

NEW AIR-STABLE TRIMETHYLSILYL-SUBSTITUTED TRIVINYLBORANES AND CARBORANES

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Summary

The reaction of B_5H_9 with $(CH_3)_3SiC\equiv CR$ ($R = (CH_3)_3Si$, CH_3 , or H) without the use of a Lewis base, heat, solvent, or large volume gas bulbs produced air-stable $[R(H)C=CSi(CH_3)_3]_3B$ and $2-(CH_3)_3Si-3-R-2,3-C_2B_4H_6$ in quantitative yields. However, this reaction was very slow. The reaction of $BH_3 \cdot THF$ with $(CH_3)_3SiC\equiv CR$ at $0^\circ C$ also quantitatively produced the corresponding trivinylborane derivative, in which the boron is bonded exclusively to the silicon bearing olefinic carbon of each of the vinyl groups. The most satisfactory method of preparation of the carborane involved the liquid phase reaction of a mixture of B_5H_9 and $(CH_3)_3SiC\equiv CR$ at $135^\circ C$ with the formation of hydroborated species in a high vacuum stainless steel reactor. The carborane product was easily isolated in gram quantities in high purity by vacuum fractionation. All new products were characterized by IR, 1H , ^{11}B , ^{13}C , and ^{29}Si NMR spectroscopy, mass spectrometry, and, where possible, elemental analysis.

Introduction

Alkenylsilanes and their monohydroborated derivatives are exceedingly versatile intermediates for a number of synthetic transformations [1]. Although the trimethylsilyl-substituted monovinylborane derivatives are known [2,3], the preparation of the corresponding trivinylborane derivatives has never been reported. We report here the results of a systematic study of the hydroboration of $(CH_3)_3SiC\equiv CR$ ($R = (CH_3)_3Si$, CH_3 or H) with B_5H_9 , and $BH_3 \cdot THF$ which produces the air-stable trivinylboranes of the type $[RCH=CSi(CH_3)_3]_3B$. We believe this to be the first example of a compound having trimethylsilyl groups on each olefinic carbon bonded to central boron atom.

There has been considerable interest in the synthesis and reaction chemistry of *nido*-2,3- $C_2B_4H_8$ [dicarbahexaborane(8)] and its *C*-alkyl-substituted derivatives [4,5]. One of the main constraints on the further development and utilization of these small carboranes has been the synthetic procedures available for their preparation

[6–8]. Recently, Grimes et al. [9,10] reported alternate routes which afford 2 to 3 grams of carboranes safely and cleanly with minimal problems of separation. However, these procedures are not convenient for the synthesis of *C*-trimethylsilyl and *C*-phenyl-substituted $C_2B_4H_8$ derivatives due to difficulties arising in separating the carboranes from side-products such as $(C_2H_5)_3NBH_3$ [11]. We also report herein several convenient routes to air-stable derivatives of *C*-trimethylsilyl-substituted $C_2B_4H_8$ in addition to tris(trimethylsilyl-1-alkenyl)borane that avoid the use of Lewis bases such as $(C_2H_5)_3N$ and hence the purification difficulties due to formation of $(C_2H_5)_3NBH_3$.

Experimental

Materials. Pentaborane(9) was obtained from Callery Chemical Co., Callery, PA, and was checked for purity by IR spectroscopy and vapor pressure measurements before use. Trimethylsilylacetylene, 1-trimethylsilyl-1-propyne, and bis(trimethylsilyl)acetylene (Petrarch Systems, Inc., Bristol, PA) were also checked for purity by IR, NMR, and vapor pressure measurements. Triethylamine (Matheson Coleman and Bell) was dried over molecular sieve, distilled into barium oxide, redistilled, passed through $-23^\circ C$ trap in vacuo and finally redistilled just prior to use. $BH_3 \cdot THF$ (0.98 *M* solution in THF) was obtained from Alfa Products, Danvers, MA and used without further purification.

Instrumentation. Boron-11, carbon-13, silicon-29, and proton pulse Fourier transform NMR spectra at 64.2, 50.3, 39.76, and 200 MHz, respectively, were recorded on an IBM-200SY multinuclear NMR spectrometer. Unit resolution mass spectra were obtained on a Dupont GC/mass spectrometer model 321. Infrared spectra were recorded on Perkin-Elmer model 283 infrared spectrometer. Elemental analyses were obtained from Galbraith Laboratories, Knoxville, TN. The molecular weight determinations were made on a Wescan Model 233 molecular weight apparatus.

Procedures. Except where otherwise indicated, all operations were conducted in vacuo. All room temperature 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. All high temperature experiments were carried out in Hoke stainless steel single ended cylinders of 500 ml capacity (obtained from Tech Controls, Inc., Dallas, TX) fitted with forged body shut-off valves of 1/4" male npt and 1/4" Swagelok fittings (obtained from Texas Valve and Fitting Co., Dallas, TX). Nonvolatile substances were manipulated in evacuable glove-bags 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.

A. Reaction of B_5H_9 with trimethylsilyl-1-alkynes

The carborane and trivinylborane yields are highly dependent on reaction conditions, particularly the ratio of reactants, and temperature. All the reactions of B_5H_9 and $(CH_3)_3SiC \equiv Si(CH_3)_3$, $(CH_3)_3SiC \equiv CCH_3$ or $(CH_3)_3SiC \equiv CH$ with or without $(C_2H_5)_3N$ were carried out using the same millimolar quantities of reagents, similar reaction vessels, warming times and temperatures as described for $(CH_3)_3SiC \equiv Si(CH_3)_3$ in each subsection of the experimental procedures.

1. In the presence of triethylamine

(a) Reactions of B_5H_9 , $(C_2H_5)_3N$ and $(CH_3)_3SiC \equiv Si(CH_3)_3$. Triethylamine

(45.0 mmol total) was added in 5.00 mmol portions to a mixture of bis(trimethylsilyl)acetylene (36.0 g; 212 mmol) and pentaborane (3.20 g; 50.0 mmol) at -196°C , with stirring for 2 h at 0°C and for 2 h at room temperature after each addition. On completion of the triethylamine addition, the mixture was stirred at room temperature for 4 days, after which the volatiles were fractionated through traps at 0, -23 , -78 , -93 , and -196°C . A small quantity of noncondensable gas, presumably H_2 , was pumped out through -196°C trap. The contents of the 0°C trap were redistilled through 0°C traps several times. The final 0°C trap contained carborane and triethylamineborane (2.70 g). The IR, ^1H , ^{11}B , and ^{13}C NMR spectroscopy identified the carborane as 2,3- $[(\text{CH}_3)_3\text{Si}]_2$ -2,3- $\text{C}_2\text{B}_4\text{H}_6$ (I). Similarly, the -23°C trap contained 50/50 mixture of the carborane and triethylamineborane (2.60 g). Complete separation of the carborane product from $(\text{C}_2\text{H}_5)_3\text{NBH}_3$ was unsuccessful despite repeated attempts at vacuum distillation. The unreacted $(\text{CH}_3)_3\text{Si}\equiv\text{CSi}(\text{CH}_3)_3$ (1.03 g; 6.06 mmol) was recovered in a -78°C trap. The -93°C trap contained a trace quantity of B_5H_9 and the -196°C trap contained pure $(\text{CH}_3)_3\text{SiH}$ (15.2 mmol). After complete removal of the volatiles, the reaction flask, containing a reddish-brown polymeric mass, was attached to a detachable U trap and was heated to 135°C for 18 h during which time the most volatile product, $(\text{CH}_3)_3\text{Si}\equiv\text{CSi}(\text{CH}_3)_3$ (3.67 g; 21.6 mmol) was collected at -196°C in a vacuum-line trap. A low volatile, colorless liquid (6.9 g), presumably a mixture of $(\text{C}_2\text{H}_5)_3\text{NBH}_3$ and the dimer of the hydroborated alkyne (see eq. 3), was distilled into the adjacent U-trap at 0°C with the aid of a heating tape wrapped around the side arms. The orange-red spongy material left in the flask was discarded.

(b) *Reaction of B_5H_9 , $(\text{C}_2\text{H}_5)_3\text{N}$ and $(\text{CH}_3)_3\text{SiC}\equiv\text{CCH}_3$.* The trap at 0°C contained a mixture of 2- $(\text{CH}_3)_3\text{Si}$ -3- $(\text{CH}_3)_2$ -2,3- $\text{C}_2\text{B}_4\text{H}_6$ (III) and $(\text{C}_2\text{H}_5)_3\text{NBH}_3$ (2.58 g) in the ratio of 25/75, and the -23°C trap contained a mixture of the same components (1.61 g) in 75/25 ratio. Trace quantities of $(\text{CH}_3)_3\text{SiC}\equiv\text{CCH}_3$ (at -78°C) and B_5H_9 (at -93°C) were identified among the products. The pure $(\text{CH}_3)_3\text{SiH}$ (7.3 mmol) was collected in -196°C trap. After complete removal of the volatiles, the reddish-orange polymeric mass yielded a white crystalline material (4.08 g) upon sublimation at 70°C . This material was resublimed 2–3 times in vacuo (3.80 g, 10.9 mmol) and was identified by its mass spectral data ($m/e = 350$, parent ion (Supplementary Table 1) as $[\text{CH}_3\text{CH}=\text{CSi}(\text{CH}_3)_3]_3\text{B}$ (IV) (m.p., 78.2°C ; 21.7% yield based on the B_5H_9 consumed). IR (CDCl_3 vs. CDCl_3): 2950(vs), 2900(s), 1640(m), 1610(w), 1565(vs), $\nu(\text{C}=\text{C})$, 1440(w), 1405(w), 1370(w), 1340(w), 1250(vs), 1170(vs), 1075(s), 1035(m), 930(m) 840(vs), 760(w), 678(s), 630(m), 610(s), 493(s), 460(w), 430(m), 385(w) cm^{-1} . Analysis Found: C, 61.12; H, 11.11; B, 2.98; Si, 24.13. $\text{C}_{18}\text{H}_{39}\text{BSi}_3$ calcd.: C, 61.65; H, 11.23; B, 3.08; Si, 24.03%.

No other volatile material was identified among the products.

(c) *Reaction of B_5H_9 , $(\text{C}_2\text{H}_5)_3\text{N}$ and $(\text{CH}_3)_3\text{SiC}\equiv\text{CH}$.* This reaction yielded pure 2-Si $(\text{CH}_3)_3$ -2,3- $\text{C}_2\text{B}_4\text{H}_7$ (V) collected at -45°C (0.75 g, 5.07 mmol; 10.6% yield based on B_5H_9 consumed). The physical properties and characterizations of this compound are: bp, 83 – 84°C at 39 Torr (Ar) and 152 – 153°C at 615 Torr (Ar); Mass spectrum (CI, 15 eV), $m/e = 149$ (protonated parent ion, $(^{12}\text{CH}_3)_3^{28}\text{Si}^{12}\text{C}_2^{11}\text{B}_4\text{H}_8^+$). A mixture of $[\text{H}_2\text{C}=\text{CSi}(\text{CH}_3)_3]_3\text{B}$ (VI) and $(\text{C}_2\text{H}_5)_3\text{NBH}_3$ was collected at both 0 and -23°C (4.00 g). The separation of VI from the mixture was unsuccessful. $(\text{CH}_3)_3\text{SiH}$ was collected at -196°C (3.80 mmol). The unreacted B_5H_9 (2.00 mmol) was collected at -93°C . After complete removal of the volatiles, the polymeric mass

failed to produce any sublimable and/or distillable product(s), and hence this material was discarded.

II. In the absence of triethylamine

(a) *Reaction of B_5H_9 and $(CH_3)_3SiC\equiv CSi(CH_3)_3$ at 23°C.* A mixture of penta-borane (50.0 mmol) and bis(trimethylsilyl)acetylene (200 mmol) was stirred constantly for 15 days at room temperature. Fractionation of the volatiles through 0, -64, and -196°C traps gave 2,3-[(CH_3)₃Si]₂-2,3-C₂B₄H₆ (I) (collected at 0°C; 0.21 g, 0.95 mmol; 91% yield based on B₅H₉ consumed). B.p. 143.5 ± 0.5°C at 38 Torr (Ar) and 197.5 ± 0.5°C at 582 Torr (Ar). Mass spectrum (EI, 70 eV) m/e = 220 (parent ion, (¹²CH₃)₆²⁸Si₂¹²C₂¹¹B₄H₆⁺), 206 (parent ion minus one ¹²CH₃ unit [(¹²CH₃)₅²⁸Si₂¹²C₂¹¹B₄H₇⁺]), 73 [(¹²CH₃)₃²⁸Si⁺], 59[(¹²CH₃)₂²⁸SiH⁺] and 45 [¹²CH₃²⁸SiH₂⁺]. IR (CDCl₃ vs. CDCl₃): 2955(vs) and 2900(s) (C-H), 2590(vs) (B-H), 1948(m) and 1922(w,br) (B-H-B), 1530(w), 1495(w), 1465(w), 1410(s), 1375(ms), 1330(ms), 1250(vs), 1155(ms), 1100(m), 1070(m), 1030(m), 1000(s), 960(m), 930(vs), 845(vs), 680(vs), 655(ms), 620(vs), 520(s), 480(m), 400(vs), 368(vs), and 275(w) cm⁻¹. Analysis. Found: C, 43.28; H, 10.74; Si, 25.09. C₈H₂₄B₄Si₂ calcd.: C, 43.64; H, 10.91; Si, 25.45%. (CH_3)₃SiC≡CSi(CH₃)₃ (195 mmol) and B₅H₉ (48.95 mmol) were collected in -64 and -196°C traps, respectively. A nonvolatile white crystalline material remained in the reaction flask and was identified as [(CH_3)₃SiCH=CSi(CH₃)₃]₃B (II) (0.51 g, 0.97 mmol; 92.7% yield based on B₅H₉ consumed). M.p. 68.5 ± 0.5°C. Mass spectrum: m/e = 524, parent ion (Supplementary Table 1). IR (CDCl₃ vs. CDCl₃): 2950(vs) and 2900(s) (C-H), 1500(w) (C=C), 1410(ms), 1310(ms), 1250(vs), 1110(vs), 840(vs), 770(ms), 680(s), 628(s), 575(w), 550(w), 482(vs), 440(ms), 412(ms) cm⁻¹. This solid II failed to sublime in vacuo below 100°C. When the sublimation was attempted above 100°C, the material gave (CH_3)₃SiC≡CSi(CH₃)₃ (0.071 g, 0.42 mmol; condensed at -78°); a trace quantity of (CH_3)₃SiH (condensed at -196°C) and a colorless liquid, presumably a dimer of II (collected at 0°C; 0.29 g). The EI mass spectrum of this liquid exhibited a strong grouping with the tallest peak at m/e = 354 corresponding to [(¹²CH₃)₃²⁸Si¹²CH = ¹²C²⁸Si(¹²CH₃)₃]₂¹¹BH⁺. Molecular weight: Found (by v.p.o. in CHCl₃), 710 ± 5; calculated for the monomer, 354.

(b) *Reaction of B_5H_9 and $(CH_3)_3SiC\equiv CCH_3$ at 23°C.* This reaction yielded pure 2-[(CH_3)₃Si]-3-CH₃-2,3-C₂B₄H₆ (III) (collected at -23°C; 0.13 g; 0.80 mmol, 81.6% yield based on B₅H₉ consumed). The physical properties and characterizations of this compound are: b.p. 108°C at 58 Torr (Ar) and 178°C at 551 Torr (Ar). Mass spectrum (CI, 15 eV) m/e : 163 (parent ion, (¹²CH₃)₄²⁸Si¹²C₂¹¹B₄H₇⁺), 149 [(¹²CH₃)₃²⁸Si¹²C₂¹¹B₄H₈⁺], 74 [(¹²CH₃)₃²⁸SiH⁺], 60 [(¹²CH₃)₂²⁸SiH₂⁺] and 46 [(¹²CH₃)²⁸SiH₃⁺]. IR (CDCl₃ vs. CDCl₃): 2960(vs) and 2900(s) (C-H), 2590(vs) (B-H), 1970(sh), 1935(s), and 1885(w,br) (B-H-B), 1495(ms), 1408(ms), 1375(ms), 1330(s), 1250(vs), 1165(s), 1100(s), 1043(s), 1020(sh), 995(sh), 980(s), 943(s), 840(vvs), 770(m,br), 683(ms), 655(w), 622(vs), 568(vw), 510(s), 402(vs), 323(s) cm⁻¹. Analysis. Found: C, 44.31; H, 11.04; Si, 17.34. C₆H₁₈B₄Si calcd.: C, 44.44; H, 11.11; Si, 17.28. (CH_3)₃SiC≡CCH₃ (196 mmol) and B₅H₉ (49.02 mmol) were recovered in traps at -78 and -196°C, respectively. The least volatile, white crystalline material, [CH₃CH=CSi(CH₃)₃]₃B (IV) (0.295 g; 0.84 mmol, 86% yield based on B₅H₉ consumed) was sublimed out of the reaction flask at 70°C.

(c) *Reaction of B_5H_9 and $(CH_3)_3SiC\equiv CH$ at 23°C.* Trap-to-trap distillation of

the volatile products gave $[\text{H}_2\text{C}=\text{CSi}(\text{CH}_3)_3]_3\text{B}$ (VI) (collected at 0°C ; 0.151 g; 0.49 mmol, 98% yield based on B_5H_9 consumed). The physical properties and characterizations of this compound are: b.p. $> 180^\circ\text{C}$ with polymerization; Mass spectrum, $m/e = 308$, parent ion (Supplementary Table 1); IR (CDCl_3 vs. CDCl_3): 3010(s), 2960(vs), 2900(ms), 1562(s) $\nu(\text{C}=\text{C})$, 1410(vs), 1355(w), 1250(s), 1200(s), 1125(w), 1085(w), 1023(vs), 955(s), 850(vs), 765(ms), 680(vs), 630(ms), 623(ms), 580(ms), 510(w), 460(ms), 370(ms), 330(w) cm^{-1} . The carborane, 2- $(\text{CH}_3)_3\text{Si}$ -2,3- $\text{C}_2\text{B}_4\text{H}_7$ (V), was collected at -45°C (0.071 g, 0.48 mmol; 96% yield based on B_5H_9 consumed). The unreacted $(\text{CH}_3)_3\text{SiC}\equiv\text{CH}$ (condensed at -196°C ; 197.4 mmol) and B_5H_9 (condensed at -83°C ; 49.5 mmol) were recovered. A trace quantity of the polymeric mass remained at the bottom of the reaction flask and was not identified.

III. At 135°C in Stainless Steel Reactor

(a) *Reaction of B_5H_9 and $(\text{CH}_3)_3\text{SiC}\equiv\text{CSi}(\text{CH}_3)_3$ at 135°C .* Pentaborane (6.40 g; 100 mmol) and bis(trimethylsilyl)acetylene (68.0 g; 400 mmol) were condensed at -196°C into a 500 ml single-ended stainless steel reactor fitted with a high vacuum (10^{-6} Torr) Swagelok shut-off valve. Extreme care was taken to keep the upper end of the reactor at room temperature (occasional warming with a heat gun) during the condensation of the reactants. The mixture was later warmed to room temperature and then only the lower half of the reactor was immersed in an oil bath maintained at a temperature of 135°C . The heating was continued for 48 h. After cooling the mixture to -196°C , accumulated noncondensable gas, presumably H_2 (2.00 mmol) was pumped out. After transferring the most volatile products from the reactor into a vacuum line trap at -196°C , the remaining mixture was heated to 100°C . A low volatile, colorless liquid was distilled into a vacuum line trap at -78°C over a period of 24 h. An efficient distillation of this liquid was achieved when the operating section of the vacuum line manifold was heated to 70°C by using a heating tape and the liquid carborane pumped through -23 and -196°C traps at 10^{-6} Torr. All the distillable and/or volatile products were transferred to the main vacuum line traps and were mixed and fractionated through traps at 0, -23 , -78 , -93 , and -196°C . The unreacted $(\text{CH}_3)_3\text{SiC}\equiv\text{CSi}(\text{CH}_3)_3$ (0.84 g; 4.94 mmol) and B_5H_9 (1.28 g; 20.0 mmol) were collected in -78 and -93°C traps, respectively. The most volatile product, $(\text{CH}_3)_3\text{SiH}$ (96.0 mmol) was condensed into a -196°C trap. The liquids, collected at 0 and -23°C , were mixed and fractionated once again through 0 and -23°C over a period of 3 days while pumping through -196°C . The pure carborane, 2,3- $[(\text{CH}_3)_3\text{Si}]_2$ -2,3- $\text{C}_2\text{B}_4\text{H}_6$ (I) (12.8 g, 58.2 mmol; 72.7% yield based on B_5H_9 consumed) was collected at -23°C . A pale yellow syrupy liquid (0.60 g) was collected at 0°C . The mass spectrum of a portion of this liquid exhibited an intense grouping with the tallest peak at $m/e = 354$ corresponding to $[(^{12}\text{CH}_3)_3^{28}\text{Si}^{12}\text{CH} = ^{12}\text{C}^{28}\text{Si} (^{12}\text{CH}_3)_3]_2^{11}\text{BH}^+$, along with other, more complex, fragmentation patterns. The ^1H NMR spectrum of this material showed several trimethylsilyl protons and vinyl protons. The molecular weight determination in CHCl_3 gave different values for each portion of this material. A further fractionation of this liquid was unsuccessful.

In a second experiment, B_5H_9 (6.40 g; 100 mmol) and $(\text{CH}_3)_3\text{SiC}\equiv\text{CSi}(\text{CH}_3)_3$ (51.0 g; 300 mmol) were allowed to react at 135°C for 48 h. The volatile products consisted of I (11.2 g, 50.9 mmol; 61.3% yield based on B_5H_9 consumed); unreacted alkyne (0.18 g, 1.06 mmol) and B_5H_9 (1.09 g; 17.0 mmol); and trimethylsilane (42.6 mmol).

(b) Reaction of B_5H_9 and $(CH_3)_3SiC\equiv CCH_3$ at $135^\circ C$. Trap-to-trap distillation of all the volatile products gave carborane III (collected at $-23^\circ C$; 4.68 g, 28.9 mmol; 33.4% yield based on B_5H_9 consumed); unreacted alkyne (collected at

TABLE 1

 1H FT NMR DATA (200.132 MHz) ^a

Compound	δ^b (rel. area)	Assignment
2,3- $[(CH_3)_3Si]_2$ -2,3- $C_2B_4H_6$ (I)	0.48 (18), singlet 3.99 (3), quartet, $^1J(BH)$ 158 Hz -0.72 (1), quartet, $^1J(BH)$ 173 Hz -1.66, broad peak	$(CH_3)_3Si$ H_t (base) H_t (apex) B-H-B
$[(CH_3)_3Si(H)C=CSi(CH_3)_3]_3B$ (II)	6.56 (1), singlet, $^2J(HC^{29}Si)$ 26.0 Hz 0.15 (9), singlet 0.10 (9), singlet	$\cdot C=$ H $(CH_3)_3Si$ $(CH_3)_3Si$
2- $[(CH_3)_3Si]$ -3- (CH_3) -2,3- $C_2B_4H_6$ (III)	2.35 (3), singlet 0.33 (9), singlet 3.60 (3), quartet, $^1J(BH)$ 156 Hz -0.68 (1), quartet, $^1J(BH)$ 177 Hz -2.08, broad peak	CH_3 $(CH_3)_3Si$ H_t (base) H_t (apex) B-H-B
$[(CH_3)(H)C=CSi(CH_3)_3]_3B$ (IV)	6.22 (1), quartet, $^3J(HCCH)$ 6.80 Hz 1.88 (3), doublet, $^3J(HCCH)$ 6.80 Hz 0.08 (9), singlet	$\cdot C=$ H CH_3 $(CH_3)_3Si$
2- $[(CH_3)_3Si]$ -2,3- $C_2B_4H_7$ (V)	6.1 (1), broad singlet ^c -0.4 (9), singlet ^c 3.2 (3), quartet, $^1J(BH)$ 160 Hz -0.72 (1), quartet, $^1J(BH)$ 176 Hz -1.75, broad peak	CH $(CH_3)_3Si$ H_t (base) H_t (apex) B-H-B
$[H_2C=CSi(CH_3)_3]_3B$ (VI)	6.40 (1), doublet; 6.23 (1), doublet, $^2J(HCH)$ 5.10 Hz 0.45 (9), singlet	H $\cdot C=$ H $(CH_3)_3Si$

^a $CDCl_3$ was used as solvent and an internal standard for II and IV; for I, III, V, and VI $CDCl_3$ was used as an external standard. ^b Chemical shifts are relative to $(CH_3)_4Si$ with a positive sign indicating a downfield shift. ^c Previously reported by Grimes et al. [17].

–64°C; 0.81 g, 7.23 mmol) and B_5H_9 (collected at –93°C; 0.86 g, 13.4 mmol); and trimethylsilane (collected at –196°C; 34.69 mmol). A small quantity (0.81 g) of white crystalline material IV was collected at 0°C.

(c) *Reaction of B_5H_9 and $(CH_3)_3SiC\equiv CH$ at 135°C.* The volatile products were found to consist of carborane V (collected at –45°C; 2.08 g, 14.0 mmol; 14% yield based on B_5H_9 consumed); unreacted alkyne (at –93°C; 1.03 mmol) and trimethylsilane (collected at –196°C; 35.84 mmol). The unreacted pentaborane was not detected among the products. The trap at 0°C contained a colorless liquid VI (1.86 g, 6.04 mmol; 6.04% yield based on B_5H_9 consumed).

B. Reaction of $BH_3 \cdot THF$ with trimethylsilyl-1-alkynes

$BH_3 \cdot THF$ (9.80 mmol) solution was transferred under argon to a 250 ml greaseless Pyrex reactor containing a magnetic stirring bar. The flask was cooled to –196°C and the argon was pumped out. The gas dissolved in the solution was removed by freeze-thaw process. Freshly distilled trimethylsilyl-1-alkyne, $(CH_3)_3SiC\equiv CR$ (32.0 mmol) was condensed into the reactor at –196°C, after which the mixture in the flask was warmed to 0°C and stirred at that temperature for 6 h. The volatiles were then distilled out of the flask at 0°C, leaving behind a white crystalline solid (when $R = Si(CH_3)_3$ or CH_3) or a colorless liquid (when $R = H$). Further purification via a chromatographic separation on silica-gel column in pure $CHCl_3$, vacuum sublimation at 78°C, and vacuum fractional distillation at 70°C gave $[(CH_3)_3SiCH=CSi(CH_3)_3]_3B$ (II) (4.46 g, 8.51 mmol; 86.8% yield based on $BH_3 \cdot THF$ consumed), $[(CH_3CH=CSi(CH_3)_3)]_3B$ (IV) (2.68 g, 7.66 mmol; 78.1% yield based on $BH_3 \cdot THF$ consumed), and $[H_2C=CSi(CH_3)_3]_3B$ (VI) (1.86 g, 6.04 mmol; 61.6% yield based on $BH_3 \cdot THF$ consumed), respectively.

C. The air stability of $C-Si(CH_3)_3-C'-(R)$ -nido-2,3- $C_2B_4H_6$ and tris(trimethylsilyl-1-alkenyl)borane derivatives

In separate experiments, the pure I, II, III, IV, V, and VI were exposed to air and/or atmospheric moisture for several days, during which time the spectroscopic data (Tables 1–4) on the materials gave no indication of their decomposition.

TABLE 2

^{11}B FT NMR DATA (64.2 MHz)^a

Compound	δ^b (J, Hz)	Rel. areas
I	[+1.85, +1.56 (156)] ^c , –50.05 (173)	3/1
II	+68.68 ^d	–
III	+0.14 (153), –0.73 (153) ^e , (47) ^f , –1.54 (153) ^e (47) ^f , –48.26 (176)	1/1/1/1
IV	+69.93 ^d	–
V ^g	[+0.49; –0.11 (160) ^e , (43) ^f] ^c , –51.82 (176)	3/1
VI	+74.39 ^d	–

^a For I, III, V, and VI a neat liquid sample was taken in an 8-mm sample tube, sealed off, and inserted in a 10-mm standard NMR tube containing $CDCl_3$ for deuterium lock; $CDCl_3$ solution was used for II and IV. ^b Chemical shifts are relative to $BF_3 \cdot O(C_2H_5)_2$ with a positive sign denoting a downfield shift. ^c Superimposed resonances (apparent doublets) which collapse to overlapping singlets in the 1H -decoupled spectrum. ^d Singlet arising from $^{11}B-Cl[Si(CH_3)_3]$. ^e Primary splitting assigned to $H_{term}-^{11}B(4,6)$ coupling. ^f Secondary splitting assigned to $H_{bridge}-^{11}B$ coupling. ^g The NMR parameters reported herein are different from the published data [17].

However, compound II appeared to be extremely hygroscopic when it was exposed to atmospheric moisture for a brief period of time.

In other experiments, each compound (8.00 mmol) was taken separately in an ordinary sample tube with a plastic screw cap under argon atmosphere. Upon storing the materials at room temperature for 7 months, the caps were unscrewed to recover almost all the quantity of I (7.96 mmol) and II (7.92 mmol), a little reduced quantity of III (6.98 mmol) and IV (7.03 mmol), and a substantially reduced quantity of V (5.11 mmol) and VI (4.97 mmol).

Results and discussion

Reaction of B_5H_9 , $(CH_3)_3SiC\equiv CR$ in the presence of $(C_2H_5)_3N$

The reaction not only yielded the expected side product, triethylamineborane, but

TABLE 3

^{13}C FT NMR DATA (50.32 MHz)

Compound	δ^a (J, Hz)	Assignment
I ^b	143.52; broad singlet 1.95 (121); quartet	cage carbons (CH ₃) ₃ Si B
II ^c	174.17 (50) ^d , broad singlet 158.90 (126), (65) ^d , (45) ^e ; doublet 2.47 (118), (51) ^d ; quartet 0.96 (118), (52) ^d ; quartet	C= Si Si C= H (CH ₃) ₃ Si (CH ₃) ₃ Si
III ^f	142.86 (59) ^g ; 134.15 (50) ^g ; broad quartets 22.74 (130); quartet 0.43 (121); quartet	cage carbons CH ₃ (CH ₃) ₃ Si
IV ^c	152.67; broad singlet 148.63 (152) (6.8) ^h ; doublet of quartets 20.50 (126) (6.8) ^h ; quartet of doublets 1.46 (118)	B C= Si C= H CH ₃ (CH ₃) ₃ Si
V ^f	136.5 (42) ^g ; broad quartet 126.4 (154) (35) ^g ; doublet of quartets -1.35 (119); quartet	Si Cage carbon (C) B Cage CH (CH ₃) ₃ Si
VI ^f	162.26; broad singlet 134.70 (156); triplet 0.49 (119); quartet	B C= Si H ₂ C= (CH ₃) ₃ Si

^a Chemical shifts are relative to (CH₃)₄Si with a positive sign indicating a downfield shift. ^b Neat liquid; C₆D₆ as an external standard. ^c CDCl₃ was used as solvent and an internal standard of δ 77.0 ppm.

^d Satellites due to ^{29}Si - ^{13}C coupling (1J) in the 1H -decoupled spectrum. ^e Satellites due to a long-range $^2J(^{29}Si$ - $^{13}C)$ coupling in the 1H -decoupled spectrum. ^f Neat liquid; CDCl₃ as an external standard.

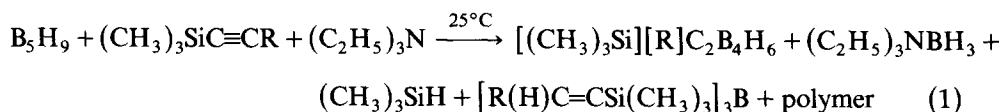
^g Tentatively assigned splitting due to $^{13}C_{(cage)}$ - $^{11}B_{(apex)}$ coupling. ^h Secondary splitting (6.8 Hz) assigned to $^3J(H_{vinyl}$ - $H_{methyl})$ coupling.

TABLE 4

²⁹Si FT NMR DATA (39.76 MHz)

Compound	δ^a (J, Hz) ^b	Rel. area
I ^c	-3.97 (6.0)	-
II ^d	-10.71, -10.42 (5.9) (7.0)	1/1
III ^c	-4.20 (4.3)	-
IV ^d	-10.30 (6.7)	-
V ^c	-1.71 (4.9)	-
VI ^c	-4.86 (6.0)	-

^a Chemical shifts are relative to (CH₃)₄Si with a positive sign indicating a downfield shift. ^b Multiplets of ten lines were observed in the uncoupled spectrum. ^c Neat liquid was taken in an 8-mm sample tube, sealed off, and inserted in a 10-mm standard NMR tube containing CDCl₃ for deuterium lock. ^d CDCl₃ solution was used.



also a new trivinylborane derivative (eq. 1). Complete separation of the carborane product, [(CH₃)₃Si]₂C₂B₄H₆ (I) or [(CH₃)₃Si][CH₃]C₂B₄H₆ (III), from triethylamineborane was unsuccessful. Since (C₂H₅)₃NBH₃ is not an effective hydroborating agent, it was not possible to react this side-product away by hydroboration of simple alkyne or alkene. When R = CH₃, a white crystalline solid, which was characterized as [CH₃(H)C=CSi(CH₃)₃]₃B (IV), was isolated from the remaining polymeric mass by vacuum sublimation. Both the novel trivinylborane derivatives, [H₂C=CSi(CH₃)₃]₃B (VI) and [(CH₃)₃Si(H)C=CSi(CH₃)₃]₃B (II) were isolatable when (C₂H₅)₃N was avoided in reaction 1.

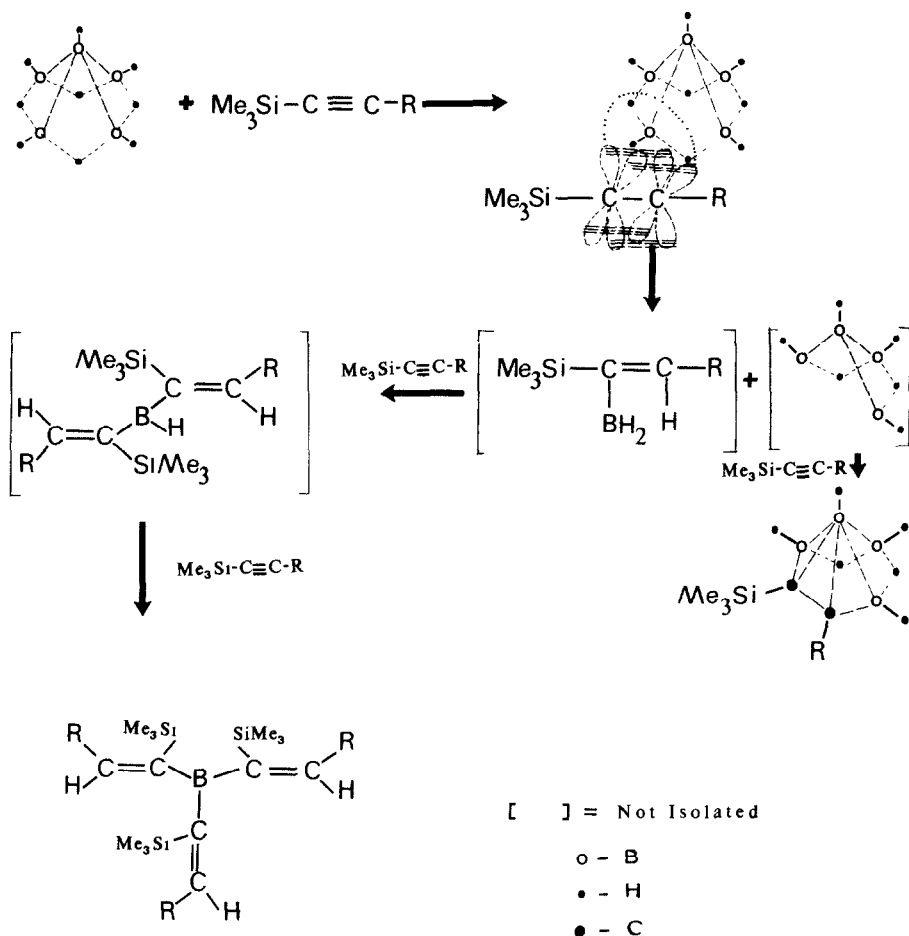
A yellow polymeric material was obtained in all these reactions and was partially identified as one of the products of pyrolysis of the corresponding trivinylborane derivative. The formation of tris(trimethylsilyl-1-alkenyl)borane in all these reactions suggested that at least two additional competing reactions were involved in the carborane synthesis. One involved a B₅H₉ · 2L adduct intermediate [12] and the other was a hydroboration involving only one BH₃ unit [2,3,13,14].

Reaction of B₅H₉ and (CH₃)₃SiC≡CR in the absence of (C₂H₅)₃N

In the absence of (C₂H₅)₃N complications due to (C₂H₅)₃NBH₃ were eliminated and the carborane could be easily separated from the trivinylborane derivative. Apparently, the trimethylsilylalkyne is basic enough to extract a BH₃ unit from B₅H₉ to initiate reaction 2.



Although this reaction quantitatively produced the carborane and the corresponding trivinylborane derivative as sole products, the absolute quantities of both products obtained were very small and the reactions were extremely slow. Scheme 1 outlines the observed reactions, proposed intermediates, and probable sequences of product formation for the B₅H₉/(CH₃)₃SiC≡CR system.



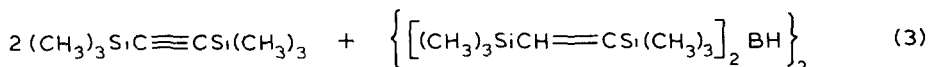
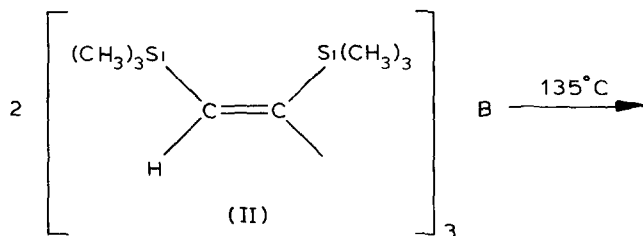
SCHEME 1

Reaction of B_5H_9 and $(CH_3)_3SiC\equiv CR$ in the liquid phase at $135^\circ C$

Although a large quantity of trimethylsilane was obtained among the products, the reaction (when $R=Si(CH_3)_3$) afforded 12.8 g of $2,3-[(CH_3)_3Si]_2C_2B_4H_6$ with minimal problems of separation. The least volatile material was a reddish-brown polymeric mass, which, upon distillation at elevated temperature in high vacuum, yielded a syrupy liquid whose mass spectrum indicated the presence of the dimer of II among other compounds of higher molecular weights. This might have been produced from the pyrolysis of tris[1,2-bis(trimethylsilyl)ethenyl]borane. This is consistent with our observation [15] that the controlled thermal decomposition of II yields a dimer (see eq. 3) and that the trimer, tetramer and higher polymeric units are obtained at higher temperatures.

In any case, the isolation of the dimer among the reaction products proves the occurrence of hydroboration involving one BH_3 unit even at 135°C .

When B_5H_9 and $(CH_3)_3SiC\equiv CSi(CH_3)_3$ were employed in the ratio of 1/3, the yield of the carborane was not reduced substantially. This is not very surprising considering reaction 3 where one mole of alkyne is produced from each mole of II.

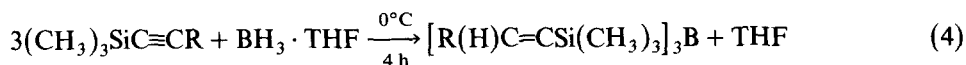


Under similar conditions, the reaction of B_5H_9 with 1-trimethylsilylpropyne or trimethylsilyl acetylene produced 2- $[(\text{CH}_3)_3\text{Si}]\text{-3-(CH}_3\text{)-2,3-C}_2\text{B}_4\text{H}_6$ (III) or 2- $[(\text{CH}_3)_3\text{Si}]\text{-2,3-C}_2\text{B}_4\text{H}_7$ (V) in much lower yields. Because of other side reactions such as di-, tri-, tetra-, and/or polymerization of the hydroborated species, at elevated temperature, the yield of $[\text{CH}_3\text{CH}=\text{CSi}(\text{CH}_3)_3]_3\text{B}$ (IV) was not very high. It was not possible to determine the exact boiling point of VI due to the polymerization of this species above 180°C .

The stabilities of the carborane and trivinylborane derivatives toward air and/or moisture decrease in the following order: $\text{I} = \text{II} > \text{III} = \text{IV} > \text{V} = \text{VI}$ (see Experimental section). Air oxidation of $\text{R,R}'\text{-C}_2\text{B}_4\text{H}_6$ or $[\text{RCH}=\text{CSi}(\text{CH}_3)_3]_3\text{B}$ is minimum when $\text{R} = \text{R}' = \text{Si}(\text{CH}_3)_3$. Thus, it seems that the rate of oxidation depends on steric factors as well as electronic factors. (This dependence on steric factors would explain why the rate of oxidation decreases with increasing trimethylsilyl and/or methyl substitution on cage or olefinic carbons). However, all of these materials can be stored in bottles under argon for indefinite periods (see Experimental section).

Reaction of $\text{BH}_3 \cdot \text{THF}$ and $(\text{CH}_3)_3\text{SiC}\equiv\text{CR}$

The trihydroboration of 1-trimethylsilyl-1-alkyne with $\text{BH}_3 \cdot \text{THF}$, shown in eq. 4, proceeds in a stereo- [2] and regio-selective [3] manner, placing the boron nearly exclusively at the silicon bearing olefinic carbon regardless of the steric requirements of the alkyl substituent attached at the β -carbon [16]. This was confirmed by an X-ray diffraction study of IV [16a].



Although compound IV could be purified further by sublimation in vacuo at 70°C , a substantial loss of the material forming a colorless liquid of very low volatility was noticed. However, solid II failed to sublime in vacuo at 70°C and decomposed at 135°C to give $(\text{CH}_3)_3\text{SiC}\equiv\text{CSi}(\text{CH}_3)_3$ as described in eq. 3. Although the formation of the $(\text{CH}_3)_3\text{SiC}\equiv\text{CSi}(\text{CH}_3)_3$ from II is very intriguing, we are unable to state the exact mechanism of this decomposition reaction.

When trimethylsilylacetylene was hydroborated with $\text{BH}_3 \cdot \text{THF}$, other isomers of VI were identified as minor products in the ^{13}C NMR spectroscopy. This is consistent with the observation made by Brown et al. [13] when terminal acetylene was used for hydroboration.

It is now obvious that this is the most convenient method for the preparation of II, IV, and VI since it avoids altogether a handling of volatile pentaborane and formation of carboranes.

*Characterization of tris(trimethylsilyl-1-alkenyl)borane **

The trivinylboranes, II, IV, and VI were structurally characterized from their EI mass spectra (Supplementary Table 1), ^1H , ^{11}B , ^{13}C and ^{29}Si NMR spectra (Table 1–4), infrared spectra and, where possible, elemental analysis (Experimental section). The formulations (Table 1) of the trivinylborane derivatives are consistent with their spectroscopic parameters and were further confirmed in our X-ray crystal structure study of $[\text{CH}_3\text{CH}=\text{CSi}(\text{CH}_3)_3]_3\text{B}$ [16a].

*Characterization of the C-trimethylsilyl substituted $\text{C}_2\text{B}_4\text{H}_8$ derivatives **

The carboranes were structurally characterized from their unit-mass spectra, ^1H , ^{11}B , ^{13}C , and ^{29}Si NMR spectra (Tables 1–4), infrared spectra, and elemental analysis (Experimental section). The IR, ^1H , and ^{11}B NMR spectroscopic parameters for I and III are consistent with those of 2,3- $(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_6$ [7] and 2-Si $(\text{CH}_3)_3$ -2,3- $\text{C}_2\text{B}_4\text{H}_7$ [17].

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