aldehydes to produce the desired allylic alcohols.[19] Presence of a donor ligand on nickel such as triphenylphosphine proved to accelerate the homo-coupling of alkenyl triflates.[20] For example, addition of a catalytic amount of NiCl$_2$(PPh$_3$)$_2$ (5 mol % of CrCl$_2$) instead of NiCl$_2$ in the reaction of triflate **1** and benzaldehyde under the same condition described above provided 2,3-didecyl-1,3-butadiene (**7**) in 37% yield along with the desired alcohol **2** (35%).

Acknowledgment. We are grateful to Professor Yoshito Kishi at Harvard University for valuable discussions.

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(19) Attempt to complete the Grignard-type reaction between triflate **1** (1.0 equiv) and benzaldehyde (0.5 equiv) with NiCl$_2$ (0.2) and zinc (2.0) in DMF at 25 °C for 6 h resulted in recovery of the starting materials.

(20) (a) Kende, A. S.; Liebeskind, L. S.; Braitsch, D. M. *Tetrahedron Lett.* **1975**, 3375. (b) Zembayashi, M.; Tamao, K.; Yoshida, J.; Kumada, M. *Tetrahedron Lett.* **1977**, 4089.

(21) Bp 112 °C (bath temperature, 2 torr); IR (neat) 3434, 2926, 2854, 1714, 1646, 1459, 1359, 1047, 718 cm^{-1}; NMR (CDCl$_3$) δ 0.92 (t, 3, J = 7 Hz), 1.15–1.75 (m, 18), 1.90–2.15 (m, 3), 2.13 (s, 3), 2.42 (t, 2, J = 7 Hz), 4.06 (t, 1, J = 6 Hz), 4.84 (s, 1), 5.00 (s, 1). Anal. Calcd for C$_{17}$H$_{32}$O$_2$: C, 76.06; H, 12.02. Found: C, 75.97; H, 12.26.

Synthesis and Structure of 2,2′,3,3′-Tetrakis(trimethylsilyl)[1,1′-*commo*-bis(2,3-dicarba-1-germa-*closo*-heptaborane)] (12): A Germanocene Analogue?

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Recent theoretical calculations[1,2] coupled with synthetic[3] and structural investigations, unambiguously show that the lone pair of electrons on the divalent tin in stannocene[4,5] and stannacarborane derivatives[6] is chemically inactive and the metal does not act as a donor atom. But the stannocinium cations[7] and the stannacarboranes behave as Lewis acids when forming complexes with tetrahydrofuran and 2,2′-bipyridine.[8,9] Although a similar study in the analogous germanocene,[10,11] germacarboranes,[6,12] and germaboranes[13] began in early 1970, convenient synthetic methods and crystal structures of (η^5-C$_5$H$_5$)$_2$Ge,[14] (η^5-CH$_3$C$_5$H$_4$)$_2$Ge,[15] (η^5-C$_5$Me$_5$)$_2$Ge,[16] and (η^5-C$_5$CH$_2$Ph$_5$)$_2$Ge[17] were reported only during the last few years. To date, a stannocene or a germanocene analogue in the stanna- or germacarboranes, in which the heteroatom is sandwiched by two carborane cages, has not been reported. We report herein the synthesis, characterization, and crystal structure of [2,3-(Me$_3$Si)$_2$C$_2$B$_4$H$_4$]$_2$Ge^{IV} (I) which may be the first example of a germanocene analogue.

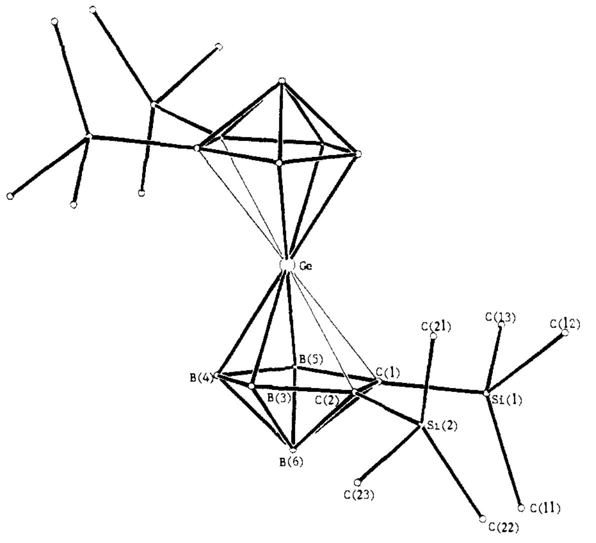

Figure 1, Side view of I; atoms are represented as circles of arbitrary radii. The central Ge atom lies at a center of symmetry. The weaker Ge–C interactions are shown by thinner lines.

Table I. Selected Bond Lengths (Å) with Standard Deviations in Parentheses

Ge–C(1)	2.38 (2)	C(2)–Si(2)	1.88 (2)
Ge–C(2)	2.39 (2)	C(2)–B(3)	1.63 (4)
Ge–B(3)	2.14 (3)	C(2)–B(6)	1.72 (3)
Ge–B(4)	2.08 (3)	B(3)–B(4)	1.56 (4)
Ge–B(5)	2.15 (2)	B(3)–B(6)	1.73 (4)
C(1)–C(2)	1.43 (3)	B(4)–B(5)	1.56 (3)
C(1)–B(5)	1.61 (3)	B(4)–B(6)	1.72 (3)
C(1)–B(6)	1.72 (2)	B(5)–B(6)	1.71 (3)
C(1)–Si(1)	1.89 (2)		

A 6.60-mmol sample of Li$^+$[(Me$_3$Si)$_2$C$_2$B$_4$H$_5$]$^-$ in tetrahydrofuran (50 mL) was allowed to react with anhydrous GeCl$_4$ (0.71 g; 3.3 mmol), in a procedure identical with that employed in the synthesis of stannacarboranes,[6] to produce ca. 0.338 g (collected at 0 °C; 0.67 mmol, 20% yield based on GeCl$_4$ consumed; mp 107 °C) of colorless [(Me$_3$Si)$_2$C$_2$B$_4$H$_4$]$_2$Ge^{IV} (I) as a pure sublimed crystalline product.[18] In addition, neutral *nido*-carborane (Me$_3$Si)$_2$C$_2$B$_4$H$_6$ (II)[19] (0.69 g, 3.14 mmol) and *closo*-germacarborane [(Me$_3$Si)$_2$C$_2$B$_4$H$_4$]Ge^{II} (III) (pale yellow liquid, 0.26 g, 0.90 mmol, 27% yield based on GeCl$_4$ consumed; bp 205 °C) were collected in traps held at −23 and −15 °C, respectively.

The electron-impact (EI) mass spectrum of I (supplementary material, Table IV) exhibited a parent grouping [^{76}Ge(^{12}CH$_3$)$_{12}$^{28}Si$_4$^{12}C$_4$^{11}B$_8$H$_8$]$^+$ with the major cutoff at m/z 512.

The most significant features in both the infrared spectrum[20] and ^{1}H pulse Fourier-transform NMR spectrum[21] of I are the

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(1) Jutzi, P.; Kohl, F.; Hoffmann, P.; Krüger, C.; Tsay, Y.-H. *Chem. Ber.* **1980**, *113*, 757.

(2) (a) Baxter, S. G.; Cowley, A. H.; Lasch, J. G.; Lattman, M.; Sharnn, W. P.; Stewart, C. A. *J. Am. Chem. Soc.* **1982**, *104*, 4064. (b) Dewar, M. J. S.; Grady, G. L.; Kuhn, D. R.; Merz, K. M., Jr. *J. Am. Chem. Soc.* **1984**, *106*, 6773.

(3) (a) Dory, T. S.; Zuckerman, J. J.; Barnes, C. L., *J. Organomet. Chem.*, **1985**, *281*, C1. (b) Dory, T. S.; Zuckerman, J. J.; Rausch, M. D. *J. Organomet. Chem.* **1985**, *281*, C8.

(4) Cowley, A. H.; Jones, R. A.; Stewart, C. A.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Chem. Commun.* **1981**, 921.

(5) Heeg, M. J.; Janiak, C.; Zuckerman, J. J. *J. Am. Chem. Soc.* **1984**, *106*, 4259.

(6) (a) Hosmane, N. S.; Sirmokadam, N. N.; Herber, R. H. *Organometallics* **1984**, *3*, 1665. (b) Wong, K.-S.; Grimes, R. N. *Inorg. Chem.* **1977**, *16*, 2053. (c) Grimes, R. N. *Rev. Silicon, Germanium, Tin Lead Compd.* **1977**, 223. (d) Rudolph, R. W.; Voorhees, R. L.; Cochoy, R. E. *J. Am. Chem. Soc.* **1970**, *92*, 3351. (e) Voorhees, R. L.; Rudolph, R. W. *Ibid.* **1969**, *91*, 2173. (f) Chowdhry, V.; Pretzer, W. R.; Rai, D. N.; Rudolph, R. W. *Ibid.* **1973**, *95*, 4560.

(7) (a) Jutzi, P.; Kohl, F.; Krüger, C.; Wolmershäuser, G.; Hofmann, P.; Stauffert, P. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 70. (b) Kohl, F. X.; Schlüter, E.; Jutzi, P.; Krüger, C.; Wolmershäuser, G.; Hofmann, P.; Stauffert, P. *Chem. Ber.* **1984**, *117*, 1178.

(8) Cowley, A. H.; Galow, P.; Hosmane, N. S.; Jutzi, P.; Norman, N. C. *J. Chem. Soc., Chem. Commun.* **1984**, 1564.

(9) Hosmane, N. S.; de Meester, P.; Maldar, N. N.; Potts, S. B.; Chu, S. S. C.; Herber, R. H., *Organometallics* **1986**, *5*, 772.

(10) Scibelli, J. V.; Curtis, M. D. *J. Am. Chem. Soc.* **1973**, *95*, 924.

(11) Dousse, G.; Satge, J. *Helv. Chim. Acta* **1977**, *60*, 1381.

(12) Todd, L. J.; Wikholm, G. S. *J. Organomet. Chem.* **1974**, *71*, 219.

(13) Loffredo, R. E.; Norman, A. D. *J. Am. Chem. Soc.* **1971**, *93*, 5587.

(14) Grenz, M.; Hahn, E.; du Mont, W.-W.; Pickardt, J. *Angew. Chem.* **1984**, *96*, 69; *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 61.

(15) Almlöf, J.; Fernholt, L.; Faegri, K.; Haaland, A.; Schilling, B. E. R.; Seip, R.; Taugbol, K. *Acta Chem. Scand., Ser. A* **1984**, *A37*, 131.

(16) Fernholt, L.; Haaland, A.; Jutzi, P.; Kohl, F. X.; Seip, R., *Acta Chem. Scand. Ser. A* **1984**, *A38*, 211.

(17) Schumann, H.; Janiak, C.; Hahn, E.; Loebel, J.; Zuckerman, J. J. *Angew. Chem.* **1985**, *97*, 765; *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 773.

(18) Compound I is soluble in THF, CHCl$_3$, CDCl$_3$, CH$_2$Cl$_2$, and C$_6$H$_{14}$ and is moderately stable in air for brief periods of time.

(19) Hosmane, N. S.; Sirmokadam, N. N.; Mollenhauer, M. N. *J. Organomet. Chem.* **1985**, *279*, 359.

(20) IR (CDCl$_3$ vs. CDCl$_3$): 2960 (m, s) and 2900 (w) [ν(C–H)], 2600 (vs) [ν(B–H)], 1410 (w, br) [δ(CH), asym], 1270 (sh), 1260 (vs) [δ(CH), sym], 1190 (m, br), 1130 (vw), 980 (m, br), 841 (vvs, br) [ρ(CH)], 680 (w), 630 (m, s) [ν(Si–C)], 520 (w, br), 450 (w), 380 (s, br), 325 (w) cm^{-1}.

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absence of a stretching mode of vibration and a resonance near −2 ppm, respectively, arising from B–H–B bridge bonds.

The IR, NMR, and mass spectroscopic data for I are all consistent with its X-ray crystal structure[22] that shows two distorted pentagonal bipyramids joined by a germanium atom at the commo-apical position. A side view of the molecular structure of I is shown in Figure 1. Table I, where selected bond lengths are presented, shows that the Ge–C distances of 2.38 (2) and 2.39 (2) Å are substantially longer than the Ge–B distances [2.14 (3), 2.08 (3), and 2.15 (2) Å] as found previously in stannacarborane–bipyridine complexes.[8,9] The η^5-bonding (ca. 2.1–2.4 Å) of the germanium atom to each of the pentagonal faces of carborane ligands in I is comparable to that found in germanocene and its derivatives. This type of slippage from η^5 to η^3 has been observed in many of the stannocene,[3-5] stannacarborane complex,[8,9] germanocene,[14-17] silicocene,[23] and other metallacarborane[24] derivatives.

We believe that the compound I, along with $[C_2B_9H_{11}]_2Si^{IV}$[25] and $[(Me_3Si)_2C_2B_4H_4]_2Si^{IV}$,[26] the only examples reported to date in which a group 4 atom is sandwiched by two carborane cages. In these compounds, the group 4 atom is 10-coordinated, indicating the use of d-orbitals by the germanium atom and the silicon atom in bonding to the carborane cages. It is clear that in I the germanium atom interacts only weakly with the cage carbon atoms. However, the germanium in I is in its +4 oxidation state. With the exception of this difference in oxidation state, the title compound I can be regarded as a carborane analogue germanocene.

Studies on the reactivities of $[(Me_3Si)(R)C_2B_4H_4]^{2-}$ ions with MX_4 (R = Me₃Si, Me, H; M = Si, Sn, Pb; X = Cl, Br) are now in progress. The characterization and the chemistry of III will be reported later.

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Supplementary Material Available: Tables of positional and thermal parameters (Table I), bond distances and angles (Table II), and mass spectrometric data (Table IV) (3 pages); listing of observed and calculated structure factors (Table III) (6 pages). Ordering information is given on any current masthead page.

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(21) FT NMR Data of I: ^{1}H NMR ($CDCl_3$, relative to external Me_4Si) δ 4.07 [q br (overlapping), 6 H, basal H_t, $^1J(^1H-^{11}B)$ = 110 Hz], 0.62 [br q, 2 H, apical H_t, $^1J(^1H-^{11}B)$ = 171 Hz], 0.35 [br s, 36 H, $(CH_3)_3Si$]; ^{11}B NMR ($CDCl_3$, relative to external $BF_3\cdot OEt_2$) δ 17.87 [d, 4 B, basal BH, $^1J(^{11}B-^1H)$ = 112 Hz], 4.20 [d, 2 B, basal BH, $^1J(^{11}B-^1H)$ = 108 Hz], −39.14 [d, 2 B, apical BH, $^1J(^{11}B-^1H)$ = 172 Hz]; ^{13}C NMR ($CDCl_3$, relative to external Me_4Si) δ 132.27 [br s, cage carbons], 1.67 [q, $(CH_3)_3Si$, $^1J(^{13}C-^1H)$ = 119 Hz]; ^{29}Si NMR ($CDCl_3$, relative to Me_4Si) δ −1.47 [m, $Si(CH_3)_3$, $^2J(^{29}Si-^1H)$ = 6.5 Hz].

(22) Crystal and experimental data for I. $C_{16}H_{44}B_8Si_4Ge$, mol wt 507.95, monoclinic, space group $P2_1/n$, 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, Z = 2, d_{calcd} = 1.060 g/cm^3, μ(Mo Kα) = 11.00 cm^{-1}. Data were collected on a Syntex P2$_1$ diffractometer with a crystal coated in an epoxy resin. A total of 1280 independent reflections was measured in the range $3 < 2\theta < 38°$ ($\theta/2\theta$ scan type, graphite monochromatized MoKα radiation). The data were corrected for decay (ca. 16%) and for Lp effects but not for absorption. Only the 808 observed reflections with $I > 3\sigma(I)$ were used subsequently. The structure was solved by standard Patterson and difference Fourier methods. All non-H atoms were refined 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 were used (SHELX76, Sheldrick, G. M., 1976. Program for crystal structure determination, Cambridge, U.K.), the function minimized being $\sum w(|F_0| - |F_c|)^2$. One reflection $\bar{1}01$, possibly affected by extinction, was taken out during the final refinement which converged $[(\Delta/\sigma)_{max} = 0.05]$ to R = 0.079 and R_w = 0.084, the weight used being $w^{-1} = \sigma_F{}^2 + 0.000816F^2$. $\Delta\rho_{max}$ = 0.45 e/Å^3. Scattering factors for C, H, B, and Si used were those stored in SHELX76. Scattering factors and $\Delta f'$ and $\Delta f''$ for Ge were taken from: *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. IV.

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

(24) Grimes, R. N.; Rademaker, W. J.; Denniston, M. L.; Bryan, R. F.; Greene, P. T. *J. Am. Chem. Soc.* **1972**, *94*, 1865.

(25) Hawthorne, M. F.; Rees, W. S.; Schubert, D. M.; Knobler, C. B. *Abstracts of Papers*, 191st National Meeting of the American Chemical Society, New York, NY, American Chemical Society: Washington, DC, 1986; ORGN 142. Rees, W. S.; Schubert, D. M.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1986**, *108*, 5367 and 5369.

(26) Hosmane, N. S.; de Meester, P.; Siriwardane, U.; Islam, M. S.; Chu, S. S. C. *J. Chem. Soc., Chem. Commun.*, in press.

Carboxylative Trimethylenemethane Cycloadditions Catalyzed by Palladium

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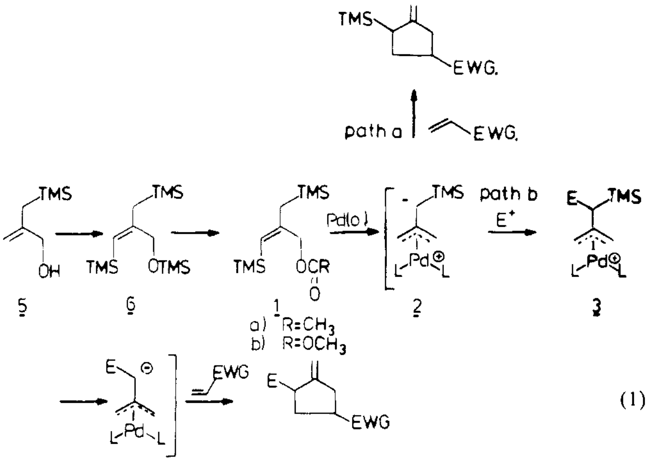
In developing a cycloaddition strategy to the synthesis of cyclopentanoids,[1,2] we designed the silyl-substituted trimethylenemethane precursor **1** as a dual-purpose conjunctive reagent. The notion was to create a silyl-substituted TMM–Pd complex **2** as a reactive intermediate which could directly cycloadd to give silyl-substituted methylenecyclopentanes (path a) or could be intercepted by an electrophile that is more reactive than the normal TMM–Pd acceptors (path b, i.e., **2** → **3**). The product, still bearing a silicon substituent, could regenerate a substituted TMM–Pd complex **4** for subsequent cycloaddition (eq 1). We wish to report the achievement of this goal and an unusual dichotomy in the reactions of **1** as a function of leaving group.



(1)

The silyl-substituted TMM precursor **1** was prepared by metallation–silylation of **5**[3] (n-C_4H_9Li, TMEDA, THF, −30 °C, then TMS–Cl, −60 °C, 91% yield), chemoselective aqueous sulfuric acid hydrolysis of the *O*-silyl ether **6** (H_2SO_4, H_2O, THF, room temperature), and acylation (AcCl, C_5H_5N, CH_2Cl_2, 0 °C, 77% yield for two steps to **1a**[4] or nC_4H_9Li, THF, $CH_3OC(=O)Cl$, −6 °C, 80% yield for two steps to **1b**[4]). Performing cycloadditions

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(1) For a recent review: Trost, B. M. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1.

(2) For some recent related work, see: (a) Shimizu, I.; Ohashi, Y.; Tsuji, J. *Tetrahedron Lett.* **1984**, *25*, 5183. (b) *Tetrahedron Lett.* **1985**, *26*, 3825. (c) Binger, P.; Lu, Q.-H.; Wedemann, P. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 316. (d) Trost, B. M.; Bonk, P. *J. Am. Chem. Soc.* **1985**, *107*, 8277.

(3) Trost, B. M.; Chan, D. M. T.; Nanninga, T. N. *Org. Synth.* **1984**, *62*, 58. As in the original procedure, the hexane solution of n-butyllithium is concentrated to remove as much of the hexane as possible. It was subsequently found that the yield could be increased to 98% by leaving the hexane and not adding the THF.

(4) This compound has been fully characterized spectrally and elemental composition determined by high-resolution mass spectroscopy and/or combustion analysis.

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