

# Germanium(II)-Inserted $\eta^5$ -*closo*-Germacarboranes and Their Donor-Acceptor Complexes. Crystal Structure of 1-Ge(C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>)-2,3-(Me<sub>3</sub>Si)<sub>2</sub>-2,3-C<sub>2</sub>B<sub>4</sub>H<sub>4</sub>

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The reaction of GeCl<sub>4</sub> with the *nido*-carborane dianionic salts NaLi[(Me<sub>3</sub>Si)(R)C<sub>2</sub>B<sub>4</sub>H<sub>4</sub>] (R = SiMe<sub>3</sub>, Me, or H) in a molar ratio of 1:2 in THF produced *closo*-1-Ge<sup>II</sup>-2,3-(SiMe<sub>3</sub>)<sub>2</sub>-2,3-C<sub>2</sub>B<sub>4</sub>H<sub>4</sub> (I), *closo*-1-Ge<sup>II</sup>-2-(SiMe<sub>3</sub>)-3-(Me)-2,3-C<sub>2</sub>B<sub>4</sub>H<sub>4</sub> (II), and *closo*-1-Ge<sup>II</sup>-2-(SiMe<sub>3</sub>)-2,3-C<sub>2</sub>B<sub>4</sub>H<sub>5</sub> (III) as air-sensitive, pale yellow liquids, in 36, 49, and 23% yields, respectively. In addition to the corresponding neutral *nido*-carborane precursors, the Ge(IV)-inserted derivatives of *commo*-bis(germacarborane), [(Me<sub>3</sub>Si)(R)C<sub>2</sub>B<sub>4</sub>H<sub>4</sub>]<sub>2</sub>Ge<sup>IV</sup>, were also produced in 9.0, 7.4, and 9.5% yields when R = SiMe<sub>3</sub>, Me, and H, respectively. The *closo*-germacarboranes I, II, and III react slowly with 2,2'-bipyridine in benzene to form the electron donor-acceptor complexes 1-Ge<sup>II</sup>-(C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>)-2,3-(SiMe<sub>3</sub>)<sub>2</sub>-2,3-C<sub>2</sub>B<sub>4</sub>H<sub>4</sub> (IV), 1-Ge<sup>II</sup>-(C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>)-2-(SiMe<sub>3</sub>)-3-(Me)-2,3-C<sub>2</sub>B<sub>4</sub>H<sub>4</sub> (V), and 1-Ge<sup>II</sup>-(C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>)-2-(SiMe<sub>3</sub>)-2,3-C<sub>2</sub>B<sub>4</sub>H<sub>5</sub> (VI) in 73, 42, and 48% yields, respectively. Both the visible/UV and <sup>11</sup>B NMR spectroscopic results on IV-VI indicate that at least two different kinetic processes are taking place: a slow formation of the bipyridine-germacarborane adduct, followed by a rapid intramolecular process which causes all the basal and apical boron atoms to become equivalent on an NMR time scale. The X-ray crystal structure of IV shows an extreme displacement of the germanium from the centroidal position above the C<sub>2</sub>B<sub>3</sub> face in its distorted pentagonal-bipyramidal geometry with the Lewis base tilted significantly away from the cage carbons. The slippage of the apical germanium is such that it could be considered as  $\eta^2$ -bonded to the C<sub>2</sub>B<sub>3</sub> face of the carborane cage. Although some similarities between the *closo*-germacarborane and the *closo*-stannacarborane systems exist, the donor-acceptor complexes of the two metallocarboranes seem to be quite different. Compound IV crystallizes in the monoclinic space group P2<sub>1</sub>/n with *a* = 7.102 (5) Å, *b* = 34.61 (2) Å, *c* = 9.774 (4) Å,  $\beta$  = 102.55 (4)°, *U* = 2345 (2) Å<sup>3</sup>, and *Z* = 4. Full-matrix least-squares refinement converged at *R* = 0.040 and *R*<sub>w</sub> = 0.038.

## Introduction

In the early 1970s Rudolph and co-workers<sup>1</sup> reported the synthesis of the series 1,2,3-MC<sub>2</sub>B<sub>9</sub>H<sub>11</sub> (M = Ge, Sn, Pb) in which the apical heteroatom, in its 2+ oxidation state, replaced a BH unit in the parent C<sub>2</sub>B<sub>10</sub>H<sub>12</sub> icosahedron. The structures were assigned on the basis of infrared, mass, and NMR spectroscopy. Structural assignment by X-ray crystallography was not possible, presumably due to disorder in the solid-state structures of these almost spherically symmetric compounds. At about the same time, the synthesis of *closo*-MeGeCB<sub>9</sub>H<sub>11</sub>, -GePCB<sub>9</sub>H<sub>10</sub>, and -GeAsCB<sub>9</sub>H<sub>10</sub> and *nido* species, such as (Me)<sub>3</sub>MB<sub>10</sub>H<sub>12</sub> (M = Ge and Sn) were reported.<sup>1,2</sup> More recently, the aluminacarborane *closo*-2,3-(Me)<sub>2</sub>-1-C<sub>2</sub>H<sub>5</sub>-1,2,3-AlC<sub>2</sub>B<sub>9</sub>H<sub>9</sub> was found to be a convenient carbollyl-transfer reagent when reacted with a number of main-group halides to produce 2,3-(Me)<sub>2</sub>-1,2,3-MC<sub>2</sub>B<sub>9</sub>H<sub>9</sub> (M = Ge, Sn) and 2,3-(Me)<sub>2</sub>-1,1'-(Me)<sub>2</sub>-1,2,3-Sn<sup>IV</sup>C<sub>2</sub>B<sub>9</sub>H<sub>9</sub>. However, as in the previous cases, the solid-state structures of these compounds have not yet been reported.<sup>3</sup>

In 1977, Wong and Grimes reported the synthesis of the smaller carborane homologues M<sup>II</sup>C<sub>2</sub>B<sub>4</sub>H<sub>6</sub> (M<sup>II</sup> = Ge, Sn, Pb).<sup>4</sup> From infrared, mass, and NMR spectroscopic data, the group 14 heteroatom was proposed to occupy one of the apical positions in a pentagonal bipyramid. The existence of GeC<sub>2</sub>B<sub>4</sub>H<sub>6</sub> was inferred from mass spectral data

only, and could not be isolated.<sup>4</sup> As with the MC<sub>2</sub>B<sub>9</sub>H<sub>11</sub> compounds, no X-ray crystal structures could be obtained for any of these species. Although the synthesis and structures of several *C*-trimethylsilyl-substituted *closo*-stannacarboranes and their donor-acceptor complexes have been documented during the past 4 years or so,<sup>1</sup> little is known about the *closo*-germacarboranes, particularly of the small carborane species such as 1-Ge-2,3-C<sub>2</sub>B<sub>4</sub>H<sub>6</sub>. In our earlier communication, the preliminary results of the synthesis and structure of a donor-acceptor complex 1-Ge(2,2'-C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>)-2,3-(Me<sub>3</sub>Si)<sub>2</sub>-2,3-C<sub>2</sub>B<sub>4</sub>H<sub>4</sub> have been reported.<sup>5</sup> Here we describe, in detail, the preparation, characterization, and properties of *C*-trimethylsilyl-substituted  $\eta^5$ -*closo*-germacarboranes (I-III) and their donor-acceptor complexes with 2,2'-bipyridine (IV-VI). In addition, the single-crystal X-ray analysis of one of the donor-acceptor complexes, 1-(2,2'-bipyridine)-2,3-bis(trimethylsilyl)-2,3-dicarba-1-germa-*closo*-heptaborane(6) (IV), will be presented in detail.

## 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.<sup>6-8</sup> Solutions of the sodium salts of the *nido*-carborane anions [2-(SiMe<sub>3</sub>)-3-(R)-2,3-C<sub>2</sub>B<sub>4</sub>H<sub>5</sub>]<sup>-</sup> (R = SiMe<sub>3</sub>, Me, or H) in THF were prepared by the method of Onak and Dunks.<sup>9</sup> Prior to use, anhydrous tetrachlorogermane (Strem Chemicals, Inc., Newburyport, MA) was

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passed through a  $-78$  °C trap in vacuo to remove any 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  $\text{LiAlH}_4$  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, and silicon-29 pulse Fourier transform NMR spectra, at 200, 64.2, 50.3, and 39.76 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  $^1\text{H}$  NMR spectra with those of authentic samples.

**Synthesis of closo-1-Ge<sup>II</sup>-2-(Me<sub>3</sub>Si)-3-(R)-2,3-C<sub>2</sub>B<sub>4</sub>H<sub>4</sub> (R = Me<sub>3</sub>Si, Me, and H).** A THF (50-mL) solution of  $\text{Na}^+[(\text{Me}_3\text{Si})_2\text{C}_2\text{B}_4\text{H}_5]^-$  (3.10 g, 12.83 mmol),  $\text{Na}^+[(\text{Me}_3\text{Si})(\text{Me})\text{C}_2\text{B}_4\text{H}_5]^-$  (3.56 g, 19.38 mmol), or  $\text{Na}^+[(\text{Me}_3\text{Si})\text{C}_2\text{B}_4\text{H}_5]^-$  (1.13 g, 6.66 mmol) was added in vacuo to a THF solution (15 mL) of BuLi (0.822 g, 12.83 mmol; 1.242 g, 19.39 mmol; or 0.427 g, 6.66 mmol) at 0 °C, and the resulting mixture was stirred constantly at this temperature for 2 h. This mixture was then allowed to react with  $\text{GeCl}_4$  (6.42 mmol, 9.69 mmol, or 3.33 mmol) with constant stirring at 0 °C for 2 h. After removal of THF via vacuum distillation for 6 h, the reaction flask containing a dark residue was attached to a series of detachable high-vacuum U traps. With identical distillation and/or sublimation procedures, temperatures and times as described for the synthesis of *commo*-bis(germacarborane) derivatives,<sup>10</sup> the dark residue gave  $[(\text{Me}_3\text{Si})_2\text{C}_2\text{B}_4\text{H}_4]\text{Ge}^{\text{II}}$  (I) (1.34 g, 4.62 mmol; collected at  $-10$  °C; 36% yield),  $[(\text{Me}_3\text{Si})(\text{Me})\text{C}_2\text{B}_4\text{H}_4]\text{Ge}^{\text{II}}$  (II) (2.20 g, 9.47 mmol; collected at  $-23$  °C; 49% yield), or  $[(\text{Me}_3\text{Si})\text{C}_2\text{B}_4\text{H}_5]\text{Ge}^{\text{II}}$  (III) (0.33 g, 1.51 mmol; collected at  $-23$  °C; 23% yield) in high purity along with *commo*-bis(germacarborane)  $[(\text{Me}_3\text{Si})_2\text{C}_2\text{B}_4\text{H}_4]\text{Ge}^{\text{IV}}$  (0.58 g, 1.15 mmol; 9.0% yield; mp 107 °C),  $[(\text{Me}_3\text{Si})(\text{Me})\text{C}_2\text{B}_4\text{H}_4]\text{Ge}^{\text{IV}}$  (0.57 g, 1.44 mmol; 7.4% yield; bp 130 °C), or  $[(\text{Me}_3\text{Si})\text{C}_2\text{B}_4\text{H}_5]\text{Ge}^{\text{IV}}$  (0.23 g, 0.63 mmol; 9.5% yield; bp 81 °C) which was collected at 0 °C. In addition to the isolation of *closo*- and *commo*-germacarborane derivatives, the corresponding neutral carborane, *nido*- $[(\text{Me}_3\text{Si})(\text{R})\text{C}_2\text{B}_4\text{H}_6]$  (0.92 g, 4.19 mmol; 0.49 g, 3.03 mmol; or 0.14 g, 0.94 mmol), was also recovered in a trap held at  $-78$  °C.

The physical properties and characterization of I are as follows: pale yellow liquid; bp 205 °C; sensitive to air and moisture; at 25 °C, highly soluble in both polar and nonpolar organic solvents;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , relative to external  $\text{Me}_4\text{Si}$ )  $\delta$  3.81 [q (br), 3 H, basal  $\text{H}_b$ ,  $^1J(^1\text{H}-^{11}\text{B}) = 126$  Hz], 1.25 [q (br), 1 H, apical  $\text{H}_a$ ,  $^1J(^1\text{H}-^{11}\text{B}) = 163$  Hz], 0.45 (s, 18 H,  $\text{Me}_3\text{Si}$ );  $^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , relative to external  $\text{BF}_3\text{-OEt}_2$ )  $\delta$  24.10 [d, 3 B, basal BH,  $^1J(^{11}\text{B}-^1\text{H}) = 126$  Hz],  $-1.53$  [d, 1 B, apical BH,  $^1J(^{11}\text{B}-^1\text{H}) = 163$  Hz];  $^{13}\text{C}$  NMR (relative to external  $\text{Me}_4\text{Si}$ )  $\delta$  135.07 [s (br), cage carbon], 1.68 [q,  $\text{Me}_3\text{Si}$ ,  $^1J(^{13}\text{C}-^1\text{H}) = 120$  Hz];  $^{29}\text{Si}$  NMR (relative to external  $\text{Me}_4\text{Si}$ )  $\delta$   $-0.53$  [m,  $\text{SiMe}_3$ ,  $^2J(^{29}\text{Si}-^1\text{H}) = 6.8$  Hz]. The IR and mass spectral data of I together with their assignments are summarized in Tables S1 and S2.

The physical properties and characterization of II are as follows: light pale yellow liquid; bp 134 °C ( $10^{-6}$  Torr); sensitive to air and moisture; at 25 °C, highly soluble in both polar and nonpolar organic solvents;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , relative to external  $\text{Me}_4\text{Si}$ )  $\delta$  3.87 [q (br), 3 H, basal  $\text{H}_b$ ,  $^1J(^1\text{H}-^{11}\text{B}) = 108$  Hz], 2.10 [q (br), 1 H, apical  $\text{H}_a$ ,  $^1J(^1\text{H}-^{11}\text{B}) = 160$  Hz], 2.71 (s, 3 H, Me), 0.38 (s, 9 H,  $\text{Me}_3\text{Si}$ );  $^{11}\text{B}$  NMR (relative to external  $\text{BF}_3\text{-OEt}_2$ )  $\delta$  20.52 [d,

3 B, basal BH,  $^1J(^{11}\text{B}-^1\text{H}) = 108$  Hz],  $-0.02$  [d, 1 B, apical BH,  $^1J(^{11}\text{B}-^1\text{H}) = 160$  Hz];  $^{13}\text{C}$  NMR (relative to external  $\text{Me}_4\text{Si}$ )  $\delta$  133.96 [s (br), cage carbon (SiCB)], 129.56 [s (br), cage carbon (CCB)], 25.0 [q, 1 C, Me,  $^1J(^{13}\text{C}-^1\text{H}) = 130$  Hz], 0.36 [q, 3 C,  $\text{Me}_3\text{Si}$ ,  $^1J(^{13}\text{C}-^1\text{H}) = 120$  Hz];  $^{29}\text{Si}$  NMR (relative to external  $\text{Me}_4\text{Si}$ )  $\delta$   $-1.83$  [m,  $\text{SiMe}_3$ ,  $^2J(^{29}\text{Si}-^1\text{H}) = 5.8$  Hz]. The IR and mass spectral data of II together with their assignments are summarized in Tables S1 and S2.

The physical properties and characterization of III are as follows: clear liquid; bp 112 °C ( $10^{-6}$  Torr); sensitive to air and moisture; at 25 °C, highly soluble in both polar and nonpolar organic solvents;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , relative to external  $\text{Me}_4\text{Si}$ )  $\delta$  6.65 [s (br), 1 H, cage CH], 3.55 [q (br, overlapping), 3 H, basal  $\text{H}_b$ ,  $^1J(^1\text{H}-^{11}\text{B}) = 143$  Hz], 1.84 [q (br), 1 H, apical  $\text{H}_a$ ,  $^1J(^1\text{H}-^{11}\text{B}) = 168$  Hz], 0.49 [s, 9 H,  $\text{Me}_3\text{Si}$ ];  $^{11}\text{B}$  NMR (relative to external  $\text{BF}_3\text{-OEt}_2$ )  $\delta$  14.21 [d, 1 B, basal BH,  $^1J(^{11}\text{B}-^1\text{H}) = 146$  Hz], 10.11 [d, 2 B, basal BH,  $^1J(^{11}\text{B}-^1\text{H}) = 141$  Hz],  $-0.08$  [d, 1 B, apical BH,  $^1J(^{11}\text{B}-^1\text{H}) = 168$  Hz];  $^{13}\text{C}$  NMR (relative to external  $\text{Me}_4\text{Si}$ )  $\delta$  124.32 [s (br), cage carbon (SiCB)], 106.9 [d (br), cage CH,  $^1J(^{13}\text{C}-^1\text{H}) = 190$  Hz], 0.08 [q,  $\text{Me}_3\text{Si}$ ,  $^1J(^{13}\text{C}-^1\text{H}) = 119$  Hz];  $^{29}\text{Si}$  NMR (relative to external  $\text{Me}_4\text{Si}$ )  $\delta$   $-1.30$  [m,  $\text{SiMe}_3$ ,  $^2J(^{29}\text{Si}-^1\text{H}) = 6.2$  Hz]. The IR and mass spectral data of III together with their assignments are summarized in Tables S1 and S2.

**Synthesis of 1-Ge( $\text{C}_{10}\text{H}_8\text{N}_2$ )-2-(SiMe<sub>3</sub>)-3-(R)-2,3-C<sub>2</sub>B<sub>4</sub>H<sub>4</sub> (R = SiMe<sub>3</sub>, Me, and H).** A benzene solution (10–15 mL) of  $\text{Ge}(\text{SiMe}_3)_2\text{C}_2\text{B}_4\text{H}_4$  (I) (0.62 g, 2.13 mmol),  $\text{Ge}(\text{SiMe}_3)(\text{Me})\text{C}_2\text{B}_4\text{H}_4$  (II) (0.58 g, 2.50 mmol), or  $\text{Ge}(\text{SiMe}_3)\text{C}_2\text{B}_4\text{H}_5$  (III) (2.22 g, 10.17 mmol) was poured in vacuo into a reaction flask containing anhydrous 2,2'-bipyridine,  $\text{C}_{10}\text{H}_8\text{N}_2$  (0.333 g, 2.13 mmol; 0.390 g, 2.497 mmol; or 1.59 g, 10.17 mmol when I, II, or III was used), at  $-78$  °C. When the reaction flask was placed in an ice bath, a bright red and clear solution formed slowly. This mixture was constantly stirred for 8 h at 0 °C. Since the boron-11 NMR spectra of this mixture showed no significant change from its precursor, the stirring of the mixture was continued for 7 days at room temperature during which time the solution turned to dark brown and no gas evolution was detected. The boron-11 NMR spectra of this dark brown solution indicated that the reaction was complete. The solvent, benzene, was then removed slowly by pumping the reaction mixture at 0 °C. After removal of all  $\text{C}_6\text{H}_6$ , the reaction flask was heated to 45–50 °C and pumped through a detachable U trap, held at  $-196$  °C, over a period of 16 h to remove unreacted 2,2'-bipyridine from the product mixture by mild sublimation. A substantial quantity (0.11, 0.19, and 0.74 g when R = SiMe<sub>3</sub>, Me, and H, respectively) of 2,2'-bipyridine was recovered in the U trap held at  $-196$  °C. After removal of all the unreacted 2,2'-bipyridine, the reaction flask was then attached to another detachable U trap held at  $-23$  °C. When the reaction flask was heated to 90 °C in vacuo, over a period of 18 h, a bright red crystalline solid of  $(\text{C}_{10}\text{H}_8\text{N}_2)\text{Ge}(\text{SiMe}_3)_2\text{C}_2\text{B}_4\text{H}_4$  (IV) (0.46 g, 1.030 mmol; 73% yield based on 2,2'-bipyridine consumed), bright reddish orange solid of  $(\text{C}_{10}\text{H}_8\text{N}_2)\text{Ge}(\text{SiMe}_3)(\text{Me})\text{C}_2\text{B}_4\text{H}_4$  (V) (0.21 g, 0.541 mmol; 42% yield based on 2,2'-bipyridine consumed), or a dark red solid of  $(\text{C}_{10}\text{H}_8\text{N}_2)\text{Ge}(\text{SiMe}_3)\text{C}_2\text{B}_4\text{H}_5$  (VI) (0.98 g, 2.62 mmol; 48% yield based on 2,2'-bipyridine consumed) was collected on the inside walls of the U trap. The side arms of both the reaction flask and the U trap were maintained at 90 °C with heating tape during the sublimation.

The physical properties, characterization, and preliminary results of the X-ray analysis of  $(\text{C}_{10}\text{H}_8\text{N}_2)\text{Ge}(\text{SiMe}_3)_2\text{C}_2\text{B}_4\text{H}_4$  (IV) have been reported in an earlier communication.<sup>5</sup> The IR spectral data of this compound are summarized in Table S1. Both the electron-impact (EI) and the chemical ionization (CI) mass spectra of IV do not exhibit the parent ion grouping. The  $^{11}\text{B}$  NMR spectra ( $^1\text{H}$ -coupled and  $^1\text{H}$ -decoupled) of IV at 25 °C in  $\text{CD}_2\text{Cl}_2$  exhibit a broad singlet at 8.01 ppm. However, at low temperature ( $-80$  °C), the proton-coupled boron-11 NMR spectrum of this complex shows three doublets of intensity 1:2:1 at 23.26, 7.72, and  $-0.62$  ppm, respectively. In addition to the coupling constants ( $J$ ) in the boron-11 NMR spectrum, the proton, carbon-13, and silicon-29 NMR spectral data of IV have already been published in an earlier communication.<sup>5</sup>

The physical properties and characterization of V are as follows: mp 49–50 °C at  $10^{-6}$  Torr; very sensitive to air and moisture; at room temperature highly soluble in THF,  $\text{C}_6\text{D}_6$ ,  $\text{CCl}_4$ ,  $\text{CH}_2\text{Cl}_2$ ,

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and  $\text{CDCl}_3$ ;  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , relative to external  $\text{Me}_4\text{Si}$ )  $\delta$  8.68 [d, 2 H, bpy ring,  $^3J(^1\text{H}-^1\text{H}) = 4.1$  Hz], 8.15 [d, 2 H, bpy ring,  $^3J(^1\text{H}-^1\text{H}) = 7.6$  Hz], 7.19 [t, 2 H, bpy ring,  $^3J(^1\text{H}-^1\text{H}) = 7.3$  Hz], 6.72 [t, 2 H, bpy ring,  $^3J(^1\text{H}-^1\text{H}) = 5.5$  Hz], 3.98 [q (br), 3 H, basal  $\text{H}_t$ ,  $^1J(^1\text{H}-^{11}\text{B}) = 139$  Hz], 2.46 (s, 3 H, Me), 1.63 [q (br), 1 H, apical  $\text{H}_t$ ,  $^1J(^1\text{H}-^{11}\text{B}) = 157$  Hz], 0.28 [s, 9 H,  $\text{Me}_3\text{Si}$ ];  $^{11}\text{B}$  NMR ( $\text{CD}_2\text{Cl}_2$ , relative to external  $\text{BF}_3\cdot\text{OEt}_2$ , at  $-80$  °C)  $\delta$  18.79 [d, 1 B, basal BH,  $^1J(^{11}\text{B}-^1\text{H}) = 138$  Hz], 9.05 [d, 2 B, basal BH,  $^1J(^{11}\text{B}-^1\text{H}) = 141$  Hz], 0.154 [d, 1 B, apical BH,  $^1J(^{11}\text{B}-^1\text{H}) = 157$  Hz]; at 25 °C, a broad singlet at 9.72 ppm was observed in both proton-coupled and proton-decoupled  $^{11}\text{B}$  NMR spectra;  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ , relative to external  $\text{Me}_4\text{Si}$ )  $\delta$  154.05 (s, 2,2'-C, bpy ring), 148.72 [d, bpy ring,  $^1J(^{13}\text{C}-^1\text{H}) = 180$  Hz], 136.78 [d, bpy ring,  $^1J(^{13}\text{C}-^1\text{H}) = 165$  Hz], 121.00 [d, bpy ring,  $^1J(^{13}\text{C}-^1\text{H}) = 160$  Hz], 113.66 [d, bpy ring,  $^1J(^{13}\text{C}-^1\text{H}) = 164$  Hz], 134.22 [s (br), cage carbon (SiCB)], 123.76 [s (br), cage carbon (CCB)], 22.46 [q, 1 C, Me,  $^1J(^{13}\text{C}-^1\text{H}) = 130$  Hz], 0.26 [q, 3 C,  $\text{Me}_3\text{Si}$ ,  $^1J(^{13}\text{C}-^1\text{H}) = 120$  Hz];  $^{29}\text{Si}$  NMR (relative to external  $\text{Me}_4\text{Si}$ )  $\delta$  -6.24 [m (br),  $\text{SiMe}_3$ ,  $^2J(^{29}\text{Si}-^1\text{H}) = 6.1$  Hz]. The IR spectral data of V are summarized in Table S1. Both the EI and CI mass spectra of V do not exhibit the parent ion grouping.

The physical properties and characterization of VI are as follows: mp 45–46 °C at  $10^{-6}$  Torr; very sensitive to air and moisture; at room temperature highly soluble in almost all of the organic solvents;  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , relative to external  $\text{Me}_4\text{Si}$ )  $\delta$  8.64 [d, 2 H, bpy ring,  $^3J(^1\text{H}-^1\text{H}) = 7.60$  Hz], 8.60 [d, 2 H, bpy ring,  $^3J(^1\text{H}-^1\text{H}) = 8.56$  Hz], 8.51 [t, 2 H, bpy ring,  $^3J(^1\text{H}-^1\text{H}) = 3.84$  Hz], 7.30 [t, 2 H, bpy ring,  $^3J(^1\text{H}-^1\text{H}) = 7.50$  Hz], 6.97 [s (br), 1 H, cage CH], 3.85 [q (br), 3 H, basal  $\text{H}_t$ ,  $^1J(^1\text{H}-^{11}\text{B}) = 133$  Hz], 1.48 [q (br), 1 H, apical  $\text{H}_t$ ,  $^1J(^1\text{H}-^{11}\text{B}) = 150$  Hz];  $^{11}\text{B}$  NMR ( $\text{CD}_2\text{Cl}_2$ , relative to external  $\text{BF}_3\cdot\text{OEt}_2$ , at  $-80$  °C)  $\delta$  17.65 [d, 1 B, basal BH,  $^1J(^{11}\text{B}-^1\text{H}) = 143$  Hz], 10.34 [d (br), 2 B, basal BH,  $^1J(^{11}\text{B}-^1\text{H}) = 122$  Hz], -2.69 [d, 1 B, apical BH,  $^1J(^{11}\text{B}-^1\text{H}) = 150$  Hz]; at 25 °C, a broad singlet at 11.01 ppm was observed in both proton-coupled and proton-decoupled  $^{11}\text{B}$  NMR spectra;  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ , relative to external  $\text{Me}_4\text{Si}$ )  $\delta$  156.58 (s, 2,2'-C, bpy ring), 149.26 [d, bpy ring,  $^1J(^{13}\text{C}-^1\text{H}) = 178$  Hz], 136.54 [d, bpy ring,  $^1J(^{13}\text{C}-^1\text{H}) = 161$  Hz], 123.64 [d, bpy ring,  $^1J(^{13}\text{C}-^1\text{H}) = 131$  Hz], 121.07 [d, bpy ring,  $^1J(^{13}\text{C}-^1\text{H}) = 134$  Hz], 116.94 [s (br), cage carbon SiCB], 113.91 [d (br), cage CH,  $^1J(^{13}\text{C}-^1\text{H}) = 159$  Hz], -1.39 [q, 3 C,  $\text{Me}_3\text{Si}$ ,  $^1J(^{13}\text{C}-^1\text{H}) = 121$  Hz].  $^{29}\text{Si}$  NMR ( $\text{C}_6\text{D}_6$ , relative to external  $\text{Me}_4\text{Si}$ )  $\delta$  0.71 [m (br),  $\text{SiMe}_3$ ,  $^2J(^{29}\text{Si}-^1\text{H}) = 6.3$  Hz]. The IR spectra data of VI are summarized in Table S1. Both the EI and CI mass spectral of VI do not exhibit the parent ion grouping.

**X-ray Analysis of 1-(2,2'-Bipyridine)-2,3-bis(trimethylsilyl)-[2,3-dicarba-1-germa-closo-heptaborane](6) (IV).** Several large red crystals of the title compound (IV) were grown by vacuum sublimation onto a glass surface. Crystals quickly turned white upon brief exposure to air. One of the crystals was coated with an epoxy resin and mounted on an automatic Syntex  $P_2$  diffractometer, approximately along the  $a$  axis. The unit-cell parameters were determined by least-squares fit of 15 reflections in the range  $15 \leq 2\theta \leq 25^\circ$ . Systematic absences were consistent with 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 did not show any significant decay 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 direct methods (SHELXS 86, G. M. Sheldrick Programs for Structure Solution)<sup>11</sup> and subsequent difference Fourier methods. Full-matrix least-squares refinements were used throughout, the function minimized being  $\sum w(|F_o| - |F_c|)^2$ . The four cage hydrogen atoms were located on difference Fourier maps. The methyl and the aromatic ring hydrogen atomic positions were calculated. All hydrogen atoms were refined isotropically. In the final stages of refinement, a weighting scheme was used (see Table I). Calculations were carried out with the SHELX 76 system of programs (G. M. Sheldrick, University of Cambridge, Cambridge, England).<sup>12</sup> Scattering factors used for

Table I. Crystallographic Data<sup>a</sup> for IV

formula	$\text{C}_{18}\text{H}_{30}\text{B}_4\text{N}_2\text{Si}_2\text{Ge}$
fw	446.46
cryst system	monoclinic
space group	$P2_1/n$
$a$ , Å	7.102 (5)
$b$ , Å	34.61 (2)
$c$ , Å	9.774 (4)
$\beta$ , deg	102.55 (4)
$U$ , Å <sup>3</sup>	2345 (2)
$Z$	4
$D_{\text{calcd}}$ , g cm <sup>-3</sup>	1.26
cryst dimens, mm	0.40 × 0.30 × 0.17
$\mu$ (Mo $K\alpha$ ), cm <sup>-1</sup>	13.94
scan type	$\theta/2\theta$
scan speed, deg min <sup>-1</sup>	2.9–14.0
$2\theta$ range	$3 < 2\theta < 40$
data collected	$\pm hkl$
$T$ , K	295
decay, %	2
unique data	2209
obsd reflcns, $I > 3\sigma(I)$	1793
$R^b$	0.040
$R_w$	0.038
$\Delta\rho$ (max, min), e/Å <sup>3</sup>	0.28, -0.39

<sup>a</sup> Graphite-monochromatized Mo  $K\alpha$  radiation,  $\lambda = 0.71069$  Å. <sup>b</sup>  $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ ,  $R_w = [\sum w(F_o - F_c)^2 / \sum (F_o)^2]^{1/2}$ , and  $w = 1/\sigma^2(F_o) + k(F_o)^2$ , where  $k = 0.000065$ .

Table II. Fractional Atomic Coordinates with Equivalent Isotropic Parameters for the Non-Hydrogen Atoms (Esd's in Parentheses)

	$x$	$y$	$z$	$U(\text{eq})$ , Å <sup>2</sup>
Ge	0.5667 (1)	0.10359 (2)	0.7307 (1)	0.0556 (1)
C(1)	0.8439 (7)	0.1406 (1)	0.8920 (5)	0.040 (1)
C(2)	0.8852 (7)	0.1370 (1)	0.7505 (5)	0.041 (1)
B(3)	0.8679 (10)	0.0938 (2)	0.6984 (7)	0.051 (2)
B(4)	0.8182 (10)	0.0683 (2)	0.8303 (7)	0.054 (2)
B(5)	0.7927 (10)	0.1011 (2)	0.9483 (7)	0.052 (2)
B(6)	0.9961 (10)	0.1034 (2)	0.8722 (6)	0.052 (2)
Si(7)	0.8642 (2)	0.18330 (5)	1.0117 (2)	0.0499 (4)
Si(8)	0.9846 (3)	0.17405 (5)	0.6454 (2)	0.0554 (4)
N(9)	0.4007 (6)	0.0455 (1)	0.7180 (5)	0.051 (1)
N(10)	0.4675 (6)	0.0781 (1)	0.4893 (4)	0.049 (1)
C(11)	0.3738 (8)	0.0300 (2)	0.8381 (7)	0.062 (2)
C(12)	0.2818 (9)	-0.0046 (2)	0.8430 (7)	0.076 (2)
C(13)	0.2155 (8)	-0.0246 (2)	0.7198 (7)	0.067 (2)
C(14)	0.2389 (8)	-0.0084 (2)	0.5970 (7)	0.056 (2)
C(15)	0.3302 (7)	0.0270 (2)	0.5971 (6)	0.045 (2)
C(16)	0.3547 (7)	0.0468 (2)	0.4695 (5)	0.046 (1)
C(17)	0.2645 (8)	0.0349 (2)	0.3371 (6)	0.057 (2)
C(18)	0.2862 (9)	0.0560 (2)	0.2241 (7)	0.069 (2)
C(19)	0.3981 (9)	0.0887 (2)	0.2436 (7)	0.068 (2)
C(20)	0.4871 (9)	0.0988 (2)	0.3781 (6)	0.060 (2)
C(21)	0.7939 (11)	0.2300 (2)	0.9182 (7)	0.080 (2)
C(22)	0.6890 (10)	0.1760 (2)	1.1260 (7)	0.084 (2)
C(23)	1.1125 (8)	0.1858 (2)	1.1252 (6)	0.067 (2)
C(24)	1.0787 (10)	0.1503 (2)	0.5034 (6)	0.080 (2)
C(25)	1.1935 (10)	0.2009 (2)	0.7549 (7)	0.076 (2)
C(26)	0.7865 (10)	0.2071 (2)	0.5589 (7)	0.084 (2)

all atoms as well as  $\Delta f'$  and  $\Delta f''$  for Si were those stored in SHELX 76. Scattering factors and  $\Delta f'$  and  $\Delta f''$  for Ge were taken from ref 13. The final atomic coordinates are given in Table II. Selected bond lengths, bond angles, and torsion angles are presented in Table III.

## Results and Discussion

**Synthesis.** In recent preliminary communications<sup>10a,14</sup> and articles,<sup>10b,15</sup> we have described that the reaction of

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Table III. Selected Bond Lengths (Å), Bond Angles (deg), and Torsion Angles (deg)

Bond Lengths			
Ge-C(1)	2.579 (5)	Ge-C(2)	2.510 (5)
Ge-B(3)	2.255 (7)	Ge-B(4)	2.208 (7)
Ge-B(5)	2.371 (7)	Ge-N(9)	2.321 (4)
Ge-N(10)	2.474 (4)	C(1)-C(2)	1.480 (6)
C(1)-B(5)	1.546 (8)	C(1)-B(6)	1.719 (8)
C(1)-Si(7)	1.871 (5)	C(2)-B(3)	1.576 (8)
C(2)-B(6)	1.726 (8)	C(2)-Si(8)	1.875 (5)
B(3)-B(4)	1.662 (10)	B(3)-B(6)	1.776 (10)
B(4)-B(5)	1.656 (10)	B(4)-B(6)	1.736 (10)
B(5)-B(6)	1.764 (10)	N(9)-C(11)	1.342 (8)
N(9)-C(15)	1.342 (7)	N(10)-C(16)	1.336 (7)
N(10)-C(20)	1.334 (7)		
Selected Bond Angles			
C(1)-Ge-C(2)	33.8 (1)	C(1)-Ge-B(3)	62.5 (2)
C(1)-Ge-B(4)	64.4 (2)	C(1)-Ge-B(5)	36.1 (2)
C(1)-Ge-N(9)	140.7 (1)	C(1)-Ge-N(10)	141.4 (1)
C(2)-Ge-B(3)	38.1 (2)	C(2)-Ge-B(4)	65.9 (2)
C(2)-Ge-B(5)	61.6 (2)	C(2)-Ge-N(9)	147.4 (2)
C(2)-Ge-N(10)	107.6 (1)	B(3)-Ge-B(4)	43.7 (3)
B(3)-Ge-B(5)	69.0 (2)	B(3)-Ge-N(9)	110.4 (2)
B(3)-Ge-N(10)	84.0 (2)	B(4)-Ge-B(5)	42.2 (2)
B(4)-Ge-N(9)	84.1 (2)	B(4)-Ge-N(10)	105.0 (2)
B(5)-Ge-N(9)	104.7 (2)	B(5)-Ge-N(10)	147.1 (2)
N(9)-Ge-N(10)	66.7 (1)	Ge-C(1)-C(2)	70.5 (2)
Ge-C(1)-B(3)	52.4 (2)	Ge-C(1)-B(4)	50.8 (2)
Ge-C(1)-B(5)	64.6 (3)	Ge-C(1)-B(6)	88.5 (3)
Ge-C(1)-Si(7)	136.0 (2)	Ge-C(2)-C(1)	75.7 (3)
Ge-C(2)-B(3)	62.1 (3)	Ge-C(2)-B(4)	51.4 (2)
Ge-C(2)-B(5)	56.5 (2)	Ge-C(2)-B(6)	90.7 (3)
Ge-C(2)-Si(8)	135.5 (2)	Ge-B(3)-C(1)	65.0 (2)
Ge-B(3)-C(2)	79.7 (3)	Ge-B(3)-B(4)	66.6 (3)
Ge-B(3)-B(6)	98.2 (4)	Ge-B(4)-C(1)	64.8 (2)
Ge-B(4)-C(2)	62.7 (2)	Ge-B(4)-B(3)	69.6 (3)
Ge-B(4)-B(5)	74.2 (4)	Ge-B(4)-B(6)	101.2 (4)
Ge-B(5)-C(1)	79.3 (3)	Ge-B(5)-C(2)	61.9 (2)
Ge-B(5)-B(4)	63.6 (3)	Ge-B(5)-B(6)	94.4 (4)
Torsion Angles			
N(9)-Ge-B(4)-B(3)	128.0 (8)	N(9)-Ge-B(4)-B(5)	-119 (1)
N(10)-Ge-B(4)-B(3)	64.1 (9)	N(10)-Ge-B(4)-B(5)	176.5 (7)
N(9)-Ge-B(3)-C(1)	177 (1)	N(9)-Ge-B(3)-C(2)	-169 (1)
N(10)-Ge-B(3)-C(1)	129 (1)	N(10)-Ge-B(3)-C(2)	109 (1)
N(9)-Ge-C(1)-Si(7)	-107.2 (8)	N(9)-Ge-C(2)-Si(8)	-164.2 (8)
N(10)-Ge-C(1)-Si(7)	130.8 (8)	N(10)-Ge-C(2)-Si(8)	50 (1)

$M^{IV}Cl_4$  with the lithium or the sodium lithium salt of *nido*-[( $Me_3Si$ )( $R$ ) $C_2B_4H_4$ ] $^{2-}$  ( $R = SiMe_3, Me, \text{ or } H$ ) produces a mixture of  $M(IV)$  ( $M = Si$  and  $Ge$ ) sandwiched *commo*-bis(sila- or germacarborane) and the  $M(II)$ -inserted *closo*-sila- or germacarborane in varying yields. However, when  $SnCl_4$  was used, the only metallacarborane product was  $Sn(II)$ -inserted *closo*-stannacarborane.<sup>10b</sup> These reactions, involving reductive insertion to yield a *closo*-metallacarborane and nonreductive insertion to a *commo* product, presumably depend on the oxidation potential of the group 14 heteroatom. It is important to point out that the reaction of  $Ge^{IV}Cl_4$  with the monolithium salt of *nido*-[( $Me_3Si$ ) $_2C_2B_4H_5$ ] $^-$  produces both *commo*-1- $Ge^{IV}$ -[2,3-( $Me_3Si$ ) $_2$ -2,3- $C_2B_4H_4$ ] $_2$  and *closo*-1- $Ge^{II}$ -2,3-( $Me_3Si$ ) $_2$ -2,3- $C_2B_4H_4$  in 20 and 27% yields, respectively, and use of the dilithium salt gave low, irreproducible yields.<sup>10</sup> However, in the present study, the predominant heterocarborane product of the reaction of  $GeCl_4$  with  $NaLi$  [( $Me_3Si$ )( $R$ ) $C_2B_4H_4$ ] $^-$  ( $R = SiMe_3, Me, H$ ) is the  $Ge(II)$ -inserted *closo*-germacarborane 1- $Ge$ -2,3-( $Me_3Si$ ) $_2$ -2,3- $C_2B_4H_4$  (I), 1- $Ge$ -2-( $Me_3Si$ )-3-( $Me$ )-2,3- $C_2B_4H_4$  (II), or 1- $Ge$ -2-

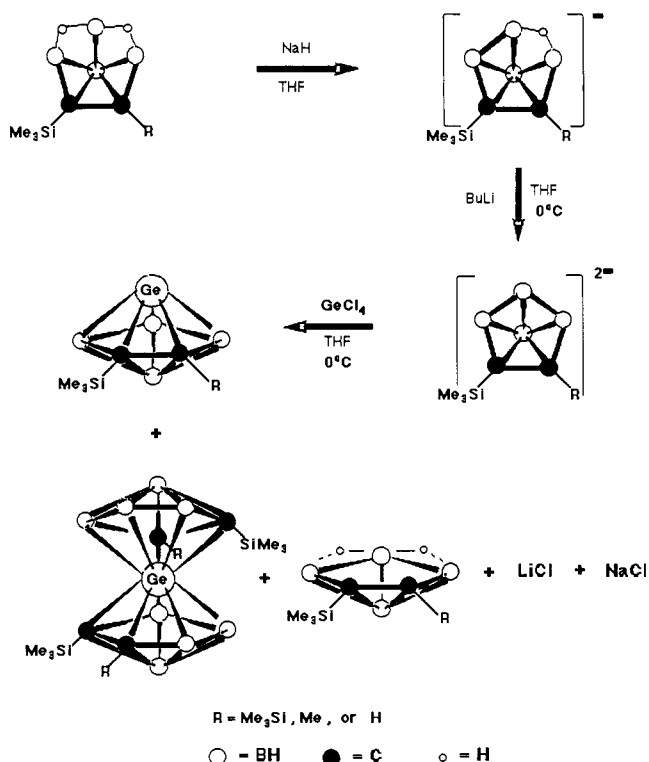


Figure 1. A reaction scheme describing the reductive and non-reductive insertions of germanium atoms into  $C_2B_4$  carborane systems with the formation of the corresponding neutral *nido*-carborane precursors.

( $Me_3Si$ )-2,3- $C_2B_4H_5$  (III) in 36, 49, or 23% yields (see Figure 1 and Experimental Section). The yields of the corresponding *commo*-bis(germacarborane) derivatives are 9.0, 7.4, and 9.5%, respectively. Since the results obtained using the  $NaLi$  salt of the  $C_2B_4$  carborane are substantially different from those of either the mono- or dilithium salts, it is apparent that the size of the cation plays a major role in the selectivity and the extent of either the reductive or the nonreductive heteroatom insertion. This observation is consistent with the results of Hawthorne and co-workers who have shown that the reaction of  $SiCl_4$  with 2 equiv of the dilithium salt of *nido*-[7,8- $C_2B_9H_{11}$ ] $^{2-}$  produces the *commo*-3,3'- $Si(3,1,2-C_2B_9H_{11})_2$ ,<sup>16,17</sup> while the reaction with the disodium salt of the dicarborane anion does not produce the desired *commo*-bis(silacarborane).<sup>18</sup>

Unlike the stannacarborane systems,<sup>19-22</sup> the *closo*-germacarboranes I, II, and III do not readily form the donor-acceptor complexes 1- $Ge(C_{10}H_8N_2)$ -2,3-( $Me_3Si$ ) $_2$ -2,3- $C_2B_4H_4$  (IV), 1- $Ge(C_{10}H_8N_2)$ -2-( $Me_3Si$ )-3-( $Me$ )-2,3- $C_2B_4H_4$  (V), and 1- $Ge(C_{10}H_8N_2)$ -2-( $Me_3Si$ )-2,3- $C_2B_4H_5$  (VI) with 2,2'-bipyridine in benzene. Even though the extent of Lewis acidity of I-III for the formation of their donor-acceptor complexes IV-VI and their solution behavior, discussed in the following section, are quite different from those of the stannacarborane systems, the solid-state X-ray

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structural analysis of the donor-acceptor complex (IV) shows a somewhat similar bonding position of the apical heteroatom with respect to the  $C_2B_3$  face of the carborane fragment. The details of the X-ray analysis are presented below.

**Characterization.** The *closo*-germacarboranes I, II, and III, and their donor-acceptor complexes 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). The donor-acceptor complex IV was also characterized by single-crystal X-ray diffraction (Tables I-III).

**Mass Spectra.** The electron-impact (EI) mass spectra of I-III exhibit characteristic groupings corresponding to their molecular ions (see Table S2). The absence of the parent ion and the presence of a bipyridine ion fragment with 100% relative intensity along with the parent grouping of the corresponding germacarborane precursor have been observed in the EI mass spectrum of each of the donor-acceptor complexes, IV-VI. This indicates that the Ge-N bonds in the complexes are weak; consequently, these bonds were broken during the ionization at 70 eV. The most intense peak for all the *closo*-germacarboranes I-III corresponded to the parent minus one methyl group and is a common phenomenon observed for all the  $Me_3Si$  containing compounds.<sup>6,10b,19,23</sup>

**NMR, IR, and Visible/Ultraviolet Spectra.** The  $^1H$ ,  $^{11}B$ ,  $^{13}C$ , and  $^{29}Si$  NMR spectra, as well as the infrared (IR) spectra, of I-III are all consistent with an apical position of the germanium(II) in a pentagonal-bipyramidal cluster. Except for a very small shift of the apical  $^{11}B$  resonance, the  $^{11}B$  NMR spectra of I-III bear striking similarities to those of the corresponding stannacarboranes<sup>24</sup> which have been shown by X-ray crystal structure determination to have a *closo* geometry.<sup>19,25</sup> The apical position, rather than a terminal position of the germanium in I-III, can be further inferred from the absence of a separate  $^{11}B$ -Ge singlet in the proton-coupled spectra and the large  $^{11}B$  chemical shifts of the apical and basal boron resonances on complexation with germanium. If the germanium is in a 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 the precursors.<sup>26,27</sup> In addition, neither the  $^{11}B$ ,  $^1H$  NMR spectra nor the IR spectra of I-III show any evidence of B-H-B bridges.

However, the solution properties of complexes IV-VI are quite different from those of their tin analogues.<sup>19,20,22</sup> At room temperature, the  $^{11}B$  NMR spectrum ( $^1H$ -coupled and  $^1H$ -decoupled) of each donor-acceptor complex (IV, V, or VI) in both polar and nonpolar solvents exhibits a broad, symmetric singlet. This broad singlet, in between the basal and apical BH resonances, appears to be very small in intensity when the spectra were run on the solution mixture immediately after the addition of 2,2'-bipyridine to the solutions of *closo*-germacarboranes. Over a period of about 7 days, this symmetric singlet grows in intensity at the expense of both the basal and apical BH resonances. The  $-80^\circ C$   $^{11}B$  NMR spectrum of each of the donor-acceptor complexes, IV-VI, in  $CD_2Cl_2$  weakly ex-

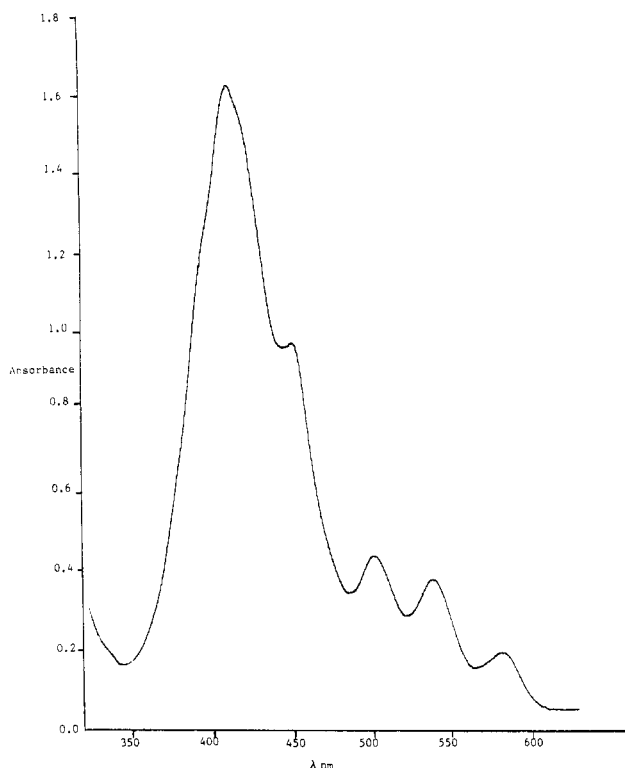
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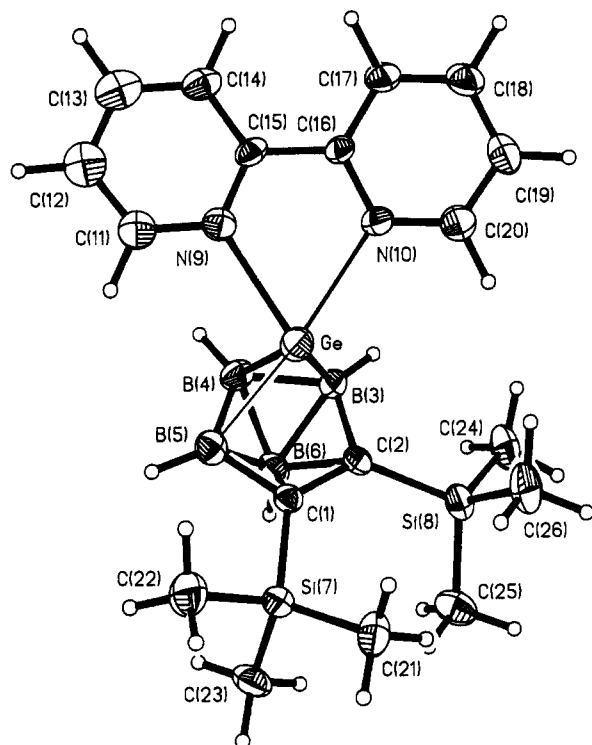
**Figure 2.** Typical visible and ultraviolet spectrum of 1-Ge<sup>II</sup>(C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>)-2-(SiMe<sub>3</sub>)-3-(Me)-2,3-C<sub>2</sub>B<sub>4</sub>H<sub>4</sub> (V).

hibits three BH doublets of 1:2:1 intensities, despite the fact that these complexes are not very soluble in  $CD_2Cl_2$  at  $-80^\circ C$  (see Experimental Section). Due to this limited solubility, spectra could not be obtained below  $-80^\circ C$ .

Figure 2 shows the visible/ultraviolet (UV) absorption spectrum of V in benzene, which is typical of these donor-acceptor complexes. The maximum at about 400 nm gives rise to the characteristic deep red color of these complexes. Since neither bipyridine nor the germacarboranes absorb in this region, complex formation can be followed by monitoring the visible/UV spectra of mixtures of I-III and bipyridine. When benzene solutions of the donor and acceptor molecules are mixed, absorption peaks such as those shown in Figure 2 developed slowly with time over a period of several days that parallels the slow  $^{11}B$  NMR spectral changes observed for IV-VI. Due to instability of the complexes and the long reaction times, reliable kinetic and equilibrium results could not be obtained for the bipyridine-germacarborane complexes. However, both the visible/UV and  $^{11}B$  NMR spectroscopic results indicate that at least two different kinetic processes are taking place; a slow formation of the bipyridine-germacarborane adduct, followed by a rapid intra- or intermolecular process which causes all the basal and apical boron atoms to become equivalent on an NMR time scale.

This fluxional behavior has not been observed in the bipyridine-stannacarborane system. The X-ray crystallographic structure of IV, discussed in the following section, is not too helpful in explaining the solution behavior. It has the same general structural features of the bipyridine-stannacarboranes,<sup>19-21</sup> that is, the bipyridine is coordinated to a slipped germanium atom and is oriented away from the cage carbons of the carborane (see Figure 3). It is more consistent with the  $^{11}B$  NMR spectrum at  $-80^\circ C$  than it is with the room-temperature spectrum and could represent only one of several isomeric forms of IV that exist in solution.

**Crystal Structure of 1-Ge(C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>)-2,3-(Me<sub>3</sub>Si)<sub>2</sub>-2,3-C<sub>2</sub>B<sub>4</sub>H<sub>4</sub> (IV).** The X-ray crystal structure of IV, rep-



**Figure 3.** ORTEP view of 1-Ge<sup>II</sup>(C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>)-2,3-(SiMe<sub>3</sub>)<sub>2</sub>-2,3-C<sub>2</sub>B<sub>4</sub>H<sub>4</sub> (IV) showing the atom numbering scheme and thermal ellipsoids at the 30% probability level. The thinner lines represent weaker interactions between Ge and B(5) and between Ge and N(10).

resented in Figure 3, shows an extreme displacement of the germanium from the centroidal position above the C<sub>2</sub>B<sub>3</sub> face in its distorted pentagonal-bipyramidal geometry, and the Lewis base 2,2'-bipyridine is tilted significantly away from the cage carbons with particular B-Ge-N orientation angles of about 84–105°. The average Ge-C(cage) distance of 2.544 (5) Å is 0.336 Å longer than the germanium-unique boron distance [2.208 (7) Å] (see Table III). The corresponding differences in the 2,2'-bipyridine complexes of the stannacarborane 1-Sn-2-(SiMe<sub>3</sub>)<sub>2</sub>-3-(R)-2,3-C<sub>2</sub>B<sub>4</sub>H<sub>4</sub> are 0.36 and 0.459 Å when R = SiMe<sub>3</sub> and Me, respectively.<sup>19,20</sup> In the case of the 2,2'-bipyrimidine complex of the *closo*-1-Sn-2,3-(Me<sub>3</sub>Si)<sub>2</sub>-2,3-C<sub>2</sub>B<sub>4</sub>H<sub>4</sub>, the Sn-C(cage) distance is 0.267 Å longer than the Sn-B(unique) distance.<sup>28</sup> Surprisingly, one of the germanium-nitrogen distances [Ge-N(10) = 2.474 (4) Å] is significantly longer than the other by about 0.15 Å. As a result of the elongation of one of the Ge-N bonds, the Ge-bound 2,2'-bipyridine is not exactly opposite the C-C(cage) bond, rather it is tilted toward two of the basal borons [B(3) and B(4)] above the C<sub>2</sub>B<sub>3</sub> face. Thus, the apical germanium exhibits stronger bonding interactions with one of the nitrogens of the 2,2'-bipyridine [Ge-N(9) = 2.321 (4) Å] and two consecutive borons [Ge-B(4) = 2.208 (7) and Ge-B(3) = 2.255 (7) Å] of the C<sub>2</sub>B<sub>3</sub> face than with the other similar atoms in IV. Consequently, Ge-B(5) and Ge-N(10) distances of

2.371 (7) and 2.474 (4) Å are significantly longer than the other similar bond distances in IV. The slippage of the apical germanium is such that it could be considered as  $\eta^2$ -bonded to the C<sub>2</sub>B<sub>3</sub> face of the carborane cage.

The dihedral angle between the planes formed by the C<sub>2</sub>B<sub>3</sub> face of the carborane cage and the 2,2'-bipyridine ring is -49 (2)° (see Table S4) and is quite different from those of the complexes of the stannacarboranes where tilting of the bipyridine ring toward one side of the cage is not evident.<sup>19,20</sup> Since the 2,2'-bipyridine nitrogens are equivalent and the *closo*-germacarborane I is, presumably, symmetric to a plane bisecting the C-C cage bond and containing B(4) and B(6), there is no apparent reason for the tilting of the bipyridine and the differences in the Ge-N and Ge-B(3), B(5) bond lengths in IV. Recent MNDO-SCF calculations of the model compound 1-Sn-(2,2'-C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>)-2,3-C<sub>2</sub>B<sub>4</sub>H<sub>6</sub><sup>29</sup> indicate that such distortions would arise as the bipyridine molecule is twisted about the tin-carborane cage bond. Such a twisting may be due to crystal packing forces, or it may be that IV is just one of several isomeric forms (see above). Preliminary MNDO-SCF calculations<sup>30</sup> on IV predict the germanium atom to be  $\eta^1$ -bonded to B(4) which is not in accord with its X-ray crystal structure.

Our results indicate that although some similarities between the *closo*-germacarborane and the *closo*-stannacarborane systems of the type 1-M-2-(SiMe<sub>3</sub>)<sub>2</sub>-3-(R)-2,3-C<sub>2</sub>B<sub>4</sub>H<sub>4</sub> (M = Ge, Sn; R = SiMe<sub>3</sub>, Me, H) exist, the donor-acceptor complexes of the two metallacarboranes seem to be quite different. Presently, there is no ready explanation for the kinetically slow formation of compounds IV-VI or of their room-temperature spectra. A study of the properties of other donor-acceptor complexes of the *closo*-germacarboranes may give information on the various processes taking place. Such studies are currently underway in our laboratories.

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**Registry No.** I, 104034-07-3; II, 116466-56-9; III, 116466-57-0; IV, 110510-82-2; V, 116502-67-1; VI, 116466-58-1; Na[(Me<sub>3</sub>Si)<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>5</sub>], 91633-70-4; Na[(Me<sub>3</sub>Si)(Me)C<sub>2</sub>B<sub>4</sub>H<sub>5</sub>], 91633-71-5; Na[(Me<sub>3</sub>Si)C<sub>2</sub>B<sub>4</sub>H<sub>6</sub>], 91633-72-6; GeCl<sub>4</sub>, 10038-98-9; [(Me<sub>3</sub>Si)<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>4</sub>]<sub>2</sub>Ge, 104069-93-4; [(Me<sub>3</sub>Si)(Me)C<sub>2</sub>B<sub>4</sub>H<sub>4</sub>]<sub>2</sub>Ge, 109284-52-8; [(Me<sub>3</sub>Si)C<sub>2</sub>B<sub>4</sub>H<sub>5</sub>]<sub>2</sub>Ge, 109284-53-9; Li[(Me<sub>3</sub>Si)<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>5</sub>], 104034-08-4; 2,2'-bipyridine, 366-18-7.

**Supplementary Material Available:** Listings of IR absorptions (Table S1) of I, II, III, IV, V, and VI, mass spectrometric data (Table S2) of I, II, and III, a table of anisotropic temperature factors of IV (Table S3), a table of atomic displacements from the least-squares planes of IV (Table S4), and a table of hydrogen atom coordinates and isotropic displacement parameters of IV (Table S5) (6 pages); a listing of structure factors of IV (10 pages). Ordering information is given on any current masthead page.

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