Selected bond distances and angles are presented in Table V. The Co-N distances and angles are typical of complexes of first-row transition metal ions with this ligand. There are no unusual features in this regard.

Summary

The 1,5-cyclooctanediylbis(pyrazol-1-yl)borate ligand is in many ways preferable to the other known dialkylbis(pyrazol-1-yl)borates for the study of C-H-M interactions, as it has a single bridgehead hydrogen well-directed at the coordinated metal. Not only is the ligand readily prepared from convenient starting materials, but its salts and complexes are more stable to storage and have better crystallinity. L* is quite flexible and adapts itself through distortion of other ligands present on the metal. This flexibility suggests the use of L* in situations where it may act as a temporary blocker of a coordination site on the metal, which can be unblocked later under appropriate conditions.

Supplementary Material Available: Listings of crystal data (Table S1), thermal parameters (Tables S2 and S6), hydrogen atom positions (Tables S3 and S7), and all bond distances and angles (Tables S4 and S8) (11 pages); listings of observed and calculated structure factors (Tables S5 and S9) (29 pages). Ordering information is given on any current masthead page.

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Synthesis and Chemistry of $B_{11}H_{11}Sn^{2-}$ and Its Germanium and Lead Analogues. Crystal Structure of $[B_{11}H_{11}SnCH_3]PPh_3CH_3{\cdot}CH_2Cl_2$

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The heteroborane dianions $B_{11}H_{11}E^{2-}$ (E = Ge, Sn) have been prepared in good yield starting with the $B_{11}H_{14}^-$ ion, ECl_2, and *n*-butyllithium. The $B_{11}H_{11}Pb^{2-}$ ion was made from $B_{11}H_{14}^-$ and $PbCl_2$ in aqueous sodium hydroxide solution. Methylation of the respective heteroborane dianion formed the $B_{11}H_{11}GeCH_3^-$ and $B_{11}H_{11}SnCH_3^-$ ions in good yield. The compound $[1\text{-}CH_3\text{-}1\text{-}SnB_{11}H_{11}]PPh_3CH_3{\cdot}CH_2Cl_2$ has been characterized by a single-crystal X-ray structure determination (space group $P\bar{1}$, $a = 11.659$ (3) Å, $b = 13.580$ (3) Å, $c = 9.980$ (2) Å, $\alpha = 109.65$ (1)°, $\beta = 94.91$ (1)°, $\gamma = 99.83$ (1)°, $Z = 2$).

Introduction

In the 1970's, Union Carbide developed a synthesis of $B_{11}H_{14}^-$ which gave the anion in 63% isolated yield as an alkyl ammonium salt. With sodium borohydride as the starting material, the overall chemical reaction of this process is as follows:[1,2]

$$17NaBH_4 + 20BF_3{\cdot}O(C_2H_5)_2 \xrightarrow[105\ ^\circ C]{\text{diglyme solvent}} 15NaBF_4 + 2NaB_{11}H_{14} + 20H_2 + 20O(C_2H_5)_2$$

It has been demonstrated that this product can be made safely in pilot plant quantities using simple equipment. Thus, the $B_{11}H_{14}^-$ ion has become an attractive starting material for the production of higher boron hydride derivatives because it is accessible from $NaBH_4$ by a safe procedure using general laboratory glassware.

We have previously investigated the syntheses of several icosahedral heteroboranes of the type $B_{11}H_{11}E$ using $B_{11}H_{14}^-$ as the starting reagent. Thus, reaction of $NaB_{11}H_{14}$ with excess $NaHSeO_3$ or solid TeO_2 in a water/heptane mixture at room temperature over 24 h formed $B_{11}H_{11}Se$ or $B_{11}H_{11}Te$ in 18% and 25% yield, respectively.[3] More recently we have found that $HNEt_3[B_{11}H_{14}]$ will react with KOH/As_2O_3 in water to form the $B_{11}H_{11}As^-$ ion in 48% yield.[4] An anhydrous protocol was employed to form the $B_{11}H_{11}Sb^-$ and $B_{11}H_{11}Bi^-$ ions. Treatment of $Me_3NH[B_{11}H_{14}]$ with excess butyllithium followed by $SbCl_3$ or $BiCl_3$ formed $B_{11}H_{11}Sb^-$ and $B_{11}H_{11}Bi^-$ in 13% and 25% yields, respectively.[5,6] Similar results for the syntheses of the $B_{11}H_{11}E^-$ (E = As, Sb, Bi) ions were recently reported by Frange and co-workers.[7]

There have been many examples of the incorporation of Ge, Sn, and Pb atoms into carborane structures.[8] For example, reaction of $1,2\text{-}C_2B_9H_{11}^{2-}$ with the element dihalides EX_2 (E = Sn, Ge, Pb) formed the icosahedra $1,2,3\text{-}(CH)_2EB_9H_9$.[9] A similar series of smaller carborane derivatives such as $(CH)_2EB_4H_4$ (E = Ge, Sn, Pb)[10] and the trimethylsilyl-containing compounds $1\text{-}E\text{-}2\text{-}[Si(CH_3)_3]\text{-}2,3\text{-}C_2B_4H_5$ (E = Si, Ge, Sn) have been reported.[11-14] For most of the compounds reported, the group 14 element is in the +2 oxidation state. More recently, the first fully cage-incorporated silacarborane derivatives have been reported.[15,16] For most of these compounds, the silicon atom is in the +4 oxidation state.

The incorporation of group 14 elements into boron hydride cage structures has not been investigated as extensively. Bridge-substituted compounds having the general formula $R_3MB_5H_8$ (M = Si, Ge, Sn, Pb) were formed in the low-temperature reaction of LiB_5H_8 with R_3MX (X = Cl, Br, I). In the presence of a Lewis base, these compounds isomerized to $2\text{-}R_3MB_5H_8$ compounds in

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which the R_3M group is attached via a single bond to the exterior of the pentaborane cage.[17,18] The nido 11-atom derivatives $(CH_3)_2MB_{10}H_{12}$ (M = Ge, Sn) have been prepared by reaction of $NaB_{10}H_{13}$ with Me_2SnCl_2.[19,20] In a more recent report, $(Ph_4As)_2B_{10}H_{12}$ was reacted with $SnCl_2$ and R_2SnCl_2 to form the dianion products $(Ph_4As)_2B_{10}H_{12}SnCl_2$ and $(Ph_4As)_2B_{10}H_{12}SnR_2Cl_2$, respectively.[21] These two interesting compounds have ^{119}Sn Mössbauer isomer shifts of δ 3.17 ± 0.03 mm s^{-1} and δ 1.75 ± 0.01 mm s^{-1}, suggesting that they are Sn^{II} and Sn^{IV} compounds, respectively.

Recently, an unexpected route for the synthesis of 1,2-$(CH_3Si)_2B_{10}H_{10}$ from $B_{10}H_{14}$ was discovered.[22] This is the first silicon analogue of the extensively-studied class of compounds known as *ortho*-carboranes (e.g., 1,2-$(CH_3C)_2B_{10}H_{10}$). The two silicon atoms of this new compound are formally in the +4 oxidation state.

In this paper, we describe the use of the $B_{11}H_{14}^-$ ion to prepare $B_{11}H_{11}E^{2-}$ (E = Ge, Sn, Pb) salts. The germanium- and tin-containing dianions can be alkylated. The single-crystal X-ray structure determination of one of these alkylated derivatives will also be described.

Experimental Section

Physical Measurements. Boron (^{11}B) NMR spectra were obtained at 115.85 MHz with a Nicolet NT-360 spectrometer and were externally referenced to $BF_3{\cdot}O(C_2H_5)_2$ (positive values downfield). Proton NMR spectra were recorded on the same instrument at 361.1 MHz and were referenced to residual solvent protons. Proton chemical shift values were reported relative to tetramethylsilane. Tin (^{119}Sn) NMR spectra were recorded on the same instrument at 134.61 MHz and were externally referenced to Me_4Sn (positive values downfield). Infrared spectra were obtained on a Perkin-Elmer 283 spectrometer as KBr wafers. Melting points were obtained in sealed, evacuated capillaries and are uncorrected. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, NY. The ^{119m}Sn Mössbauer spectrum was recorded at 77.7 ± 0.06 K on a Ranger Engineering constant-acceleration spectrometer equipped with a proportional counter and with $Ca^{119m}SnO_3$ (New England Nuclear Corp.) used as the γ-ray source. The zero velocity was based upon $CaSnO_3$, and velocity calibrations were based on β-tin and natural iron foils. Standard, nonlinear least-squares techniques were used to fit the data to Lorentzian curves.

Materials. All reactions were performed under an atmosphere of prepurified nitrogen, while the workup and isolation of products were performed in air. Tetrahydrofuran (THF) was freshly distilled from sodium benzophenone ketyl and stored under nitrogen. Anhydrous stannous chloride ($SnCl_2$) was obtained from the dihydrate according to a published procedure.[23] Germanium diiodide (Alfa), lead chloride ($PbCl_2$, Fisher), and methyl iodide (Aldrich) were used as received. *n*-Butyllithium (Aldrich) was purchased as a 2.5 M solution in hexane and titrated prior to use.[24] The $B_{11}H_{14}^-$ ion was prepared by the method of Dunks and co-workers[25] and was utilized as the trimethylammonium salt after crystallization from ethanol.

Preparation of $[Ph_3PCH_3]_2[B_{11}H_{11}Sn]$ (1). A 100-mL, three-neck flask fitted with two pressure-equalized dropping funnels with septa, nitrogen inlet, and magnetic stir bar was charged with $[(CH_3)_3NH][B_{11}H_{14}]$ (2.00 g, 10.4 mmol). The system was evacuated and flushed with nitrogen prior to addition of THF (40 mL) via syringe. Into one dropping funnel, *n*-butyllithium (18.6 mL, 46.6 mmol) was added by syringe. The reaction vessel was cooled to 0 °C with an ice bath, and the *n*-butyllithium was added dropwise at a rate of 0.5 mL/min. The resulting white suspension was allowed to stir for an additional 30 min. Anhydrous stannous chloride (2.95 g, 15.5 mmol) was cannula transferred to the remaining funnel as a suspension in THF (30 mL) and added at a rate of 0.5 mL/min. The resulting brown-orange solution was allowed to stir for an additional 4 h at ambient temperature. The solvent was removed by rotary evaporation, and the residue was extracted twice with 20-mL aliquots of 1 M aqueous NaOH. The extract was filtered through a fine sintered-glass frit and then was precipitated by addition of aqueous triphenylmethylphosphonium bromide. The white precipitate was filtered and dried in vacuo, yielding 7.5 g of $[Ph_3PCH_3]_2[B_{11}H_{11}Sn]$ (90% yield). Organic impurities were removed by crystallization from ethylene dichloride, yielding 7.3 g of crystalline product. The ^{11}B NMR data of **1** and related compounds are presented in Table II. Infrared spectrum of **1** (KBr): 3060 (w), 2985 (m), 2907 (m), 2470 (s), 2390 (sh), 1590 (m), 1487 (m), 1445 (s), 1435 (sh), 1390 (m), 1340 (m), 1325 (m), 1280 (m), 1170 (m), 1120 (s), 1080 (sh), 1030 (s), 1000 (m), 950 (w), 910 (sh), 900 (s), 872 (w), 795 (m), 752 (s), 750 (sh), 722 (s), 690 (s), 673 (sh), 650 (m), 520 (m), 510 (m), 490 (sh), 440 (w) cm^{-1}.

Table I. Crystallographic Data for $[B_{11}H_{11}SnCH_3]PPh_3CH_3{\cdot}CH_2Cl_2$

chem formula	$C_{21}H_{34}B_{11}Cl_2PSn$	space group	$P\bar{1}$
a, Å	11.659 (3)	*T*, °C	−156
b, Å	13.580 (3)	λ, Å	0.71069
c, Å	9.980 (2)	ρ_{calcd}, g cm^{-3}	1.435
β, deg	94.94 (1)	μ(Mo Kα), cm^{-1}	11.367
V, $Å^3$	1448.73	*R*	0.0315
Z	2	R_w	0.0329
fw	625.98		

Preparation of $Ph_3PCH_3[B_{11}H_{11}SnCH_3]$ (2). Compound **1** (2.00 g, 2.49 mmol) was added to a 100-mL two-neck flask fitted with a nitrogen inlet, stir bar, and septum. The system was evacuated and flushed with nitrogen prior to the addition of THF (30 mL) via syringe. Methyl iodide (0.60 mL, 9.6 mmol) was added by syringe, and the suspension was allowed to stir for 5 h at room temperature resulting in an orange suspension. The solvent was removed in vacuo, and the crude product was washed with two 5-mL aliquots of distilled water to extract excess triphenylmethylphosphonium iodide. The crude product was dried under vacuum and crystallized from CH_2Cl_2/5% hexane (v/v), giving 1.2 g of $[Ph_3PCH][B_{11}H_{11}SnCH_3]$ in 89% yield. Anal. Calcd for $C_{20}H_{32}B_{11}PSn$: C, 44.4; H, 5.96. Found: C, 43.7; H, 5.82. ^1H NMR (acetone-d_6): δ 1.66 (3 H, $SnCH_3$), 2.87 (3 H, P–CH_3) (J_{PH} = 13 Hz). ^{119}Sn NMR (acetone-d_6): δ −196.5. IR (KBr): 2870 (m), 2800 (m), 2500 (s), 2450 (sh), 1582 (m), 1478 (m), 1431 (s), 1380 (m), 1315 (w), 1255 (w), 1190 (w), 1160 (w), 1110 (s), 1022 (s), 995 (sh), 890 (s), 780 (w), 735 (s), 710 (m), 680 (s), 500 (s), 485 (sh) cm^{-1}.

Preparation of $[(CH_3)_4N]_2[B_{11}H_{11}Ge]$ (3). The method of synthesis is the same as that employed for compound **1**. The orange residue obtained after rotary evaporation of the reaction mixture was dissolved in 40 mL of aqueous 1 M NaOH, and the extract was filtered through a fine sintered-glass frit. The filtrate was treated with concentrated tetramethylammonium chloride solution, giving a white precipitate which was filtered and dried, giving $[(CH_3)_4N]_2[B_{11}H_{11}Ge]$ (90% yield). Organic impurities were removed by precipitation from CH_2Cl_2 with hexane. IR (KBr): 3010 (m), 2500 (s), 2470 (sh), 1486 (s), 1402 (m), 1320 (w), 1030 (w), 950 (s), 920 (sh) cm^{-1}.

Preparation of $(CH_3)_4N[B_{11}H_{11}GeCH_3]$ (4). A 100-mL two-neck flask equipped with magnetic stir bar, nitrogen inlet, and septum was charged with $[(CH_3)_4N]_2[B_{11}H_{11}Ge]$ (2.0 g, 5.7 mmol), evacuated, and flushed with nitrogen. THF (30 mL) was added via syringe, followed by the addition of methyl iodide (1.09 mL, 17.1 mmol). The suspension was allowed to stir for 8 h at room temperature, during which time it changed in color from white to orange. The solvent was removed in vacuo, and the solid was recrystallized from an acetone/10% water (v/v) mixture, giving 1.5 g of $(CH_3)_4N[B_{11}H_{11}GeCH_3]$ (90% yield). ^1H NMR (acetone-d_6): δ 1.39 (3 H, $GeCH_3$), 3.46 [12 H, $N(CH_3)_4$]. IR (KBr): 3025 (m), 2922 (w), 2510 (s), 2350 (sh), 1480 (s), 1415 (m), 1388 (w), 1032 (s), 952 (m), 827 (m), 732 (m), 648 (m), 302 (m) cm^{-1}.

Preparation of $[(CH_3)_4N]_2[B_{11}H_{11}Pb]$ (5). In a well-ventilated hood, aqueous NaOH (2.0 M, 20 mL) was added to a 50-mL Erlenmeyer flask equipped with magnetic stir bar. Solid $[(CH_3)_3NH][B_{11}H_{14}]$ (0.500 g, 2.59 mmol) was added, and the suspension was allowed to stir until everything dissolved (approximately 30 min). Lead chloride ($PbCl_2$) (1.50 g, 5.40 mmol) was added, and the solution was allowed to stir for 4 h. The resulting gray suspension was filtered with a medium sintered-glass frit and the filtrate was treated with concentrated tetramethylammonium hydroxide solution. Hydrochloric acid (1.0 M) was added dropwise with stirring until the solution had reached pH 8 to enhance precipitation. The suspension was filtered with a fine sintered-glass frit and dried in vacuo, yielding 0.71 g of $[(CH_3)_4N]_2[B_{11}H_{11}Pb]$ (56%). IR (KBr): 3005 (m), 2450 (s), 2350 (sh), 1478 (s), 1381 (m), 1025 (s), 947 (s), 725 (w), 675 (s) cm^{-1}.

X-ray Structure Determination for $Ph_3PCH_3[B_{11}H_{11}SnCH_3]{\cdot}CH_2Cl_2$. Crystals of **2** were obtained by crystallization from CH_2Cl_2 and 5%

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Table II. ^{11}B NMR Data for $B_{11}H_{11}E^{2-}$ (E = Ge, Sn, Pb) Salts and Their Methylated Derivatives

compd	solvent	rel areas	chem shift, ppm ($J_{^{11}B-H}$, Hz) B(12)	B(2–6)	B(7–11)
$[Ph_3PCH_3]_2[B_{11}H_{11}Sn]$ (**1**)	*a*	1:5:5	−5.1 (125)	−10.6[d]	−11.9
$Ph_3PCH_3[B_{11}H_{11}SnCH_3]$ (**2**)	*b*	1:5:5	−10.9 (136)	−16.6	−15.9
$[(CH_3)_4N]_2[B_{11}H_{11}Ge]$ (**3**)	*c*	1:5:5	−5.0 (135)	−9.6	−11.1
$(CH_3)_4N[B_{11}H_{11}GeCH_3]$ (**4**)	*b*	1:5:5	−10.9 (134)	−16.2	−14.6
$[(CH_3)_4N]_2[B_{11}H_{11}Pb]$ (**5**)	*c*	1:5:5	−2.9	−5.0 (122)[e]	−10.3 (129)

[a] DMSO solvent. [b] Acetone solvent. [c] DMF solvent. [d] $J_{^{11}B-^{117,119}Sn}$ = 59 ± 2 Hz. [e] $J_{^{11}B-^{207}Pb}$ = 260 Hz.

hexane (v/v). A suitable small clear crystal was selected and transferred to the goniostat where it was cooled to −156 °C for characterization and data collection.[26] A systematic search of a limited hemisphere of reciprocal space yielded a set of reflections which exhibited no symmetry (other than a center) and no systematic extinctions. The reflections were indexed on a triclinic lattice, and the choice of the centrosymmetric space group $P\bar{1}$ was confirmed by the subsequent solution and refinement of the structure. The crystal diffracted very strongly, and the data collection was carried out to $2\theta = 55°$. A total of 10032 reflections were collected. After data processing and averaging of equivalent reflections, 6677 unique reflections remained. The *R* for the averaging was 0.023 for 2918 reflections measured more than once. Of the unique data, 6058 reflections were considered observed by the criterion $\geq 3.0{*}\sigma(F)$. Details concerning crystal and data collection are summarized in Table I. The crystal structure was solved by a combination of direct methods and Fourier techniques. The Sn atom was located by MULTAN, and the remaining atoms were located in successive difference maps. The asymmetric unit contains one $B_{11}H_{11}SnMe$ anion, one PPh_3Me cation, and one molecule of methylene chloride as solvent. All hydrogen atoms were located in a difference map following initial refinement of the non-hydrogen atoms. The full-matrix least-squares refinement was completed using anisotropic thermal parameters on the non-hydrogen atoms and isotropic thermal parameters on the hydrogen atoms. The final *R* was 0.032. The final difference map was essentially featureless; the largest peak was 0.7 e/Å^3 in the vicinity of the Sn atom. The closest approach between the anion and the cation is 3.60 Å for C(13) to C(18), the closest approach from the solvent to the anion is 3.71 Å for Cl(34) to B(10), and the closest approach from the solvent to the cation is 3.50 Å for Cl(34) to C(32).

Results and Discussion

The reaction of $[(CH_3)_3NH]B_{11}H_{14}$ with 4 equiv of *n*-butyllithium followed by addition of 1 equiv of a metal halide (GeI_2 or $SnCl_2$) at 0 °C in tetrahydrofuran produced the closo heteroborane anions $B_{11}H_{11}E^{2-}$ (E = Ge, Sn) in good yield as illustrated in the following equation:

$$[(CH_3)_3NH]B_{11}H_{14} + 4n\text{-BuLi} + GeI_2 \text{ (or } SnCl_2) \xrightarrow[\text{THF}]{0\ °C} B_{11}H_{11}E^{2-}$$

$$E = Ge, Sn$$

All samples of the $B_{11}H_{11}E^{2-}$ products were contaminated by small amounts of the $B_{11}H_{11}{}^{2-}$ ion. While these impurities prevented the acquisition of an acceptable elemental analysis, the compounds were characterized by ^1H, ^{11}B, and, for the tin compound, ^{119}Sn NMR spectroscopy. In addition, these salts could be directly converted to methylated derivatives which were fully characterized (vide infra). Allowing the pot temperature, in the reactions described above, to rise above 0 °C resulted in increased formation of the $B_{11}H_{11}{}^{2-}$ ion byproduct. The synthesis of the lead derivative was achieved by the reaction of $[(CH_3)_3NH][B_{11}H_{14}]$ in 2.0 M aqueous NaOH with $PbCl_2$.

The ^{11}B NMR spectra of compounds **1**, **3**, and **5** (see Table II) have a 1:5:5 area ratio pattern of doublets consistent with an icosahedral structure. A two-dimensional (^{11}B–^{11}B) NMR study of **1**, **3**, and **5** clearly showed that the low-field resonance of area one was cross-coupled to the highest field resonance of area five. The high-field resonance is thus assigned to the five boron atoms not adjacent to the hetero atom. This assignment was further confirmed by performing line narrowing of the proton-decoupled ^{11}B NMR spectrum of **1**. The area five resonance of −10.6 ppm (assigned to B2–B6) exhibits satellite peaks due to spin coupling with the adjacent tin atom (^{117}Sn, 7.61% natural abundance; ^{119}Sn, 8.58% natural abundance; $J_{^{11}B-^{117,119}Sn}$ = 59 ± 2 Hz).

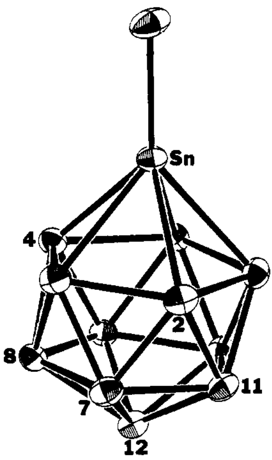

Figure 1. ORTEP drawing of the $B_{11}H_{11}SnCH_3{}^-$ ion. (The numbering system for the cage structure is included.)

Table III. Selected Interatomic Distances for $[B_{11}H_{11}SnCH_3]PPh_3{\cdot}CH_2Cl_2$

Sn(1)–C(13)	2.105 (3)	B(10)–B(5)	1.774 (4)
Sn(1)–B(5)	2.288 (3)	B(10)–B(6)	1.772 (4)
Sn(1)–B(6)	2.295 (3)	B(11)–B(7)	1.794 (4)
Sn(1)–B(2)	2.306 (3)	B(11)–B(6)	1.775 (4)
Sn(1)–B(3)	2.299 (3)	B(11)–B(2)	1.771 (4)
Sn(1)–B(4)	2.291 (3)	B(7)–B(8)	1.794 (4)
B(12)–B(9)	1.773 (4)	B(7)–B(2)	1.782 (4)
B(12)–B(10)	1.785 (4)	B(7)–B(3)	1.787 (4)
B(12)–B(11)	1.782 (4)	B(8)–B(3)	1.780 (4)
B(12)–B(7)	1.787 (4)	B(8)–B(4)	1.770 (4)
B(12)–B(8)	1.777 (4)	B(5)–B(6)	1.909 (4)
B(9)–B(10)	1.788 (4)	B(5)–B(4)	1.909 (4)
B(9)–B(8)	1.781 (4)	B(6)–B(2)	1.904 (4)
B(9)–B(5)	1.775 (4)	B(2)–B(3)	1.915 (4)
B(9)–B(4)	1.775 (4)	B(3)–B(4)	1.891 (4)
B(10)–B(11)	1.789 (4)		

The proton-decoupled ^{11}B NMR spectrum of **5** clearly showed lead-207 to boron spin coupling ($J_{^{11}B-^{207}Pb}$ = 260 Hz) on the −5.0 ppm resonance. The size of the lead satellite peaks is consistent with the ^{207}Pb natural abundance of 22.6%. Poorly-resolved lead–boron coupling ($J_{^{11}B-^{207}Pb}$ = 175 Hz) was previously reported for $1\text{-Pb-}2,3\text{-}C_2B_9H_{11}$ from the 32.1-MHz ^{11}B NMR spectrum.[9]

The $B_{11}H_{11}E^{2-}$ (E = Ge, Sn) ions reacted at room temperature in 5–8 h with methyl iodide in THF to form orange $B_{11}H_{11}ECH_3{}^-$ ions. This contrasts sharply with the carboranyl–tin derivatives [i.e., $2,3\text{-}(CH_3)_2\text{-}1\text{-Sn-}2,3\text{-}C_2B_9H_9$ and $2,3\text{-}[Si(CH_3)_3]_2\text{-}1\text{-Sn-}2,3\text{-}C_2B_4H_4$], which show no tendency to use the lone pair of electrons on the tin atom to interact with Lewis acids such as BF_3 nor with electrophiles such as CH_3I or $CH_3SO_3CF_3$.[11,27] The lead derivative **5** did not react with methyl iodide under similar reaction conditions to those used for **1** and **3**.

The structure of **2** was determined by a single-crystal X-ray structure study. The structure of the monoanion of **2** is illustrated

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Table IV. ^{119m}Sn Mössbauer Data for Tin-Containing Boron Cage Compounds

compd	IS, mm/s	QS, mm/s	ref
3-Sn-1,2-$C_2H_2B_9H_9$	4.67 ± 0.04	3.86 ± 0.04	32
2,3-$(Me_3Si)_2$-1,2,3-$SnC_2B_4H_4$	3.253 ± 0.008	2.743 ± 0.010	33
1-Sn(bpy)-2,3-$(Me_3Si)_2$-2,3-$C_2B_4H_4$	3.102 ± 0.012		33
$(Ph_4As)_2[B_{10}H_{12}SnCl_2]$	3.17 ± 0.03		21
$(Ph_4As)_2[B_{10}H_{12}Sn(CH_3)_2Cl_2]$	1.75 ± 0.01		21

in Figure 1. The distorted icosahedral geometry for this anion is confirmed. The methyl–Sn vector of this anion is slightly bent away from the 5-fold axis defined by the tin atom and B(12) of the icosahedral cage. This small distortion is probably due to crystal packing forces. A similar type of distortion was observed previously for $CH_3PB_{11}H_{11}$.[28]

The Sn–B bond distances of **2** (Table III) were found to be in the range of 2.288 (3)–2.306 (3) Å. This is very similar to the Sn–B bond distances of *nido*-1-(bipyr)-1-Sn-2,3-$(CH_3)_2$-2,3-$C_2B_9H_9$, which are in the range 2.35 (2)–2.56 (2) Å.[27] The X-ray structure studies of two other related icosahedral heteroboranes $MeAlB_{11}H_{11}^{2-}$ and $MePB_{11}H_{11}$ have been reported.[28,29] In these studies, the Al–B and P–B distances were found to be in the range 2.131 (4)–2.140 (4) Å and 1.927 (2)–1.978 (3) Å, respectively. There is also the expected lengthening of the B–B distances of the B_2–B_6 ring in each of these heteroborane derivatives relative to the B–B distance of $B_{12}H_{12}^{2-}$.

A two-dimensional ^{11}B–^{11}B NMR study of **2** and **4** clearly showed that the low-field resonance of area one was cross-coupled to the *lowest field resonance* of area five. Thus, there is a switch in assignments of the area five resonances when the $B_{11}H_{11}E^{2-}$ compounds and their methylated derivatives are compared. No tin–boron coupling was observed in the line-narrowed, proton-decoupled ^{11}B NMR spectrum of **2**.

The ^{119}Sn NMR spectra of **1** (triethylammonium salt) and **2** contained single, broad resonances at −546 ($W_{1/2}$ = 690 ± 23 Hz) and −196.5 ppm ($W_{1/2}$ = 330 ± 2 Hz), respectively. The ^{119}Sn signal for **2** narrowed considerably ($W_{1/2}$ = 51 ± 0.1 Hz) with proton decoupling. This suggested that there is unresolved proton coupling between the ^{119}Sn nucleus and the attached methyl group in the undecoupled spectrum of **2**. Generally, the lower oxidation state of ^{119}Sn is found at higher fields.[30] Unfortunately, the chemical shift ranges for reported Sn(II) and Sn(IV) compounds[31] overlap badly and are strongly solvent-dependent, so that no definitive statement can be made about the oxidation state of the tin atoms in **1** and **2** on the basis of the ^{119}Sn NMR data. The neutral Sn(II) derivative, 2,3-$(Me_3Si)_2$-1,2,3-$SnC_2B_4H_4$, has a ^{119}Sn chemical shift of −205.9 ppm, which is quite different from our dianion Sn(II) derivative (**1**).

The ^{119}Sn Mössbauer spectra of several tin-containing boron cage compounds have been reported previously as illustrated in Table IV. In general, Sn(II) compounds exhibit an isomer shift of 2.3–4.2 mm s^{-1} and Sn(IV) compounds have an isomer shift of less than 2.0 mm s^{-1}.[34–36] Thus, the isomer shift values suggest that all the compounds in Table IV contain Sn(II) atoms with the exception of the last compound, which has a Sn(IV) atom within the $B_{10}H_{12}Sn(CH_3)_2Cl_2^{2-}$ ion.

Table V. Fractional Coordinates and Isotropic Thermal Parameters for $[B_{11}H_{11}SnCH_3]PPh_3CH_3\cdot CH_2Cl_2$

	10^4x	10^4y	10^4z	$10B_{iso}$, Å^2
Sn(1)	5498.6 (2)	5053.7 (1)	7509.7 (2)	14
B(2)	6321 (3)	3949 (2)	5730 (3)	17
B(3)	6953 (2)	4128 (2)	7653 (3)	16
B(4)	5679 (2)	3847 (2)	8617 (3)	14
B(5)	4247 (2)	3502 (2)	7316 (3)	13
B(6)	4650 (3)	3566 (2)	5529 (3)	15
B(7)	6874 (3)	2927 (2)	6153 (3)	17
B(8)	6486 (2)	2865 (2)	7829 (3)	15
B(9)	4922 (2)	2508 (2)	7633 (3)	13
B(10)	4323 (2)	2347 (2)	5844 (3)	14
B(11)	5530 (3)	2605 (2)	4930 (3)	16
B(12)	5660 (3)	1935 (2)	6175 (3)	15
C(13)	5567 (3)	6711 (2)	8315 (3)	24
P(14)	8400 (1)	10219.2 (5)	12482 (1)	12
C(15)	7536 (3)	10289 (2)	13895 (3)	19
C(16)	7479 (2)	10105 (2)	10882 (3)	14
C(17)	7516 (2)	9332 (2)	9553 (3)	17
C(18)	6851 (3)	9318 (2)	8308 (3)	21
C(19)	6170 (3)	10081 (3)	8410 (3)	25
C(20)	6141 (3)	10849 (3)	9724 (4)	25
C(21)	6789 (2)	10867 (2)	10969 (3)	20
C(22)	9099 (2)	9096 (2)	12156 (3)	14
C(23)	10320 (2)	9245 (2)	12182 (3)	17
C(24)	10853 (2)	8374 (2)	11931 (3)	21
C(25)	10189 (3)	7359 (2)	11636 (3)	21
C(26)	8969 (3)	7204 (2)	11600 (3)	19
C(27)	8421 (2)	8070 (2)	11869 (3)	16
C(28)	9534 (2)	11406 (2)	12958 (3)	14
C(29)	10252 (2)	11809 (2)	14310 (3)	20
C(30)	11207 (3)	12657 (2)	14610 (3)	23
C(31)	11436 (2)	13113 (2)	13581 (3)	21
C(32)	10726 (3)	12727 (2)	12256 (3)	21
C(33)	9779 (2)	11863 (2)	11931 (3)	18
Cl(34)	−49 (1)	4738 (1)	6758 (1)	29
C(35)	1286 (3)	5563 (3)	6710 (4)	29
Cl(36)	2152 (1)	6139 (1)	8422 (1)	48
H(1)	574 (3)	112 (3)	583 (4)	30 (8)
H(2)	446 (3)	206 (2)	820 (3)	17 (6)
H(3)	348 (3)	178 (3)	529 (4)	23 (7)
H(4)	552 (3)	221 (3)	380 (4)	27 (7)
H(5)	768 (3)	275 (3)	577 (4)	22 (7)
H(6)	704 (3)	263 (3)	857 (3)	19 (6)
H(7)	339 (3)	365 (2)	770 (3)	17 (6)
H(8)	406 (3)	371 (3)	473 (3)	20 (6)
H(9)	675 (3)	435 (3)	510 (4)	22 (7)
H(10)	779 (3)	467 (2)	826 (3)	10 (5)
H(11)	571 (3)	417 (2)	975 (3)	16 (6)
H(12)	569 (4)	696 (3)	925 (5)	39 (9)
H(13)	602 (5)	705 (4)	786 (6)	61 (12)
H(14)	486 (5)	683 (4)	799 (6)	63 (13)
H(15)	801 (3)	1038 (3)	1474 (4)	23 (7)
H(16)	711 (3)	1087 (3)	1402 (4)	34 (8)
H(17)	700 (3)	962 (3)	1366 (4)	30 (8)
H(18)	797 (3)	884 (2)	952 (3)	13 (6)
H(19)	688 (3)	878 (3)	739 (4)	30 (8)
H(20)	575 (3)	1003 (3)	759 (4)	31 (8)
H(21)	574 (3)	1138 (3)	982 (4)	30 (8)
H(22)	676 (3)	1140 (3)	1183 (4)	22 (7)
H(23)	1076 (3)	987 (3)	1237 (4)	25 (7)
H(24)	1164 (3)	849 (3)	1196 (4)	23 (7)
H(25)	1054 (3)	681 (3)	1144 (3)	20 (6)
H(26)	853 (3)	650 (3)	1141 (3)	21 (7)
H(27)	762 (3)	794 (2)	1187 (3)	13 (6)
H(28)	1005 (3)	1152 (3)	1498 (4)	20 (7)
H(29)	1166 (3)	1290 (3)	1551 (4)	33 (8)
H(30)	1204 (3)	1369 (2)	1378 (3)	13 (6)
H(31)	1086 (3)	1307 (3)	1160 (4)	24 (7)
H(32)	931 (3)	1159 (3)	1105 (3)	19 (6)
H(33)	181 (4)	513 (4)	610 (5)	51 (11)
H(34)	110 (4)	618 (3)	640 (4)	41 (9)

The tin-119m Mössbauer spectrum of solid Ph_3PCH_3-$[B_{11}H_{11}SnCH_3]$ at 77 K exhibits a typical, small, positive isomer shift, 1.177 ± 0.010 mm s^{-1} relative to $BaSnO_3$, characteristic of the formal tin(IV) oxidation state. The quadrupole splitting (0.946

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± 0.010 mm s^{-1}) is well resolved and is consistent with the expected low axial symmetry at the tin coordination center.

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Supplementary Material Available: Complete listings of crystallographic details, anisotropic thermal parameters, and bond lengths and angles (9 pages); a listing of observed and calculated structure factors (16 pages). Ordering information is given on any current masthead page. A complete MSC structure report (No. 87158) is available on request from the Indiana University Chemistry Library.

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[Tris(3-*tert*-butylpyrazolyl)hydroborato]beryllium Hydride: Synthesis, Structure, and Reactivity of a Terminal Beryllium Hydride Complex

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The terminal beryllium hydride complex {η^3-HB(3-Bu^{t}pz)$_3$}BeH (3-Bu^{t}pz = 3-$C_3N_2Bu^tH_2$) has been synthesized by the reactions of either {η^3-HB(3-Bu^{t}pz)$_3$}BeCl or {η^3-HB(3-Bu^{t}pz)$_3$}BeBr with $LiAlH_4$. The molecular structure of {η^3-HB(3-Bu^{t}pz)$_3$}BeH has been investigated by X-ray diffraction, thus determining d(Be–H) = 1.23 (7) Å. ^{1}H NMR studies on {η^3-HB(3-Bu^{t}pz)$_3$}BeH have determined the magnitude of $^1J_{^9\text{Be–H}}$ to be 28 Hz, the first report of $^1J_{^9\text{Be–H}}$ for a terminal beryllium hydride moiety. IR studies demonstrate that the Be–H stretching frequency is observed at 1865 cm^{-1} and shifts to 1410 cm^{-1} ($\nu_H/\nu_D = 1.32$) upon deuterium substitution. Other half-sandwich [tris(pyrazolyl)hydroborato]beryllium complexes of the series {η^3-HB(3-Bu^{t}pz)$_3$}BeX (X = Cl, Br, I, SH) have also been synthesized, and the molecular structure of the bromide derivative {η^3-HB(3-Bu^{t}pz)$_3$}BeBr has been determined by X-ray diffraction. The series of complexes {η^3-HB(3-Bu^{t}pz)$_3$}BeX (X = H, Cl, Br, I, SH) have been investigated by ^{9}Be NMR spectroscopy and are characterized by ^{9}Be resonances in the range δ 1–4 ppm (relative to $[Be(H_2O)_4]^{2+}$). {η^3-HB(3-Bu^{t}pz)$_3$}BeH is rhombohedral, *R*3*m* (No. 160), with a = 15.739 (3) Å, b = 15.739(3) Å, c = 8.228 (3) Å, α = 90.0°, β = 90.0°, γ = 120.0°, V = 1765.3 (8) Å^3, and Z = 3. {η^3-HB(3-Bu^{t}pz)$_3$}BeBr is monoclinic, *Pn* (No. 7), with a = 8.455 (1) Å, b = 15.242(3) Å, c = 9.643 (2) Å, β = 100.54 (1)°, V = 1221.8 (4) Å^3, and Z = 2.

Introduction

Our recent investigations have described the use of the sterically demanding tris(3-*tert*-butylpyrazolyl)hydroborato ligand, [HB(3-Bu^{t}pz)$_3$]$^-$ (3-Bu^{t}pz = 3-$C_3N_2Bu^tH_2$),[1] to provide a well-defined coordination environment for zinc and magnesium, which has allowed an investigation of the synthesis and reactivity of 4-coordinate monomeric zinc and magnesium alkyl and hydride derivatives {η^3-HB(3-Bu^{t}pz)$_3$}MR (M = Zn, Mg) and {η^3-HB(3-Bu^{t}pz)$_3$}ZnH.[2-4] Here we report the first tris(pyrazolyl)hydroborato complexes of beryllium and, in particular, the synthesis and characterization of the terminal hydride complex {η^3-HB(3-Bu^{t}pz)$_3$}BeH.

Results

The [tris(pyrazolyl)hydroborato]beryllium halide complexes {η^3-HB(3-Bu^{t}pz)$_3$}BeCl and {η^3-HB(3-Bu^{t}pz)$_3$}BeBr are readily obtained by reaction of Tl{η^3-HB(3-Bu^{t}pz)$_3$} with $BeCl_2 \cdot xH_2O$ and $BeBr_2(OEt_2)_2$, respectively (eq 1). The molecular structure of

$$\text{BeX}_2 + \text{Tl}\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\} \xrightarrow{\text{Et}_2\text{O}} \{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}\text{BeX} + \text{TlX} \quad (1)$$

the bromide derivative {η^3-HB(3-Bu^{t}pz)$_3$}BeBr has been determined by X-ray diffraction, as shown in Figure 1. Selected bond lengths and angles are presented in Tables I and II, with atomic coordinates in Table III.

The hydride derivative {η^3-HB(3-Bu^{t}pz)$_3$}BeH is obtained by metathesis of either {η^3-HB(3-Bu^{t}pz)$_3$}BeCl or {η^3-HB(3-Bu^{t}pz)$_3$}BeBr with $LiAlH_4$ in Et_2O at room temperature (Scheme I). However, the reaction of $LiAlH_4$ with {η^3-HB(3-Bu^{t}pz)$_3$}BeBr proceeded faster than that with {η^3-HB(3-Bu^{t}pz)$_3$}BeCl. The deuteride derivative {η^3-HB(3-Bu^{t}pz)$_3$}BeD was obtained by the corresponding reaction with $LiAlD_4$ in benzene. The molecular structure of {η^3-HB(3-Bu^{t}pz)$_3$}BeH has also been determined by X-ray diffraction, as shown in Figure 2. Selected bond lengths and angles are presented in Tables IV and V, with atomic coordinates in Table VI.

Table I. Selected Bond Lengths (Å) for {η^3-HB(3-Bu^{t}pz)$_3$}BeBr

Be–Br	2.122 (7)	Be–N(12)	1.793 (8)
Be–N(22)	1.788 (8)	Be–N(32)	1.810 (7)
N(11)–N(12)	1.377 (6)	N(11)–B	1.506 (7)
N(21)–N(22)	1.386 (6)	N(21)–B	1.541 (8)
N(31)–N(32)	1.382 (6)	N(31)–B	1.534 (8)

Table II. Selected Bond Angles (deg) for {η^3-HB(3-Bu^{t}pz)$_3$}BeBr

Br–Be–N(12)	117.2 (3)	Br–Be–N(22)	117.2 (4)
Br–Be–N(32)	114.1 (4)	N(12)–Be–N(22)	100.7 (4)
N(12)–Be–N(32)	102.2 (4)	N(22)–Be–N(32)	103.2 (4)
N(12)–N(11)–B	121.6 (4)	Be–N(12)–N(11)	107.3 (4)
N(22)–N(21)–B	119.5 (4)	Be–N(22)–N(21)	108.5 (4)
N(32)–N(31)–B	120.2 (4)	Be–N(32)–N(31)	107.7 (4)
N(11)–B–N(21)	107.6 (4)	N(11)–B–N(31)	107.5 (5)
N(21)–B–N(31)	104.6 (4)		

The reactivity of {η^3-HB(3-Bu^{t}pz)$_3$}BeH, leading to the formation {η^3-HB(3-Bu^{t}pz)$_3$}BeI and {η^3-HB(3-Bu^{t}pz)$_3$}BeSH, is illustrated in Scheme I. The series of complexes {η^3-HB(3-Bu^{t}pz)$_3$}BeX (X = H, Cl, Br, I, SH) have been investigated by ^{9}Be NMR spectroscopy, and the data are presented in Table VII, while ^{1}H and ^{13}C NMR data on all new compounds are presented in Table VIII.

Discussion

The cyclopentadienyl ligand has played a central role in the development of the organometallic chemistry of the transition metals due to its ability to stabilize well-defined coordination environments.[5] However, the cyclopentadienyl ligand frequently exhibits a variety of coordination modes with s- and p-block

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