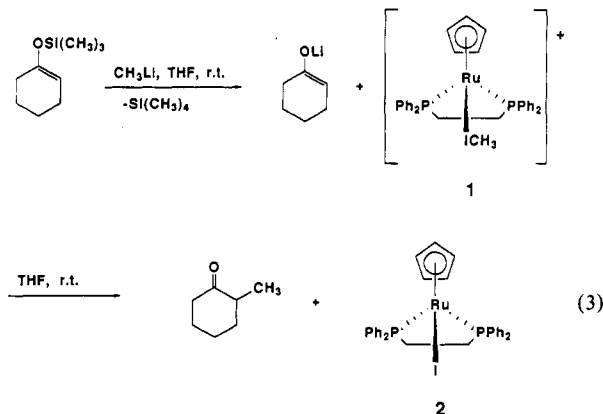
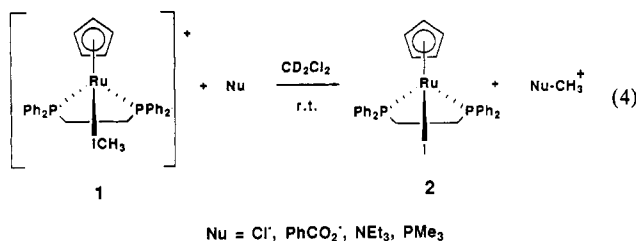


is isolated in >80% yield, after aqueous workup. This reaction demonstrates the first application of a transition-metal halocarbon complex in a selective carbon-carbon bond formation reaction.

Other carbon nucleophiles are also methylated by 1. The lithium enolate, shown in eq 3 and obtained via desilylation of the corresponding trimethylsilyl enol ether, reacts with 1b in THF to yield 2-methylcyclohexanone (60%, by GC<sup>10</sup>) as shown in eq 3. The silyl enol ether itself, however, is not sufficiently nucleophilic to react with 1.

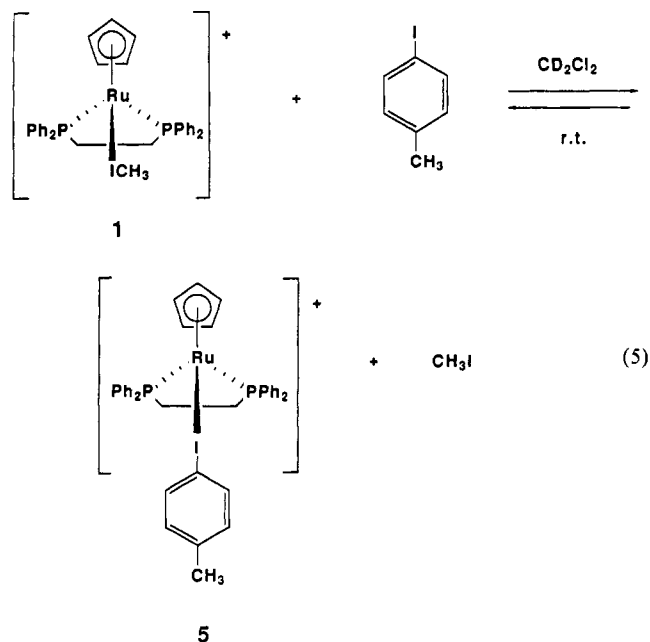


In addition to carbon nucleophiles, the iodomethane complex 1 also reacts with a wide range of other nucleophiles (eq 4). In all cases, addition of the nucleophile to



the iodomethane complex 1b results in rapid and quantitative formation of the ruthenium iodide complex 2 and the corresponding methylation products, as identified by <sup>1</sup>H NMR. Similar reactions with hindered amines<sup>28</sup> and phosphines<sup>21</sup> are known for other iodomethane complexes. In striking contrast, the iridium complex [IrH<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>(IME)<sub>2</sub>][SbF<sub>6</sub>]<sup>28</sup> gives ligand displacement, rather than methylation, with these nucleophiles. Reaction of 1b with less nucleophilic species such as acetone, acetonitrile, and pyridine resulted in complete displacement to generate free iodomethane and the cationic complexes [Cp(dppe)Ru(L)]PF<sub>6</sub> (L = (CH<sub>3</sub>)<sub>2</sub>CO, CH<sub>3</sub>CN, C<sub>5</sub>H<sub>5</sub>N), the identities of which were verified by independent synthesis.<sup>11</sup>

A new iodoarene complex, [Cp(dppe)Ru(IC<sub>6</sub>H<sub>4</sub>-p-CH<sub>3</sub>)]PF<sub>6</sub> (5), can also be prepared by a procedure similar to that employed for 1b and is characterized by <sup>1</sup>H NMR.<sup>12</sup> Iodomethane and *p*-iodotoluene compete for the coordi-



nation site at ruthenium as depicted in eq 5. The equilibrium constant for eq 4 is  $0.17 \pm 0.02$  (298 K), determined by <sup>1</sup>H NMR. The value of *K* apparently reflects both the increased steric demands and lower basicity of the *p*-iodotoluene ligand. Further experiments to quantify the relative and absolute M-XR bond strengths in ruthenium(II) halocarbon complexes are in progress.

In conclusion, we have shown a new synthetic route to a transition-metal iodomethane complex, which we expect to be general for the reaction of carbon electrophiles with other coordinatively saturated, oxidation-resistant halide complexes.

Furthermore, we have demonstrated the first example of selective carbon-carbon bond formation by a transition-metal halocarbon complex. We suspect that this reaction may have implications for methylation in organic synthesis and are currently investigating its scope and limitations.

**Acknowledgment.** We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work and Martin McGrath for obtaining the <sup>31</sup>P NMR spectrum.

### Synthesis and Structure of 2,3-Bis(trimethylsilyl)-5-(trichlorogermyl)-2,3-dicarba-1-germa-closo-heptaborane(6): A Novel, Potential Intermediate for Extended Germacarboranes of Mixed Valences

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**Summary:** The reaction of *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> (I) with a slight excess of GeCl<sub>4</sub> at 135 °C in the absence of solvent produced a novel germacarborane,

(9) In a typical procedure, to a cooled (0 °C) solution of 1b (100 mg, 0.117 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (15 mL) was added the enamine (0.37 mL, 2.35 mmol, 20 equiv). After being warmed to room temperature (1 h), the reaction mixture was hydrolyzed with acetate buffer (15 mL, 0.2 M, pH 4) for 1 h, the organic layer separated, washed with dilute HCl, NaHCO<sub>3</sub>, and brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and evaporated. The residue was dissolved in hexanes, filtered through a short column of silica to remove the ruthenium complex, and analyzed by GC.

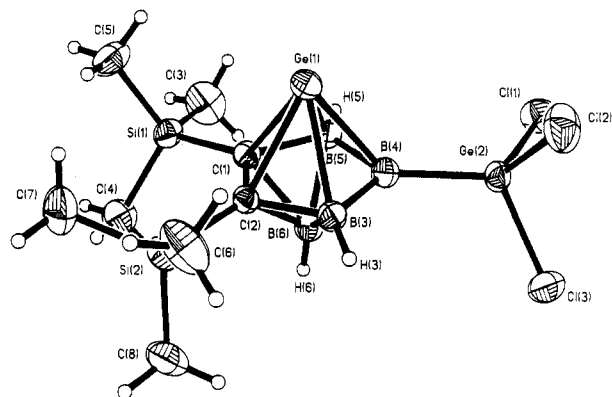
(10) The aqueous workup employed precluded quantification of any O-methylation products which may have been formed.

(11) Davies, S. G.; Scott, F. J. *Organomet. Chem.* 1980, 188, C41.  
(12) <sup>1</sup>H NMR (250 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 7.75-7.20 (c, PPh), 6.649 (d, <sup>3</sup>J<sub>HH</sub> = 8.1 Hz, ArI), 6.500 (d, <sup>3</sup>J<sub>HH</sub> = 8.1 Hz, ArI), 4.902 (s, C<sub>5</sub>H<sub>5</sub>), 2.75-2.20 (c, CH<sub>2</sub>CH<sub>2</sub>), 2.243 (s, ArMe). We have not yet been able to prepare analytically pure samples of 5; the major contaminants appear to be 2 and *p*-iodotoluene, by <sup>1</sup>H NMR.

*closo*-1-Ge<sup>II</sup>-2,3-(Me<sub>3</sub>Si)<sub>2</sub>-5-(Ge<sup>IV</sup>Cl<sub>3</sub>)-2,3-C<sub>2</sub>B<sub>4</sub>H<sub>3</sub> (II), as an air-sensitive, colorless, crystalline, and sublimable solid, in 44% yield. The X-ray crystal structure of II unambiguously shows that one germanium atom, formally in a +2 oxidation state, is  $\eta^5$ -bonded to the planar face of the C<sub>2</sub>B<sub>4</sub> carborane ligand and is located directly in the centroidal position above the C<sub>2</sub>B<sub>3</sub> face and the other germanium atom, formally in a +4 oxidation state, is involved in an exopolyhedral GeCl<sub>3</sub> moiety that is bonded to the unique boron of the planar face via B-Ge  $\sigma$  bond.

Icosahedral germacarboranes incorporating a Ge(II) atom as the apical heteroatom were first reported by Rudolph and co-workers in 1969.<sup>1</sup> Since then there has been a number of reports<sup>2-4</sup> in the literature concerning the synthesis of either *closo* germanium species such as MeGeCB<sub>10</sub>H<sub>11</sub>, GePCB<sub>9</sub>H<sub>10</sub>, GeAsCB<sub>9</sub>H<sub>10</sub>, or Ge-(CMe)<sub>2</sub>B<sub>9</sub>H<sub>9</sub> or *nido* species such as (Me)<sub>2</sub>GeB<sub>10</sub>H<sub>12</sub>. Their structures were assigned solely on the basis of infrared, mass, and NMR spectroscopic data, and solid-state structures have not been reported to date.<sup>2-4</sup> In the latter part of the 1970s, Wong and Grimes reported the existence of a smaller germacarborane GeC<sub>2</sub>B<sub>4</sub>H<sub>6</sub> from mass spectral data but could not be isolated.<sup>5</sup> As in the cases of icosahedral group 14 heterocarborane systems, no X-ray crystal structures could be obtained for any of the smaller carborane homologues MC<sub>2</sub>B<sub>4</sub>H<sub>6</sub> (M = Ge, Sn, Pb). However, during the past 5 years or so, there have been several reports from our laboratories on the syntheses and structures of a number of C-trimethylsilyl-substituted *commo*-bis(sila- or germacarborane) derivatives, *closo*-stannacarboranes, and their donor-acceptor complexes.<sup>4</sup> Although little is known about the *closo*-germacarboranes, particularly of the smaller carborane species such as 1-Ge-2,3-C<sub>2</sub>B<sub>4</sub>H<sub>6</sub>, we have recently reported that the C-SiMe<sub>3</sub>-substituted germacarboranes can be prepared in macroscale by a reductive insertion of germanium into the Na/Li salt of the carborane dianion [2-(Me<sub>3</sub>Si)-3-(R)-2,3-C<sub>2</sub>B<sub>4</sub>H<sub>4</sub>]<sup>2-</sup> (R = SiMe<sub>3</sub>, Me or H) in tetrahydrofuran.<sup>6</sup> Since these germacarboranes are liquids at 25 °C and glassy solids at low temperatures, X-ray structures could not be obtained. The only solid-state structural information available to date for any germacarboranes have been for the Ge<sup>IV</sup>-inserted *commo*-1,1'-Ge-[2,3-(Me<sub>3</sub>Si)<sub>2</sub>-2,3-C<sub>2</sub>B<sub>4</sub>H<sub>4</sub>]<sub>2</sub><sup>7a,b</sup> and Ge<sup>II</sup>-incorporated 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>.<sup>6,8</sup> Here we report the synthesis and structure of the first germacarborane that contains germanium atoms formally in both +2 and +4 oxidation states at reactive sites of the C<sub>2</sub>B<sub>4</sub> polyhedron.

A 4.49-mmol (1.51-g) sample of *closo*-1-Sn-2,3-(SiMe<sub>3</sub>)<sub>2</sub>-2,3-C<sub>2</sub>B<sub>4</sub>H<sub>4</sub> (I) was allowed to react with anhydrous



**Figure 1.** ORTEP view of II showing the atom numbering scheme and thermal ellipsoids at the 30% probability level. Pertinent parameters include Ge(1)-C(1) = 2.251 (4), Ge(1)-C(2) = 2.244 (4), Ge(1)-B(3) = 2.265 (6), Ge(1)-B(4) = 2.243 (6), Ge(1)-B(5) = 2.250 (6), Ge(2)-B(4) = 1.995 (6), and Ge(2)-Cl(1-3) = 2.145 (2) Å.

GeCl<sub>4</sub> (1.01 g, 4.71 mmol) at 135 °C in the absence of solvent, in a procedure identical with that employed in the synthesis of *commo*-germacarboranes<sup>7b</sup> to produce ca. 0.92 g (collected at 0 °C; 1.96 mmol, 44% yield based on stannacarborane (I) consumed; mp 67 °C at 10<sup>-5</sup> mmHg) of colorless 1-Ge<sup>II</sup>-2,3-(SiMe<sub>3</sub>)<sub>2</sub>-5-(Ge<sup>IV</sup>Cl<sub>3</sub>)-2,3-C<sub>2</sub>B<sub>4</sub>H<sub>3</sub> (II) as a sublimed crystalline product.<sup>9</sup> In addition, a substantial quantity of known neutral *nido*-carborane (Me<sub>3</sub>Si)<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>6</sub> (III) (0.22 g, 1.00 mmol) and *commo*-[(Me<sub>3</sub>Si)<sub>2</sub>C<sub>2</sub>B<sub>4</sub>H<sub>4</sub>]<sub>2</sub>Ge<sup>IV</sup> (IV) (0.33 g, 0.65 mmol) were collected in traps held at -196 and 10 °C, respectively. After sublimation of all the volatile products, an off-white solid, identified as SnCl<sub>2</sub> (not measured), remained in the reaction flask.

The infrared, NMR, and mass spectroscopic data<sup>11</sup> for II are all consistent with its X-ray crystal structure<sup>12</sup> that

(9) Compound II is soluble in THF, CCl<sub>4</sub>, CHCl<sub>3</sub>, CDCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, C<sub>6</sub>H<sub>6</sub>, and C<sub>6</sub>H<sub>14</sub> and is sensitive to air and moisture.

(10) Hosmane, N. S.; Sirmokadam, N. N. *Organometallics* 1984, 3, 1119.

(11) Spectroscopic Data. IR (CDCl<sub>3</sub> vs CDCl<sub>3</sub>): 2945 (s, s), 2900 (sh), 2840 (sh) [ $\nu$ (C-H)], 2575 (s, br), [ $\nu$ (B-H)], 1400 (sh), 1310 (w, br), [ $\delta$ (CH), asym], 1250 (s) [ $\delta$ (CH), sym], 1160 (w, br), 977 (w, br), 830 (vs, br) [ $\rho$ (CH)], 720 (w, br), 620 (w, br), 525 (w, br), 441 (s, s) [ $\delta$ (Ge-Cl), asym], 382 (s, br) [ $\delta$ (Ge-Cl), sym] cm<sup>-1</sup>. FT NMR Data: <sup>1</sup>H NMR (CDCl<sub>3</sub>, relative to external Me<sub>4</sub>Si)  $\delta$  3.79 [q(br), 2 H, basal H, <sup>1</sup>J(<sup>1</sup>H-<sup>13</sup>B) = 133 Hz], 1.40 [q(br), 1 H, apical H, <sup>1</sup>J(<sup>1</sup>H-<sup>13</sup>B) = 175 Hz], 0.46 [s, 18 H, (CH<sub>3</sub>)<sub>2</sub>Si]; <sup>13</sup>B NMR (CDCl<sub>3</sub>, relative to external BF<sub>3</sub>·OEt<sub>2</sub>)  $\delta$  26.21 [d, 2B, basal BH, <sup>1</sup>J(<sup>13</sup>B-H) = 132.5 Hz], 24.68 [s, 1 B, basal B-Ge], -1.70 [d, 1 B, apical BH, <sup>1</sup>J(<sup>13</sup>B-H) = 174.4 Hz]; <sup>13</sup>C NMR (CDCl<sub>3</sub>, relative to external Me<sub>4</sub>Si)  $\delta$  135.04 [s(br), cage carbons], 1.60 [q, (CH<sub>3</sub>)<sub>2</sub>Si, <sup>1</sup>J(<sup>13</sup>C-<sup>1</sup>H) = 120.9 Hz]; <sup>29</sup>Si NMR (CDCl<sub>3</sub>, relative to external Me<sub>4</sub>Si)  $\delta$  1.81 [m, Si(CH<sub>3</sub>)<sub>2</sub>, <sup>2</sup>J(<sup>29</sup>Si-H) = 6.3 Hz]. Mass Spectrum: the electron-impact (EI) mass spectrum of II exhibits a weak parent ion grouping [<sup>76</sup>Ge-(<sup>12</sup>CH<sub>3</sub>)<sub>2</sub>-<sup>28</sup>Si<sub>2</sub>-<sup>12</sup>C<sub>2</sub>-<sup>11</sup>B<sub>4</sub>H<sub>3</sub><sup>37</sup>Cl<sub>2</sub><sup>35</sup>Cl<sup>+</sup>] with the major cutoff at *m/z* 478. Intense groupings with the major cutoffs at *m/z* 330 and 315 corresponded to the ion fragments [<sup>76</sup>Ge-(<sup>12</sup>CH<sub>3</sub>)<sub>2</sub>-<sup>28</sup>Si<sub>2</sub>-<sup>12</sup>C<sub>2</sub>-<sup>11</sup>B<sub>4</sub>H<sub>3</sub><sup>37</sup>Cl<sup>+</sup>] and [<sup>76</sup>Ge-(<sup>12</sup>CH<sub>3</sub>)<sub>2</sub>-<sup>28</sup>Si<sub>2</sub>-<sup>12</sup>C<sub>2</sub>-<sup>11</sup>B<sub>4</sub>H<sub>3</sub><sup>37</sup>Cl<sup>+</sup>], respectively.

(12) Crystal and Experimental Data. Suitable colorless crystals of II (C<sub>8</sub>H<sub>2</sub>B<sub>4</sub>Si<sub>2</sub>Cl<sub>3</sub>Ge<sub>2</sub>, mol wt 468.22) were grown in CDCl<sub>3</sub> solution. Since the crystals were air sensitive, they were sealed in 0.5-mm capillary tubes under dry argon. Data collection was carried out at 298 K by using an automatic Nicolet R3m/V diffractometer, Mo K $\alpha$  radiation. The space group is P $\bar{1}$  with *a* = 6.845 (4) Å, *b* = 11.815 (8) Å, *c* = 12.898 (5) Å,  $\beta$  = 89.47 (4)°,  $\gamma$  = 87.46 (4)°,  $\gamma$  = 81.82 (5)°, *U* = 1031.6 (9) Å<sup>3</sup>, *Z* = 2, and  $d_{\text{calc}}$  = 1.51 g cm<sup>-3</sup>. A total of 3804 independent reflections in the range  $3 \leq 2\theta \leq 50^\circ$  were collected. Data were corrected for Lorentz-polarization and for absorption. Structure was solved by direct methods (SHELXTL-Plus) and subsequent difference Fourier methods. Final full-matrix least-squares refinement (SHELXTL-Plus-Structure Determination Software Program: Nicolet Instrument Corp., 1988) using 2818 reflections with *I* > 3 $\sigma$ (*I*) converged to *R* = 0.040 and *R*<sub>w</sub> = 0.044, *S* = 2.13, ( $\Delta$ / $\sigma$ )<sub>max</sub> = 0.01, and  $\Delta\rho$ (max, min) = 0.54, -0.62 e/Å<sup>3</sup>. All non-hydrogen atoms were refined anisotropically, and silyl methyl H atoms were constrained tetrahedrally. The function minimized being  $\sum w(|F_o| - |F_c|)^2$ , the weight used being  $w = 1/\sigma^2(F_o) + 0.000366/F_o^2$ . Scattering factors for C, H, B, Si, Cl, and Ge used were those stored in SHELXTL-Plus.

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

(2) Wikholm, G. S.; Todd, L. J. *J. Organomet. Chem.* 1974, 71, 219. (3) (a) Jutzi, P.; Galow, P. *J. Organomet. Chem.* 1987, 319, 139. (b) Loffredo, R. E.; Norman, A. D. *J. Am. Chem. Soc.* 1971, 93, 5587.

(4) Hosmane, N. S.; Maguire, J. A. *Molecular Structure and Energetics*; Greenberg, A.; Liebman, J. F., Williams, R. E., Eds.; VCH: New York, 1987, Vol 5, Chapter 14, pp 297-328 and references therein.

(5) Wong, K.-S.; Grimes, R. N. *Inorg. Chem.* 1977, 16, 2053.

(6) Hosmane, N. S.; Islam, M. S.; Pinkston, B. S.; Siriwardane, U.; Baniewicz, J. J.; Maguire, J. A. *Organometallics* 1988, 7, 0000.

(7) (a) Hosmane, N. S.; de Meester, P.; Siriwardane, U.; Islam, M. S.; Chu, S. S. C. *J. Am. Chem. Soc.* 1986, 108, 6050. (b) Islam, M. S.; Siriwardane, U.; Hosmane, N. S.; Maguire, J. A.; de Meester, P.; Chu, S. S. C. *Organometallics* 1987, 6, 1936.

(8) Hosmane, N. S.; Siriwardane, U.; Islam, M. S.; Maguire, J. A.; Chu, S. S. C. *Inorg. Chem.* 1987, 26, 3428.

shows one germanium atom, formally in a +2 oxidation state, is  $\eta^5$ -bonded to the planar face of the  $C_2B_4$  carborane ligand. This germanium is located directly in the centroidal position above the  $C_2B_3$  face [the Ge-C(cage) distances are 2.251 (4) and 2.244 (4) Å, while Ge-B distances are 2.265 (6), 2.243 (6), and 2.250 (6) Å] as represented in the ORTEP diagram of II in Figure 1. The centroidal position of the Ge(II) in II is analogous to the situation found in *closo*-1- $C_2H_5$ -1,2,3- $AlC_2B_9H_{11}$ <sup>13</sup> and *commo*-3,3'-Al[(*exo*-8,9-( $\mu$ -H)<sub>2</sub>Al( $C_2H_5$ )<sub>2</sub>-3,1,2- $AlC_2B_9H_9$ ) (3',1',2'- $AlC_2B_9H_{11}$ )]<sup>14</sup> and in the anionic bis( $C_2B_9$ -carborane)iron sandwich complexes.<sup>15</sup> With the exceptions of these aluminacarboranes and the title compound II, the solid-state structures of all main-group heterocarboranes exhibit a distinct dislocation of the apical heteroatom away from the two cage carbon atoms and toward the three boron atoms.<sup>4</sup> The other germanium atom of II, formally in a +4 oxidation state, is involved in an exopolyhedral  $GeCl_3$  moiety, which is bonded to the unique boron of the  $C_2B_3$  ring via B-Ge  $\sigma$  bond [B(4)-Ge(2) = 1.995 (6) Å]. Since the exopolyhedral  $GeCl_3$  moiety is reactive, it has the potential to undergo nonreductive insertion<sup>7</sup> into a new  $C_2B_4$  or  $C_2B_9$  polyhedron, and the title compound II can be regarded as a potential intermediate for the construction of novel extended mixed-valence germacarborane systems.

Recently, Fenske-Hall<sup>16</sup> and MNDO-SCF<sup>17</sup> molecular orbital (MO) calculations have been used to explain the slip distortion of main-group heterocarboranes and their donor-acceptor complexes. From MNDO-SCF calcula-

tions<sup>17</sup> it was predicted that electron-withdrawing groups on the unique boron should favor a centroidal location of the apical heteroatom. This is precisely what is found in II when the electron-withdrawing  $GeCl_3$  group replaces a terminal hydrogen on the unique boron, the resulting heterocarborane shows no slippage of the apical germanium within the limits of experimental errors (see ORTEP diagram in Figure 1).

The removal of the apical tin by the germanium in the present study is not surprising since the tin is known to be loosely ligated and the stannacarboranes have been used as precursors for the preparation of several *commo*-bis-(germacarborane) and *closo*-osmacarborane derivatives.<sup>7b,10</sup> The unusual aspect of this reaction is the substitution of  $GeCl_3$  moiety for the terminal hydrogen on the unique boron when the molar ratio between  $GeCl_4$  and the stannacarborane precursor is essentially 1:1. The mechanism of this synthetic route is presently under investigation.

A further study on the chemistry of the title compound II, particularly involving the construction of extended mixed-valence germacarboranes, is also currently underway in our laboratories.

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**Supplementary Material Available:** Tables of positional and thermal parameters (Table S1) bond distances and angles (Table S2), torsion angles (Table S3), anisotropic temperature factors (Table S4), and H-atom coordinates and isotropic displacement parameters (Table S5) (5 pages); a listing of observed and calculated structure factors (Table S6) (13 pages). Ordering information is given on any current masthead page.

(13) Churchill, M. R.; Reis, A. H., Jr. *J. Chem. Soc., Dalton Trans.* 1972, 1317.

(14) Rees, W. S., Jr.; Schubert, D. M.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* 1986, 108, 5367.

(15) (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.

(16) Barreto, R. D.; Fehner, T. P.; Hosmane, N. S. *Inorg. Chem.* 1988, 27, 453.

(17) Maguire, J. A.; Ford, G. P.; Hosmane, N. S. *Inorg. Chem.* 1988, 27, 0000.