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Silicon(IV) π-Complexes of *C*-Trimethylsilyl-Substituted Carboranes. Syntheses of $[(Me_3Si)(R)C_2B_4H_4]_2Si$ and $[(Me_3Si)(Me)C_2B_4H_4]SiH(R')$ [R = Me_3Si, Me, or H; R′ = H or Cl]. Crystal Structure of 2,2′-Bis(trimethylsilyl)-3,3′-dimethyl-[1,1′-*commo*-bis(2,3-dicarba-1-sila-*closo*-heptaborane)](12)

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Abstract: The reaction of $SiCl_4$ with the *nido*-carborane dianionic salts, $NaLi[(Me_3Si)(R)C_2B_4H_4]$ (R = Me_3Si, Me, or H), in a molar ratio of 1:2 in THF produced $[(Me_3Si)_2C_2B_4H_4]_2Si^{IV}$ (I) and $[(Me_3Si)(Me)C_2B_4H_4]_2Si^{IV}$ (II) as air-stable, sublimable white crystalline solids and $[(Me_3Si)C_2B_4H_5]_2Si^{IV}$ (III) as an air-stable colorless liquid, in yields ranging from 18 to 57%. A minute amount of the silicon(II) inserted carborane was also produced as a byproduct in each reaction. These silicon(II) species are extremely sensitive to air and/or moisture. The reaction of SiH_2Cl_2 with $NaLi[(Me_3Si)(Me)C_2B_4H_4]$ in THF in a molar ratio of 2:1 produced $[(Me_3Si)(Me)C_2B_4H_4]SiH(Cl)$ (IV) as a colorless liquid in 58% yield. In each of these reactions, the neutral *nido*-carborane precursor, $(Me_3Si)(R)C_2B_4H_6$, was isolated in varying yields. The reaction of IV with NaH in THF produced $[(Me_3Si)(Me)C_2B_4H_4]SiH_2$ (V) in virtually quantitative yield. The spectroscopic characterizations indicated that the silicon atoms in IV and V could be either η^3- or η^5-bonded to the C_2B_3 faces of the carborane cages. The infrared spectra, mass spectra, ^1H, ^{11}B, ^{13}C, and ^{29}Si NMR spectra of I, II, and III are all consistent with the crystal structures of I and II that show two distorted pentagonal bipyramids joined by a silicon atom at the commo apical position. Compound II crystallizes in the monoclinic space group $P2_1/n$ with $a = 9.041$ (3) Å, $b = 10.174$ (3) Å, $c = 13.222$ (4) Å, $\beta = 105.53$ (2)°, $U = 1171.8$ (6) Å^3, and $Z = 2$. Full-matrix least-squares refinement converged at $R = 0.063$ and $R_w = 0.069$.

The incorporation of main group heteroatoms as either integral parts of carborane cages or in B–M–B three-center, two-electron bonds on the open face of a *nido*-carborane is well known and has been extensively reviewed.[1-4] In the case of group 14 elements, many carborane species containing stable B–M^{IV}–B (M^{IV} = Si, Ge, Sn, and Pb) three-center bridging bonds are known.[3,4] However, until quite recently, the only group 14 elements to be incorporated into carborane cage molecules have been Ge, Sn, and Pb in their 2+ oxidation states. In 1986 the synthesis and structures of several silicon(II) and silicon(IV) π-complexes were reported by Jutzi et al.,[5] Hawthorne et al.,[6] and from this laboratory.[7] In several preliminary communications[7,8] we have shown that both silicon(IV) and germanium(IV) undergo reductive and nonreductive insertion reactions with *C*-$SiMe_3$-substituted *nido*-carboranes to yield η^5- and bis-η^5-sila– and germa–carborane complexes. We describe herein the details of the synthesis, characterization, and crystal structure determination of *commo*-bis(2,3-dicarba-1-sila-*closo*-heptaborane). In addition, we also report the synthesis and partial characterization of an unusual silacarborane in which the metalloid could be in either a 2+ or a 4+ oxidation state.

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.[9-11] Solutions of the sodium salts of the *nido*-carborane anions, $[2\text{-}Si(CH_3)_3\text{-}3\text{-}R\text{-}2,3\text{-}C_2B_4H_5]^-$ (R = $Si(CH_3)_3$, CH_3, or H), in THF were prepared by the method of Onak and Dunks.[12] Prior to use, tetrachlorosilane and dichlorosilane (Petrarch Systems, Inc., Bristol, PA) were passed through −120 °C traps in vacuo to remove any traces of HCl impurity. Purity was checked by IR, NMR, and vapor pressure measurements. A 2.5 molar 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

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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, and silicon-29 pulse Fourier transform NMR spectra, at 200, 64.2, 50.3, and 39.76 MHz, respectively, were recorded on an IBM-200SY 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. Elemental analyses were obtained from Galbraith Laboratories, Knoxville, TN.

Synthetic Procedures. All experiments were carried out in Pyrex glass round-bottomed 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 2,2′-$(SiMe_3)_2$-3,3′-$(R)_2$-*commo*-1,1′-Si(1,2,3-$SiC_2B_4H_4)_2$ (R = $SiMe_3$, Me, and H). A THF (50-mL) solution of Na^+-$[(Me_3Si)_2C_2B_4H_5]^-$ (1.43 g, 5.92 mmol), $Na^+[(Me_3Si)(Me)C_2B_4H_5]^-$ (1.53 g, 8.35 mmol), or $Na^+[(Me_3Si)C_2B_4H_6]^-$ (1.83 g, 10.63 mmol) was added to a THF (10 mL) solution of *n*-BuLi (0.384 g, 6.00 mmol; 0.538 g, 8.40 mmol; or 0.68 g, 10.65 mmol) in vacuo, and the resulting mixture was allowed to react with $SiCl_4$ (2.96, 4.18, or 5.32 mmol) with constant stirring at 0 °C for 6 h. After removal of THF at 0 °C via vacuum distillation for 4 h, the reaction flask was attached to a series of detachable high-vacuum U-traps. With identical sublimation procedures, temperatures and times as described for stannacarboranes,[1k] $[(Me_3Si)_2C_2B_4H_4]_2Si^{IV}$ (I) (0.24 g, 0.52 mmol; collected at 25 °C; 18% yield), $[(Me_3Si)(Me)C_2B_4H_4]_2Si^{IV}$ (II) (0.82 g, 2.36 mmol; collected at 0 °C; 57% yield), or $[(Me_3Si)C_2B_4H_5]_2Si^{IV}$ (III) (0.57 g, 1.79 mmol; collected at 0 °C; 34% yield) were obtained in high purity along with the neutral carborane, *nido*-$[(Me_3Si)(R)C_2B_4H_6]$ (0.55 g, 2.50 mmol; 0.51 g, 3.15 mmol; or 0.58 g, 3.92 mmol; collected at −45 °C). When R = $SiMe_3$, 0.015 g (0.061 mmol; 1% yield) of $[(Me_3Si)_2C_2B_4H_4]Si^{II}$ was collected at 0 °C. When R = Me or H, only traces of $[(Me_3Si)$-$(R)C_2B_4H_4]Si^{II}$ could be identified among the products.

The physical properties and characterization of $[(Me_3Si)_2C_2B_4H_4]Si^{II}$ and $[(Me_3Si)_2C_2B_4H_4]_2Si^{IV}$ (I) have been described in an earlier communication.[7] The infrared spectrum and electron-impact (EI) mass spectrum of I together with their assignments are summarized in Supplementary Tables I and II.

The physical properties and characterization of II are as follows: transparent crystals; mp 78 °C; 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 4.43 [q (br overlapping), 4 H, basal H_t, $^1J(^1H-^{11}B)$ = 133 Hz], 3.15 [q (br), 2 H, basal H_t, $^1J(^1H-^{11}B)$ = 124 Hz], 0.70 [q (br), 2 H, apical H_t, $^1J(^1H-^{11}B)$ = 177 Hz], 2.45 [s, 3 H, CH_3], 0.40 [s, 9 H, $(CH_3)_3Si$]; ^{11}B NMR ($CDCl_3$, relative to external $BF_3{\cdot}OEt_2$) δ 14.78 [d, 4 B, basal BH, ^1J-$(^{11}B-^1H)$ = 133 Hz], −0.14 [d, 2 B, basal BH, $^1J(^{11}B-^1H)$ = 124 Hz], −43.09 [d, 2 B, apical BH, $^1J(^{11}B-^1H)$ = 177 Hz]; ^{13}C NMR ($CDCl_3$, relative to external Me_4Si) δ 124.43 [s (br), cage SiCB], 121.68 [s (br), cage CCB], 21.01 [q, CH_3, $^1J(^{13}C-^1H)$ = 130 Hz], 0.11 [q, $(CH_3)_3Si$, $^1J(^{13}C-^1H)$ = 119 Hz]; ^{29}Si NMR ($CDCl_3$, relative to external Me_4Si) δ −2.15 [m, $Si(CH_3)_3$, $^2J(^{29}Si-^1H)$ = 6.5 Hz], −128.77 [s (br), cage silicon]. Anal. Calcd for $C_{12}H_{32}B_8Si_3$: C, 41.52; H, 9.29; B, 24.92; Si, 24.27. Found: C, 41.61; H, 9.20; B, 24.57; Si, 24.59. The IR and mass spectral data of II together with assignments are summarized in Supplementary Tables I and II.

The physical properties and characterization of III are as follows: colorless liquid; bp 64–66 °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 6.44 [s (br), cage CH], 3.87 [q (br overlapping), 4 H, basal H_t, $^1J(^1H-^{11}B)$ = 163 Hz], 2.29 [q (br), 2 H, basal H_t, $^1J(^1H-^{11}B)$ = 160 Hz], 0.88 [q (br), 2 H, apical H_t, $^1J(^1H-^{11}B)$ = 183 Hz], 0.31 [s, 9 H, $(CH_3)_3Si$]; ^{11}B NMR ($CDCl_3$, relative to external $BF_3{\cdot}OEt_2$) δ 14.77 [d, 4 B, basal BH, $^1J(^{11}B-^1H)$ = 163 Hz], −0.22 [d, 2 B, basal BH, $^1J(^{11}B-^1H)$ = 160 Hz], −45.39 [d, 2 B, apical BH, $^1J(^{11}B-^1H)$ = 183 Hz]; ^{13}C NMR ($CDCl_3$, relative to external Me_4Si) δ 134.37 [s (br), cage carbon SiCB], 109.57 [d (br), cage CH, $^1J(^{13}C-^1H)$ = 187 Hz], −1.61 [q, $(CH_3)_3Si$, $^1J(^{13}C-^1H)$ = 120 Hz]; ^{29}Si NMR ($CDCl_3$, relative to external Me_4Si) δ −0.74 [m, $Si(CH_3)_3$, $^2J(^{29}Si-^1H)$ = 6.7 Hz], −130.25 [s (br), cage silicon]. Anal. Calcd for $C_{10}H_{28}B_8Si_3$: C, 37.64; H, 8.84; B, 27.10; Si 26.41. Found: C, 37.15; H, 9.05; B, 27.39; Si, 26.43. The IR and mass spectral data of III with assignments are summarized in Supplementary Tables I and II.

Synthesis of $[(Me_3Si)(Me)C_2B_4H_4]SiH(Cl)$. A THF (50-mL) solution of $Na^+[(Me_3Si)(Me)C_2B_4H_5]^-$ (1.85 g, 10.08 mmol) was added to a THF (10-mL) solution of *n*-BuLi (0.67 g, 10.50 mmol) in vacuo, and the resulting mixture was allowed to react with SiH_2Cl_2 (22.00 mmol) with constant stirring at −23 °C for 2 h. During this time the color of the solution changed from pale yellow to light green and finally to colorless. After removal of THF at 0 °C via vacuum distillation for 4 h, the reaction flask was attached to a series of detachable high-vacuum U-traps. With identical distillation procedures, temperatures, and times as described elsewhere[1k,m] $[(Me_3Si)(Me)C_2B_4H_4]SiH(Cl)$ (IV) (1.32 g, 5.89 mmol; 58% yield based on $(Me_3Si)(Me)C_2B_4H_6$ used) was obtained in the 0 °C trap as a moderately air-stable pale yellow liquid. *nido*-$(Me_3Si)(Me)C_2B_4H_6$ (0.64 g, 3.95 mmol) was obtained in the −45 °C trap. A solid residue, remaining in the reaction flask, was not identified. Trace quantities of unreacted SiH_2Cl_2 were collected at −78 °C.

The physical properties and characterization of IV are as follows: bp 118–122 °C (10^{-4} Torr); at 25 °C, highly soluble in THF, $CDCl_3$, $CHCl_3$, hexane, and benzene; ^1H NMR ($CDCl_3$, relative to external Me_4Si) δ 4.32 [s (br), 1 H, SiH] 3.81 [q (br overlapping), 3 H, basal H_t, $^1J(^1H-^{11}B)$ = 130 Hz], 2.51 [s, 3 H, CH_3], 1.2 [q (br), 1 H, apical H_t, $^1J(^1H-^{11}B)$ = 170 Hz], 0.32 [s, 9 H, $(CH_3)_3Si$]; ^{11}B NMR ($CDCl_3$, relative to external $BF_3{\cdot}OEt_2$) δ 13.42 [d, 1 B, basal BH, $^1J(^{11}B-^1H)$ = 148 Hz], 7.87 [d, 2 B, basal BH, $^1J(^{11}B-^1H)$ = 122 Hz], −30.09 [d, 1 B, apical BH, $^1J(^{11}B-^1H)$ = 171 Hz]; ^{13}C NMR ($CDCl_3$, relative to external Me_4Si) δ 142.42 [s (br), cage SiCB], 135.88 [s (br), cage CCB], 23.76 [q, CH_3, $^1J(^{13}C-^1H)$ = 129 Hz], 1.18 [q, $(CH_3)_3Si$, $^1J(^{13}C-^1H)$ = 118 Hz]; ^{29}Si NMR ($CDCl_3$, relative to external Me_4Si) δ −3.02 [m (br), $Si(CH_3)_3$, $^2J(^{29}Si-^1H)$ = 6.0 Hz], −47.59 [d, cage SiH, $^1J(^{29}Si-^1H)$ = 368 Hz]. Anal. Calcd for $C_6H_{17}B_4Si_2Cl$: C, 32.16; H, 7.65; B, 19.30; Si, 25.07; Cl, 15.82. Found: C, 32.21; H, 7.7; B, 18.92; Si, 25.16; Cl, 16.09. The IR and mass spectral data of IV together with assignments are summarized in Supplementary Tables I and II.

Synthesis of $[(Me_3Si)(Me)C_2B_4H_4]SiH_2$ from IV. A THF (50-mL) solution of IV (0.601 g, 2.68 mmol) was added to NaH (0.10 g, 4.17 mmol) in vacuo, and the resulting mixture was stirred for 1 h at 0 °C. The mixture was then filtered in vacuo through a glass frit to remove excess NaH and the product, NaCl. After removal of THF from the filtrate, a light yellow syrupy liquid remained in the receiving flask. Under identical distillation procedures, temperatures, and times as described above, this liquid yielded $[(Me_3Si)(Me)C_2B_4H_4]SiH_2$ (V) (0.48 g, 2.55 mmol; 95% yield based on IV used). The physical properties and characterization of V are as follows: bp 110–114 °C (10^{-4} Torr); reasonably stable in air for brief 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 4.39 [s (br), 1 H, SiH], 3.63 [q (br overlapping), 3 H, basal H_t, $^1J(^1H-^{11}B)$ = 140 Hz], 2.53 [s, 3 H, CH_3], 1.52 [q (br), 1 H, apical H_t, $^1J(^1H-^{11}B)$ = 170 Hz], 0.39 [s, 9 H, $Si(CH_3)_3$], −0.52 [s (v br), 1 H, Si–H–B]; ^{11}B NMR ($CDCl_3$, relative to external $BF_3{\cdot}OEt_2$) δ 13.43 [d, 1 B, basal BH, $^1J(^{11}B-^1H)$ = 148 Hz], 7.87 [d, 2 B, basal BH, $^1J(^{11}B-^1H)$ = 125 Hz], −31.0 [d, 1 B, apical BH, $^1J(^{11}B-^1H)$ = 170 Hz]; ^{13}C NMR ($CDCl_3$, relative to external Me_4Si) δ 142.45 [s (br), cage SiCB], 136.10 [s (br), cage CCB], 23.70 [q, CH_3, $^1J(^{13}C-^1H)$ = 127 Hz], 1.15 [q, $(CH_3)_3Si$, $^1J(^{13}C-^1H)$ = 119 Hz]; ^{29}Si NMR ($CDCl_3$, relative to external Me_4Si) δ −3.05 [m (br), $Si(CH_3)$, $^2J(^{29}Si-^1H)$ = 6.1 Hz], −64.88 [d of d, cage SiH_2, $^1J(^{29}Si-^1H)$ = 361.8 Hz, $^1J(^{29}Si-^1H_{(bridge)})$ = 42 Hz]. Anal. Calcd for $C_6H_{18}B_4Si_2$: C, 38.21; H, 9.62; Si, 29.76. Found: C, 38.18; H, 9.71; Si, 29.98. The IR and mass

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Table I. Crystallographic Data[a] for II

formula	$C_{12}H_{32}B_8Si_3$
fw	347.13
cryst system	monoclinic
space group	$P2_1/n$
a, Å	9.041 (3)
b, Å	10.174 (3)
c, Å	13.222 (4)
β, deg	105.53 (2)
U, Å^3	1171.8 (6)
Z	2
D_{calcd}, g cm^{-3}	0.984
cryst dimens, mm	0.31 × 0.09 × 0.07
μ (Mo Kα), cm^{-1}	1.63
scan type	$\theta/2\theta$
scan speed, deg min^{-1}	2.9–14.7
2θ range, deg	$3 < 2\theta < 40$
data collected	$\pm hkl$
decay, %	10
unique data	1257
obsd reflcns, $I > 3\sigma(I)$	724
R[b]	0.063
R_w	0.069
$\Delta\rho_{(max,min)}$, e/Å^3	0.28, 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 $k = 0.000989$.

Table II. Fractional Atomic Coordinates with Equivalent Isotropic Thermal Parameters for Non-Hydrogen Atoms[a]

atom	x	y	z	U_{eq}[b] (Å^2)
Si(1)	0.0000	0.0000	0.0000	0.0833 (7)
Si(2)	0.2265 (2)	−0.2582 (2)	0.8902 (2)	0.1214 (8)
C(1)	−0.1207 (7)	0.1860 (6)	0.0202 (5)	0.0899 (19)
C(2)	0.0411 (8)	0.2153 (6)	0.0225 (6)	0.0994 (23)
B(3)	0.0862 (12)	0.1550 (12)	−0.0735 (9)	0.1352 (36)
B(4)	−0.0702 (15)	0.0797 (9)	−0.1464 (6)	0.1281 (38)
B(5)	−0.2022 (10)	0.1023 (9)	−0.0783 (7)	0.1019 (26)
B(6)	−0.0903 (12)	0.2382 (10)	−0.0975 (7)	0.1221 (34)
C(7)	0.1444 (9)	0.3000 (10)	0.1044 (7)	0.1270 (31)
C(8)	−0.1111 (12)	0.2284 (15)	0.2506 (8)	0.2129 (51)
C(9)	−0.2649 (26)	0.4274 (11)	0.0844 (16)	0.3347 (91)
C(10)	−0.4106 (13)	0.1650 (16)	0.0902 (11)	0.2375 (59)

[a] esd's are in parentheses. [b] The standard deviations of U_{eq}'s were calculated according to Schomaker and Marsh (1983).

Table III. Bond Lengths (Å) and Bond Angles (deg)[a]

Bond Lengths			
Si(1)–C(1)	2.236 (6)	C(1)–B(5)	1.565 (11)
Si(1)–C(2)	2.228 (7)	C(1)–B(6)	1.734 (12)
Si(1)–B(3)	2.108 (12)	C(2)–B(3)	1.559 (14)
Si(1)–B(4)	2.037 (10)	C(2)–B(6)	1.724 (12)
Si(1)–B(5)	2.117 (9)	C(2)–C(7)	1.499 (12)
Si(2)–C(1)	1.861 (7)	B(3)–B(4)	1.669 (16)
Si(2)–C(8)	1.899 (13)	B(3)–B(6)	1.759 (15)
Si(2)–C(9)	1.770 (20)	B(4)–B(5)	1.692 (14)
Si(2)–C(10)	1.872 (14)	B(4)–B(6)	1.765 (15)
C(1)–C(2)	1.485 (10)	B(5)–B(6)	1.771 (14)
Bond Angles			
Si(1)–B(3)–C(2)	73.1 (5)	C(2)–Si(1)–B(3)	42.0 (4)
Si(1)–B(3)–B(4)	64.0 (5)	C(2)–Si(1)–B(4)	74.6 (3)
Si(1)–B(3)–B(6)	90.8 (6)	C(2)–Si(1)–B(5)	70.9 (3)
C(2)–B(3)–B(4)	106.6 (8)	B(3)–Si(1)–B(4)	47.4 (4)
C(2)–B(3)–B(6)	62.3 (6)	B(3)–Si(1)–B(5)	77.5 (4)
B(4)–B(3)–B(6)	61.9 (6)	B(4)–Si(1)–B(5)	48.0 (4)
Si(1)–B(4)–B(3)	68.5 (5)	C(1)–Si(2)–C(8)	108.7 (4)
Si(1)–B(4)–B(5)	68.5 (5)	C(1)–Si(2)–C(9)	111.8 (7)
Si(1)–B(4)–B(6)	93.0 (6)	C(1)–Si(2)–C(10)	107.5 (5)
B(3)–B(4)–B(5)	103.9 (8)	C(8)–Si(2)–C(9)	111.7 (8)
B(3)–B(4)–B(6)	61.5 (6)	C(8)–Si(2)–C(10)	106.8 (6)
B(5)–B(4)–B(6)	61.6 (6)	C(9)–Si(2)–C(10)	110.1 (8)
Si(1)–B(5)–C(1)	73.0 (4)	Si(1)–C(1)–Si(2)	139.5 (3)
Si(1)–B(5)–B(4)	63.5 (5)	Si(1)–C(1)–C(2)	70.3 (4)
Si(1)–B(5)–B(6)	90.1 (5)	Si(1)–C(1)–B(5)	64.9 (4)
C(1)–B(5)–B(4)	105.9 (7)	Si(1)–C(1)–B(6)	87.3 (4)
C(1)–B(5)–B(6)	62.3 (5)	Si(2)–C(1)–C(2)	125.4 (5)
B(4)–B(5)–B(6)	61.2 (6)	Si(2)–C(1)–B(5)	122.5 (5)
C(1)–B(6)–C(2)	50.9 (4)	Si(2)–C(1)–B(6)	133.0 (5)
C(1)–B(6)–B(3)	92.6 (6)	C(2)–C(1)–B(5)	111.6 (6)
C(1)–B(6)–B(4)	96.1 (6)	C(2)–C(1)–B(6)	64.2 (5)
C(1)–B(6)–B(5)	53.0 (5)	B(5)–C(1)–B(6)	64.7 (5)
C(2)–B(6)–B(3)	53.2 (5)	Si(1)–C(2)–C(1)	70.8 (4)
C(2)–B(6)–B(4)	95.8 (6)	Si(1)–C(2)–B(3)	64.9 (5)
C(2)–B(6)–B(5)	92.4 (6)	Si(1)–C(2)–B(6)	87.8 (4)
B(3)–B(6)–B(4)	56.5 (6)	Si(1)–C(2)–C(7)	135.3 (6)
B(3)–B(6)–B(5)	97.1 (7)	C(1)–C(2)–B(3)	112.0 (7)
B(4)–B(6)–B(5)	57.2 (5)	C(1)–C(2)–B(6)	64.9 (5)
C(1)–Si(1)–C(2)	38.9 (2)	C(1)–C(2)–C(7)	123.4 (6)
C(1)–Si(1)–B(3)	71.0 (4)	B(3)–C(2)–B(6)	64.5 (6)
C(1)–Si(1)–B(4)	74.9 (3)	B(3)–C(2)–C(7)	124.5 (7)
C(1)–Si(1)–B(5)	42.0 (3)	B(6)–C(2)–C(7)	136.9 (7)

[a] esd's are in parentheses.

spectral data of V together with assignments are summarized in Supplementary Tables I and II.

X-ray Analysis of II. Large, well-formed clear colorless crystals of II 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 b axis. 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 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. 10%) 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. Full-matrix least-squares refinements were used throughout, the function minimized being $\sum\omega(F_o - F_c)^2$. All nonhydrogen atoms were allowed to refine anisotropically. The four cage hydrogen atoms were located and refined isotropically. All methyl hydrogen atoms were calculated, and their positions were refined with fixed isothermal parameters. In the final stages of refinement, a weighting scheme was used (Table I). Calculations were carried out with the SHELX76 system of programs.[13] Scattering factors used for all atoms as well as the real and imaginary parts of the dispersion correction for Si were those stored in SHELX76. 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 recent preliminary communications,[7,8] we have shown that the reaction of tetrachlorogermane or tetrachlorosilane with the monolithium or the sodium lithium salt of *nido*-$(Me_3Si)_2C_2B_4H_6$ produces a mixture of the M(IV) (M = Ge or Si) sandwiched *commo*-bis(germa- or silacarborane) and the M(II) inserted *closo*-germa- or silacarborane in varying yields. These reactions involve reductive insertions to yield the *closo*-heterocarboranes and nonreductive insertions yielding the *commo*-bis(heterocarborane). The reactions in the present investigation demonstrate the utility of a sodium–lithium mixed salt to produce two novel silacarboranes (see Scheme I). The preparation of disodium salt of the *nido*-C_2B_4-carborane is not yet known. When the monosodium or monolithium salt of the *nido*-C_2B_4-carborane was used under reaction conditions similar to those used in Scheme I, very little, if any, silacarboranes were produced. The dilithium salt of the carborane gave very irreproducible results. However, the mixed sodium–lithium salt of the C–$SiMe_3$-substituted C_2B_4 carborane systems reacts quite readily (see Experimental Section and Scheme I). The mechanisms of both reductive and nonreductive insertions of group 14 heteroatoms in the carborane polyhedra have not been determined, and it is not known whether the two insertion reactions take place concurrently or sequentially. The tendency to form a closo or a commo product varies with the

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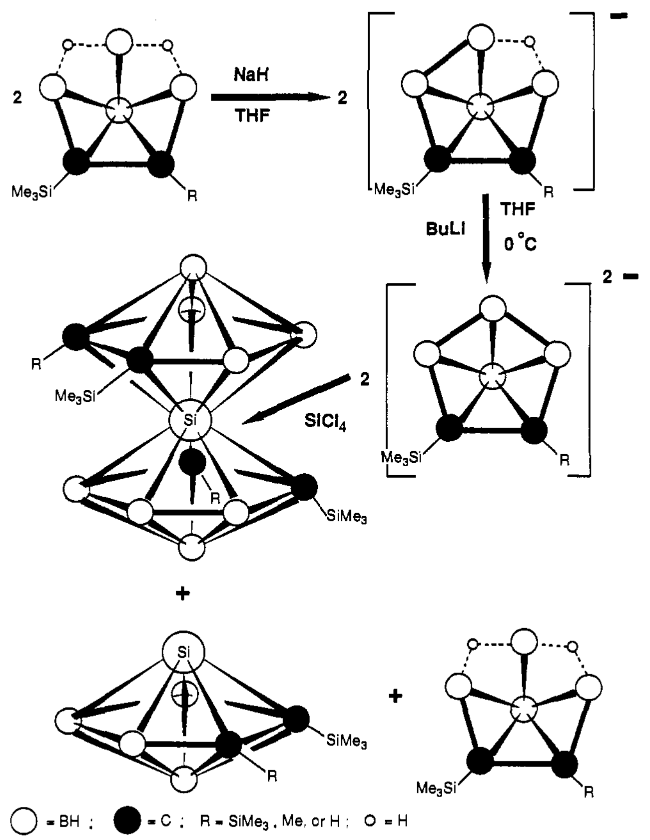
[13] Sheldrick, G. M. SHELX76, Programs for Crystal Structure Determination, University of Cambridge, England, 1976.

Scheme I



oxidation potential of the group 14 heteroatom.[7,8,14] The order of increasing oxidation potential of M(IV) is

$$\mathrm{Pb > Sn > Ge > Si}$$

Thus, only the M(II) inserted *closo*-carborane species formed when M = Pb, whereas in the case of the silicon, the predominant product was M(IV) inserted *commo*-bis(silacarborane).[7] When M = Sn, a small amount of the *commo*-Sn^{IV}-bis(carborane) was produced[14a] and an approximately 50:50 mixture of both closo and commo species was obtained when M = Ge.[8]

The reaction of SiH_2Cl_2 with the Na/Li salt of *nido*-$[(Me_3Si)(Me)C_2B_4H_4]^{2-}$ was found to produce $[(Me_3Si)(Me)C_2B_4H_4]SiH(Cl)$ (IV) as a colorless liquid of low volatility as shown in eq 1. Since SiH_2Cl_2 is an effective chlorinating agent for silanes[15] the formation of IV in reaction 1 is not surprising. Compound IV can be converted quantitatively to $[(Me_3Si)(Me)C_2B_4H_4]SiH_2$ (V) as shown in eq 2. It is known that the

$$\mathrm{NaLi[(Me_3Si)(Me)C_2B_4H_4] + 2SiH_2Cl_2 \xrightarrow[-23\ ^{\circ}C]{THF} \underset{(IV)}{[(Me_3Si)(Me)C_2B_4H_4]SiH(Cl)} + NaCl + LiCl + [(Me_3Si)(Me)C_2B_4H_6]} \quad (1)$$

$$\mathrm{[(Me_3Si)(Me)C_2B_4H_4]SiH(Cl) + NaH \xrightarrow[0\ ^{\circ}C]{THF} \underset{(V)}{[(Me_3Si)(Me)C_2B_4H_4]SiH_2} + NaCl} \quad (2)$$

reaction of *nido*-$Na[C_2B_4H_7]$ with SiH_2Cl_2 yields exclusively μ,μ'-$SiH_2(C_2B_4H_7)_2$ in which the silicon atom is doubly bridged by two three-center two-electron B–Si–B bonds.[4] Evidently, the carborane dianion in the present system induces the insertion of the heteroatom into the cage framework as in the C_2B_9 system.[16]

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

NMR and IR Spectra. The ^1H NMR and ^{13}C NMR spectra indicate the presence of a C_2B_4-carborane ring in the silacarboranes in addition to the $SiMe_3$ and Me or CH groups. The ^1H NMR spectra clearly show the presence of additional SiH protons in the case of IV and V and possibly an Si–H–B bridge hydrogen near Me_3Si region in the case of V. The ^{13}C chemical shifts of the cage carbons in each compound were not changed significantly from those of the *nido*-carborane precursors.[17] It is possible that the interaction between cage carbon atoms and the apical silicon atom is weak. This decreased interaction with the cage carbon atoms is confirmed by the crystal structures of I[7] and II (discussed in the following section) where a significant slippage of the Si away from the two carbon atoms and toward the three boron atoms of each C_2B_3 face is found. Except for a very small shift of the apical ^{11}B resonance, the ^{11}B NMR data of I, II, III, IV, and V bear striking resemblance to those of the stannacarboranes and their 2,2′-bipyridine donor–acceptor complexes.[1k,m] The commo apical or apical position, rather than a terminal position of silicon in these silacarboranes, can be inferred from the absence of a separate ^{11}B–Si singlet in the proton-coupled spectrum. If the silicon is in bridging or doubly bridging positions with one or two three-center, two-electron bonds, one would expect virtually no change from its precursor in the ^{11}B chemical shifts of the apical and basal boron resonances.[4,18] In addition, a secondary splitting of the basal BH resonances due to B–H–B bridge hydrogens[18] 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 silacarborane is further evidence for a commo apical or apical position of silicon in these molecules.

In addition to a Me_3Si multiplet, a broad singlet near −130 ppm due to a commo silicon (cage) appeared in the proton-coupled ^{29}Si NMR spectrum of each *commo*-bis(silacarborane) complex. This high field silicon resonance is perhaps indicative of π-bonding of the central silicon atom to two C_2B_3 faces. However, the ^{29}Si chemical shift of the bis(pentamethylcyclopentadienyl)silicon, the first π-complex with silicon(II) as the central atom, was observed at −577 ppm.[5]

The proton-coupled ^{29}Si NMR spectrum of IV in the region of silicon–carborane cage resonances exhibited a 1:1 doublet with a large coupling constant (^1J = 368 Hz), thus indicating that the apical silicon atom in IV is directly bonded to only one hydrogen atom. However, the proton-coupled ^{29}Si NMR spectrum of V failed to show a 1:2:1 triplet due to ^1H coupling but instead exhibited a broad major doublet with a large coupling constant (^1J = 362 Hz). Each line of this doublet was further split into doublets with a much smaller coupling constant (^1J = 42 Hz) as shown in Figure 1. The large splitting could arise from ^{29}Si–$^1H_{terminal}$ spin coupling and the secondary splitting from a much weaker coupling of the second hydrogen. This suggests a structure, such as that shown in Figure 2, in which one H is involved in a Si–H–B three-center two-electron bond. In this structure the silicon atom would formally be in a 2+ oxidation state. It is of great interest to note that there are, to our knowledge, no known examples of either B–H–Si or E–H–Si (E = main group element)

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[14] (a) Hosmane, N. S.; Dehghan, M.; Maldar, N. N. XIIth International Conference on Organometallic Chemistry, Vienna, September 1985; Abstract, 547. (b) Schubert, D. M.; Hawthorne, M. F., private communication to N.S.H., 1986.

[15] Hosmane, N. S., Ph.D. Thesis, University of Edinburgh, Scotland, 1974.

[16] (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.

[17] The ^{13}C chemical shift of the cage carbons in *closo*-$Os(CO)_3(Me_3Si)_2C_2B_4H_4$ appears as a broad singlet at 89.93 ppm due to the π-bonding between cage carbons and osmium metal: Hosmane, N. S.; Sirmokadam, N. N. *Organometallics* **1984**, *3*, 1119.

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

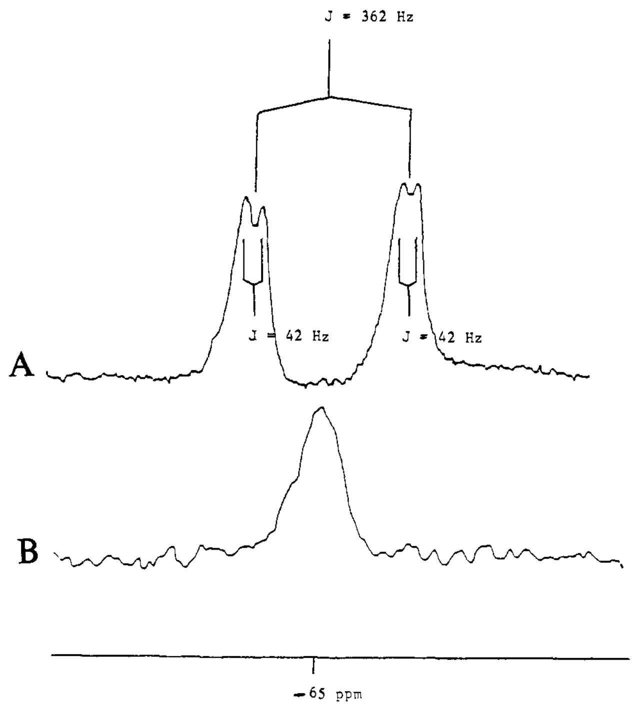

Figure 1. 39.76-MHz ^{29}Si FT NMR spectra of [$(Me_3Si)(Me)C_2B_4H_4$]SiH_2 (V) (in $CDCl_3$) in the region of $Si_{(cage)}$ resonance: A, proton coupled; B, proton decoupled.

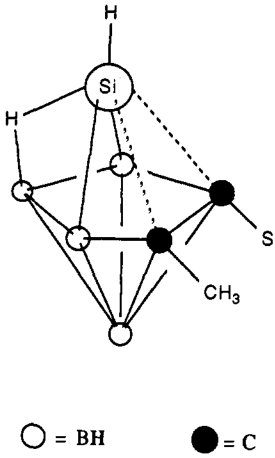

Figure 2. Possible structure for V.

bridge bonds. However, compounds containing M–H–Si (M = transition metals such as Cr and Mn) two-electron three-center bridge bonds and their crystal structures have been reported very recently.[19] Therefore, if the structure of V shown in Figure 2 is correct, it will be the first example of a compound containing E–H–Si (E = main group element) bridge bonds. However, single crystals of V of suitable dimensions at low temperatures for X-ray analysis have not yet been obtained.

The positions of the silicon atoms in I–V can also be verified by their IR spectra (Supplementary Table I) which exhibited a single B–H stretching band near 2600 cm^{-1}, a noncharacteristic feature of the vibrational spectra of all known heteroatom-bridged $C_2B_4H_8$ derivatives.[3a–c,4,18] In addition, a stretching mode due to a B–H–B bridge bond near 1900 cm^{-1} is absent in the infrared spectrum of each of the silacarboranes. The most significant feature in the IR spectra (see Supplementary Table I) of IV and V is the presence of a strong band near 2200 cm^{-1} due to a characteristic Si–H stretching. An additional Si–Cl stretching band is also present in the IR spectrum of IV.

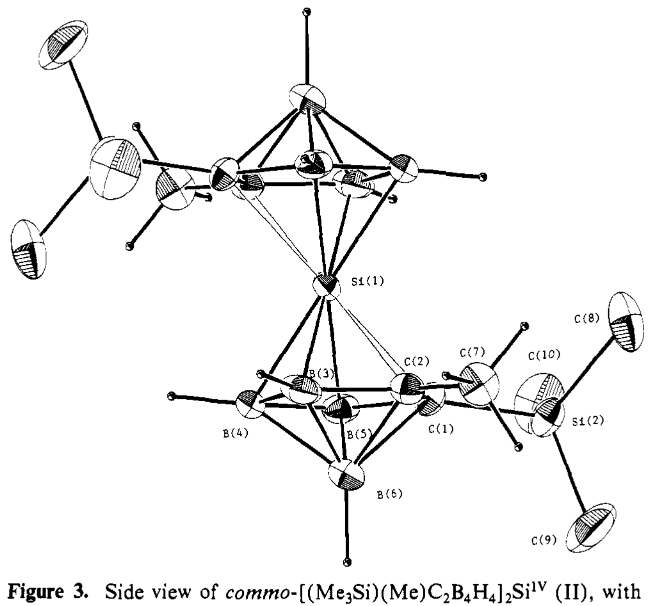

Figure 3. Side view of *commo*-[$(Me_3Si)(Me)C_2B_4H_4$]$_2$Si^{IV} (II), with thermal ellipsoids drawn at 10% probability level. The central Si atom lies at a center of symmetry. The weaker Si–C interactions are shown by thinner lines.

The structures of IV and V are not known. The structures of I and II (and presumably III) are consistent with Wade's rules[20] in that each carborane unit is part of a seven-vertex, 16 skeletal electron ($2n + 2$) closo system joined at the commo apical position by the silicon atom. These same rules would yield 18 skeletal electrons for IV and V (the SiHX being considered a four-electron donor), indicating a seven-vertex nido structure for these compounds. If this is correct, IV and V would be the first stable, neutral seven-vertex nido systems to be reported. The fact that the ^{29}Si chemical shift of the apical silicon resonances in I, II, and III are at a significantly higher field (by a difference of about 70 ppm) than those of IV and V indicates that the two systems could be based on quite different geometries. However, the consequences of such electron counting for IV and V are difficult to predict in that the SiHCl and the SiH_2 groups may not be isolobal with B–H or with one another. If, as indicated by the ^{29}Si NMR, one of the Si–H bonds in SiH_2 lies in the polyhedral surface, the group could be considered as a source of four electrons and three atomic orbitals. On the other hand, the SiHCl may be considered as a source of two electrons and two atomic orbitals. Until more structural information becomes available on complexes such as IV and V, it is not possible to say whether such compounds have closo, distorted closo, nido, or some other structures. If eq 1 proves to be a general preparative route, it may be possible to obtain silacarboranes similar to IV and V that are amenable to X-ray crystallographic structure determination.

Mass Spectra. Except for IV, the electron-impact (EI) mass spectra of both the *commo*-bis(silacarborane) and *mono*-silacarboranes exhibited characteristic groupings corresponding to their molecular ions (see Supplementary Table II). The absence of the parent ion in the case of IV indicates cleavage of Si–Cl and Si–C bonds during the ionization at 70 eV. In fact, the most intense peak for all the silacarboranes corresponded to the parent minus one methyl group. This phenomenon has been observed elsewhere.[1k,m]

Crystal Structure of *commo*-[$(Me_3Si)(Me)C_2B_4H_4$]$_2$Si^{IV} (II). The X-ray crystal structure of II, represented in Figure 3, reveals that the silicon atom at the commo apical position of two distorted pentagonal bipyramids is essentially η^5-bonded to each of the C_2B_3 faces. The distortion involves primarily the Si–C distances [2.236 (6) and 2.228 (7) Å], which are substantially longer than the Si–B distances [2.108 (12), 2.037 (10), and 2.117 (9) Å], thus con-

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(19) Schubert, U.; Müller, J.; Alt, H. G. *Organometallics* **1987**, *6*, 469 and references cited therein.

(20) Wade, K. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1. Wade, K. *Electron Deficient Compounds*; Nelson; London, 1971.

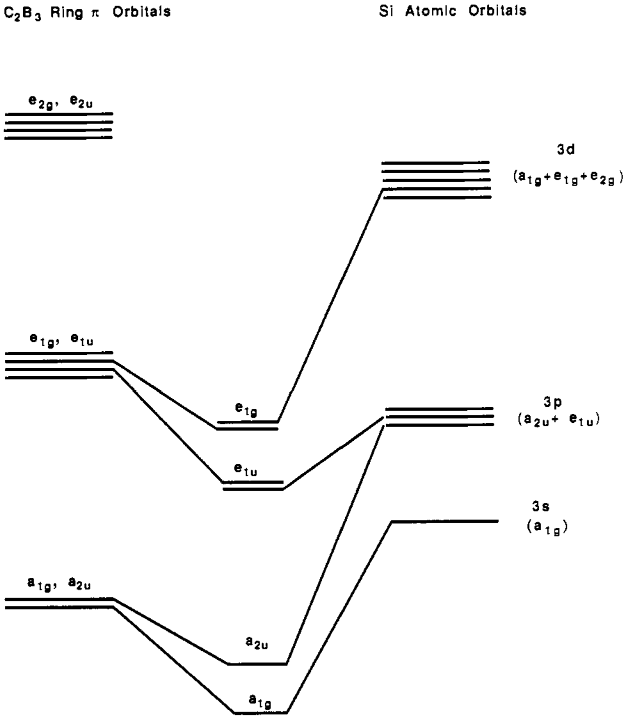

Figure 4. Schematic molecular orbital diagram showing the bonding interactions between a pair of C_2B_3 ring π MO's and Si AO's in idealized D_{5d} symmetry.

firming the NMR evidence for such an elongation (see Table III). Very similar bond distances [Si–C(1), 2.23 (1); Si–C(2), 2.25 (1); Si–B(3), 2.10 (1); Si–B(4), 2.03 (1); and Si–B(5), 2.10 (1) Å] are found in I.[7] The comparable bond distances for *commo*-$(C_2B_9H_{11})_2Si^{IV}$ are Si–C(1,2), 2.22 (1); Si–B(4,7), 2.14 (1); Si–B(8), 2.05 (1) Å, which is also distorted.[6] The same type of slippage has been observed previously in the structures of 1-$MeGaC_2B_4H_6$,[2g] stannacarboranes, and their bipyridine complexes,[1l,m] *commo*-$[(Me_3Si)_2C_2B_4H_4]_2Ge^{IV}$,[8] and 1,2,3-$(Et_3P)_2PtMe_2C_2B_4H_4$.[21] Such "slip distortions" are a very common structural feature of transition-metal–metallacarborane derivatives[16] and have been investigated theoretically.[22] It may be noted that in all of these examples, the shortest of the five metal–C_2B_3 bonds involves the boron atom opposite to the cage C–C bond.

Bonding in Silicon Sandwich *commo*-Bis(silacarborane) Compounds. Molecular orbital (MO) calculations have not been performed on I–III. Nevertheless, it is possible to discuss the bonding in this type of molecule in a qualitative fashion. To do so, we draw attention to the well-recognized isoelectronic nature of the $[C_2B_4H_6]^{2-}$ and $[C_5H_5]^-$ ligands. For simplicity, let us assume that the C_2B_3 pentagonal faces of the $[(R_1)(R_2)C_2B_4H_4]^{2-}$ ligands to be planar and to possess fivefold symmetry. Combination of a pair of such faces in a staggered conformation (i.e., D_{5d} symmetry) affords a familiar set of ring π orbitals (Figure 4).[23] The Si(3s) and Si($3p_z$) atomic orbitals (AO's) are of the correct symmetry to interact with the a_{1g} and a_{2u} ring orbitals, respectively. A further bonding interaction takes place by overlap of the e_{1u} ring orbitals with the degenerate pair of Si($3p_x$, $3p_y$) AO's. In the absence of Si(3d) orbital participation, the e_{1g} ring MO would be nonbonding. However, as implied in Figure 4, a π-type interaction can, in fact, take place between the e_{1g} ring MO and the ($3d_{xz}$, $3d_{yz}$) AO's of silicon. It is clear that the scheme accommodates a total of 12 bonding electrons. This is precisely the number of interstitial bonding electrons[24] possessed by I–III. In passing, we note that several other molecules, such as $(\eta^5\text{-}C_5H_5)_2Mg$,[25] possess 12 interstitial bonding electrons and, like I–III, exhibit sandwich-type structures. Finally, we note that the actual symmetries of the *commo*-bis(silacarborane) compounds are lower than D_{5d}. If, as in the case of II, the symmetry is C_i, all MO's will become singly degenerate (a_g or a_u). However, the qualitative conclusions presented above would remain valid.

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. We thank Dr. Randal R. Ford for setting up the parameters for ^{29}Si NMR program.

Supplementary Material Available: Listings of IR absorptions (Table S1) and mass spectrometric data (Table S2) of I, II, III, IV, and V and tables of anisotropic temperature factors and fractional coordinates of hydrogen atoms (7 pages); listings of structure factors of II (Tables S3–S5) (5 pages). Ordering information is given on any current masthead page.

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[24] Interstitial bonding electrons have been defined as electrons which bind π-bonding ligands to a central atom. See: Collins, J. B.; Schleyer, P. v. R. *Inorg. Chem.* **1977**, *16*, 152.

[25] Bunder, W.; Weiss, E. *J. Organomet. Chem.* **1975**, *92*, 1.