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Synthesis and Characterization of a New Alkenyldecaborane and Alkenyl Monocarbon Carboranes

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Decaborane(14) reacts with 1-$(CH_3)_3SiC{\equiv}CC_4H_9$ in the presence of dimethyl sulfide to give the new alkenyldecaborane 5-$(S(CH_3)_2)$-6-$[(CH_3)_3Si(C_4H_9)C{=}CH]B_{10}H_{11}$ (**I**). Crystal data for 5-$(S(CH_3)_2)$-6-$[(CH_3)_3Si(C_4H_9)C{=}CH]B_{10}H_{11}$: space group $P2_1/n$, monoclinic, $a = 9.471(1)$ Å, $b = 13.947(3)$ Å, $c = 17.678(3)$ Å, $\beta = 100.32(1)°$. A total of 3366 unique reflections were collected over the range $2.0° \le 2\theta \le 56.0°$, of which 1763 reflections had $F_o^2 \ge 3\sigma(F_o^2)$ and were used in the final refinement. $R_F = 0.083$; $R_{wF} = 0.094$. The single-crystal X-ray structure of 5-$(S(CH_3)_2)$-6-$[((CH_3)_3Si)_2C{=}CH]B_{10}H_{11}$ (**A**) is also reported. Crystal data for 5-$(S(CH_3)_2)$-6-$[((CH_3)_3Si)_2C{=}CH]B_{10}H_{11}$: space group, $P2_12_12_1$, orthorhombic, $a = 9.059$ (3) Å, $b = 12.193(4)$ Å, $c = 21.431(3)$ Å. A total of 4836 unique reflections were collected over the range $6° \le 2\theta \le 140°$, of which 3705 reflections had $F_o^2 \ge 3\sigma(F_o^2)$ and were used in the final refinement. $R_F = 0.052$; $R_{wF} = 0.059$. The reactions of 5-$(S(CH_3)_2)$6-$[(CH_3)_3Si(C_4H_9)C{=}CH]B_{10}H_{11}$ and 5-$(S(CH_3)_2)$6-$[((CH_3)_3Si)_2C{=}CH]B_{10}H_{11}$ with a variety of alkyl isocyanides were investigated. All of the alkenyl monocarbon carboranes reported are the result of incorporation of the carbon atom from the isocyanide into the alkenyldecaborane framework and reduction of N≡C bond to a N−C single bond. The characterization of these compounds is based on ^{1}H and ^{11}B NMR data, IR spectroscopy, and mass spectrometry.

Introduction

The reactivity of decaborane(14) with a number of alkyl isocyanides or the cyanide ion was first investigated by Knoth and Todd in the late 1960s, who showed that the product obtained consisted of a one−carbon-insertion monocarbon carborane and that the N≡C bond was reduced to a $NH_2{-}C$ bond.[1−6]

$$RN{\equiv}C + B_{10}H_{14} \rightarrow \textit{nido}\text{-7-}(RNH_2)\text{-7-}CB_{10}H_{12}{}^{1} \quad (1)$$

$$C{\equiv}N^- + B_{10}H_{14} \rightarrow \textit{nido}\text{-6-}(NC)B_{10}H_{12} \rightarrow \textit{nido}\text{-7-}(NH_3)\text{-7-}CB_{10}H_{12}{}^{5} \quad (2)$$

Another borane and a thiaborane, 5-$(S(CH_3)_2)$-9-(C_6H_{13})-$B_{10}H_{11}$ and SB_9H_{11}, were found to react also with $(CH_3)_3N{\equiv}C$, resulting in the incorporation of the carbon atom of the isocyanide and reduction of the N≡C bond.[2,4]

$$(CH_3)_3CN{\equiv}C + \text{5-}(S(CH_3)_2)\text{-6-}(C_6H_{11})B_{10}H_{11} \rightarrow \textit{nido}\text{-3-}(S(CH_3)_2)\text{-7-}((CH_3)_3CNH)\text{-11-}(C_6H_{11})B_{10}H_{10}{}^{4} \quad (3)$$

$$(CH_3)_3CN{\equiv}C + SB_9H_{11} \rightarrow \textit{nido}\text{-8-}((CH_3)_3CNH_2)\text{-7-}CSB_9H_9{}^{2} \quad (4)$$

In each of these reactions the alkyl isocyanide is acting as a nucleophile, while the boron hydride molecule is acting as an electrophile. The result is an attack on the negatively charged carbon atom of the isocyanide molecule, resulting in carbon incorporation into the boron-containing cage and reduction of the N≡C bond to a N−C single bond.

We have continued to investigate the reactivity of substituted boron hydrides toward isocyanides by performing experiments that involve the substituted alkenylboranes 5-$(S(CH_3)_2)$-6-$[(CH_3)_3Si(C_4H_9)C{=}CH]B_{10}H_{11}$ and 5-$(S(CH_3)_2)$-6-$[((CH_3)_3Si)_2C{=}CH]B_{10}H_{11}$, with different isocyanides.

Boron hydrides and carboranes having pendant alkenyl groups are relatively few. The formation of these alkenyl monocarbon carboranes gives an unique opportunity to investigate the reactivity not only of the carborane cage but also of the ancillary alkenyl group associated with the cage. One possibility that could be explored is the possible polymerization of the alkenyl group, producing boron-containing polymers which could be used as precursors to other materials. Another possible application for these types of materials is their subsequent conversion into molecules which could be used in boron neutron capture therapy studies.

The results presented in this communication confirm that this type of chemistry is general for boron hydrides based on the decaborane(14) framework, due to the intrinsic electrophilic character of these molecules. Their facile conversion into alkenyl monocarbon carboranes could open new synthetic pathways for the production of new and interesting compounds, which could have a variety of applications, depending on the

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Table 1. ^{11}B Nuclear Magnetic Resonance Chemical Shifts[a]

compound	δ, ppm (J, Hz)	rel intens
$5-(S(CH_3)_2)-6-[(CH_3)_3Si(C_4H_9)C{=}CH]B_{10}H_{11}$ (**I**)[b]	29.84[c] (s), 2.89 (128), −2.13,[d] −4.41 (146), −6.76,[c] −11.47,[d] −24.15 (142), −41.74 (149)	1:2:1:1:1:1:2:1
$2-(S(CH_3)_2)-7-(C_6H_5CH_2NH)-11-[((CH_3)_3Si)_2C{=}CH]-7-CB_{10}H_{10}$ (**II**)[b]	−2.62,[c] −3.48,[c] −10.64,[d] −12.61,[d] −20.11,[d] −21.82,[d] −27.38 (145), −30.59 (144), −32.75(144)	1:2:1:1:1:1:1:1:1
$2-(S(CH_3)_2)-7-((CH_3)_3CNH)-11-[((CH_3)_3Si)_2C{=}CH]-7-CB_{10}H_{10}$ (**III**)[b]	−4.31,[c] −10.39,[c] −21.84,[d] −27.96 (172), −31.10 (124), −32.44[c]	3:2:2:1:1:1
$2-(S(CH_3)_2)-7-(C_4H_9NH)-11-[((CH_3)_3Si)_2C{=}CH]-7-CB_{10}H_{10}$ (**IV**)[b]	−4.45,[c,d] −12.15,[c] −13.36,[d] −21.60,[d] −22.31,[d] −28.32 (134), −31.59 (142), −33.69 (148)	3:1:1:1:1:1:1:1
$2-(S(CH_3)_2)-7-(C_4H_9NH)-11-[(CH_3)_3Si(C_4H_9)C{=}CH]-7-CB_{10}H_{10}$ (**V**)[b]	-4.46,[c,d] −11.57,[c] −22.69,[d] −24.26 (138), −28.40 (130), −31.78 (143), −33.88 (135)	3:2:1:1:1:1:1

[a] 128.4 Hz. [b] C_6D_6 solvent. [c] Singlet. [d] Coupling constants could not be reliably calculated due to overlapping peaks. [e] $(CD_3)_2C{=}O$ solvent.

Table 2. ^{1}H Nuclear Magnetic Resonance Chemical Shifts

compound	δ, ppm
$5-(S(CH_3)_2)-6-[(CH_3)_3Si\ (C_4H_9)C{=}CH]B_{10}H_{11}$ (**I**)[a,b]	-2.352 (2, b, BHB), 0.034 (9, s, $(CH_3)_3Si$), 1.038 (3, t, CH_3), 1.454 (4, m, CH_2CH_2), 1.609 (3, s, SCH_3), 1.719 (3, s, SCH_3), 2.039 (2, m, $C{=}CCH_2$), 7.043 (1, s, $C{=}CH$)
$2-(S(CH_3)_2)-7-(C_6H_5CH_2NH)-11-[((CH_3)_3Si)_2C{=}CH]-7-CB_{10}H_{10}$ (**II**)[d,e]	-3.36 (2, b, BHB), 0.07 and 0.22 (18, s, $(CH_3)_3Si$), 1.88 (1, b, NH), 2.70 (6, s, $S(CH_3)_2$), 3.74 and 4.03 (2, d, CH_2), 5.30 (1, s, $C{=}CH$), 7.08 (1, m, C_6H_5), 7.23 (2, m, C_6H_5), 7.26 (2, m, C_6H_5)
$2-(S(CH_3)_2)-7-((CH_3)_3CNH)-11-[((CH_3)_3Si)_2C{=}CH]7-CB_{10}H_{10}$ (**III**)[b,e]	-2.547 (2, b, BHB), 0.22 and 0.45 (18, s, $(CH_3)_3Si$), 1.16 (9, s, $(CH_3)_3C$), 1.45 (3, s, SCH_3), 1.49 (3, s, SCH_3), 1.85 (1, b, NH), 7.42 (1, s, $C{=}CH$)
$2-(S(CH_3)_2)-7-(C_4H_9NH)-11-[((CH_3)_3Si)_2C{=}CH]-7-CB_{10}H_{10}$ (**IV**)[b,c]	-2.851 (2, b, BHB), 0.333 and 0.346 (18, s, $(CH_3)_3Si$), 0.871 (3, t, CH_3), 1.261 and 1.418 (4, m,CH_2CH_2) 1.569 (3, s, SCH_3), 1.638 (3, s, SCH_3), 2.287 (1, b, NH), 3.003 and 2.594 (2, m, $NHCH_2$), 6.275 (1, s, $C{=}CH$)
$2-(S(CH_3)_2)-7-(C_4H_9NH)-11-[(CH_3)_3Si(C_4H_9)C{=}CH]-7-CB_{10}H_{10}$ (**V**)[b,c]	-2.132 (2, b, BHB), 0.374 (9, s, $(CH_3)_3Si$), 1.051(6, m, CH_3 from C_4H_9 on $NHCH_2CH_2CH_2\mathbf{CH_3}$ and $C{=}CCH_2CH_2CH_2\mathbf{CH_3}$**)**, 1.413 (8, m, CH_2 from $NHCH_2\mathbf{CH_2CH_2}CH_3$ and $C{=}CCH_2\mathbf{CH_2CH_2}CH_3$), 1.593 (1, m, NH), 1.752 (3, s, SCH_3), 1.817 (3, s, SCH_3), 2.134 (2, m, $C{=}CCH_2$), 3.104 and 2.657 (2, d of d, $NH\mathbf{CH_2}$), 6.453 (1, s, $C{=}CH$)

[a] 400.0 MHz. [b] C_6D_6 solvent. [c] 200.0 MHz. [d] CD_2Cl_2 solvent. [e] 250 MHz. [f] $(CD_3)_2C{=}O$ solvent.

kind of pendant organic groups attached to the boron hydride framework.

Experimental Section

All manipulations were carried out using standard high-vacuum or inert-atmosphere techniques, when warranted, as described by Shriver.[7]

Materials. The compound *nido*-$5-(S(CH_3)_2)6-[((CH_3)_3Si)_2C{=}CH]-B_{10}H_{11}$ was prepared according to the reported literature procedure.[8] Decaborane(14) was purchased from Callery Chemical and recrystallized from boiling heptane prior to use. Anhydrous dimethyl sulfide, 1-(trimethylsilyl)-1-hexyne, and the isocyanides used in this study, *n*-$C_4H_9N{\equiv}C$, $(CH_3)_3CN{\equiv}C$, and $C_6H_5CH_2N{\equiv}C$ were purchased from Aldrich Chemical and used as received. Benzene and hexane were obtained from Fisher Scientific and dried according to literature procedures prior to use. C_6D_6, DMSO-*d*$_6$, acetone-*d*$_6$, and TMS were purchased from Isotech and used as received.

Physical Measurements. The 128.4 MHz boron-11 and 400.0 MHz proton NMR spectra were obtained on a Varian Unity-400 Fourier transform spectrometer. All boron-11 chemical shifts were referenced to $BF_3{\cdot}O(C_2H_5)_2 = 0.0$ ppm, with a negative sign indicating an upfield shift. Proton NMR spectra at 200 MHz were obtained on a Varian Gemini-200 Fourier transform spectrometer. Proton chemical shifts were referenced to TMS = 0.00 ppm, with positive values indicating downfield shifts.

Infrared spectra were recorded on a Perkin-Elmer 337 grating infrared spectrophotometer and on Perkin Elmer 1720 Fourier transform spectrophotometer. Low-resolution CI mass spectra and all high-resolution mass spectra were obtained on a VG 7070-H mass spectrometer, except that of **I**. The high-resolution mass spectral data for **I** were obtained from the Nebraska Center for Mass Spectrometry of the University of Nebraska.

X-ray diffraction data were obtained on an Enraf-Nonius four-circle CAD-4 and an AFC7R diffractometer employing Cu Kα radiation from a highly oriented monochromator.

Tables 1−3 summarize relevant ^{11}B NMR, ^{1}H NMR, and IR information for the compounds discussed on this paper.

All melting points are uncorrected.

Crystallographic Structure Determinations of $\mathbf{5-(S(CH_3)_2)-6-[((CH_3)_3Si)_2C{=}CH]B_{10}H_{11}}$ (A) and $\mathbf{5-(S(CH_3)_2)6-[(CH_3)_3Si-(C_4H_9)C{=}CH]B_{10}H_{11}}$ (I). Single-crystals of **A** and **I** were grown overnight by slow evaporation in air of a methylene chloride/heptane solution. See Table 4 for crystal data. The cell constants for both compounds were determined from a least-squares fit of the setting angles for 25 accurately centered reflections. X-ray intensity data were collected on an Enraf Nonius four-circle CAD-4 diffractometer controlled by a PDP 8/A computer for **A** and on an AFC7R diffractometer for **I**. Both diffractometers employed graphite-monochromated Cu Kα radiation ($\lambda = 1.541\ 84$ ×81Å) and used the $\omega - 2\theta$ scanning technique. X-ray data were processed, and the structures were solved and refined by using either the Molecular Structure Corp. teXsan package[9] on a Silicon Graphics Indigo R4000 computer for compound **I** or a VAX 750 minicomputer which had the Enraf-Nonius structure package[10] for compound **A**. For compound **A** , a total of 4836 reflections were measured over the ranges $6° \le 2\theta \le 140°$ and −11

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Table 3. Infrared Spectral Data

compound	ν, cm^{-1}
$5\text{-}(S(CH_3)_2)\text{-}6\text{-}[(CH_3)_3Si(C_4H_9)C{=}CH]B_{10}H_{11}$ (**I**)	2935 (m), 2927 (m), 2895 (w), 2870 (m), 2862 (m), 2582 (w), 2565 (s), 2552 (s), 2542 (sh), 2530 (sh), 2520 (s), 1554 (m), 1471 (m), 1427 (m), 1330 (w), 1261 (m), 1245 (s), 1115 (m), 1039 (s), 991 (m), 937 (w), 905 (w), 852 (m), 832 (s), 806 (m), 758 (m), 716 (w), 686 (w), 624 (w
$2\text{-}(S(CH_3)_2)\text{-}7\text{-}(C_6H_5CH_2NH)\text{-}11\text{-}[((CH_3)_3Si)_2C{=}CH]\text{-}7\text{-}CB_{10}H_{10}$ (**II**)	3325 (m), 3020 (m), 2970 (m), 2880 (sh), 2440 (s), 1630 (m), 1480 (s), 1400 (w), 1280 (w), 1250 (s), 1160 (w), 950 (m), 880 (sh), 860 (sh), 840 (m), 760 (m), 680 (m), 650 (m), 620 (w)
$2\text{-}(S(CH_3)_2)\text{-}7\text{-}((CH_3)_3CNH)\text{-}11\text{-}[((CH_3)_3Si)_2C{=}CH]\text{-}7\text{-}CB_{10}H_{10}$ (**III**)	3310 (m), 3010 (m), 2960 (m), 2900 (sh), 2800 (sh), 2540 (s), 1610 (w), 1400 (br, m), 1050 (sh), 1000 (m), 980 (sh), 900 (m), 860 (sh), 840 (m), 750 (w), 740 (w), 690 (m), 650 (w)
$2\text{-}(S(CH_3)_2)\text{-}7\text{-}(C_4H_9NH)\text{-}11\text{-}[((CH_3)_3Si)_2C{=}CH]\text{-}7\text{-}CB_{10}H_{10}$ (**IV**)	3285 (m), 3015 (m), 2950 (m), 2910 (sh), 2470 (s), 1615 (m), 1465 (s), 1390 (w), 1245 (sh), 1140 (w), 1000 (m), 980 (sh), 965 (m), 875 (sh), 845 (m), 740 (w), 645 (m)
$2\text{-}(S(CH_3)_2)\text{-}7\text{-}C_4H_9NH\text{-}11\text{-}[S(CH3)2i(C_4H_9)C{=}CH]\text{-}7\text{-}CB_{10}H_{10}$ (**V**)	3325 (m), 3005 (m), 2975 (m), 2870 (sh), 2490 (s), 1620 (m), 1470 (s), 1370 (w), 1020 (sh), 990 (m), 960 (sh), 945 (m), 835 (m), 700 (w), 620 (w)

Table 4. Data Collection and Structure Refinement Information for $5\text{-}(S(CH_3)_2)\text{-}6\text{-}[((CH_3)_3Si)_2C{=}CH]B_{10}H_{11}$ (**A**) and $5\text{-}(S(CH_3)_2\text{-}6\text{-}[(CH_3)_3Si(C_4H_9)C{=}CH]B_{10}H_{11}$ (**I**)

	A	**I**
formula	$C_{10}H_{36}B_{10}SSi_2$	$C_{11}H_{36}B_{10}SSi$
fw	352.74	336.67
space group	$P2_12_12_1$	$P2_1$
Z	4	4
crystal class	orthorhombic	monoclinic
a, Å	9.059(1)	9.471(1)
b, Å	12.193(3)	13.947(3)
c, Å	21.431(3)	17.678(3)
β, deg		100.32(1)
V, Å^3	2367.4(4)	2297.2(6)
μ, cm^{-1}	20.73	16.15
crystal size, mm	0.30 × 0.45 × 0.20	0.38 × 0.27 × 0.20
D_{calc}, g/cm^3	0.990	0.939
radiation (λ, Å)	Cu Kα (1.541 84)	Cu Kα (1.541 84)
scan range, deg	$6 \leq 2\theta \leq 140$	$2 \leq 2\theta \leq 56$
h,k,l collected	±11,±14,±26	+10,+15,±19
no. of reflns measd	4836	3366
no. of reflns for $F_o^2 > 3\sigma(F_o^2)$	3705	1763
no. of variables	244	253
R_F	0.052	0.083
R_{wF}	0.059	0.094

Table 5. Atomic Positional Parameters and Their Estimated Standard Deviations for $5\text{-}(S(CH_3)_2)\text{-}6\text{-}[((CH_3)_3Si)_2C{=}CH]B_{10}H_{11}$ (**A**)

atom	x	y	z	B_{eq}, Å^2
Si1	0.2698(2)	0.4707(1)	0.14510(6)	4.95(3)
Si2	0.5612(2)	0.3329(1)	0.09698(6)	5.06(3)
S	0.5925(1)	0.3649(1)	0.35822(6)	4.86(2)
B1	0.2878(7)	0.2776(5)	0.4036(3)	4.7(1)
B2	0.3192(6)	0.2145(5)	0.3309(3)	4.3(1)
B3	0.1377(6)	0.2178(5)	0.3625(3)	5.3(1)
B4	0.1056(7)	0.3330(5)	0.4133(3)	5.4(1)
B5	0.3874(6)	0.3468(4)	0.3474(2)	3.9(1)
B6	0.3383(3)	0.3186(4)	0.2744(2)	4.0(1)
B7	0.1657(7)	0.2475(5)	0.2816(3)	4.9(1)
B8	0.0190(5)	0.3197(5)	0.3379(3)	5.5.(1)
B9	0.0744(7)	0.4493(5)	0.3686(3)	5.5.(1)
B10	0.2584(7)	0.4425(5)	0.3954(3)	4.8(1)
C1	0.4353(5)	0.3185(3)	0.2148(2)	3.99(9)
C2	0.4257(5)	0.3713(4)	0.1592(2)	4.15(9)
CA	0.3052(8)	0.5616(5)	0.0773(2)	8.1(2)
CB	0.0960(7)	0.3922(5)	0.1305(3)	8.1(2)
CC	0.2485(7)	0.5632(4)	0.2139(2)	6.1(1)
CD	0.4603(9)	0.2258(6)	0.0365(2)	9.3(2)
CE	0.6583(7)	0.4503(5)	0.0595(3)	7.7(2)
CF	0.7068(7)	0.2415(5)	0.1294(3)	7.4(1)
CG	0.6231(6)	0.4988(5)	0.3274(3)	7.0(2)
CH	0.6285(6)	0.3874(5)	0.4389(3)	7.1(2)

[a] $B_{eq} = {}^8/_3[U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*) + 2U_{12}(aa^*bb^*)\cos\gamma) + 2U_{13}(aa^*cc^*\cos\beta) + 2U_{23}(bb^*cc^*\cos\alpha)]$.

$\leq h \leq 11$, $-14 \leq k \leq 14$, $-26 \leq l \leq 26$. For compound **I**, 3366 reflections were collected over the ranges $2° \leq 2\theta \leq 56°$ and $0 \leq h \leq 10$, $0 \leq k \leq 15$, $-19 \leq l \leq 19$. For both compounds three standard reflections were measured every 3500 s of X-ray exposure. Compound **A** showed a decay of 9.5% and compound **I** showed a decay of 12.5% over the course of data collection. A linear decay correction was applied for both compounds.

The intensity data were corrected for Lorentz and polarization effects but not for absorption. For compound **A**, 3705 reflections were unique, and for **I**, 1763 were unique, having $F^2 > 3\sigma(F^2)$, and they were used in the subsequent structure refinement.

Both structures were solved by direct methods. Refinement was full-matrix least-squares techniques based on F to minimize the quantity $\Sigma w(|F_o| - |F_c|)^2$ with $w = 1/\sigma^2(F)$.

Non-hydrogen atoms were refined anisotropically; cage hydrogens were refined isotropically; all other hydrogens were included as constant contributions to the structure factors and were not refined. For **A**, refinement converged to $R_F = 0.052$ and $R_{wF} = 0.059$; for **I**, $R_F, = 0.083$ and $R_{wF} = 0.094$. Tables containing relevant information such as data collection and structure refinement details, positional parameters of selected atoms, and selected interatomic distances for both compounds are presented in Tables 4−7. Tables containing positional parameters of hydrogen atoms, anisotropic thermal parameters, and bond angles are available as Supporting Information.

Reaction of Decaborane(14) with 1-(Trimethylsilyl)-1-hexyne. In a 250 mL round-bottom flask equipped with a high-vacuum stopcock were placed 3.13 g (25.6 mmol) of decaborane(14), 3.75 mL (51.2 mmol) of dimethyl sulfide, and 150 mL of dry benzene. The flask was sealed and degassed three times under vacuum. The resulting solution was heated to reflux for 12 h, with periodic degassing to ensure removal of hydrogen gas produced during the course of the reaction. After evolution of hydrogen gas had ceased, the flask was opened and 3.96 g (5.2 mL, 25.6 mmol) of 1-(trimethylsilyl)-1-hexyne was syringed into the yellow solution. The flask was then resealed and degassed three times. The solution was heated to reflux for an additional 48 h, at which time, the solution had turned red. The benzene solvent was removed under vacuum, along with free dimethyl sulfide, which is a byproduct of the reaction. An oily solid remained inside the flask after most of the solvent had been removed. To this solid was added dropwise 25 mL of methanol, by using an addition funnel, which resulted in the dissolution of the solid and evolution of hydrogen gas. The flask was then placed inside a refrigerator for 5 h, after which a small amount of a yellow solid had precipitated from the solution. This solid was filtered off through a medium-porosity frit, and the resulting filtrate was placed in a 400 mL beaker.

The beaker containing the methanol solution was cooled at −50 °C, and water was added very slowly via an addition funnel. The addition of water resulted in the precipitation of more of the yellow solid. The methanol/water solution was filtered through a medium-porosity frit,

Table 6. Atomic Positional Parameters and Their Estimated Standard Deviations for $5\text{-}(S(CH_3)_2)\text{-}6\text{-}[(CH_3)_3Si(C_4H_9)C{=}CH]B_{10}H_{11}$ (**I**)

atom	*x*	*y*	*z*	B_{eq},[a] Å^2
Si	0.7656(2)	−0.6173(2)	0.2696(2)	7.4(1)
S	0.2177(2)	−0.4580(2)	0.1903(1)	6.8(1)
B1	0.226(1)	−0.7565(8)	0.0945(7)	7.8(6)
B2	0.240(1)	−0.6913(8)	0.0099(7)	7.9(6)
B3	0.161(1)	−0.6397(7)	0.0843(7)	7.1(6)
B4	0.225(1)	−0.6824(7)	0.1749(7)	6.9(5)
B5	0.2774(9)	−0.5703(6)	0.1458(6)	6.3(5)
B6	0.399(1)	−0.6334(7)	0.2063(6)	6.6.(5)
B7	0.381(1)	−0.7532(8)	0.1703(6)	7.1(5)
B8	0.383(1)	−0.7666(9)	0.0563(7)	8.0(6)
B9	0.412(1)	−0.655(1)	0.0111(7)	7.7(6)
B10	0.293(1)	−0.5745(7)	0.0447(6)	6.9(5)
C1	0.4744(9)	−0.6039(6)	0.2983(5)	6.8(4)
C2	0.6144(8)	−0.5948(5)	0.3215(4)	5.8(4)
C3	0.6485(8)	−0.5628(6)	0.4034(5)	7.1(5)
C4	0.6635(9)	−0.4533(7)	0.4135(5)	7.9(5)
C5	0.720(1)	−0.4222(8)	0.4952(6)	9.9(6)
C6	0.717(1)	−0.3162(8)	0.5066(7)	12.5(8)
C7	0.738(1)	−0.5590(9)	0.1748(6)	11.0(7)
C8	0.785(1)	−0.7493(7)	0.2580(7)	10.9(7)
C9	0.9387(9)	−0.5700(9)	0.3276(6)	11.9(7)
C10	0.364(1)	−0.3798(6)	0.1874(6)	9.4(6)
C11	0.079(1)	−0.4036(6)	0.1211(6)	9.6(6)

[a] $B_{eq} = {}^8/_3[U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*) + 2U_{12}(aa^*bb^*) \cos \gamma) + 2U_{13}(aa^*cc^* \cos \beta) + 2U_{23}(bb^*cc^* \cos \alpha)]$.

Table 7. Selected Interatomic Distances (Å) for $5\text{-}(S(CH_3)_2)\text{-}[((CH_3)_3Si)_2C{=}CH]B_{10}H_{11}$ (**A**) $5\text{-}(S(CH_3)_2)\text{-}[(CH_3)_3Si(C_4H_9)C{=}CH]B_{10}H_{11}$ (**I**)

bond	**A**	**I**	bond	**A**	**B**
B1−B2	1.759(8)	1.718(15)	B9−B10	1.793(8)	1.768(15)
B1−B3	1.777(8)	1.741(14)	C1−C2	1.358(6)	1.351(9)
B1−B4	1.792(9)	1.781(15)	C1−B6	1.550(7)	1.569(13)
B1−B5	1.726(8)	1.706(14)	Si1−C2	1.886(5)	1.860(7)
B1−B10	1.796(8)	1.792(13)	Si2−C2	1.873(4)	
B2−B3	1.778(3)	1.759(15)	Si1−CA (C7)[a]	1.856(6)	1.838(10)
B2−B5	1.763(8)	1.745(12)	Si1−CB (C8)[a]	1.869(6)	1.866(10)
B2−B6	1.763(8)	1.771(13)	Si1−CC (C9)[a]	1.866(5)	1.890(9)
B2−B7	1.792(8)	1.786(14)	Si2−CD	1.845(7)	
B3−B4	1.777(9)	1.776(16)	Si2−CE	1.862(6)	
B3−B7	1.788(9)	1.799(14)	Si2−CF	1.862(6)	
B4−B8	1.766(8)	1.789(15)	C2−C3		1.495(10)
B4−B9	1.712(9)	1.702(15)	C3−C4		1.541(11)
B4−B10	1.795(9)	1.782(15)	C4−C4		1.512(12)
B5−B6	1.661(7)	1.673(13)	C5−C6		1.493(14)
B5−B10	1.810(8)	1.821(14)	S−B5	1.885(5)	1.885(9)
B6−B7	1.795(8)	1.785(13)	S−CG (C10)[a]	1.784(6)	1.771(8)
B7−B8	2.000(8)	2.028(15)	S−CH (C11)[a]	1.780(5)	1.798(8)
B8−B9	1.784(9)	1.793(17)			

[a] Notation in parentheses refers to the numbering sequence used for compound **I**.

and 2.50 g of $5\text{-}(S(CH_3)_2)\text{-}6\text{-}[(CH_3)_3Si(C_4H_9)C{=}CH]B_{10}H_{11}$ (**I**) was isolated. [7.45 mmol, 29.1% yield based on decaborane(14)]. Anal. Calcd: C, 39.24; H, 10.78. Found, C, 38.98; H, 9.84.[11] Mp: 98−100 °C. Exact mass measurement: calculated for $^{12}C_{11}{}^1H_{36}{}^{11}B_{10}{}^{32}S^{28}Si$, 338.3238; found, 338.3280.

Reaction of $5\text{-}(S(CH_3)_2)\text{-}6\text{-}[((CH_3)_3Si)_2C{=}CH]B_{10}H_{11}$ with Alkyl Isocyanides. *Caution*! Addition and transferal of alkyl isocyanides must be performed inside a well-ventilated hood. Some of these compounds are highly toxic, and even small amounts leave a pungent odor behind that lasts in the area for around 3−4 h.

(A) In a Kjedahl 100 mL flask equipped with a high-vacuum stopcock were placed 0.50 g (1.42 mmol) of $5\text{-}(S(CH_3)_2)6\text{-}[((CH_3)_3Si)_2C{=}CH]B_{10}H_{11}$ and 0.17 mL (1.40 mmol) of benzyl isocyanide. Benzene (25 mL) was then condensed in, the mixture was and stirred at room temperature for 6 h. Noncondensables were removed at 1 h intervals. Once the solution turned yellow, it was heated at reflux for an additional 18 h. The benzene was removed *in vacuo*, the resulting oily solid was dissolved in 20 mL of methanol, and the mixture was stirred at room temperature for 1 h, resulting in the evolution of hydrogen gas. The resulting solution was then cooled at −5 °C in a water−ice bath, resulting in the formation of a yellow precipitate with was filtered off and dissolved in 5 mL of methylene chloride. The mother liquor was added to 30 mL of methylene chloride, and the mixture was left until two phases were clearly visible. Then, 5.0 g of sodium bisulfite was added to the solution, and the aqueous layer was separated from the organic layer with the aid of a separatory funnel. The methylene chloride solutions were combined and evaporated under reduced pressure, resulting in the isolation of $2\text{-}(S(CH_3)_2)\text{-}7\text{-}(C_6H_5CH_2\text{-}NH)\text{-}11\text{-}[((CH_3)_3Si)_2C{=}CH]\text{-}7\text{-}CB_{10}H_{10}$ (**II**) [brown solid; 0.40 g (0.84 mmol), 60% yield; $R_f = 0.45$; mp 254−6 °C]. Mass measurements calculated for $^{12}C_{18}{}^1H_{43}{}^{11}B_{10}{}^{14}N^{32}S^{28}Si_2$, 471.3585; found, 471.3528.

(B) The procedure followed was the same as for the reaction of benzyl isocyanide, the amounts used were the following: 0.25 g (0.71 mmol) of $5\text{-}(S(CH_3)_2)6\text{-}[((CH_3)_3Si)_2C{=}CH]B_{10}H_{11}$, 0.10 mL of *tert*-butyl isocyanide, and 25 mL of dry benzene. The reaction was worked up in the same manner, resulting in the formation of 0.15 g (0.34 mmol) of $2\text{-}(S(CH_3)_2)\text{-}7\text{-}((CH_3)_3CNH)\text{-}11\text{-}[((CH_3)_3Si)_2C{=}CH]\text{-}7\text{-}CB_{10}H_{10}$ (**III**), corresponding to a 48% yield of monocarbon carborane based on starting material. Mass measurement: calculated for $^{12}C_{15}{}^1H_{45}{}^{11}B_{10}{}^{14}N^{32}S^{28}Si_2$, 437.3742; found, 437.3762. Mp: 247−8 °C.

(C) In a 100 mL round-bottom flask equipped with a stirring bar and a high-vacuum stopcock were placed 0.73 g (2.16 mmol) of $5\text{-}(S(CH_3)_2)6\text{-}[((CH_3)_3Si)_2C{=}CH]B_{10}H_{11}$, 0.25 mL of *n*-butyl isocyanide, and 50 mL of a 60:40 benzene/hexane solution. The contents of the flask were degassed three times, and the reaction mixture was heated to reflux for a period of 12 h. After the solution was cooled to room temperature a yellow precipitate containing $2\text{-}(S(CH_3)_2)\text{-}(7\text{-}C_4H_9NH)\text{-}11\text{-}[((CH_3)_3Si)_2C{=}CH]\text{-}7\text{-}CB_{10}H_{10}$ (**IV**) was observed and was removed by filtration through a medium-porosity frit. The filtrate was reduced *in vacuo* to 10 mL, resulting in the formation of additional $2\text{-}(S(CH_3)_2)\text{-}7\text{-}(C_4H_9NH)\text{-}11\text{-}[((CH_3)_3Si)_2C{=}CH]\text{-}7\text{-}CB_{10}H_{10}$ precipitate, which was also removed by filtration. The combined weight of crude $2\text{-}(S(CH_3)_2)\text{-}7\text{-}(C_4H_9NH)\text{-}11\text{-}[((CH_3)_3Si)_2C{=}CH]\text{-}7\text{-}CB_{10}H_{10}$ (**IV**) obtained was 0.59 g (67.3% based on starting material). Recrystallization from methanol/water produced 0.35 g (40.2%) of the off-white carborane $2\text{-}(S(CH_3)_2)\text{-}7\text{-}(C_4H_9NH)\text{-}11\text{-}[((CH_3)_3Si)_2C{=}CH]\text{-}7\text{-}CB_{10}H_{10}$, mp 251−3 °C. The ^{11}B NMR spectrum of **IV** was similar to those obtained for **II** and **III**. On the basis of on this information, it seems reasonable that **IV** has a similar structure.

Reaction of $5\text{-}(S(CH_3)_2)\text{-}6\text{-}[(CH_3)_3Si(C_4H_9)C{=}CH]B_{10}H_{11}$ with *n*-Butyl Isocyanide. In a 100 mL round-bottom flask, equipped with a high-vacuum stopcock, were placed 0.50 g (1.49 mmol) of $5\text{-}(S(CH_3)_2)6\text{-}[(CH_3)_3Si(C_4H_9)C{=}CH]B_{10}H_{11}$ and 0.20 mL of *n*-butyl isocyanide. The flask was then attached to a high-vacuum line, and its contents were degassed. Benzene (25 mL) was directly condensed onto the reactants, and the resulting solution was stirred at reflux for 12 h. Noncondensables were removed periodically from the reaction mixture. The benzene was then stripped off, by using the high-vacuum line, and the resulting solid was digested in methanol (20 mL) for 6 h. The methanol solution was cooled at −5 °C in a water−ice−rock salt bath until a slightly yellow precipitate was formed. The precipitate was then filtered off and dried overnight in a desiccator.

The identity of the compound was established as $2\text{-}(S(CH_3)_2)\text{-}7\text{-}((CH_3)_3CNH)\text{-}11\text{-}[(CH_3)_3Si(C_4H_9)C{=}CH]B_{10}H_{10}$ (**V**) [yellowish solid; 0.36 g (0.91 mmol), 61% yield; mp 262−3 °C]. On the basis of the similarity of the ^{11}B NMR spectrum of **V** to those of the other compounds discussed, the structure of **V** is assumed to be similar to those of **II**−**IV**.

Results and Discussion

The reaction of decaborane(14) with 1-(trimethylsilyl)-1-hexyne in the presence of dimethyl sulfide resulted in the formation of $5\text{-}(S(CH_3)_2)\text{-}6\text{-}[(CH_3)Si(C_4H_9)C{=}CH]B_{10}H_{11}$. The formation of this compound is not surprising, since under similar circumstances, reaction of $B_{10}H_{14}$ with $(CH_3)_3SiC{\equiv}CSi(CH_3)_3$

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[11] When loss of molecular hydrogen is taken into consideration, the analysis is as follows: C, 39.48; H, 10.24.

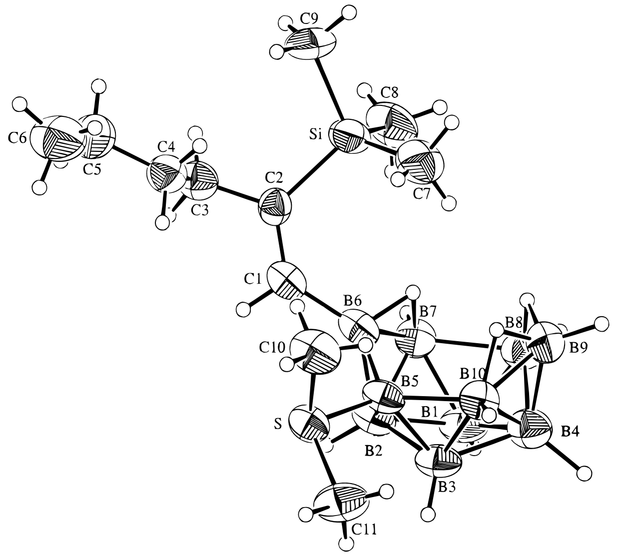

Figure 1. ORTEP Drawing of the molecular structure of 5-($S(CH_3)_2$)-6-[$(CH_3)_3Si(C_4H_9)C{=}CH$]$B_{10}H_{11}$ (**I**).

and $CH_3C{\equiv}CSi(CH_3)_3$ in the presence of dimethyl sulfide also results in the formation of compounds analogous to **I**.

$$B_{10}H_{12}(S(CH_3)_2)_2 + (CH_3)_3SiC{\equiv}CR \rightarrow \text{5-}(S(CH_3)_2)\text{-6-}[(CH_3)_3Si(R)C{=}CH]B_{10}H_{11} \quad (5)$$

$$R = (CH_3)_3Si,\ CH_3,\ C_4H_9$$

The reaction of isocyanides with boron hydrides has been previously studied by Todd and coworkers.[1−6] It was found to yield the first monocarbon carborane derived from decaborane(14). Among the analogous systems which have also been found to react with isocyanides in a similar fashion are SB_9H_{11},[2] SeB_9H_{11},[2] and 5-$S(CH_3)_2$-9-C_6H_{11}-$B_{10}H_{11}$.[4] All of these compounds have a $B_{10}H_{14}$ or, like either **A** or **I**, a $B_{10}H_{13}^-$ type structure.

Synthesis and Structural Studies of Alkenyldecaboranes. The identity of **I** was established by ^{11}B and ^1H NMR spectra, as well as single-crystal X-ray diffraction techniques. Mass spectrometric measurements were also consistent with the structure of **I**. In addition, the single-crystal X-ray structure for 5-$S(CH_3)_2$-6-[$((CH_3)_3Si)_2C{=}CH$]$B_{10}H_{11}$ (**A**) is being reported. The synthesis of this compound was first reported by Sneddon and co-workers,[8] although the data presented suggested that indeed the structure of this compound was very similar to that of 5-$S(CH_3)_2$-6-[$(CH_3)_3Si(CH_3)C{=}CH$]$B_{10}H_{11}$, which was reported in a previous Communication.[8] No structural confirmation was presented. The discussion regarding the characterization of this compound has been previously reported.[8] Figures 1 and 2 show ORTEP drawings for compounds **I** and **A**.

The ^{11}B NMR spectrum of **I** consisted of eight resonances in the ratio 1:2:1:1:1:2:1, with singlets at 29.84 and −6.76 ppm, which corresponds to substitution at two boron atoms by $(CH_3)_3Si(C_4H_9)C{=}CH$ and $S(CH_3)_2$ groups. The ^{11}B NMR spectrum of **I** is indeed very similar to those reported for 5-$S(CH_3)_2$-6-[$(CH_3)_3Si(CH_3)C{=}CH$]$B_{10}H_{11}$ and 5-$S(CH_3)_2$-6-[$((CH_3)_3Si)_2C{=}CH$]$B_{10}H_{11}$.[8] The ^1H NMR spectrum showed resonances characteristic of $(CH_3)_3Si$, C_4H_9, $S(CH_3)_2$, and $C{=}CH$ groups, as well as the presence of bridge hydrogens in the borane molecule. The single-crystal X-ray diffraction structure obtained for **I** showed intramolecular distances very similar to those reported for 5-($S(CH_3)_2$)-9-C_6H_{11}-$B_{10}H_{11}$[12] and 5-($S(CH_3)_2$)-6-[$(CH_3)_3Si(CH_3)C{=}CH$]$B_{10}H_{11}$.[8]

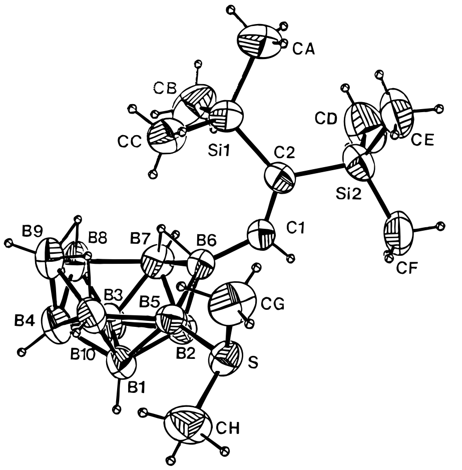

Figure 2. ORTEP drawing of the molecular structure of 5-($S(CH_3)_2$)-6-[$((CH_3)_3Si)_2C{=}CH$]$B_{10}H_{11}$ (**A**).

The structures of these compounds are very similar to those found for the isoelectronic $B_{10}H_{13}^-$ anion.[13] In $B_{10}H_{13}^-$, the B5−B6 distance is rather short, 1.65 Å,[13] whereas in $B_{10}H_{14}$ the same bond has an intramolecular distance of 1.790(3) Å.[14] This shortening could be due to the increased two-center, two-electron character of this bond. In compound **I** this distance was found to be 1.673(13) Å, in agreement with the reported distances for 5-($S(CH_3)_2$)9-C_6H_{11}-$B_{10}H_{11}$ (1.64(1) Å)[12] and 5-($S(CH_3)_2$)6-[$(CH_3)_3Si(CH_3)C{=}CH$]$B_{10}H_{11}$ (1.657(1) Å).[8] In contrast, the boron−boron distance between B7 and B8 in this compound is rather long (2.028(15) Å).

A similar situation arises for 5-($S(CH_3)_2$)-6-[$((CH_3)_3Si)_2C{=}CH$]-$B_{10}H_{11}$. The B5−B6 intermolecular distance was found to be 1.661(7) Å, while the B7−B8 distance was determined to be 2.000(8) Å. The other boron−boron, boron−carbon, and carbon−carbon distances in both compounds fall within expected ranges for molecules of this type. The presence of long boron−boron and short boron−boron bonds in both **I** and **A** should activate these molecules for reaction toward nucleophiles, such as isocyanides.

The exopolyhedral organosilyl group of **I** is bound to the 6-position of the borane, and this group is of the type RR′C=CH, suggesting that, following hydroboration of silylated acetylene, this fragment rearranged via a trimethylsilyl migration from the α−carbon to the β−carbon of the olefinic unit. This type of migration has been observed previously with other organoboron compounds.[8,15] As observed with bis(trimethylsilyl)acetylene and (trimethylsilyl)propyne, the reaction of $B_{10}H_{12}(S(CH_3)_2)_2$ with 1-(trimethylsilyl)-1-hexyne involves initial hydroboration of the acetylene, followed by trimethylsilyl migration, dissociation of one dimethyl sulfide molecule, and migration of the second dimethyl sulfide molecule from an apical position in the initial borane to a basal position in the final product. The trimethylsilyl migration in this compound could be explained in terms of steric repulsions between the silyl group and the decaborane cage. By migrating, the

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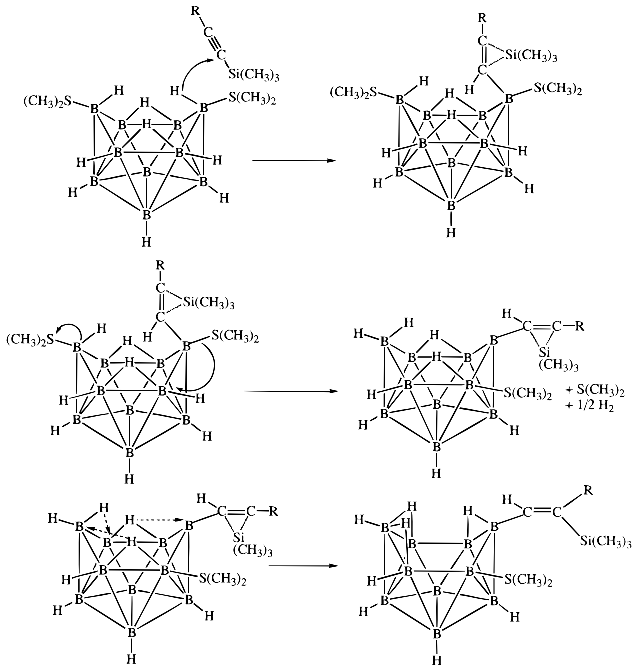

Figure 3. Proposed reaction scheme leading to the formation of alkenyldecaboranes.

trimethylsilyl group increases its distance from the decaborane cage, hence minimizing possible steric interactions with the cage. The proposed reaction scheme for the formation of **I** is shown in Figure 3. Initial attack on the alkyne results in the formation of an intermediate having both dimethyl sulfide groups still bonded to the boron cage, while the trimethylsilyl group starts its migration from the α-carbon to the *β*-carbon. In the second step, the dimethyl sulfide bonded to the boron which has the alkenyl group migrates while hydrogen and dimethyl sulfide are liberated from the intermediate; finally migration of hydrogens results in the formation of the observed product. This reaction scheme is important, since it does not lead to the formation of monocarbon carboranes, which is the case when bis(trimethylsilyl)acetylene is used. Clearly, the formation of the alkenyldecaboranes must follow a different reaction pathway.

The mass spectrum of compound **I** shows the expected fragmentation pattern. For **I**, the cutoff at *m/e* 338 corresponds to the assigned empirical formula ${}^{12}C_{11}{}^{1}H_{36}{}^{11}B_{10}{}^{32}S^{28}Si^{+}$. In addition, the fragments found at *m/e* 276, 219, and 146 are consistent with the stepwise loss of $S(CH_3)_2$, C_4H_9, and $(CH_3)_3$-Si groups, respectively.

Synthesis and Characterization of Alkenyl Monocarbon Carboranes. The reactions of 5-($S(CH_3)_2$)-6-[($(CH_3)_3Si)_2C{=}CH$]-$B_{10}H_{11}$ and 5-($S(CH_3)_2$)-6-[$(CH_3)Si(C_4H_9)$-$C{=}CH$]$B_{10}H_{11}$ with isocyanides were found to produce monocarbon carboranes via insertion of the carbon atom of the isocyanide unit, accompanied by the protonation of the nitrogen atom. The product geometry is based on an icosahedron missing one vertex, yielding an 11-vertex *nido* monocarbon carborane, the basic structure of which is shown in Figure 4.

The ${}^{11}B$ NMR spectra of these compounds are consistent with the proposed structures. For the related compound 3-($S(CH_3)_2$)-7-($(CH_3)_3CNH$)-11-(C_6H_{11})$B_{10}H_{10}$, a single-crystal X-ray structure has been reported.[4] The ${}^{11}B$ NMR spectra for these monocarbon carboranes show the lack of mirror symmetry imposed on the molecule due to the presence of three exopolyhedral groups. All the compounds show clearly the two singlets, which is consistent with two boron atoms containing organic groups directly attached to them, rather than a hydrogen. For compound **II**, ${}^{11}B$ NMR spectrum shows seven resonances with relative areas of 3:2:1:1:1:1:1; for compound **III**, the ${}^{11}B$ NMR spectrum consists of eight resonances with relative areas of 3:1:1:1:1:1:1:1; for compound **IV**, the ${}^{11}B$ NMR spectrum is somewhat simplified, with relative areas of 3:2:2:1:1:1. Finally, for compound **V**, the ${}^{11}B$ NMR spectrum shows resonances of relative intensities 1:2:1:1:1:1:1:1:1. Coincidental overlap of signals will tend to simplify the observed ${}^{11}B$ NMR. This is clearly the case for compounds **II**−**IV**. The ${}^{1}H$ NMR spectra of these compounds show lack of mirror symmetry. With the exception of the spectrum of **V**, they showed split peaks for the dimethyl sulfide groups attached to the boron cage. Likewise, for **II**−**V**, there are two distinct peaks for each of the trimethylsilyl groups, indicating the lack of a mirror plane that will make these groups magnetically equivalent during the NMR experiment. ${}^{1}H$ NMR data for these compounds are summarized in Table 3.

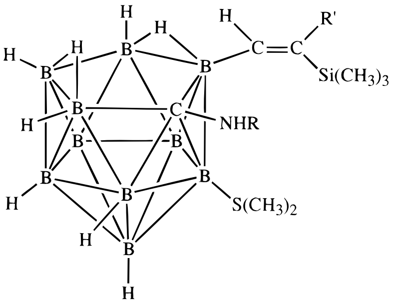

Figure 4. Cage skeletal structure of 2-($S(CH_3)_2$)-7-RNH-11-[$(CH_3)_3$-$Si(R')C{=}CH$]$B_{10}H_{10}$ (**II**, R = $C_6H_5CH_2$, R′ = $(CH_3)_3Si$; **III**, R = $(CH_3)_3C$, R′ = $(CH_3)_3Si$; **IV**, R = C_4H_9, R′ = $(CH_3)_3Si$; **V**, R = C_4H_9, R′ = C_4H_9).

The presence of N−H stretch bands in the IR spectra of these compounds suggested that their structures might be analogous to that of the previously reported carborane 3-$S(CH_3)_2$-7-(*t*-C_4H_9-NH)-8-(C_6H_{11})-7-$CB_{10}H_{10}$, which was reported by Todd and coworkers.[4] The structure of this monocarbon carborane was confirmed by single-crystal X-ray diffraction. It is important to point out that insertion of the isocyanide carbon into the decaborane frame of 5-($S(CH_3)_2$)-9-C_6H_{11}-$B_{10}H_{11}$ did not disturb the relative positions of the of the dimethyl sulfide and cyclohexyl groups. Another distinguishing feature of this compound is that, instead of reduction of the N≡C bond to an NH_2R group, the reduction was to an amino group (NHR). This behavior is clearly different from that of $B_{10}H_{14}$, which, when reacted with isocyanides, results in the formation of monocarbon carboranes having NH_2R groups.

The normal type of reaction that takes place between decaborane(14) and alkynes results in the formation of substituted *o*-carboranes.[16] Clearly, when trimethylsilyl groups are part of the alkyne, this is not the case. Sneddon and coworkers confirmed the fact that when bis(trimethylsilyl)acetylene reacts with decaborane(14), two products are formed, a monocarbon carborane, 9-$S(CH_3)_2$-7-[($(CH_3)_3Si)_2CH$]-7-$CB_{10}H_{11}$, and an alkenyldecaborane similar to **I**. When (trimethylsilyl)propyne

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(16) (a) Kutal, C. R.; Owen, D. A.; Todd, L. J. *Inorg. Synth.* **1968**, *11*, 19−23. (b) Heying, T. L.; Ager, J. W., Jr.; Clark, S. L.; Mangold, D. L.; Goldstein, H. L.; Hillman, M.; Pollack, R. J.; Szymanski, J. W. *Inorg. Chem.* **1963**, *2*, 1089−1092. (c) Fein, M. M.; Grafstein, D.; Paustian, J. E.; Bobinski, J.; Liechstein, B. M.; Mayes, N.; Schwartz, N. N.; Cohen, M. S. *Inorg. Chem.* **1963**, *2*, 1115−1119. (d) Zakharkin, L. I.; Stanko, V. I.; Brattsev, V. A.; Chapovskii, Yu. A.; Klimova, A. I.; Oxlobystin, O. Yu.; Ponomarenko, A. A. *Dokl. Akad. Nauk SSSR* **1964**, *155*, 1119−1112. (e) Dupont, J. A.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1964**, *86*, 1643. (f) Paxson, T. E.; Callahan, K. P.; Hawthorne, M. F. *Inorg. Chem.* **1973**, *12*, 708−709. (g) Fein, M. M.; Bobinski, J.; Mayes, N.; Schwartz, N.; Cohen, M. S. *Inorg. Chem.* **1963**, *2*, 1111−1115.

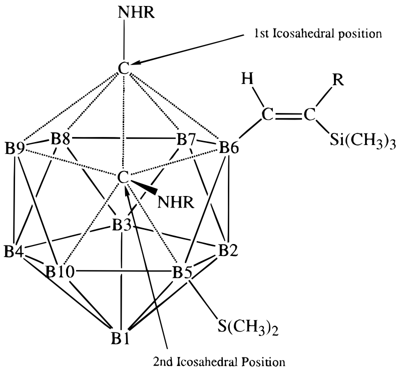

Figure 5. Possible icosahedral positions for the incorporation of the carbon atom of the isocyanide into a 10-vertex polyhedral alkenylborane.

is the alkyne used, only the alkenyldecaborane product is obtained. It was found that, for the case of bis(trimethylsilyl)-acetylene, conversion of the alkenyldecaborane into the monocarbon carborane was not possible under any circumstances.[8] This result suggests that these alkenyldecaboranes might be related to the "unreactive" isomer of $B_{10}H_{12}(S(CH_3)_2)$, which has been found not to undergo reactions with acetylenes to produce carboranes.[17]

A previous study conducted by Todd and coworkers has shown that the cyclohexyl-substituted borane derivative 5-$(S(CH_3)_2)$9-C_6H_{11}-$B_{10}H_{11}$, which might be related to the "unreactive" isomer of $B_{10}H_{12}(S(CH_3)_2)$, undergoes reaction with *tert*-butyl isocyanide, resulting in carbon insertion into the borane framework and reduction of the N≡C triple bond.[4] Thus, the compound is activated for attack by a nucleophile, such as an isocyanide.

Huckel calculations (giving Mulliken atomic charges) performed on 5-$(S(CH_3)_2)$-9-C_6H_{11}-$B_{10}H_{11}$ indicated that the boron carrying the cyclohexyl group had the higher relative positive atomic charge in the cluster.[12] This observation is in agreement with the results obtained by Tolpin and coworkers, who showed that pyridine attacked at the B9 position of the borane cluster.[12] It is significant to note that, even the presence of a bulky substituent, such as cyclohexyl, did not prevent attack by pyridine at this position.

Undoubtedly, a similar type of reaction sequence can occur upon reaction of isocyanides with the alkenylboranes reported in this communication. The attack will probably be initiated at B6, followed by formation of carbon−boron bonding interactions, resulting in the incorporation of the isocyanide carbon into the borane framework.

Todd observed that the yields obtained from the reaction of 5-$(S(CH_3)_2)$-9-C_6H_{11}-$B_{10}H_{11}$ with *tert*-butyl isocyanide were moderate and had argued that this could a consequence of the existence of a second isomer that cannot be isolated under the reaction conditions.[4] We have observed the same pattern in the reactivity of these alkenylboranes with isocyanides. A possible explanation to this observation is the fact that these alkenylboranes do not have mirror symmetry, as demonstrated by the ^{11}B NMR data. This lack of mirror symmetry will lead to the creation of two nonequivalent icosahedral positions, as shown in Figure 5, in which the carbon atom could be incorporated into the borane framework. The first configuration would be formed by B5, B6, B9, B10, and the incoming carbon atom. Attack on that side of the molecule will result in the formation of the observed product. The second possible configuration will include B6, B7, B8, B9, and the incoming carbon atom. If the attack occurs on that side of the molecule, the resulting product will have a carbon atom on the second possible icosahedral position. This will force the dimethyl sulfide associated with the cage to be placed on the open face of the monocarbon carborane and not in the position in which is found, namely, the lower belt of boron atoms in the structure. A plausible reaction sequence illustrating the products obtained on the basis of the point of attack of the isocyanide is shown in Figure 6.

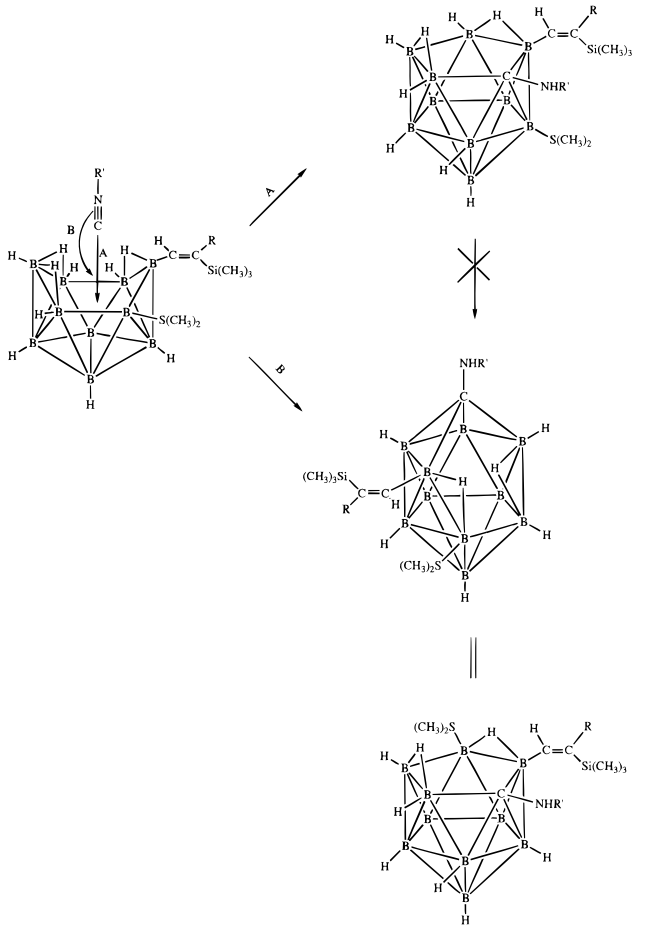

Figure 6. Possible reaction sequence leading to the formation of 2-$(S(CH_3)_2)$-7-(RNH)-11-$[(CH_3)_3Si(R)C{=}CH]B_{10}H_{10}$ (**II**, R = C_4H_9, R′ = C_4H_9; **III**, R = C_4H_9, R′ = $(CH_3)_3Si$; **IV**, R = $(CH_3)_3C$, R′ = $(CH_3)_3Si$; **V**, R = $CH_2C_6H_5$, R′ = $(CH_3)_3Si$) and the second unobserved isomer of the reaction.

The fact that the incorporation of the isocyanide molecule occurred without disturbing the relative positions of the substituents already present on the parent alkenylboranes supports the theory that attack of the isocyanide occurred on the side of the molecule having the highest electrophilic character, which is the open face formed by B5, B6, B9, and B10 atoms. It is interesting to note that although it should be expected that this side of the molecule is more sterically crowded, due to the presence of the substituent groups on the borane, electronic factors seem to be more important, since the second predicted product is not observed at all. This reactivity is in agreement with the previously reported reaction of *tert*-butyl isocyanide with 5-$(S(CH_3)_2)$9-C_6H_{11}-$B_{10}H_{11}$. In that molecule the isocyanide carbon attacked selectively at B9, the boron with the most electrophilic character on the cage, even though it had a bulky cyclohexyl group already attached at that position.[4] Another example supporting the idea that electronic factors seem to be of more importance than steric factors is that pyridine

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reacts with 5-(S(CH$_3$)$_2$)-9-C$_6$H$_{11}$-B$_{10}$H$_{11}$ resulting in the formation of 6-(C$_6$H$_{11}$)-6,9-(py)$_2$B$_{10}$H$_{11}$ in good yield.[12]

In summary, the alkenyldecaboranes 5-(S(CH$_3$)$_2$)6-[(CH$_3$)$_3$-Si(C$_4$H$_9$)C=CH]B$_{10}$H$_{11}$ and 5-(S(CH$_3$)$_2$)6-[((CH$_3$)$_3$Si)$_2$C=CH]-B$_{10}$H$_{11}$ have been shown to produce monocarbon carboranes in moderate yields. The presence of a pendant alkenyl group in these monocarbon carboranes presents an interesting possibility in expanding the chemistry of these compounds to involve the attached organic groups. It is our intention to continue research dealing with these compounds by taking advantage of this fact.

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Supporting Information Available: Tables of bond angles, anisotropic temperature factors, and hydrogen atom coordinates for compounds **I** and **A** (10 pages). Ordering information is given on any current masthead page.

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