1936 *Organometallics* 1987, *6*, 1936–1940

Chemistry of *C*-Trimethylsilyl-Substituted Stannacarboranes. 3. Conversion of *closo*-1-Sn-2-(Me$_3$Si)-3-(R)-2,3-C$_2$B$_4$H$_4$ to *commo*-1,1′-Ge-[2-(Me$_3$Si)-3-(R)-2,3-C$_2$B$_4$H$_4$]$_2$ and Structure of *commo*-1,1′-Ge-[2,3-(Me$_3$Si)$_2$-*closo*-2,3-C$_2$B$_4$H$_4$]$_2$ (R = SiMe$_3$, Me, and H)

M. Safiqul Islam, Upali Siriwardane, Narayan S. Hosmane,* John A. Maguire,
Patrice de Meester, and Shirley S. C. Chu

Departments of Chemistry and Engineering, Southern Methodist University, Dallas, Texas 75275

Received February 25, 1987

The reaction of GeCl$_4$ with the *closo*-stannacarboranes 1-Sn-2,3-(Me$_3$Si)$_2$-2,3-C$_2$B$_4$H$_4$ (I), 1-Sn-2-(Me$_3$Si)-3-(Me)-2,3-C$_2$B$_4$H$_4$ (II), and 1-Sn-2-(Me$_3$Si)-2,3-C$_2$B$_4$H$_5$ (III) in a molar ratio of 1:2 in the absence of solvents at 150–160 °C produced moderately air-stable germanium(IV) sandwiched *commo*-germabis(carborane) complexes 1,1′-Ge-[2,3-(Me$_3$Si)$_2$-2,3-C$_2$B$_4$H$_4$]$_2$ (IV) as a sublimable white crystalline solid and 1,1′-Ge-[2-(Me$_3$Si)-3-(Me)-2,3-C$_2$B$_4$H$_4$]$_2$ (V) and 1,1′-Ge-[2-(Me$_3$Si)-2,3-C$_2$B$_4$H$_5$]$_2$ (VI) as colorless liquids, in yields of 74, 76, and 34%, respectively. The stannacarborane precursors I, II, and III were prepared by a new synthetic route in which a reductive insertion of tin into a *nido*-C$_2$B$_4$-carborane polyhedron takes place. The infrared spectra, mass spectra, ^{1}H, ^{11}B, ^{13}C, and ^{29}Si NMR spectra of IV, V, and VI are all consistent with the crystal structure of IV that shows two distorted pentagonal bipyramids joined by a germanium atom at the commo-apical position. Compound IV crystallizes in the monoclinic space group $P2_1/n$ with a = 9.905 (4) Å, b = 11.649 (3) Å, c = 13.793 (3) Å, β = 91.00 (3)°, U = 1591.2 (9) Å^3, T = 295 K, and Z = 2. Full-matrix least-squares refinement converged at R = 0.079 and R_w = 0.084.

Introduction

The insertions of both main group metals and transition metals into polyhedral carborane structures were first reported in the middle 1960's. However, the chemistry of transition-metal metallacarboranes has advanced much more rapidly than that of main-group metals.[1-4] Recently, there has been increased interest in the chemistry of group 14 metallacarboranes. This renewed interest has partly been the result of more structural data being available for these compounds.[5] Until quite recently, all of the reported group 14 metallacarboranes incorporated the heteroatoms in their +2 oxidation states.[1,5] In 1986, the first synthesis and structures of several π-complexes of silicon and germanium in both +2 and +4 oxidation states have been reported by Jutzi et al.[6] and Hawthorne et al.[7] and from this laboratory.[8-11] In several preliminary communications[8-10] we have shown that silicon(IV), germanium(IV), and tin(IV) undergo reductive and nonreductive insertion reactions with C-SiMe$_3$-substituted *nido*-carboranes to yield η^5- and bis- η^5-sila-, germa-, and stannacarborane complexes. Here we describe (i) a new synthetic route for the preparation of stannadicarbaheptaboranes, (ii) the utility of these compounds in the preparation of *commo*-germabis(carborane) complexes, and (iii) the details of the characterization and crystal structure determination of *commo*-bis(2,3-dicarba-1-germa-*closo*-heptaborane), which is believed to be the first example of a carborane analogue germanocene.

---

(1) (a) Todd, L. J. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. 1, Chapter 5.6 and references therein. (b) Grimes, R. N. In *Carboranes*; Academic: New York, 1970; Chapter 9.4 and references therein. (c) Todd, L. J.; Burke, A. R.; Silverstein, H. T.; Little, J. L.; Wikholm, G. S., *J. Am. Chem. Soc.* **1969**, *91*, 3376. (d) Wikholm, G. S.; Todd, L. J. *J. Organomet. Chem.* **1974**, *71*, 219. (e) Loffredo, R. E.; Norman, A. D. *J. Am. Chem. Soc.* **1971**, *93*, 5587. (f) Wong, K.-S.; Grimes, R. N. *Inorg. Chem.* **1977**, *16*, 2053. (g) Grimes, R. N. *Rev. Silicon, Germanium, Tin, Lead Compd.* **1977**, 223. (h) Rudolph, R. W.; Voorhees, R. L.; Cochoy, R. E. *J. Am. Chem. Soc.* **1970**, *92*, 3351. (i) Voorhees, R. L.; Rudolph, R. W. *Ibid.* **1969**, *91*, 2173. (j) Chowdhry, V.; Pretzer, W. R.; Rai, D. N.; Rudolph, R. W. *Ibid.* **1973**, *95*, 4560. (k) Hosmane, N. S.; Sirmokadam, N. N.; Herber, R. H. *Organometallics* **1984**, *3*, 1665.

(2) (a) Spencer, J. L.; Green, M.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1972**, 1178. (b) Colquhoun, H. M.; Greenhough, T. J.; Wallbridge, M. G. H. *J. Chem. Soc., Chem. Commun.* **1977**, 737. (c) Mikhailov, B. M.; Potapova, T. V. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1968**, *5*, 1153. (d) Young, D. A. T.; Wiersema, R. J.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1971**, *93*, 5687. (e) Young, D. A. T.; Willey, G. R.; Hawthorne, M. F.; Churchill, M. R.; Reis, A. H., Jr. *J. Am. Chem. Soc.* **1970**, *92*, 6663. (f) Churchill, M. R.; Reis, A. H., Jr. *J. Chem. Soc., Dalton Trans.* **1972**, 1317. (g) Grimes, R. N.; Rademaker, W. J.; Denniston, M. L.; Bryan, R. F.; Greene, P. T. *J. Am. Chem. Soc.* **1972**, *94*, 1865. (h) Popp, G.; Hawthorne, M. F. *Inorg. Chem.* **1971**, *10*, 391. (i) Popp, G.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1968**, *90*, 6553. (j) Rees, W. S., Jr.; Schubert, D. M.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1986**, *108*, 5367. (k) Todd, L. J. *Pure Appl. Chem.* **1972**, *30*, 587. (l) Todd, L. J. In *Metal Interactions with Boron Clusters*; Grimes, R. N., Ed.; Plenum: New York, 1982; Chapter 4 and references therein. (m) Dunks, G. B.; Hawthorne, M. F. In *Boron Hydride Chemistry*; Muetterties, E. L., Ed.; Academic: New York, 1975 and references therein. (n) Borlin, J.; Gaines, D. F. *J. Am. Chem. Soc.* **1972**, 94, 1367.

(3) (a) Thompson, M. L.; Grimes, R. N. *Inorg. Chem.* **1972**, *11*, 1925. (b) Savory, C. G.; Wallbridge, M. G. H. *J. Chem. Soc., Chem. Commun.* **1971**, 622. (c) Savory, C. G.; Wallbridge, M. G. H. *J. Chem. Soc., Dalton Trans.* **1972**, 918. (d) Sneddon, L. G.; Beer, D. C.; Grimes, R. N. *J. Am. Chem. Soc.* **1973**, *95*, 6623. (e) Magee, C. P.; Sneddon, L. G.; Beer, D. C.; Grimes, R. N. *J. Organomet. Chem.* **1975**, *86*, 159.

(4) Tabereaux, A.; Grimes, R. N. *Inorg. Chem.* **1973**, *12*, 792.

(5) (a) Cowley, A. H.; Galow, P.; Hosmane, N. S.; Jutzi, P.; Norman, N. C. *J. Chem. Soc., Chem. Commun.* **1984**, 1564. (b) Hosmane, N. S.; de Meester, P.; Maldar, N. N.; Potts, S. B.; Chu, S. S. C.; Herber, R. H. *Organometallics* **1986**, *5*, 772. (c) Hosmane, N. S.; Maguire, J. A. In *Molecular Structure and Energetics*; Liebman, J. F., Greenberg, A., Williams, R. E., Eds.; VCH: Deerfield Beach, FL, 1987; Vol. 5, Chapter 14 and references therein. (d) Siriwardane, U.; Hosmane, N. S.; Chu, S. S. C. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1987**, *C43*, 0000.

(6) Jutzi, P.; Kanne, D.; Krüger, C. *Angew. Chem.* **1986**, *98*, 163; *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 164.

(7) Rees, W. S., Jr.; Schubert, D. M.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1986**, *108*, 5369.

(8) Hosmane, N. S.; de Meester, P.; Siriwardane, U.; Islam, M. S.; Chu, S. S. C. *J. Chem. Soc., Chem. Commun.* **1986**, 1421.

(9) Hosmane, N. S.; de Meester, P.; Siriwardane, U.; Islam, M. S.; Chu, S. S. C. *J. Am. Chem. Soc.* **1986**, *108*, 6050.

(10) Siriwardane, U.; Islam, M. S.; West, T. A.; Hosmane, N. S. *Abstract of Papers*, 193rd National Meeting of the American Chemical Society, Denver, CO; American Chemical Society: Washington, DC, 1987; INOR 213.

(11) Siriwardane, U.; Islam, M. S.; West, T. A.; Hosmane, N. S.; Maguire, J. A.; Cowley, A. H. *J. Am. Chem. Soc.* **1987**, *109*, 0000.

0276-7333/87/2306-1936$01.50/0 © 1987 American Chemical Society

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 the methods of Hosmane et al.[12–14] Solutions of the sodium salts of the *nido*-carborane anions $[2\text{-Si}(CH_3)_3\text{-}3\text{-R-}2,3\text{-}C_2B_4H_5]^-$ (R = $Si(CH_3)_3$, CH_3, or H) in THF were prepared by the method of Onak and Dunks.[15] Prior to use, anhydrous tetrachlorogermane (Strem Chemicals, Inc., Newburyport, MS) and anhydrous tetrachlorostannane (Johnson Matthey, Seabrook, NH) were passed through −78 °C traps in vacuo to remove any last traces of HCl impurity. Purity was checked by IR, NMR, and vapor pressure measurements. A 2.5 M solution of *n*-butyllithium in *n*-hexane was obtained from Aldrich Chemical Co., Milwaukee, WI, and used as received. NaH (Aldrich) in mineral oil dispersion was washed repeatedly with dry pentane. Tetrahydrofuran and benzene were dried over $LiAlH_4$ and double distilled before use. All other solvents were dried over 4–8 mesh molecular sieves (Davidson) and either saturated with dry argon or degassed before use.

Spectroscopic Procedures. Proton, boron-11, carbon-13, silicon-29, chlorine-35, and tin-119 pulse Fourier transform NMR spectra, at 200, 64.2, 50.3, 39.76, 19.6, and 74.63 MHz, respectively, were recorded on an IBM -200 SY multinuclear NMR spectrometer. Mass spectral data were obtained on a Hewlett-Packard GC/MS system 5988A. Infrared spectra were recorded on a Perkin-Elmer Model 283 infrared spectrometer.

Synthetic Procedures. All experiments were carried out in Pyrex glass round-bottom flasks of 250-mL capacity, containing magnetic stirring bars and fitted with high vacuum Teflon valves. 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 ^1H NMR spectra with those of authentic samples.

Synthesis of 1-Sn-2-[Si(CH_3)$_3$]-3-[R]-2,3-$C_2B_4H_4$ (R = Si(CH_3)$_3$, CH_3, and H) by Reductive Insertion of Tin. A THF (50-mL) solution of $Na^+[(Me_3Si)_2C_2B_4H_5]^-$ (1.99 g, 8.24 mmol), $Na^+[(Me_3Si)(Me)C_2B_4H_5]^-$ (3.04 g, 16.55 mmol), or $Na^+[(Me_3Si)C_2B_4H_6]^-$ (2.68 g, 15.79 mmol) was added to a THF (10-mL) solution of BuLi (0.528 g, 8.25 mmol; 1.061 g, 16.58 mmol; or 1.011 g, 15.8 mmol) in vacuo at −78 °C, and the resulting mixture was warmed to 0 °C over a period of 2 h with constant stirring. The reaction flask containing this mixture was then cooled to −196 °C, and $SnCl_4$ (4.12, 8.28, or 7.90 mmol) was condensed into this flask at −196 °C. The final mixture was warmed to 0 °C and stirred constantly for 4 h at this temperature. After removal of THF at 0 °C via vacuum distillation for 6 h, the reaction flask was attached to a series of detachable high-vacuum U-traps. With identical sublimation procedures, temperatures, and times as described elsewhere,[1k,8,9] 1-Sn-[2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_4$] (I) (0.86 g, 2.55 mmol, 62% yield based on $SnCl_4$ consumed), 1-Sn-[2-($SiMe_3$)-3-(Me)-2,3-$C_2B_4H_4$] (II) (1.96 g, 7.04 mmol, 85% yield based on $SnCl_4$ consumed), or 1-Sn-[2-($SiMe_3$)-2,3-$C_2B_4H_5$] (III) (0.65 g, 2.46 mmol, 31% yield based on $SnCl_4$ consumed) was obtained in 0 °C trap in high purity. In addition, the neutral carborane precursors *nido*-[2-(Me_3Si)-3-(R)-2,3-$C_2B_4H_6$] (0.70 g, 3.18 mmol; 0.73 g, 4.51 mmol; or 0.92 g, 6.22 mmol) were collected in −45 °C traps. The physical properties and characterization of I, II, and III have been reported elsewhere.[1k]

Conversion of *closo*-1-Sn-2-($SiMe_3$)-3-(R)-2,3-$C_2B_4H_4$ to 2,2′-$(SiMe_3)_2$-3,3′-$(R)_2$-*commo*-1,1′-Ge-(2,3-$C_2B_4H_4$)$_2$ (R = $SiMe_3$, Me, and H). Anhydrous $GeCl_4$ (1.58, 0.70, or 0.49 mmol) was condensed into a 250-mL round-bottom flask containing 1-Sn-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_4$ (I) (1.06 g, 3.15 mmol), 1-Sn-2-($SiMe_3$)-3-(Me)-2,3-$C_2B_4H_4$ (II) (0.39 g, 1.40 mmol), or 1-Sn-2-($SiMe_3$)-2,3-$C_2B_4H_5$ (III) (0.26 g, 0.98 mmol) and a magnetic stirring bar. After the mixture was stirred and heated for 24 h at 150–160 °C, the reaction flask was cooled and then attached to a series of detachable high-vacuum U-traps. With identical sublimation procedures, temperatures, and times as described elsewhere,[1k,8,9] 1,1′-Ge^{IV}-[2,3-$(Me_3Si)_2$-2,3-$C_2B_4H_4$]$_2$ (IV) (0.59 g, 1.16 mmol; 74% yield based on I consumed), 1,1′-Ge^{IV}-[2-(Me_3Si)-3-(Me)-2,3-$C_2B_4H_4$]$_2$ (V) (0.21 g, 0.53 mmol, 76% yield based on II consumed), or 1,1′-Ge^{IV}-[2-(Me_3Si)-2,3-$C_2B_4H_5$]$_2$ (VI) (0.06 g, 0.165 mmol, 34% yield based on III consumed) was obtained in 0 °C trap in high purity. A white solid residue remaining in the reaction flask was identified as $SnCl_2$ by comparing its IR, mass, and ^{119}Sn and ^{35}Cl NMR spectra with those of authentic sample.

The physical properties, characterization, and a preliminary X-ray analysis of 1,1′-Ge^{IV}-[2,3-$(Me_3Si)_2$-2,3-$C_2B_4H_4$]$_2$ (IV) have been reported in an earlier communication.[9] The IR and mass spectral data of IV together with their assignments are summarized in Tables S1 and S2.

The physical properties and characterization of V are as follows: clear liquid; bp 130 °C at 10^{-6} torr; reasonably stable in air for short periods of time; at 25 °C, highly soluble in both polar and nonpolar organic solvents; ^1H NMR ($CDCl_3$, relative to external Me_4Si) δ 3.72 [q (br), 2 H, basal H_t, $^1J(^1H{-}^{11}B)$ = 152 Hz], 2.69 [q (br), 4 H, basal H_t, $^1J(^1H{-}^{11}B)$ = 158 Hz], 0.45 [q (br), 2 H, apical H_t, $^1J(^1H{-}^{11}B)$ = 178 Hz], 2.46 [s, 3 H, CH_3], 0.32 [s, 9 H, $(CH_3)_3Si$]; ^{11}B NMR ($CDCl_3$, relative to external $BF_3{\cdot}OEt_2$) δ 20.08 [d, 2 B, basal BH, $^1J(^{11}B{-}^1H)$ = 152 Hz], 9.62 [d, 4 B, basal BH, $^1J(^{11}B{-}^1H)$ = 145 Hz], −38.02 [d, 2 B, apical BH, $^1J(^{11}B{-}^1H)$ = 178 Hz]; ^{13}C NMR ($CDCl_3$, relative to external Me_4Si) δ 136.90 [s (br), cage SiCB], 132.90 [s (br), cage CCB], 22.31 [q, CH_3, $^1J(^{13}C{-}^1H)$ = 128 Hz], 0.27 [q, $(CH_3)_3Si$, $^1J(^{13}C{-}^1H)$ = 120 Hz]; ^{29}Si NMR ($CDCl_3$, relative to external Me_4Si) δ −2.31 [m, $Si(CH_3)_3$, $^2J(^{29}Si{-}^1H)$ = 6.1 Hz]. The IR and mass spectral data of V together with their assignments are summarized in Tables S1 and S2.

The physical properties and characterization of VI are as follows: colorless liquid; bp 81 °C (10^{-6} torr); moderately air-stable for short periods of time; at 25 °C, highly soluble in both polar and nonpolar organic solvents; ^1H NMR ($CDCl_3$, relative to external Me_4Si) δ 6.85 [s (br), cage CH], 4.24 [q (br), 2 H, basal H_t, $^1J(^1H{-}^{11}B)$ = 147 Hz], 2.79 [q (br, overlapping), 4 H, basal H_t, $^1J(^1H{-}^{11}B)$ = 156 Hz], 0.83 [q (br), 2 H, apical H_t, $^1J(^1H{-}^{11}B)$ = 180 Hz], 0.33 [s, 9 H, $(CH_3)_3Si$]; ^{11}B NMR ($CDCl_3$, relative to external $BF_3{\cdot}OEt_2$) δ 19.20 [d, 2 B, basal BH, $^1J(^{11}B{-}^1H)$ = 143 Hz], 9.27 [d, 2 B, basal BH, $^1J(^{11}B{-}^1H)$ = 156 Hz], −2.49 [d, 2 B, basal BH, $^1J(^{11}B{-}^1H)$ = 170 Hz], −40.64 [d, 2 B, apical BH, $^1J(^{11}B{-}^1H)$ = 180 Hz]; ^{13}C NMR ($CDCl_3$, relative to external Me_4Si) δ 131.46 [s (br), cage carbon SiCB], 120.88 [d (br), cage CH, $^1J(^{13}C{-}^1H)$ = 166 Hz], −1.49 [q, $(CH_3)_3Si$, $^1J(^{13}C{-}^1H)$ = 120 Hz]; ^{29}Si NMR ($CDCl_3$, relative to external Me_4Si) δ −0.32 [m (br), $Si(CH_3)_3$, $^2J(^{29}Si{-}^1H)$ = 6.1 Hz]. The IR and mass spectral data of VI together with their assignments are summarized in Tables S1 and S2.

X-ray Analysis of IV. Large platelike colorless crystals of IV were grown by sublimation onto a glass surface. Preliminary experiments indicated that the compound was sensitive to both air and X-rays. One of the crystals was coated with an epoxy resin and mounted on an automatic Syntex $P2_1$ diffractometer, approximately along the *a* axis. Data collection was carried out at 295 K. The unit-cell parameters were determined by least-squares fit of 15 reflections measured in the range $15 < 2\theta < 25°$. Systematic absences were consistent with the space group $P2_1/n$, and this was confirmed by the successful solution and refinement of the structure. The pertinent crystallographic data are summarized in Table I. Three standard reflections, remeasured after every 100 reflections, showed a substantial decay (ca. 15%) at the end of the data collection. Data were corrected for decay and Lorentz–polarization effects but not for absorption. Only the observed reflections with $I > 3\sigma(I)$ were used in the subsequent solution and refinement of the structure. The structure was solved by standard Patterson and difference Fourier methods. All non-hydrogen atoms were allowed to refine anisotropically. The four cage hydrogen atoms were located and included in the refinement with *U*'s set at 0.06 Å^2 but not refined. Full-matrix least-squares refinements were used throughout, the function minimized being $\sum w(|F_o| - |F_c|)^2$. One reflection $\bar{1}01$, possibly affected by extinction, was taken out during the final refinement by using the weighting

---

[12] Hosmane, N. S.; Sirmokadam, N. N.; Mollenhauer, M. N. *J. Organomet. Chem.* **1985**, *279*, 359.

[13] Hosmane, N. S.; Mollenhauer, M. N.; Cowley, A. H.; Norman, N. C. *Organometallics* **1985**, *4*, 1194.

[14] Hosmane, N. S.; Maldar, N. N.; Potts, S. B.; Rankin, D. W. H.; Robertson, H. E. *Inorg. Chem.* **1986**, *25*, 1561.

[15] Onak, T.; Dunks, G. B. *Inorg. Chem.* **1966**, *5*, 439.

Table I. Crystallographic Data[a] for IV

formula	$C_{16}H_{44}B_8Si_4Ge$
fw	507.95
cryst system	monoclinic
space group	$P2_1/n$
a, Å	9.905 (4)
b, Å	11.649 (3)
c, Å	13.793 (3)
β, deg	91.00 (3)
U, Å^3	1591.2 (9)
Z	2
D_{calcd}, g cm^{-3}	1.060
cryst dimens, mm	0.31, 0.09, 0.07
μ(Mo Kα), cm^{-1}	11.00
scan type	$\theta/2\theta$
scan speed, deg min^{-1}	2.9–14.7
2θ range, deg	$3 < 2\theta < 38°$
data collected	$\pm h,k,l$
decay, %	16
unique data	1280
obsd reflctns, $I > 3\sigma(I)$	808
R^b	0.079
R_w	0.084
$\Delta\rho_{(max,\ min)}$, e/Å^3	0.45, 0.18

[a] Graphite-monochromatized Mo Kα radiation; $\lambda = 0.71069$ Å. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$, $R_w = [\sum w(F_o - F_c)^2/\sum(F_o)^2]^{1/2}$, and $w = 1/\sigma^2(F_o) + k(F_o)^2$, where $k = 0.000816$.

Table II. Fractional Atomic Coordinates (Esd's in Parentheses)

atom	x	y	z
Ge	0.0000 (0)	0.0000 (0)	0.0000 (0)
Si(1)	0.2672 (9)	0.2148 (6)	−0.1076 (6)
Si(2)	−0.1190 (10)	0.2802 (5)	−0.1411 (6)
C(1)	0.1165 (20)	0.1741 (13)	−0.0326 (11)
C(2)	−0.0247 (24)	0.1974 (12)	−0.0440 (14)
B(3)	−0.1028 (26)	0.1495 (21)	0.0510 (27)
B(4)	0.0065 (35)	0.1021 (17)	0.1238 (14)
B(5)	0.1438 (21)	0.1122 (16)	0.0700 (17)
B(6)	0.0421 (20)	0.2308 (15)	0.0688 (10)
C(11)	0.3010 (26)	0.3714 (19)	−0.1007 (16)
C(12)	0.197 (12)	0.1846 (49)	−0.2416 (42)
C(13)	0.3734 (42)	0.1183 (30)	−0.1167 (56)
C(21)	−0.2153 (27)	0.1863 (19)	−0.2130 (17)
C(22)	−0.0569 (47)	0.4194 (20)	−0.1616 (24)
C(23)	−0.2679 (67)	0.3466 (49)	−0.0906 (43)
H(3)	−0.206	0.185	0.063
H(4)	0.029	0.061	0.195
H(5)	0.240	0.102	0.101
H(6)	0.049	0.323	0.110

Table III. Bond Lengths (Å) and Bond Angles (deg)

Bond Lengths			
Ge–C(1)	2.38 (2)	C(1)–C(2)	1.43 (3)
Ge–C(2)	2.39 (2)	C(1)–B(5)	1.61 (3)
Ge–B(3)	2.14 (3)	C(1)–B(6)	1.72 (3)
Ge–B(4)	2.08 (3)	C(2)–B(3)	1.63 (4)
Ge–B(5)	2.15 (2)	C(2)–B(6)	1.72 (3)
Si(1)–C(1)	1.89 (2)	B(3)–B(4)	1.56 (4)
Si(1)–C(11)	1.86 (3)	B(3)–B(6)	1.73 (4)
Si(1)–C(12)	2.00 (8)	B(4)–B(5)	1.57 (3)
Si(1)–C(13)	1.55 (6)	B(4)–B(6)	1.72 (3)
Si(2)–C(2)	1.89 (2)	B(5)–B(6)	1.71 (3)
Si(2)–C(21)	1.75 (3)		
Si(2)–C(22)	1.76 (4)		
Si(2)–C(23)	1.82 (6)		

Bond Angles			
C(1)–Ge–C(2)	34.9 (6)	Si(2)–C(2)–C(1)	130.3 (15)
C(1)–Ge–B(3)	66.7 (9)	Si(2)–C(2)–B(3)	120.6 (16)
C(1)–Ge–B(4)	70.1 (8)	Si(2)–C(2)–B(6)	134.7 (13)
C(1)–Ge–B(5)	41.2 (7)	C(1)–C(2)–B(3)	108.9 (18)
C(2)–Ge–B(3)	41.8 (9)	C(1)–C(2)–B(6)	65.5 (12)
C(2)–Ge–B(4)	70.1 (9)	B(3)–C(2)–B(6)	62.1 (14)
C(2)–Ge–B(5)	66.0 (8)	Ge–B(3)–C(1)	61.2 (9)
B(3)–Ge–B(4)	43.5 (11)	Ge–B(3)–C(2)	77.3 (14)
B(3)–Ge–B(5)	70.9 (10)	Ge–B(3)–B(4)	66.2 (15)
B(4)–Ge–B(5)	43.4 (9)	Ge–B(3)–B(5)	54.7 (9)
C(1)–Si(1)–C(11)	111.2 (10)	Ge–B(3)–B(6)	95.4 (15)
C(1)–Si(1)–C(12)	101.2 (25)	C(2)–B(3)–B(4)	107.7 (21)
C(1)–Si(1)–C(13)	114.0 (21)	C(2)–B(3)–B(6)	61.6 (14)
C(11)–Si(1)–C(12)	106.3 (25)	B(4)–B(3)–B(6)	62.6 (16)
C(11)–Si(1)–C(13)	126.6 (22)	Ge–B(4)–C(1)	60.4 (8)
C(12)–Si(1)–C(13)	91.4 (31)	Ge–B(4)–C(2)	60.6 (8)
C(2)–Si(2)–C(21)	110.0 (11)	Ge–B(4)–B(3)	70.4 (15)
C(2)–Si(2)–C(22)	114.6 (14)	Ge–B(4)–B(5)	70.6 (13)
C(2)–Si(2)–C(23)	110.0 (21)	Ge–B(4)–B(6)	98.0 (13)
C(21)–Si(2)–C(22)	132.4 (15)	B(3)–B(4)–B(5)	105.5 (21)
C(21)–Si(2)–C(23)	92.6 (22)	B(3)–B(4)–B(6)	63.5 (16)
C(22)–Si(2)–C(23)	87.6 (23)	B(5)–B(4)–B(6)	62.5 (14)
Ge–C(1)–Si(1)	135.0 (9)	Ge–B(5)–C(1)	77.1 (11)
Ge–C(1)–C(2)	72.9 (11)	Ge–B(5)–C(2)	61.7 (7)
Ge–C(1)–B(3)	52.1 (8)	Ge–B(5)–B(3)	54.4 (9)
Ge–C(1)–B(4)	49.5 (7)	Ge–B(5)–B(4)	66.0 (12)
Ge–C(1)–B(5)	61.7 (10)	Ge–B(5)–B(6)	95.8 (11)
Ge–C(1)–B(6)	87.6 (9)	C(1)–B(5)–B(4)	108.5 (17)
Si(1)–C(1)–C(2)	132.2 (14)	C(1)–B(5)–B(6)	62.5 (12)
Si(1)–C(1)–B(5)	118.2 (13)	B(4)–B(5)–B(6)	63.2 (14)
Si(1)–C(1)–B(6)	134.5 (12)	C(1)–B(6)–C(2)	49.0 (10)
C(2)–C(1)–B(5)	109.3 (15)	C(1)–B(6)–B(3)	92.3 (14)
C(2)–C(1)–B(6)	65.5 (12)	C(1)–B(6)–B(4)	96.8 (14)
B(5)–C(1)–B(6)	61.7 (12)	C(1)–B(6)–B(5)	55.8 (11)
Ge–C(2)–Si(2)	136.1 (10)	C(2)–B(6)–B(3)	56.3 (13)
Ge–C(2)–C(1)	72.2 (11)	C(2)–B(6)–B(4)	97.1 (14)
Ge–C(2)–B(3)	61.0 (12)	C(2)–B(6)–B(5)	92.5 (13)
Ge–C(2)–B(4)	49.3 (7)	B(3)–B(6)–B(4)	53.9 (14)
Ge–C(2)–B(5)	52.3 (7)	B(3)–B(6)–B(5)	92.6 (15)
Ge–C(2)–B(6)	87.2 (10)	B(4)–B(6)–B(5)	54.3 (13)

scheme as shown in *Table* I. All calculations were carried out with the SHELX76 system of programs.[16] Scattering factors used for C, H, B, and Si were calculated from the data stored in SHELX76. Scattering factors and $\Delta f'$ and $\Delta f''$ for Ge were taken from: *International Tables for X-ray Crystallography*; Kynoch: Birmingham, U.K., 1974; Vol IV. The final atomic coordinates are given in Table II. Selected bond lengths and bond angles are presented in Table III.

Results and Discussion

Synthesis. In our earlier work we have shown that the reaction of Na[(Me$_3$Si)(R)C$_2$B$_4$H$_5$] with SnCl$_2$ in THF produces an air-sensitive THF–stannacarborane intermediate, $(C_4H_8O)_2Sn(Me_3Si)(R)C_2B_4H_4$ (R = Me$_3$Si, Me or H), which decomposes to give THF and the corresponding stannacarborane as a sublimable white solid, in gram quantities.[1k,5b,c] In the present investigation, the reaction of SnCl$_4$ with the Na/Li salt of *nido*-[2-(Me$_3$Si)-3-(R)-2,3-C$_2$B$_4$H$_4$]$^{2-}$ produces the corresponding *closo*-stannacarborane in good yields. More recently, Hawthorne and co-workers have also observed the reductive insertion of the tin atom into *nido*-[7,8-C$_2$B$_9$H$_{11}$]$^{2-}$ to yield the *closo*-stannacarborane 1-Sn-2,3-C$_2$B$_9$H$_{11}$ in which the "bare" tin atom occupies one of the apical positions of the icosahedron.[17]

The mechanism of reductive insertion of the tin in the carborane cage framework has not been determined, and the oxidized product has as yet to be identified. However, it has been observed that this reductive insertion is accompanied by the formation of *nido*-2-(Me$_3$Si)-3-(R)-2,3-C$_2$B$_4$H$_6$. The recovery of this neutral *nido*-carborane suggests that at least one or more competing reactions take place during the formation of stannadicarbaheptaborane. Apparently, these reactions produce HCl that converts the excess carborane dianion [(Me$_3$Si)(R)C$_2$B$_4$H$_4$]$^{2-}$ to the

---

(16) Sheldrick, G. M. SHELX-76, Programs for Crystal Structure Determination, University of Cambridge, England, 1976.

(17) Schubert, D. M.; Hawthorne, M. F., private communication to N.S.H., 1986.

neutral *nido*-carborane $(Me_3Si)(R)C_2B_4H_6$. Although the specific side reactions are not known, reactions such as chlorination of one or more of the B–H(terminal) bonds of the polyhedron or chlorination and cleavage of the C–H, C–C, and C–O bonds of the solvent THF by $SnCl_4$ or $Cl_2Sn[(Me_3Si)(R)C_2B_4H_4]$ may be taking place either concurrently or sequentially. Such reactions are considered to be the potential source of HCl for the formation of neutral *nido*-$(Me_3Si)(R)C_2B_4H_6$ (R = Me_3Si, Me, or H). Since the mechanism of this reductive insertion is not known, the HCl could be formed in the insertion reaction itself or be the result of subsequent reaction of the oxidized species. It is of great interest to note the recent report of Jutzi and Galow that the reaction of $Na_2[7,8\text{-}(Me)_2\text{-}7,8\text{-}C_2B_9H_9]$ with $SnCl_4$ produced *closo*-2,3-$(Me)_2$-2,3-$C_2B_9H_9$, and no Sn(II)- or Sn(IV)-containing carborane derivative was either identified or isolated among the products.[18]

The stannacarboranes have also been found to be useful starting materials for the synthesis of other metallacarboranes.[1f,19,20] Hosmane and Sirmokadam[20] have reported the reaction of $Os_3(CO)_{12}$ with *closo*-1-Sn-2,3-$(Me_3Si)_2$-2,3-$C_2B_4H_4$, in the absence of solvent, to yield the *closo*-osmacarborane 1-$Os(CO)_3$-2,3-$(Me_3Si)_2$-2,3-$C_2B_4H_4$ in high yield, thus showing that the apical tin in the stannacarborane is loosely ligated and can be replaced by other metal moieties. In the present investigation, the stannacarborane precursor undergoes a high yield conversion to a corresponding *commo*-germabis(carborane) derivative at elevated temperatures in the absence of solvents. The reaction is described in eq 1. When R = SiMe$_3$, the germacarborane product is a white crystalline, moderately air-stable material whose crystal structure has been determined and is discussed below. When R = Me or H, the germacarborane is a colorless liquid. It is now known that the carborane anions effectively reduce the tetravalent group 14 metals to their divalent states during the preparation of sila-, germa-, and stannacarboranes.[8-11,17,21] However, this reduction process is not apparent in the present study where the stannacarborane precursor undergoes a simple, nonreductive substitution reaction with Ge(IV) chloride. Thus the present work clearly demonstrates the utility of stannacarboranes for the preparation of tetravalent metal–carborane species.

$$2\,closo\text{-}1\text{-}Sn^{II}\text{-}[2\text{-}(Me_3Si)\text{-}3\text{-}(R)\text{-}2,3\text{-}C_2B_4H_4] + GeCl_4 \xrightarrow[\text{no solvent}]{150\text{–}160\ °C} commo\text{-}1,1'\text{-}Ge^{IV}\text{-}[2\text{-}(Me_3Si)\text{-}3\text{-}(R)\text{-}2,3\text{-}C_2B_4H_4]_2 + 2SnCl_2 \quad (1)$$

Characterization. The germacarboranes IV, V, and VI were characterized on the basis of ^1H, ^{11}B, ^{13}C, and ^{29}Si pulse Fourier transform NMR, IR, and mass spectroscopy (Experimental Section and Tables S1 and S2). Compound IV was also characterized by single-crystal X-ray diffraction[9] (Tables I–III).

NMR and IR Spectra. The ^1H NMR and ^{13}C NMR spectra indicate the presence of the C_2B_4 ring in the germacarboranes in addition to the $SiMe_3$ and Me or CH groups. The ^{13}C chemical shifts of the cage carbons in each compound were not changed significantly from those of the *nido*-carborane precursors.[12] It may be that the interaction between cage carbon atoms and the apical germanium atom is weak. This decreased interaction with the cage carbon atom is consistent with the crystal structure of IV[9] that shows a significant slippage of the Ge away from the two carbon atoms and toward the three boron atoms of each C_2B_3 face. Except for a very small shift of the apical ^{11}B resonance, the ^{11}B NMR data of IV, V, and VI bear striking similarities to those of the stannacarborane–2,2′-bipyridine donor–acceptor complexes,[5b-d] and *commo*-silabis(carborane) derivatives.[8,11] The commo-apical position, rather than a terminal position of germanium in these germacarboranes, can be inferred from the absence of a separate ^{11}B–Ge singlet in the proton-coupled spectrum. If the germanium is in bridging or doubly bridging positions with one or two three-center, two-electron bonds, one would expect virtually no change in the ^{11}B chemical shifts of the apical and basal boron resonances from those of the precursors.[4,22] In addition, a secondary splitting of the basal BH resonances due to B–H–B bridge hydrogens[22] should appear in their proton-coupled ^{11}B NMR spectra. The absence of a broad B–H–B resonance near −2 ppm in the ^1H NMR spectrum of each germacarborane is further evidence for a commo-apical position of the germanium atom in these molecules. The ^{29}Si NMR spectrum shows a multiplet for Me_3Si group in each of these compounds.

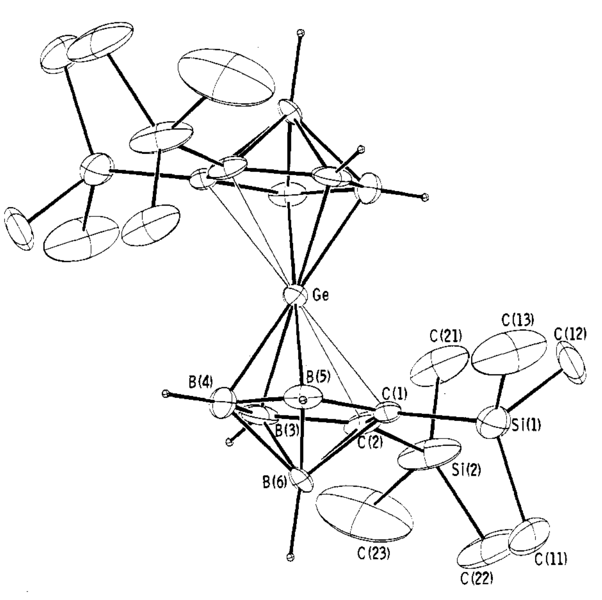

Figure 1. ORTEP view of *commo*-1,1′-Ge^{IV}-$[2,3\text{-}(SiMe_3)_2\text{-}2,3\text{-}C_2B_4H_4]_2$ (IV), showing the atom numbering scheme and thermal ellipsoids drawn at the 10% probability level. The central Ge atom lies at a crystallographic center of symmetry. The weaker Ge–C interactions are shown by thinner lines.

The position of the germanium atom in IV–VI can also be verified by their IR spectra. A characteristic feature of the vibrational spectra of all known heteroatom-bridged $C_2B_4H_8$ derivatives[3a-c,4,23] is a split B-H stretching band near 2600 cm^{-1}. However, this feature is absent in the IR spectra of *commo*-germabis(carborane) derivatives IV–VI, where a single B–H stretching band appears near 2600 cm^{-1} (see Table S1). In addition, a stretching mode of vibration due to a B–H–B bridge bond near 1900 cm^{-1} is absent in the infrared spectrum of each of the germacarboranes.

Mass Spectra. The electron-impact (EI) mass spectra of the *commo*-germabis(carborane) exhibited characteristic groupings corresponding to their molecular ions (see Table S2). The most intense peak for IV to VI corresponded to the parent ion minus one methyl group. This phenomenon has also been observed elsewhere.[1k,5b,8,11-13,20,23]

---

[18] Jutzi, P.; Galow, P. *J. Organomet. Chem.* **1987**, *319*, 139.

[19] Maxwell, W. M.; Wong, K.-S.; Grimes, R. N. *Inorg. Chem.* **1977**, *16*, 3094.

[20] Hosmane, N. S.; Sirmokadam, N. N. *Organometallics* **1984**, *3*, 1119.

[21] This work.

[22] Hosmane, N. S.; Grimes, R. N. *Inorg. Chem.* **1979**, *18*, 2886.

[23] Gaines, D. F.; Iorns, T. V. *J. Am. Chem. Soc.* **1968**, *90*, 6617.

Crystal Structure of *commo*-1,1′-Ge^{IV}-[2,3-$(Me_3Si)_2$-2,3-$C_2B_4H_4]_2$ (IV). Preliminary data on the structure of IV have been reported in an earlier communication.[9] The X-ray crystal structure of IV, shown in Figure 1, reveals that the germanium atom at the commo-apical position of two pentagonal bipyramids adopts an essentially η^5-bonding posture with respect to each of the C_2B_3 faces. The molecule is required to be centrosymmetric with the Ge atom at the origin (as there are only two molecules in the unit cell). However, there is a significant "slip distortion" of the germanium away from the two cage carbon atoms and toward the three boron atoms. This distortion involves primarily the Ge–C distances [2.38 (2) and 2.39 (2) Å], which are substantially longer than the Ge–B distances [2.14 (3), 2.08 (3), and 2.15 (2) Å], thus confirming the NMR evidence for such an elongation (see Table III). Although the extent of distortion will vary from complex to complex, such "slip distortions" due to elongated M–C (M = metal) bonds are a common structural feature in similar *commo*-silabis(carborane) derivatives.[7,8,11] Slippages of this type have also been observed in 1-MeGa-2,3-$C_2B_4H_6$,[2g] stannacarboranes, and their 2,2′-bipyridine donor–acceptor complexes,[5] as well as in a number of transition-metalcarboranes[24-28] and have been investigated theoretically.[27,29,30]

Bonding in *commo*-Germabis(carborane) Complexes. There has been no detailed calculations on the group 14 *commo*-bis(carborane) complexes. Theoretical calculations by Mingos and co-workers[30] indicate that both the *nido*-C_2B_4 and *nido*-C_2B_9 ligands use similar orbitals in bonding to metals. These workers have also shown that the orbitals on the open face of the *nido*-C_2B_9 ligand used in metal bonding are similar to those in the cyclopentadienyl ligand except that the symmetric a_1 orbital in C_2B_9 is less available for bonding and the degeneracy of the e_1 is lifted, with the resulting a′ and a″ orbitals being localized toward the boron atoms in the C_2B_3 open face.[27,31,32] The presence of the adjacent cage carbons in the C_2B_3 face stabilizes a slip distortion toward the boron atoms.[30] The *commo*-1,1′-Ge^{IV}-[2,3-$(Me_3Si)_2$-2,3-$C_2B_4H_4]_2$ (IV) has C_{2h} symmetry. Thus, the a_1 and a′ carborane orbitals each give rise to sets of a_g and b_u symmetry orbitals, and the a″ orbitals yield b_g and a_u orbitals. The 4s atomic orbital (AO) on a Ge atom that is dislocated toward the boron side of the C_2B_3 face can interact with both the $a_g(a_1)$ and $a_g(a')$ orbitals. If one adopts the convention that the z axis is the C_2 axis and the C_2B_3 faces are perpendicular to the x axis, the Ge($4p_x$) AO can interact with the $b_u(a_1)$ and $b_u(a')$ orbitals. The Ge($4p_z$) and Ge($4p_y$) AO's can undergo π interactions with the $a_u(a'')$ and the $b_u(a')$ orbitals, respectively. If the carborane orbitals are localized toward the borons, a slight slippage would increase the p_y–$b_u(a')$ overlap; however, this interaction would become antibonding for large distortions. In the absence of Ge(4d) participation, the $b_g(a'')$ orbital would be nonbonding. With Ge(4d) participation, this orbital could bond with the Ge($4d_{xz}$) AO. This scheme can accommodate a total of 12 bonding electrons, which is the number of interstitial electrons in IV. These qualitative arguments cannot assess the relative importance of the competing bonding interactions that determine the extent of the slip distortion in these complexes. One dominant factor is the increased σ interaction with orbitals arising from the a′ carborane orbitals. This increased importance in σ bonding has been used to explain the increased slippage found when the stannacarboranes complex with 2,2′-bipyridine.[5c] A completely satisfactory explanation must await theoretical calculations.

Acknowledgment. This work was supported by grants from the National Science Foundation, the Robert A. Welch Foundation, and the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Registry No. I, 90388-43-5; II, 91670-63-2; III, 91686-40-7; IV, 104069-93-4; V, 109284-52-8; VI, 109284-53-9; $Na^+[(Me_3Si)_2C_2B_4H_5]^-$, 91633-70-4; $Na^+[(Me_3Si)(MeC_2B_4H_5]^-$, 91633-71-5; $Na^+[(Me_3Si)C_2B_4H_6]^-$, 91633-72-6; $SnCl_4$, 7646-78-8; $GeCl_4$, 10038-98-9.

Supplementary Material Available: Listings of IR absorptions (Table S1) and mass spectrometric data (Table S2) of IV, V, and VI and a table of anisotropic temperature factors of IV (Table S3) (5 pages); a listing of structure factors of IV (6 pages). Ordering information is given on any current masthead page.

---

(24) (a) Hawthorne, M. F.; Young, D. C.; Wegner, P. A. *J. Am. Chem. Soc.* **1965**, *87*, 1818. (b) Hawthorne, M. F.; Young, D. C.; Andrews, T. D.; Howe, D. V.; Pilling, R. L.; Pitts, A. D.; Reintjes, M.; Warren, L. F., Jr.; Wegner, P. A. *J. Am. Chem. Soc.* **1968**, *90*, 879. (c) Hawthorne, M. F.; Dunks, G. B. *Science (Washington, DC)* **1972**, *178*, 462. (d) Hawthorne, M. F. *Pure Appl. Chem.* **1972**, *29*, 547. (e) Francis, J. N.; Hawthorne, M. F. *Inorg. Chem.* **1971**, *10*, 863.

(25) Green, M.; Howard, J. A. K.; James, A. P.; Jelfs, A. N. de M.; Nunn, C. M.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1985**, 1778.

(26) Colquhoun, H. M.; Greenough, T. J.; Wallbridge, M. G. H. *J. Chem. Soc., Dalton Trans.* **1985**, 761.

(27) Mingos, D. M. P.; Forsyth, M. I.; Welch, A. J. *J. Chem. Soc., Dalton Trans.* **1978**, 1363.

(28) Barker, G. K.; Green, M.; Onak, T. P.; Stone, F. G. A.; Ungermann, C. B.; Welch, A. J. *J. Chem. Soc., Chem. Commun.* **1978**, 169 and references therein.

(29) Canadell, E.; Eisenstein, O.; Rubio, J. *Organometallics* **1984**, *3*, 759.

(30) Calhorda, M. J.; Mingos, D. M. P.; Welch, A. J. *J. Organomet. Chem.* **1982**, *228*, 309.

(31) Mingos, D. M. P. *J. Chem. Soc., Dalton Trans.* **1977**, 602.

(32) Mingos, D. M. P.; Forsyth, M. I.; Welch, A. J. *J. Chem. Soc., Chem. Commun.* **1977**, 605.