cm^{-1}) of the nitrile group was observed.

Reductive Silylation of 1. General Procedure. In a dry flask equipped with a magnetic stirring bar, flushed with an inert gas, and stoppered with a septum were introduced lithium sand (3.2 g, 450 mmol), THF (40 mL), and TMCS (42 g, 400 mmol); the mixture was cooled to −10 °C. Nitrile 1 (50 mmol) was added via syringe: an exothermic reaction took place and the reaction mixture turned progressively cloudy due to the formation of lithium chloride and cyanide. The temperature of the mixture was kept at 0 °C for 6 h and then left at ambient temperature with stirring overnight. Precipitated salts and unreacted lithium were eliminated by filtration, washed with brine until neutral, extracted with ether, and dried over sodium sulfate. Solvents and low-boiling materials were rotatory evaporated, a mixture of 3 and unreacted 1 was distilled off, and the residue was, in general, passed on a short column of silica gel (eluent hexane), yielding 2 as a colorless jellylike mass. Products 1 and 3 were separated by preparative gas chromatography.

In an effort to consume all of nitrile 1 engaged, the following variations from this general procedure were made but were unsuccessful:[13] lithium chips instead of lithium sand; lithium sand added in three portions during the course of the reaction; pieces of glass introduced in the reaction medium in order to scour the lithium, as the sand, which floated on the surface of the reaction mixture and progressively sank to the bottom; diluted reaction medium (three times with more solvent); large excess of trimethylchlorosilane (two times).

No significant changes in the yield of products 2 and 3 were observed. Moreover, contact times of the reactants were prolonged to 3 days and we observed competitive formation of hexamethyldisilane that occurred via a Barbier-type reaction in a yield directly proportional to the reaction time without any substantial progress in the formation of compounds 2 and 3.

Results and description of the products obtained are reported in Tables I (yields) and III–V.

Registry No. 1a, 18296-11-2; **1b**, 91390-80-6; **1c**, 40326-26-9; **1d**, 91409-34-6; **1e**, 91390-81-7; **1f**, 25438-35-1; **1g**, 24731-36-0; **1h**, 91390-82-8; **1i**, 91390-83-9; **1j**, 76454-61-0; **1k**, 88522-73-0; **1l**, 60550-36-9; **2q**, 91390-84-0; (*E*)-**2b**, 91390-85-1; (*Z*)-**2b**, 91390-92-0; **2c**, 91390-86-2; (*E*)-**2d**, 91390-87-3; (*Z*)-**2d**, 91390-93-1; **2e**, 91390-88-4; **2f**, 91390-89-5; **2g**, 91390-90-8; **2h**, 91409-35-7; (*E*)-**2k**, 91390-91-9; (*Z*)-**2k**, 91390-94-2; **3a**, 40965-53-5; **3b**, 91390-95-3; **3c**, 55942-13-7; **3d**, 91390-96-4; **3e**, 91390-97-5; **3f**, 60745-14-4; **3g**, 55942-15-9; **3h**, 91409-36-8; **3i**, 91390-98-6; **3j**, 91390-99-7; 4, 91391-00-3; TMCS, 75-77-4; Li, 7439-93-2; Me_3SiCN, 7077-24-9; $(Me_3Si)_2SO_4$, 18306-29-1; KCN, 151-50-8; ZnI_2, 10139-47-6; Me_2CO, 67-64-1; *n*-PrCOMe, 107-87-9; Et_2CO, 96-22-0; *n*-BuCOMe, 591-78-6; *t*-BuCHO, 630-19-3; $MeCOCH{=}CH_2$, 78-94-4; cyclobutanone, 1191-95-3; cyclopentanone, 120-92-3; cyclohexanone, 108-94-1; cycloheptanone, 502-42-1; 2,2,6,6-tetramethylcyclohexanone, 1195-93-3; adamantanone, 700-58-3.

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Chemistry of *C*-Trimethylsilyl-Substituted Stannacarboranes. 1. Synthesis, Characterization, and Tin-119 Mössbauer Effect Study of 1-Sn-2-[$Si(CH_3)_3$]-3-[R]-2,3-$C_2B_4H_4$ Derivatives [R = $Si(CH_3)_3$, CH_3, or H]

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The reaction of $Na^+[C\text{-}Si(CH_3)_3\text{-}C'\text{-}R\text{-}C_2B_4H_5]^-$ (R = $Si(CH_3)_3$, CH_3, or H) with $SnCl_2$ in THF produces $Sn[(CH_3)_3Si][R]C_2B_4H_4$ as a sublimable white solid in gram quantities. For each stannacarborane, the ^{119m}Sn Mössbauer effect spectrum exhibits a quadrupole split doublet, having an isomer shift (at 78 K) which is characteristic of tin in the tin(II) oxidation state. The isomer shift observed in the spectrum is significantly less positive than that associated with a "bare" Sn^{2+} ion, and these data differ from those reported for $(\eta^5\text{-}C_5H_5)_2Sn$ and $SnB_9C_2H_{11}$. The infrared spectra, mass spectra, ^1H, ^{11}B, ^{13}C, ^{29}Si, and ^{119}Sn NMR, and ^{119m}Sn Mössbauer spectra of these compounds are all consistent with a pentagonal-bipyramidal structure with the tin atom occupying an apical position and directing its unshared electron-pair outward from the polyhedron. All the stannacarboranes quantitatively react with anhydrous HCl in THF to yield the corresponding neutral carboranes. The stannacarboranes do not react with $BH_3\cdot THF$ or BF_3 to form electron donor–acceptor complexes.

Introduction

Polyhedral carboranes in which a Group 4A heteroatom is present either as an integral part of the cage framework, except silicon,[1-3] or in a B–M^{IV}–B three-center, two-electron bond on the open face of a carborane skeleton,[4,5] with the exception of carbon, have been synthesized. More recently, Wong and Grimes described[6] the synthesis of

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Table I. Summary of ^{119m}Sn Mössbauer Data

sample	I	II	III
IS(78 K), mm s^{-1} [a]	3.253 ± 0.008	3.281 ± 0.008	3.233 ± 0.010
d(IS)/dT, mm s^{-1} K^{-1}		5.4 × 10^{-4}	4.4 × 10^{-4}
correl coeff (n)		0.88 (10)	0.97 (10)
QS (78 K), mm s^{-1} [a]	2.743 ± 0.010	2.743 ± 0.010	2.790 ± 0.010
d(ln A)/dT, K^{-1}	2.11 × 10^{-2}	2.32 × 10^{-2}	1.54 × 10^{-2}
correl coeff (n)[b]	0.999 (6)	0.995 (10)	0.989 (10)
Γ[c]	0.819 ± 0.043	0.883 ± 0.020	0.963 ± 0.031
R	1.29 ± 0.05	0.957 ± 0.040	d
T range, K	78–120	78–140	81–170

[a] The quoted errors are those derived from computer reduction of the data and do not reflect systematic experimental errors in the data. [b] n is the number of data points used to effect the linear regression. [c] The two components of the quadrupole doublet spectra had equal line widths within the quoted errors. No systematic broadening of either component was observed. [d] R value appears to be temperature dependent; going from a low-temperature limit of 0.90 ± 0.01 at 78 K to ~0.87 at 170 K.

several lower homologues of the $MC_2B_{n-2}H_n$ (M = Sn, Pb, or Ge) series as well as a novel cage system that incorporated both main-group and transition metals. These substances were obtained in yields less than 5%; typically, 3–25 mg was produced in reactions involving 2–4 mmol of carborane. A closo species of the type $MC_2B_{n-2}H_n$ is an interesting electronic system because of the unusual configuration involving a "bare" metal atom being incorporated in a polyhedron with its unshared electron pair directed away from the polyhedral surface. A ^{119m}Sn Mössbauer examination[7] of $SnC_2B_9H_{11}$ at 77 K established that the tin was present in this molecule as Sn(II) and had an isomer shift and quadrupole splitting that were highly atypical for tin. A similar study on the small stannacarboranes has not been reported to date.

Recently, we have developed[8] several high-yield methods for the preparation of air-stable *C*-trimethylsilyl-substituted $C_2B_4H_8$ [dicarbahexaborane(8)] derivatives. These carboranes *C*-$Si(CH_3)_3$-*C'*-R-$C_2B_4H_6$ and their sodium salts are highly reactive toward $M_3(CO)_{12}$ and $M'X_2$ (M = Os, Ru, or Fe; M' = main-group or transition metal; X = Cl, Br, or I) even in the absence of a solvent.[9] In almost all of the reactions involving these species, single products are formed in very high yield and are isolatable in gram quantities. Here we describe the preparation, characterization, ^{119m}Sn Mössbauer study, and some chemical properties of *C*-trimethylsilyl-substituted 1-stanna-2,3-dicarba-*closo*-heptaborane derivatives.

Results and Discussion

The object of this work is to establish the versatility of *C*-trimethylsilyl-substituted $C_2B_4H_8$ derivatives as effective η^5-coordinate ligands for transition metals and group 4A metals.[10] In attempting to insert tin atoms into small carborane frameworks having bulky $Si(CH_3)_3$ groups, methods that have proven successful in incorporating transition metals[11] and group 4A metals[6] into other cage systems were followed.

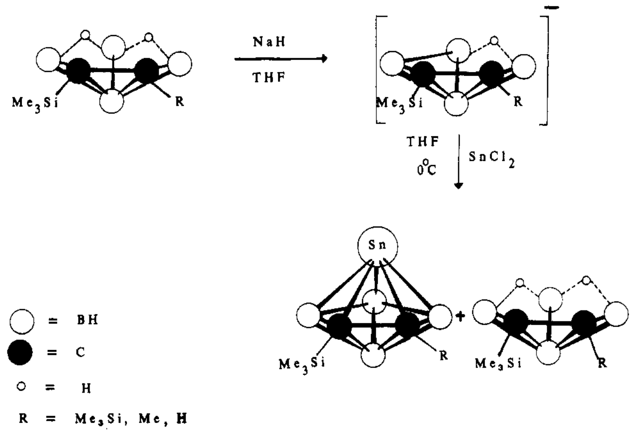

Figure 1. Reaction scheme showing proposed structure of stannacarboranes I, II, and III.

Reaction of $Na^+[C\text{-}Si(CH_3)_3\text{-}C'\text{-}R\text{-}C_2B_4H_5]^-$ with $SnCl_2$ in Tetrahydrofuran (THF). The reaction not only yielded a *closo*-stannacarborane, $Sn[(CH_3)_3Si]_2C_2B_4H_4$ (I), $Sn[(CH_3)_3Si][CH_3]C_2B_4H_4$ (II), or $Sn[(CH_3)_3Si]C_2B_4H_5$ (III), but also the corresponding neutral *nido*-carborane in nearly equimolar quantities (Figure 1).

In each of the reactions, a substantially large quantity of $SnCl_2$ also was recovered. All the stannacarboranes reacted readily with anhydrous HCl in dry THF according to eq 1 and produced the corresponding neutral carboranes in quantitative yields (see Experimental Section).

$$Sn[(CH_3)_3Si][R]C_2B_4H_4 + 2HCl \xrightarrow[THF]{0\,°C} [(CH_3)_3Si][R]C_2B_4H_6 + SnCl_2 \quad (1)$$

Reaction 1 is comparable to the one reported by Rudolph et al.[1a] and Norman et al. (who noted that $(CH_3)_2SnB_{10}H_{12}$ reacted readily with HCl to generate $B_{10}H_{14}$ and $(CH_3)_2SnCl_2$ in 95% yield[3]). The recovery of the neutral carborane in addition to large quantities of $SnCl_2$ from each reaction suggests that at least one or more of the competing reaction(s) given in eq 2 and 3 may occur.

$$Na^+[(Si(CH_3)_3)(R)C_2B_4H_5]^- + SnCl_2 \xrightarrow[THF]{0°C} Sn[(CH_3)_3Si][R]C_2B_4H_4 + NaCl + HCl \quad (2)$$

$$Na^+[((CH_3)_3Si)(R)C_2B_4H_5]^- + HCl \xrightarrow[THF]{0\,°C} [(CH_3)_3Si][R]C_2B_4H_6 + NaCl \quad (3)$$

The product ratios obtained in each reaction, coupled with eq 1, suggest that competing reactions, such as those given in eq 2 and 3, are involved in the synthesis of I, II, and III. Any HCl produced in reaction 2 would react via reaction 1 or 3.

Characterization of $Sn[(CH_3)_3Si][R]C_2B_4H_4$. Compounds I, II, and III were characterized from their ^{1}H, ^{11}B,

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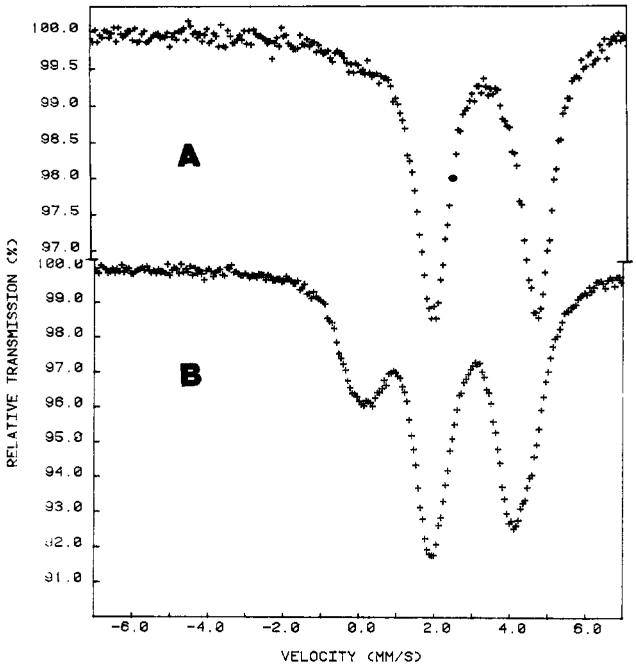

Figure 2. A. ^{119m}Sn Mössbauer spectrum of sample II at 82 K. The isomer shift scale is with respect to a $BaSnO_3$ absorber spectrum at 295 K. The intensity asymmetry is largely temperature independent and arises from preferential orientation of the sample with respect to the optical axis of the experiment. B. ^{119m}Sn Mössbauer spectrum of sample III that had been briefly exposed to air at room temperature at 83 K. A component of the absorption near 0 mm s^{-1} presumably arises from tin that has been oxidized to the +4 valent state.

^{13}C, ^{29}Si, and ^{119}Sn pulse Fourier transform NMR, IR, and mass spectra, elemental analysis, and ^{119m}Sn Mössbauer studies (Experimental Section and Table I) and were assigned the structures shown in Figure 1. Except for the large chemical shift of the ^{11}B resonances, the ^{11}B and ^1H NMR spectral data of I and II bear striking similarities to those of the $MC_2B_4H_6$ series and their dimethyl[6] and C-$Si(CH_3)_3$-C'-R-2,3-$C_2B_4H_6$ derivatives.[8] When R = H, the spectrum exhibits four signals of 1:1:1:1 ratio, indicating the presence of four nonequivalent borons. These peaks were not observed for II or $[(CH_3)_3Si]C_2B_4H_7$.[8] The ^{29}Si chemical shifts and ^{13}C NMR spectra of I, II, and III are also similar to those of the corresponding *nido*-carboranes,[8] except for the large shielding of the cage carbons. This large shielding is expected for all cage carbon atoms bonded to a metal.[9,12] A splitting of these cage carbon resonances owing to a $^1J(^{13}C-^{11}B)$ coupling was not observed, unlike their precursors, *nido*-$[(CH_3)_3Si][R]C_2B_4H_6$.[8] This splitting was also not observed for similar compounds in which a metal atom is in one of the apical positions.[9] The ^{119}Sn NMR spectra of I, II, and III exhibit very broad singlets with large negative chemical shifts. The broadness of these peaks is in accord with the NMR results for other nuclei bonded to boron atoms.[8,9]

The electron-impact (EI) mass spectra of I, II, and III (supplementary Table II) exhibit intense groupings with the major cutoffs at m/e 338, 280, and 266, corresponding to the parent ions, $^{120}Sn(^{12}CH_3)_6{}^{28}Si_2{}^{12}C_2{}^{11}B_4H_4{}^+$, $^{120}Sn(^{12}CH_3)_4{}^{28}Si^{12}C_2{}^{11}B_4H_4{}^+$, and $^{120}Sn(^{12}CH_3)_3{}^{28}Si^{12}C_2{}^{11}B_4H_5{}^+$, respectively.

Mössbauer Effect Study and Vibrational Spectroscopy of $Sn[(CH_3)_3Si][R]C_2B_4H_4$ Derivatives. The ^{119m}Sn Mössbauer data are summarized in Table I, and representative Mössbauer spectra are shown in Figure 2. From these data it is clear that there is a single (unique) metal atom in the structure of the compounds examined in the present study. The quadrupole-split doublets have an isomer shift (at 78 K) that is characteristic of tin in the tin(II) oxidation state. In contrast to the data reported for $SnB_9C_2H_{11}$ by Rudolph and Chowdry[7] and for the crown ether complexes of $Sn(ClO_4)_2$ by Herber et al.[13,14] both the isomer shift and quadrupole splitting observed in the present study are indicative of a significant covalent contribution to the bonding of the metal atom to its nearest-neighbor environment. It is also interesting to note that the Mössbauer parameters for the stannacarboranes differ significantly from those reported for $(\eta^5-C_5H_5)_2Sn$ by Harrison and Zuckerman,[15] especially in terms of the much larger quadrupole splittings observed in the present samples.

While the temperature dependence of the area under the resonance curve ($d(\ln A)/dT$) is nearly the same for I and II, it is some 30% smaller for III, indicating a significantly higher "Mössbauer temperature" for the latter. The present results suggest that in III the metal atom executes a significantly smaller thermal vibration than in I and II due to the reduced steric hindrance (with a hydrogen atom bonded to one of the cage carbon atoms) as compared to I (with a tetrahedral trimethylsilyl group) and II (with a tetrahedral methyl group).

Finally, in the context of the present discussion, it should be noted that a strong vibrational anisotropy with respect to the local symmetry axis through the metal atom should be observable as a temperature-dependent intensity asymmetry, the so-called Gol'danskii–Karyagin effect.[16-18] A careful examination of the present data show that for I and II this intensity ratio, which is given by

$$R(T) = A_+(T)/A_-(T)$$

(where A_+ and A_- are the areas of the quadrupole doublet component at velocities more and less positive than the spectrum centroid, respectively), is essentially temperature independent, whereas for III, this ratio shows a weak temperature dependence. Again, these data are suggestive of a closer approach of the metal atom to the carborane cage portion of the molecule in III as compared to I and II.

The considerable chemical reactivity of the present stannacarboranes can also be readily demonstrated by ^{119m}Sn Mössbauer effect spectroscopy. As already noted, a fresh sample of III gives rise to a resonance spectrum consisting of a well-resolved doublet. When such a sample is exposd even briefly to normal ambient (atmospheric) conditions and subsequently examined by Mössbauer spectroscopy, an additional absorption maximum at an isomer shift of ~0 mm s^{-1} appears along with the broadening of the line located at ~4.2 mm s^{-1} (Figure 2B). The former absorption quite probably has a contribution from tin oxidized to the +4 oxidation state while the latter may

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either arise from a singlet absorption of divalent tin or be part of a quadrupole doublet which is accompanied by a second component which overlies one of the majority tin atom resonance peaks. This chemical reactivity is also clearly evident in a comparison of the infrared spectra of the fresh and exposed samples of the stannacarboranes.

The IR assignments of the stannacarboranes I, II, and III (supplementary Table III) are in agreement with those of similar compounds reported by Rudolph et al.,[1a] Hosmane et al.,[19] and Grimes et al.[20]

The infrared spectrum of the (heterogeneous) material which was isolated from a sample of III stored in a vacuum dessicator after short exposure to air and moisture shows marked differences in part from the corresponding spectrum obtained with an unexposed sample. In particular, the three medium strong and sharp bands at 1126, 1064, and 975 cm^{-1} are almost completely missing in the spectrum of the stored sample, and the medium weak absorption at 1404 cm^{-1} becomes unresolved from the background.

Reaction of $Sn[(CH_3)_3Si][R]C_2B_4H_4$ with HCl, BH_3·THF, or BF_3. The stannacarboranes all reacted quantitatively with anhydrous HCl in THF at 0 °C to yield the corresponding neutral carborane as described in eq 1. However, these tin compounds failed to react with BH_3·THF or BF_3. The failure of I, II, and III to form electron-donor complexes with BF_3 or BH_3 is in line with the interpretation that the exo-polyhedral lone pair of electrons on the tin atom is diffuse, with relatively little directional character,[7,21] and that the metal atom shows a chemical behavior that is typical of Sn(II) bonded covalently to its nearest-neighbor atoms in the structure.

Summary

The proposed pentagonal-bipyramidal structure of *closo*-1-Sn-2-$[Si(CH_3)_3]$-3-[R]-2,3-$C_2B_4H_4$ (Figure 1) is consistent with its spectroscopic data, which has been unambiguously confirmed by our recent single-crystal X-ray diffraction study of II.[22] A detailed study of the chemistry of the $Sn[(CH_3)_3Si][R]C_2B_4H_4$ system is now being conducted and will be described in subsequent reports.

Experimental Section

Materials. 2,3-Bis(trimethylsilyl)-2,3-dicarba-*nido*-hexaborane(8), 2-(trimethylsilyl)-3-methyl-2,3-dicarba-*nido*-hexaborane(8), and 2-(trimethylsilyl)-2,3-dicarba-*nido*-hexaborane(8) were prepared by using methods described elsewhere.[8] Solutions of the sodium salts of these carborane anions, $Na^+[C\text{-}Si(CH_3)_3\text{-}C'\text{-}R\text{-}2,3\text{-}C_2B_4H_5]^-$ (R = $Si(CH_3)_3$, CH_3, or H), in THF were prepared by the method of Onak and Dunks.[23] Anhydrous tin(II) chloride was obtained from Johnson Matthey, Inc., Seabrook, NH, and used without further purification. Gaseous boron trifluoride and hydrogen chloride (Matheson, LaPorte, TX) were purified by passing through −120 °C traps in vacuo. Their purity was checked by IR spectroscopy. BH_3·THF (0.98 M solution in THF) was obtained from Alfa products, Danvers, MA. THF was dried over $LiAlH_4$ before use. All other solvents were dried over 4–8 mesh molecular sieve (Davidson) and either saturated with dry argon or degassed before use.

Spectroscopic Procedures. Boron-11, carbon-13, silicon-29, tin-119, and proton pulse Fourier transform NMR spectra at 64.2, 50.3, 39.76, 74.63, and 200 MHz, respectively, were recorded on an IBM-200SY multinuclear NMR spectrometer. Mass spectral data were obtained at Cornell University[24] using an AEI MS902/CI S-2 VG Data no. system 2040. Infrared spectra were obtained by using both dispersive and Fourier transform spectrometers. The former were run on a Perkin-Elmer Model 283 microprocessor controlled instrument, and the latter were acquired on an IBM Model 32 nitrogen-purged spectrometer in which 100–200 scans were taken at 2 cm^{-1} resolution. ^{119m}Sn Mössbauer spectra were obtained in the temperature range $78 \leq T \leq 160$ K by using the constant-acceleration spectrometer described earlier.[13] Spectrometer calibration was effected by using NBS SRM 0.85 mil iron foil and the magnetic hyperfine splitting data of Spijkerman et al.[25] Data reduction was carried out by using the SPECTRA program of Trooster and Viegers[26] modified to run on the Rutgers NAS-9000 computer. All isomer shifts are reported with respect to a reference spectrum of $BaSnO_3$ at 295 K obtained by using the same ^{119m}Sn Mössbauer source. All samples were examined as powders in high purity aluminum foil thermally clamped to copper sample holders mounted in a cryostat.[13] Elemental analyses were obtained from Galbraith Laboratories, Knoxville, TN.

Synthetic Procedures. All experiments were carried out in Pyrex glass round-bottom flasks of 250-mL capacity, containing a magnetic stirring bar and fitted with a high vacuum Teflon valve. Nonvolatile substances were manipulated in evacuable glovebags under an atmosphere of dry argon. All known compounds among the products were identified by comparing their infrared and ^{1}H NMR spectra with those of authentic samples.

Reaction of $SnCl_2$ with $Na^+[((CH_3)_3Si)_2C_2B_4H_5]^-$. A THF solution of $Na^+[((CH_3)_3Si)_2C_2B_4H_5]^-$ was prepared by the vacuum distillation of 2,3-$[(CH_3)_3Si]_2C_2B_4H_6$ (5.15 g, 23.4 mmol) into 100 mL of THF containing 0.60 g (26.1 mmol) of NaH. The solution was then filtered through a frit under high vacuum onto anhydrous $SnCl_2$ (4.84 g, 25.5 mmol) contained in a 250-mL round-bottom flask maintained at −78 °C. The reaction flask was then placed in an ice bath and stirred for 4 h at 0 °C. As the solution warmed to 0 °C, it changed slowly from a pale yellow to a blood red color, with the formation of a reddish brown precipitate. No gas evolution was detected. The THF was then removed by pumping the reaction mixture, still maintained at 0 °C, for another 4 h. After removal of THF, the reaction vessel was attached to a U-trap sublimator. The U-trap was immersed in a slush bath at −78 °C. On heating the dark residue to 100 °C in vacuo (10^{-6} torr), off-white $Sn[(CH_3)_3Si]_2C_2B_4H_4$ (I) and a colorless liquid, identified as the starting material $[(CH_3)_3Si]_2C_2B_4H_6$, collected on the inside walls and at the bottom of the U-trap, respectively. The sublimation was complete after 18 h. In order to facilitate the sublimation, the side arm of the reaction flask and the side arm of the U-trap sublimator were maintained at 100 °C with heating tape during the sublimation. The U-trap was then warmed to 10 °C and pumped through a trap at −196 °C for a period of 18 h. The neutral carborane $[(CH_3)_3Si]_2C_2B_4H_6$ (1.82 g, 8.27 mmol) collected in the −196 °C trap while the stannacarborane I remained in the sublimator. The stannacarborane was resublimed under high vacuum at 70 °C into a second U-trap to give ca. 3.39 g (10.1 mmol, 66.7% yield based on $[(CH_3)_3Si]_2C_2B_4H_6$ consumed) of pure I. After completion of the first sublimation at 100 °C, a gray-white residue remained in the reaction flask. This residue was heated to 220 °C in vacuo for 24 h, and an off-white solid was collected on the inside wall of the U-trap sublimator. The mass spectra and ^{119}Sn NMR[27] showed this solid to be pure $SnCl_2$ (2.49 g, 13.1 mmol). The physical properties and characterizations of I are as follows: mp 48–49 °C; solubility, at room temperature, highly

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soluble in CH_2Cl_2, $CDCl_3$, CCl_4, C_6H_6, THF, and acetone; ^1H NMR ($CDCl_3$), (relative external Me_4Si), δ 4.87 [q (br), 3 H, basal H_t, $^1J(^1H-^{11}B) = 148$ Hz], 3.78 [q (br), 1 H, apical H_t, $^1J(^1H-^{11}B) = 166$ Hz], 0.38 [s, 18 H, $(CH_3)_3Si$]; ^{11}B NMR (relative external BF_3OEt_2) δ 24.48 [d, 3 B, basal BH, $^1J(^{11}B-^1H) = 146$ Hz], -4.74 [d, 1 B, apical BH, $^1J(^{11}B-^1H) = 168$ Hz]; ^{13}C NMR (relative external Me_4Si) δ 133.6 [s(br), cage carbon, $^1J(^{13}C-^{119}Sn) = 67$ Hz], 2.26 [q, $(CH_3)_3Si$, $^1J(^{13}C-^1H) = 118.3$ Hz, $^3J(^{13}C-^{119}Sn) = 54$ Hz]; ^{29}Si NMR (relative external Me_4Si) δ -2.78 [m, $Si(CH_3)_3$, $^2J(^{29}Si-^1H) = 5.5$ Hz]; ^{119}Sn NMR (relative external TMT) δ -205.9 [s(br), cage Sn]. Anal. Calcd for $C_8H_{22}B_4Si_2Sn$: C, 28.51; H, 6.53; B, 13.07; Si, 16.63; Sn, 35.25. Found: C, 28.38; H, 6.66; B, 12.89; Si, 16.61; Sn, 35.15.

Reaction of $SnCl_2$ with $Na^+[((CH_3)_3Si)(CH_3)C_2B_4H_5]^-$. In a procedure identical with that employed in the synthesis of $Sn[(CH_3)_3Si]_2C_2B_4H_4$ (I), 13.8 mmol of $Na^+[((CH_3)_3Si)(CH_3)C_2B_4H_5]^-$ was reacted with 14.0 mmol of anhydrous $SnCl_2$ in THF. After removal of THF, a dark brown solid remained in the reaction flask. The same sublimation procedures and times described above for I yielded 1.61 g (5.78 mmol, 60.6% yield based on the carborane consumed) of $Sn[(CH_3)_3Si][CH_3]C_2B_4H_4$ (II) (as an off-white solid), 0.69 g (4.26 mmol) of neutral carborane, $[(CH_3)_3Si][CH_3]C_2B_4H_6$, and 1.54 g (8.12 mmol) of $SnCl_2$. The physical properties and characterization of II are as follows: mp 62–63 °C; solubility, highly soluble at 25 °C in THF, C_6H_6, $CDCl_3$, CCl_4, and CH_2Cl_2; ^1H NMR ($CDCl_3$), (relative external Me_4Si) δ 4.24 [q(br, overlapping), 3 H, basal H_t, $^1J(^1H-^{11}B) = 140$ Hz], 3.18 [q(br), 1 H, apical H_t, $^1J(^1H-^{11}B) = 168$ Hz], 2.55 [s, 3 H, CH_3], 0.24 [s, 9 H, $(CH_3)_3Si$]; ^{11}B NMR (relative external BF_3OEt_2] δ 22.32 [d, 1 B, basal BH, $^1J(^{11}B-^1H) = 140$ Hz], 20.34 [d, 2 B, basal BH, $^1J(^{11}B-^1H) = 140$ Hz], -6.71 [d, 1 B, apical BH, ^1J-$(^{11}B-^1H) = 167$ Hz], ^{13}C NMR (relative external Me_4Si) δ 131.8 [s(br), cage carbon (SiCB), $^1J(^{13}C-^{119}Sn) = 110$ Hz], 127.7 [s(br), cage carbon (CCB)], 23.02 (q, 1 C, CH_3, $^1J(^{13}C-^1H) = 127$ Hz], 0.82 [q, 3 C, $(CH_3)_3Si$, $^1J(^{13}C-^1H) = 121$ Hz, $^3J(^{13}C-^{119}Sn) = 52$ Hz]; ^{29}Si NMR (relative external Me_4Si) δ -3.18 [m, $Si(CH_3)_3$, ^2J $(^{29}Si-^1H) = 4.3$ Hz]; ^{119}Sn NMR (relative external TMT) δ -170.9 [s(br), cage Sn]. Anal. Calcd for $C_6H_{16}B_4SiSn$: C, 25.84; H, 5.74; B, 15.79; Si, 10.05; Sn, 42.59. Found: C, 25.69; H, 5.78; B, 15.56; Si, 9.83; Sn, 42.34.

Reaction of $SnCl_2$ with $Na^+[(CH_3)_3SiC_2B_4H_6]^-$. In a procedure identical with that employed in the synthesis of I or II above, 19.6 mmol of $Na^+[(CH_3)_3SiC_2B_4H_6]^-$ was allowed to react with 20.0 mmol of anhydrous $SnCl_2$ in THF at 0 °C for 4 h. After removal of THF at −23 °C via vacuum distillation for 8 h, the reaction flask was attached to a high vacuum U-trap sublimator. With identical sublimation procedures and times as described for I and II, 1.63 g (6.16 mmol, 44.3% yield based on the carborane consumed) of $Sn[(CH_3)_3Si]C_2B_4H_5$ (III), 0.84 g (5.68 mmol) of the neutral carborane, $(CH_3)_3SiC_2B_4H_7$, and 2.24 g (11.8 mmol) of $SnCl_2$ were obtained. The physical properties and characterization of III are as follows: mp 53–54 °C; solubility, at 25 °C, highly soluble in THF and acetone, slightly soluble in $CDCl_3$, CCl_4, CH_2Cl_2, or C_6H_6; ^1H NMR ($CDCl_3$), (relative external Me_4Si) δ 6.92 [s (br), 1 H, cage CH], 4.31 [q, (br, overlapping), 3 H, basal H_t, $^1J(^1H-^{11}B) = 136$ Hz], 3.35 [q (br), 1 H, apical H_t, $^1J(^1H-^{11}B) = 170$ Hz], 0.25 [s, 9 H, $(CH_3)_3Si$]; ^{11}B NMR (relative external BF_3OEt_2) δ 23.74 [d, 1 B, basal BH, $^1J(^{11}B-^1H) = 151.72$ Hz], 19.74 [d, 1 B, basal BH, $^1J(^{11}B-^1H) = 136$ Hz], 18.58 [d, 1 B, basal BH, $^1J(^{11}B-^1H) = 134.28$ Hz], -6.71 [d, 1 B, apical BH, $^1J(^{11}B-^1H) = 170.9$ Hz]; ^{13}C NMR (relative external Me_4Si) δ 126.8 [s(br), cage carbon (SiCB), $^1J(^{13}C-^{119}Sn) = 91$ Hz], 115.1 [d (br), cage CH, $^1J(^{13}C-^1H) = 171.1$ Hz, $^1J(^{13}C-^{119}Sn) = 89$ Hz], -0.61 [q, $(CH_3)_3Si$, $^1J(^{13}C-^1H) = 119.8$ Hz, $^3J(^{13}C-^{119}Sn) = 52$ Hz]; ^{29}Si NMR (relative external Me_4Si) δ -2.20 [m, $Si(CH_3)_3$, $^2J(^{29}Si-^1H) = 5.49$ Hz]; ^{119}Sn NMR (relative external TMT) δ -187.0 [s(br), cage Sn]. Anal. Calcd for $C_5H_{14}B_4SiSn$: C, 22.67; H, 5.29; B, 16.62; Si, 10.58; Sn, 44.84. Found: C, 22.47; H, 5.21; B, 16.49; Si, 10.52; Sn, 44.79.

Reaction of $Sn[(CH_3)_3Si][R]C_2B_4H_4$ and HCl. Pure I (1.110 g, 3.30 mmol), II (0.812 g, 2.91 mmol), or III (0.819 g, 3.09 mmol) was transferred under argon to a 250-mL greaseless Pyrex reactor containing magnetic stirring bar. The reactor was cooled to −196 °C and evacuated. Freshly distilled THF (~50 mL) and then pure HCl (10.00 mmol) were condensed into the reactor at −196 °C, after which the mixture in the flask was warmed to 0 °C and stirred at that temperature for 4 h. After removal of THF and unreacted HCl via a vacuum distillation for 8 h at −23 °C, a white crystalline solid and a colorless liquid remained in the reactor. At 25 °C, this liquid was transferred to a −196 °C trap and was identified as the carborane of the respective stannacarborane. The white solid was identified as $SnCl_2$ by its melting point (244–247 °C) and ^{119}Sn NMR spectrum in THF solution. The quantities and yields for each stannacarborane are as follows: for I, 0.70 g of $[(CH_3)_3Si]_2C_2B_4H_6$ (3.18 mmol, 95.5% yield based on the stannacarborane consumed) and 0.61 g (3.22 mmol) of $SnCl_2$; for II, 0.46 g of $[(CH_3)_3Si][CH_3]C_2B_4H_6$ (2.84 mmol, 97.6% yield based on the stannacarborane consumed) and 0.54 g (2.85 mmol) of $SnCl_2$; for III, 0.44 g of $(CH_3)_3SiC_2B_4H_7$ (2.97 mmol, 96.1% yield based on the stannacarborane consumed) and 0.57 g (3.00 mmol) of $SnCl_2$.

Reaction of $Sn[(CH_3)_3Si][R]C_2B_4H_4$ and BF_3 or $BH_3 \cdot THF$. A 3.00-mmol sample of each compound was allowed to react with 3.00 mmol of BF_3 at room temperature. After the mixture was stirred at room temperature for 4 h, the volatiles were condensed into a −196 °C trap. A white solid remained in the reaction flask. The volatile product consisted of only BF_3 (2.98 mmol); the white solids in the reaction flask were identified as I (2.91 mmol), II (2.96 mmol), and III (2.93 mmol) by IR and ^1H and ^{11}B NMR spectroscopy.

In another experiment, pure I (2.85 mmol), II (2.90 mmol), or III (2.88 mmol) was allowed to react with $BH_3 \cdot THF$ (3.40 mL of 0.98 M solution = 3.33 mmol) in THF at room temperature, with constant stirring, for a period of 4 h. After this period, the volatiles were condensed into a −196 °C trap. A white solid remained in the flask. The volatiles were found to consist of THF and $BH_3 \cdot THF$ (not measured). The white solids were identified as I (0.94 g, 2.79 mmol), II (0.78 g, 2.80 mmol), and III (0.74 g, 2.80 mmol), respectively. In addition, the room-temperature ^{11}B and ^{119}Sn NMRs of mixtures of BH_3 and the stannacarboranes in THF were identical with those of pure BH_3 and the pure stannacarboranes in THF.

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Registry No. I, 90388-43-5; II, 91670-63-2; III, 91686-40-7; $[(CH_3)3Si]_2C_2B_4H_6$, 91686-41-8; $[(CH_3)_3Si][CH_3]C_2B_4H_6$, 91686-42-9; $(CH_3)_3SiC_2B_4H_7$, 31259-72-0; $Na^+[((CH_3)_3Si)_2C_2B_4H_5]^-$, 91633-70-4; $Na^+[((CH_3)_3Si)(CH_3)C_2B_4H_5]^-$, 91633-71-5; Na^+-$[(CH_3)_3SiC_2B_4H_6]^-$, 91633-72-6.

Supplementary Material Available: Listings of mass spectrometric data (Table II) and FT-IR absorptions (Table III) of the stannacarboranes I, II, and III (5 pages). Ordering information is given on any current masthead page.