{11}{}^+$	223.0254	223.0257
IV	$^{208}Pb^{12}C_4{}^{11}B_4{}^1H_{11}{}^+$	311.0999	311.1006
V	$^{120}Sn^{59}Co^{12}C_9{}^{11}B_3{}^{10}B_1{}^1H_{15}{}^+$	344.9935	344.9928

[a] Mass of P + 1 ion (protonated parent ion) obtained in methane under chemical ionizing conditions. [b] Highest mass peak of several selected for peak-matching to avoid multiple overlap caused by the large number of tin isotopes. Several lower mass peaks were also measured and gave comparable agreement with calculated values.

Table IV. Infrared Absorptions, cm^{-1}

I[a]	2860 m, 2560 vs, sh, 1450 m, br, 1370 w, 1010 w, 975 m, 955 m, 840 w, 725 m
II[a]	2855 w, 2830 s, 2765 m, 2555 vs, 1455 w, 1285 m, sh, 1220 vs, sh, 880 vs, sh, 840 w
III[a]	2990 m, 2960 m, 2930 s, sh, 2870 m, sh, 2550 vs, 1455 s, 1445 s, 1305 w, 1105 s, 995 w, 880 s, 770 w
IV[b]	2950 w, 2920 s, 2880 m, 2540 vs, 1445 w, 1375 m, 1265 s, sh, 1220 s, sh, 1110 w, 1035 w, 930 m, 885 s, sh, 735 w
V[a]	2980 w, 2930 s, 2850 s, 2550 s, 2475 vs, 1980 vs, 1935 m, 1705 s, 1605 w, 1540 w, 1365 s, 1225 m, 1120 w, 1020 vs, 825 vs, 750 m

[a] CH_2Cl_2 vs. CH_2Cl_2. [b] $CHCl_3$ vs. $CHCl_3$.

Compounds I and II were characterized from their ^{11}B and ^{1}H pulse Fourier transform NMR, infrared, and mass spectra (Tables I–IV) and were assigned the structures shown in Figure 1. The NMR spectra of the lead species clearly reveal three different boron environments, but the ^{11}B and ^{1}H spectra of the stannacarborane each exhibit only two BH resonances due to coincidental superposition of an area 2 and an area 1 peak (the same effect is seen in the spectra of the *C*,*C'*-dimethyl derivative, III). This situation is common (but not universal) in pyramidal and bipyramidal carboranes and is found, for example, in $C_2B_4H_8$,[15] 1,2,4-$(\eta^5\text{-}C_5H_5)CoC_2B_4H_6$,[12]

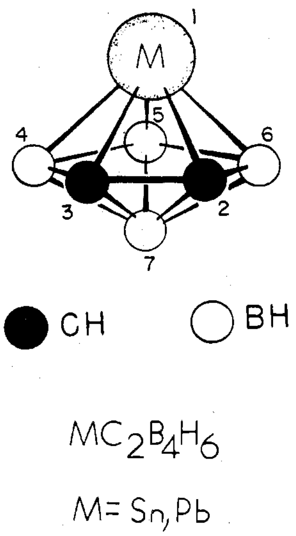

Figure 1. Proposed structures of $SnC_2B_4H_6$ and $PbC_2B_4H_6$.

1,2,3-(η^5-C_5H_5)$Fe^{II}H(C_2B_4H_6)$,[10] and 1,2,4-$(CO)_3FeC_2B_4H_6$.[10] Curiously, the ^{11}B spectrum of $PbC_2B_9H_{11}$ also exhibits better resolution than do those of $GeC_2B_9H_{11}$ or $SnC_2B_9H_{11}$.[1a]

The pentagonal-bipyramidal geometry is as expected for these molecules, which contain 16 skeletal valence electrons (assigning two from the metal, three from each CH, and two from each BH unit), and is directly analogous to 2,3-$C_2B_5H_7$ with a "bare" Sn or Pb atom replacing an apex BH group in that system. Compounds I and II are also, of course, close relatives of the seven-vertex transition metal metallocarboranes such as (η^5-C_5H_5)$CoC_2B_4H_6$ and $(CO)_3FeC_2B_4H_6$; all of these analogies proceed from the fact that $(C_5H_5)Co$, $(CO)_3Fe$, HB, :Sn, and :Pb are formal two-electron donors[16] to a polyhedral cage system and can be regarded, up to a point, as interchangeable building blocks. The new compounds are also lower homologues of the known icosahedral species[1] $MC_2B_9H_{11}$ (M = Ge, Sn, Pb) and like the latter are assumed to have an exopolyhedral lone pair of electrons on the metal atom. Both I and II are readily sublimed at room temperature and are air sensitive but differ in thermal stability. The tin species is unchanged when stored at room temperature under vacuum, but the lead compound decomposes to yield $C_2B_4H_8$ and solids.

An attempt to synthesize the analogous germanium species $GeC_2B_4H_6$ by the reaction of GeI_2 with the $C_2B_4H_7^-$ ion gave a reddish yellow mixture whose mass spectrum contained peaks assigned to $GeC_2B_4H_6$, but efforts to isolate this material were precluded by its extreme thermal instability.

The reactions of $SnCl_2$ and of $PbBr_2$ with $Na^+[C,C'$-$(CH_3)_2C_2B_4H_5]^-$ in THF produced the corresponding 1,2,3-$M(CH_3)_2C_2B_4H_4$ species. The tin compound III, collected as sublimable colorless crystals, and the lead analogue IV, a sublimable pale yellow solid, were characterized spectroscopically (Tables I–IV) and assigned structures identical with those of the parent compounds I and II with methyl substitution at the cage carbon positions. As in the case of the parent molecules, the tin species III is thermally stable in vacuo at room temperature, while IV slowly decomposes; both III and IV, however, are more stable than the parent compounds.

Treatment of the $(CH_3)_2C_2B_4H_5^-$ ion with GeI_2 gave an orange residue from which a trace of a brownish red solid sublimate was obtained. Mass spectroscopic analysis of this material indicated the presence of $Ge(CH_3)_2C_2B_4H_4$ and $Ge[(CH_3)_2C_2B_4H_4]_2$ but again we were unable to isolate these materials.

Synthesis of (η^5-C_5H_5)$CoSn(CH_3)_2C_2B_4H_4$. As part of an investigation of the chemistry of the dimethyltin species III, an attempt was made to insert transition metals into the cage by the gas-phase direct-insertion[17] reaction of III with (η^5-C_5H_5)$Co(CO)_2$ in a hot–cold reactor maintained at 70 and 150 °C. The principal products, isolated by extraction of the product residue with methylene chloride and chromatography on silica gel plates, were yellow 1,2,3-(η^5-C_5H_5)Co-$(CH_3)_2C_2B_4H_4$ (a compound previously obtained[13] from the reaction of $CoCl_2$ and NaC_5H_5 with $Na^+(CH_3)_2C_2B_4H_5^-$) and red (η^5-C_5H_5)$CoSn(CH_3)_2C_2B_4H_4$ (V), in yields of 40 and 5%, respectively. The attack of the cobalt reagent thus effects two results: metal insertion into the cage to create the eight-vertex species V and replacement of tin by the $(C_5H_5)Co$ group to give the seven-vertex cobaltacarborane. Furthermore, although V is air stable in the solid state, in solution (and especially on TLC plates) it loses tin, forming the same cobaltacarborane that is obtained as a coproduct of its synthesis.

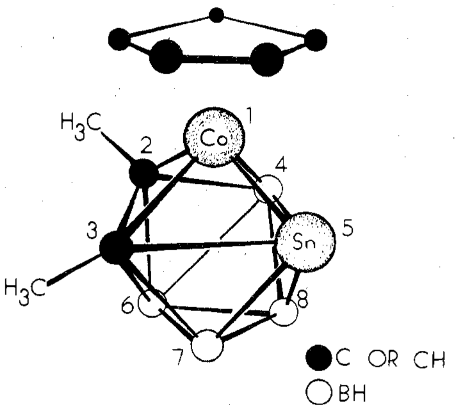

Figure 2. Proposed structure of (η^5-C_5H_5)$CoSn(CH_3)_2C_2B_4H_4$.

$$Sn(CH_3)_2C_2B_4H_4 \xrightarrow[-2CO]{(C_5H_5)Co(CO)_2} (C_5H_5)CoSn(CH_3)_2C_2B_4H_4$$

$$\xrightarrow{-Sn} (C_5H_5)Co(CH_3)_2C_2B_4H_4$$

An analogous displacement of lead by cobalt was observed in the reactions of II and IV with the cobalt reagent, but in these cases no mixed-metal species were obtained.

A possible structure for V is depicted in Figure 2. We assume that this 18 skeletal electron, $2n + 2$ system obeys the usual electron-counting rules[16] which dictate, in this case, a closo cage (all faces triangular) of eight vertices. While there are a number of ways to arrange the Sn, Co, two C, and four B atoms on such a polyhedron, the scope of possibilities is limited by (1) the absence of a low-field signal in the ^{11}B NMR spectrum, which implies that there are no four-coordinate BH units adjacent to cobalt,[12,18] (2) the facile elimination of tin to generate the 1,2,3-CoC_2B_4 cage, indicating that the framework carbon atoms remain adjacent[19] in V, (3) the nonequivalence of the CH_3 groups, as shown by the ^1H NMR spectrum, and (4) our earlier observations[17,20,21] that the insertion of a second metal atom by direct gas-phase reaction into a monometallocarborane tends to occur at a location adjacent to the first metal atom, even if the second metal must thereby assume a low-coordinate vertex.

The structure proposed in Figure 2 is consistent with these restrictions and is plausible in that its formation by cobalt insertion into 1,2,3-$Sn(CH_3)_2C_2B_4H_4$ (geometry shown in Figure 1) is readily visualized. It will be noted that ejection of tin from V and subsequent linkage of cobalt to B(7) and B(8) produce 1,2,3-$(C_5H_5)Co(CH_3)_2C_2B_4H_4$, in accordance with observation.

In common with several other eight-vertex boron cage systems,[22] it would not be surprising if V exhibited fluxional behavior in solution; indeed, the observation of only two ^{11}B NMR signals rather strongly implies that this is the case. One possible mechanism involves the reversible cleavage of the C(3)–B(6) link and formation of a C(2)–B(7) bond, producing a time-averaged NMR geometry in which the C(2)–C(3)–B(7)–B(6) group forms an open square. An attractive feature of such a process is that both CH_3–C units assume an average framework coordination number of 4.5, which is consistent with the ^1H NMR observation of very similar chemical shifts for the two methyl resonances and also allows each carbon to spend part of its time in a low-coordinate situation.

Summary

These findings together with earlier studies of icosahedral group 4 carboranes indicate that although heteroatoms of germanium, tin, and lead can be inserted into carborane polyhedra under certain conditions, this chemistry is limited in versatility and is not likely to rival the transition metal metallocarboranes of which several hundred have been characterized.[23] Nevertheless, the *closo*-$MC_2B_{n-2}H_n$ species are interesting electronic systems in respect to the unusual environment of the "bare" metal atoms with their unshared electron pairs directed away from the polyhedral surface. A ^{119}Mössbauer examination[24] of $SnC_2B_9H_{11}$ at 77 K established that the valence state of tin in this molecule is Sn(II) and disclosed an isomer shift and quadrupole splitting which are highly atypical for tin. Similar studies of the small stanna- and plumbacarboranes as well as x-ray structure determinations (which have not yet been conducted for any group 4 carborane) will be the subject of future investigations.

Experimental Section

Materials. 2,4-Dicarba-*closo*-heptaborane(7) ($C_2B_5H_7$) was purchased from Chemical Systems, Inc., Irvine, Calif., and purified by GLC (30% Apiezon L on Chromosorb W) at 35–45 °C. Solutions of sodium 2,3-dicarba-*nido*-hexaborate(1–) ($NaC_2B_4H_7$) and sodium 2,3-dimethyl-2,3-dicarba-*nido*-hexaborate(1–) ($Na(CH_3)_2C_2B_4H_5$) in tetrahydrofuran (THF) were prepared from 2,3-$C_2B_4H_8$ and 2,3-$(CH_3)_2C_2B_4H_6$ as described elsewhere.[25] Germanium diiodide (INC, Inc.), stannous chloride (PCR, Inc.), lead(II) bromide (Alfa), and other reagents were reagent grade and used as received. THF was dried over $LiAlH_4$ before use. All other solvents were dried over 4–8 mesh molecular sieve beads (Davidson) and saturated with dry nitrogen or degassed before use.

Spectra. Boron-11 FTNMR spectra at 32.1 MHz and proton FTNMR spectra at 100 MHz were obtained on a JEOL-PS-100P pulse Fourier transform spectrometer interfaced to a JEOL Texas Instrument EC-100 computer system. Unit-resolution mass spectra were obtained on a Hitachi Perkin-Elmer RMU-6E mass spectrometer. High-resolution mass spectra were recorded on an AEI MS-902 double-focusing instrument equipped with an SRI chemical ionization source and interfaced to a PDP-8I computer. All high-resolution spectra were obtained under chemical ionizing conditions in argon–water. Infrared spectra were recorded on a Beckman IR-8 instrument.

General Procedures. Except where otherwise indicated, all reactions were run in a high-vacuum system or in an inert atmosphere. Thin-layer and preparative-layer chromatography studies were conducted in air or in an inert atmosphere on precoated plates of silica gel F-254 purchased from Brinckmann Instruments, Inc.

Reaction of $Na_2C_2B_5H_7$ with $SnCl_2$. Finely divided sodium metal (2.6 mmol) and ca. 2.0 mmol of naphthalene were placed in a 25 mL flask under a nitrogen atmosphere. The flask was transferred to a vacuum line and about 10 mL of THF was added. The mixture was allowed to stir at room temperature for about 5 h, during which all of the sodium was consumed. 2,4-$C_2B_5H_7$ (2.5 mmol) was distilled *in vacuo* into the mixture and stirred at room temperature for 5 h. During the course of the reaction a color change from green to amber was noted. The carborane solution was filtered into a 50-mL flask containing 2.3 mmol of $SnCl_2$ in 5 mL of THF under vacuum at –196 °C. The reaction vessel was then slowly warmed to room temperature, and the solution became dark brown as a black material precipitated. After the mixture was stirred magnetically for 1.5 h at room temperature, all volatile materials were distilled into a –196 °C trap. The mixture of THF and other volatiles was repeatedly passed through a –31 °C cold trap several times in order to remove most of the THF and then passed through a –45 °C trap several times to remove the last traces of THF. A 0.28-mmol quantity of 2,4-$C_2B_5H_7$ was recovered and was identified from its gas-phase infrared spectrum. The resulting dark brown to black reaction residue in the reaction vessel was opened under nitrogen atmosphere and a vacuum sublimator was attached to the vessel. After most of the naphthalene was removed by sublimation at room temperature, the collection tube was replaced by a clean sublimator cooled to –78 °C, and the residue was heated at 70 °C under vacuum (10^{-4} to 10^{-5} Torr). Over an 8-h period a very small amount (~1 mg) of pale white and brown substances was slowly collected on the –78 °C cold finger. A mass spectrum of the sublimate exhibited major groupings having cutoffs at *m/e* 210 and 198, corresponding to the $^{124}SnC_2B_5H_7^+$ and $^{124}SnC_2B_4H_6^+$ parent ions, respectively. Attempts to separate this mixture did not succeed. Reactions of $Na_2C_2B_5H_7$ with $PbBr_2$ and GeI_2 conducted under essentially identical conditions produced small quantitities of 2,4-$C_2B_5H_7$ but did not yield other isolable products.

Reaction of $Na^+C_2B_4H_7^-$ with $SnCl_2$. A THF solution of $Na^+C_2B_4H_7^-$ was prepared by distillation of 2,3-$C_2B_4H_8$ (3.0 mmol) onto NaH (6.0 mmol) in 15 mL of THF in vacuo. The solution was filtered in the vacuum line onto anhydrous $SnCl_2$ (3.1 mmol) at –196 °C in a 100 mL round-bottom flask. The reaction vessel was placed in an ice bath; as the solution warmed to 0 °C, it changed slowly from pale yellow to amber to reddish brown, with formation of a black precipitate. No evolution of gas was detected. After stirring of the mixture for 0.5–1 h followed by removal of THF and a small amount of 2,3-$C_2B_4H_8$ via vacuum distillation over a 5-h period, dry nitrogen was introduced into the reaction vessel and the vessel was quickly attached to a vacuum sublimator. On heating of the dark residue at 70–120 °C under vacuum (10^{-4} to 10^{-5} Torr), off-white $SnC_2B_4H_6$ (I) mixed together with a thick yellow liquid collected slowly on the dry ice cooled (–78 °C) cold finger. After 8 h, nitrogen was introduced into the flask, and the flask was removed to a nitrogen-filled glovebag. The product (I) was washed from the cold finger with degassed methylene chloride to a 100-mL round-bottom flask, CH_2Cl_2 was removed via vacuum distillation, and the material was resublimed at room temperature to give ca. 3 mg of pure I.

Reaction of $PbBr_2$ with $Na^+C_2B_4H_7^-$. A THF solution of $Na^+C_2B_4H_7^-$ (2.0 mmol) was added to 2.0 mmol of $PbBr_2$ in 5 mL of THF, and the reaction and workup were conducted exactly as in the reaction of $SnCl_2$ described above. A 3-mg quantity of $PbC_2B_4H_6$ (II) was collected on a dry ice cooled finger by sublimation at room temperature and 10^{-4} to 10^{-5} Torr from the yellowish brown reaction residue which contained black solids. Pure II is a light yellow, easily sublimable solid which undergoes thermal decomposition at room temperature in vacuo but can be stored indefinitely at 0 °C.

Reaction of GeI_2 with $Na^+C_2B_4H_7^-$. A THF solution of $Na^+C_2B_4H_7^-$ (2.0 mmol) was added to 2.0 mmol of GeI_2 in THF, and the reaction and subsequent workup were conducted as in the $SnCl_2$ reaction. Heating the red-orange reaction residue at 100 °C and 10^{-4} Torr caused a small quantity of yellowish red material to sublime onto the dry ice cooled cold finger. The mass spectrum of this material contained groupings having cutoffs at *m/e* 354 and 150 which may be assigned to $(C_2B_4H_7)_2{}^{76}GeHI$ and $^{76}GeC_2B_4H_6$, but all attempts at separation of the mixture resulted in decomposition.

Reaction of $SnCl_2$ with $Na^+[(CH_3)_2C_2B_4H_5]^-$. In a procedure identical with that employed in the synthesis of $SnC_2B_4H_6$ (I) above, 7.0 mmol of $Na^+[(CH_3)_2C_2B_4H_5]^-$ was allowed to react with 7.0 mmol of $SnCl_2$ in THF. Following the reaction, the workup and purification of $Sn(CH_3)_2C_2B_4H_4$ (III) were conducted by two different methods. (a) After the removal of THF via vacuum distillation for 8 h, dry nitrogen was introduced into the reaction vessel and the vessel was quickly attached to a vacuum sublimator. On heating of the dark brown reaction residue at about 120 °C and 10^{-4} to 10^{-5} Torr, off-white $Sn(CH_3)_2C_2B_4H_4$ (III) collected slowly on the dry ice cooled cold finger. Purification of III was achieved by resublimation at room temperature and 10^{-5} Torr.

(b) After the removal of THF via vacuum distillation for 5 h, the dark brown reaction residue was dissolved in degassed methylene chloride and filtered under dry nitrogen into a 1 × 40 cm Pyrex tube which had one end closed and the other end equipped with a vacuum stopcock and ball joint. After removal of solvent by vacuum distillation, the stopcock was closed and the bottom of the tube was immersed in a 120 °C bath. The stopcock was opened occasionally to remove THF vapor which had been trapped in the residue. After 7–8 h, semitransparent needles had deposited on the cold surface of the tube.

The vessel was opened in a nitrogen-filled glovebag, the lower portion containing the gray-brown nonvolatile residue was cut off and removed, and the $Sn(CH_3)_2C_2B_4H_4$ (III) was washed with degassed methylene chloride and resublimed at room temperature to produce 50 mg (4% yield) of pure product.

Reaction of $PbBr_2$ with $Na^+[(CH_3)_2C_2B_4H_5]^-$. A 4.0-mmol quantity of the carborane salt in THF was allowed to react with 3.9 mmol of $PbBr_2$ in a procedure identical with the preceding synthesis. Sublimation of $Pb(CH_3)_2C_2B_4H_4$ (IV) from the yellowish-brown residue at room temperature onto a −78 °C cold finger gave 22 mg of light yellow product.

Reaction of $Sn(CH_3)_2C_2B_4H_4$ (III) with $(\eta^5\text{-}C_5H_5)Co(CO)_2$. A "hot–cold" reactor, consisting of a cylindrical Pyrex tube 24 mm in diameter and equipped with a greaseless Teflon stopcock at one end for attachment to the vacuum line, was charged with 1.2 mmol of $Sn(CH_3)_2C_2B_4H_4$ and 1.8 mmol of $(\eta^5\text{-}C_5H_5)Co(CO)_2$. The central portion of the tube was maintained at 150 °C by a Variac-controlled heating tape while the lower end was held at 70 °C in an oil bath. After 24 h the tube was cooled in liquid nitrogen and the noncondensables were removed on the vacuum line. On warming of the system to room temperature the volatile materials were removed by distillation. Extraction of the residue with methylene chloride gave a dark brown solution which was separated by preparative thin-layer chromatography. Development on silica gel plates with a 2:1 chloroform–hexane mixture gave yellow $1,2,3\text{-}(\eta^5\text{-}C_5H_5)Co(CH_3)_2C_2B_4H_4$ (100 mg, 0.48 mmol, R_f 0.77) identified from its ^{11}B NMR and mass spectra,[13] and dark red $(\eta^5\text{-}C_5H_5)CoSn(CH_3)_2C_2B_4H_4$ (V) (20 mg, 0.06 mmol; R_f 0.58). A trace of $(\eta^5\text{-}C_5H_5)_2Co_2(CH_3)_2C_2B_4H_4$[12,17] was also obtained and identified from its mass spectroscopic cutoff at m/e 350. The partial decomposition of V to produce $(\eta^5\text{-}C_5H_5)Co(CH_3)_2C_2B_4H_4$ was observed during development on silica gel; most of the latter compound could be removed by vacuum sublimation onto a −78 °C cold finger, leaving behind the less volatile V.

The reaction of the same two reagents in refluxing n-nonane at 151 °C under dry nitrogen for 4 h, followed by elution of the dark brown residue on silica gel with hexane, gave $(\eta^5\text{-}C_5H_5)Co(CH_3)_2C_2B_4H_4$ but no V was detected.

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Registry No. I, 63181-06-6; II, 63181-05-5; III, 63181-04-4; IV, 63181-03-3; V, 63230-65-9; $Na_2C_2B_5H_7$, 63230-64-8; $Na^+[(CH_3)_2C_2B_4H_5]^-$, 54244-93-8; $Na^+C_2B_4H_7^-$, 63231-39-0; $PbBr_2$, 10031-22-8; GeI_2, 13573-08-5; $SnCl_2$, 7772-99-8; $(\eta^5\text{-}C_5H_5)Co(CO)_2$, 12078-23-8; $1,2,3\text{-}(\eta^5\text{-}C_5H_5)Co(CH_3)_2C_2B_4H_4$, 50932-66-6; $(\eta^5\text{-}C_5H_5)_2Co_2(CH_3)_2C_2B_4H_4$, 63269-89-6.

References and Notes

(1) (a) R. W. Rudolph, R. L. Voorhees, and R. E. Cochoy, *J. Am. Chem. Soc.*, **92**, 3351 (1970); (b) R. L. Voorhees and R. W. Rudolph, *ibid.*, **91**, 2173 (1969); (c) V. Chowdhry, W. R. Pretzer, D. N. Rai, and R. W. Rudolph, *ibid.*, **95**, 4560 (1973).

(2) L. J. Todd, A. R. Burke, H. T. Silverstein, J. L. Little, and G. S. Wikholm, *J. Am. Chem. Soc.*, **91**, 3376 (1969).

(3) G. S. Wikholm and L. J. Todd, *J. Organomet. Chem.*, **71**, 219 (1974).

(4) D. C. Beer and L. J. Todd, *J. Organomet. Chem.*, **50**, 93 (1973).

(5) R. E. Loffredo and A. D. Norman, *J. Am. Chem. Soc.*, **93**, 5587 (1971).

(6) (a) M. L. Thompson and R. N. Grimes, *Inorg. Chem.*, **11**, 1925 (1972); (b) A. Tabereaux and R. N. Grimes, *ibid.*, **12**, 792 (1973).

(7) (a) C. G. Savory and M. G. H. Wallbridge, *Chem. Commun.*, 622 (1971); (b) C. G. Savory and M. G. H Wallbridge, *J. Chem. Soc., Dalton Trans.*, 918 (1972).

(8) A review of group 4 carborane chemistry is given by R. N. Grimes, *Rev. Silicon, Germanium, Tin Lead Compd.*, in press.

(9) R. N. Grimes, W. J. Rademaker, M. L. Denniston, R. F. Bryan, and P. T. Greene, *J. Am. Chem. Soc.*, **94**, 1865 (1972).

(10) L. G. Sneddon, D. C. Beer, and R. N. Grimes, *J. Am. Chem. Soc.*, **95**, 6623 (1973).

(11) R. N. Grimes, *Pure Appl. Chem.*, **39**, 455 (1974), and references therein.

(12) V. R. Miller and R. N. Grimes, *J. Am. Chem. Soc.*, **95**, 2830 (1973).

(13) R. N. Grimes, D. C. Beer, L. G. Sneddon, V. R. Miller, and R. Weiss, *Inorg. Chem.*, **13**, 1138 (1974).

(14) 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. Am. Chem. Soc.*, **90**, 879 (1968).

(15) T. P. Onak, R. P. Drake, and G. B. Dunks, *Inorg. Chem.*, **3**, 1686 (1964).

(16) (a) K. Wade, *Adv. Inorg. Chem. Radiochem.*, **18**, 1 (1976), and references therein; (b) R. E. Williams, *ibid.*, **18**, 67 (1976); (c) R. W. Rudolph, *Acc. Chem. Res.*, **9**, 446 (1976).

(17) V. R. Miller, L. G. Sneddon, D. C. Beer, and R. N. Grimes, *J. Am. Chem. Soc.*, **96**, 3090 (1974).

(18) W. J. Evans, G. B. Dunks, and M. F. Hawthorne, *J. Am. Chem. Soc.*, **95**, 4565 (1973).

(19) This observation is consistent with the finding[20] that $1,2,3\text{-}(\eta^5\text{-}C_5H_5)CoC_2B_4H_6$ requires much higher temperature (400 °C) for rearrangement than was employed in the synthesis of V.

(20) V. R. Miller and R. N. Grimes, *J. Am. Chem. Soc.*, **97**, 4213 (1975).

(21) W. M. Maxwell, V. R. Miller, and R. N. Grimes, *J. Am. Chem. Soc.*, **98**, 4818 (1976).

(22) (a) F. N. Tebbe, P. M. Garrett, and M. F. Hawthorne, *J. Am. Chem. Soc.*, **90**, 869 (1968); (b) F. Klanberg, D. R. Eaton, L. J. Guggenberger, and E. L. Muetterties, *Inorg. Chem.*, **6**, 1271 (1967); (c) M. L. Thompson and R. N. Grimes, *J. Am. Chem. Soc.*, **93**, 6677 (1971).

(23) For a comprehensive review of metallocarborane chemistry see R. N. Grimes in "Organometallic Reactions and Syntheses", Vol. 6, Plenum Press, New York, N.Y., 1977, Chapter 2, pp 63–221.

(24) R. W. Rudolph and V. Chowdhry, *Inorg. Chem.*, **13**, 248 (1974).

(25) T. Onak and G. B. Dunks, *Inorg. Chem.*, **5**, 439 (1966).

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Hydrogen–Deuterium Exchange between MBH_4 and MBD_4 (M = Li, Na). Isotope Effects on the ^1H and ^{11}B NMR Spectra of the BH_nD_{4-n} Anions and a Discussion of Exchange Reactions in Some Covalent Tetrahydroborate Systems

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The ^1H NMR spectra of lithium and sodium borohydrides, in various solvents, have been recorded. The resulting chemical shift and coupling constant data do not yield any clear indications of variations in solution structure. Hydrogen–deuterium exchange between $LiBH_4$ and $LiBD_4$ occurs in some ethereal solvents yielding a mixture of partially substituted species, $LiBH_nD_{4-n}$ (n = 0 to 4). These observations are relevant to the isotopic distribution in the products of exchange reactions involving some covalent borohydrides. Isotope effects in the ^1H and ^{11}B NMR spectra of $LiBH_nD_{4-n}$ (THF solvent) and $NaBH_nD_{4-n}$ (alkaline aqueous solvent) are described. Chemical shifts (^{11}B and ^1H) and coupling constants, $J(^{11}B\text{–}H)$, decrease approximately monatonically with deuterium substitution. These isotope effects are considered to arise from the modification of the vibrational characteristics of the $(BH_nD_{4-n})^-$ species.

Introduction

In 1952, Brown and co-workers demonstrated that tritium gas exchanged with the hydrogen in lithium and sodium tetrahydroborates at elevated temperatures.[2] Their method was later extended by Mesmer and Jolly into a convenient preparation for KBD_4, in which the anions BH_3D^-, $BH_2D_2^-$, and BHD_3^- were shown to occur as intermediates.[3] It has since been demonstrated[4] that a mixture of $LiBH_4$ and $LiBD_4$