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Transition-Metal-Promoted Reactions of Boron Hydrides. 2.[1] Synthesis and Thermolysis Reactions of Alkenylpentaboranes. A New Synthesis of Monocarbon Carboranes

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Although alkenylpentaboranes have been proposed to be initial intermediates in thermally induced carborane syntheses, no such compounds have previously been isolated. The results described herein, however, demonstrate that the reactions of pentaborane(9) under mild conditions with either acetylene, propyne, or 2-butyne, in the presence of catalytic amounts of $Ir(CO)Cl[P(C_6H_5)_3]_2$, result in the synthesis of the corresponding alkenylpentaboranes, 2-($CHR{=}CR'$)B_5H_8 (R, R′ = H or CH_3). The reaction corresponds to a BH addition to the alkyne in a cis fashion with the reaction of propyne occurring in a predominately anti-Markownikoff manner. Similarly, it was found that complexes of the general formula $(RC_2R')Co_2(CO)_6$ (R, R′ = H or CH_3) also activate acetylenes for BH addition with pentaborane(9), but, in contrast to the results obtained with $Ir(CO)Cl[P(C_6H_5)_3]_2$, internal alkynes were found to be more reactive than terminal and the reaction with propyne gave predominately Markownikoff addition. The thermolysis reactions of these new alkenylpentaboranes were investigated, and it was found that quick passage of the compounds through a heated tube (355 °C) in vacuo results in high yields of carborane products which are predominately alkyl derivatives of 2-CB_5H_9. Thus, thermolysis of 2-(*cis*-2-but-2-enyl)-B_5H_8 yields mainly 2-CH_3-3-C_2H_5-2-CB_5H_7 (36%) and 2-CH_3-4-C_2H_5-2-CB_5H_7 (39%), 2-(2-propenyl)-B_5H_8 gives mainly 2-CH_3-3-CH_3-2-CB_5H_7 (28%) and 2-CH_3-4-CH_3-2-CB_5H_7 (18%), 2-(1-*trans*-1-propenyl)-B_5H_8 gives mainly 3-C_2H_5-2-CB_5H_8 (26%) and 4-C_2H_5-2-CB_5H_8 (16%), and 2-(ethenyl)-B_5H_8 gives predominantly 2-CH_3-2-CB_5H_8 (15%), 3-CH_3-2-CB_5H_8 (23%), and 4-CH_3-2-CB_5H_8 (13%). The products observed in these thermolysis reactions are consistent with the reaction sequence originally proposed for the thermal reaction of pentaborane(9) and alkynes, and an appropriate mechanism is discussed.

Introduction

The development and economic exploitation of small carborane chemistry has been hampered by the lack of high-yield, selective synthetic routes for these compounds. Although an important, good yield procedure has recently been demonstrated[3,4b] for the selective preparation of the C-substituted derivatives of 2,3-$C_2B_4H_8$ under mild conditions, the remaining synthetic routes employed for small carboranes have generally involved the reaction of a borane and alkyne using relatively severe conditions such as, heat,[4] electric discharge,[5] or ultraviolet light[6] and have resulted in considerable cage fragmentation. The products of these energy reactions, therefore, usually include several carborane cage systems and substantial quantities of organic side products, necessitating the use of tedious separation procedures.

The actual steps involved in the reaction of a borane with an acetylene to produce carboranes are still not well-defined; however, Williams has previously proposed[4c,7] that the initial step in thermally induced reactions of pentaborane(9) may involve hydroboration of the alkyne by a BH group of the boron hydride to form alkenylborane intermediates. Such alkenylpentaborane compounds have not heretofore been isolated, suggesting that if formed they can readily convert to carborane products under the conditions normally employed. If this reaction sequence is correct, and the hydroboration reaction is indeed the rate-determining step in thermally induced carborane syntheses, then it would be expected that the activation of the acetylene and borane for addition would allow the use of lower temperature reactions and thereby result in higher yields and greater selectivity of carborane products. Since it is now well established that similar addition reactions of acetylenes such as hydrogenations[8a] and hydrosilations[8b] are promoted by various transition-metal catalysts, it is reasonable to expect that the addition of a BH group to an acetylene could also be induced under mild conditions by similar transition-metal reagents, yet surprisingly this approach has been previously unexplored. The work described herein deals with the effect of two different types of transition-metal catalysts, chlorocarbonylbis(triphenylphosphine)iridium(I) and μ-acetylene-dicobalt hexacarbonyl complexes, on the reaction of pentaborane(9) with various acetylenes. The study was undertaken in order to determine the utility of transition-metal reagents for the development of new mild synthetic routes to small carboranes, as well as to gain further insight into the basic steps involved in carborane syntheses.

Experimental Section

Materials. Dicobalt octacarbonyl and chlorocarbonylbis(triphenylphosphine)iridium(I) were purchased from Strem Chemicals and used as received. The acetylene complexes, $(RC_2R')Co_2(CO)_6$, were either synthesized[9] in situ or prepared by the direct reaction of $Co_2(CO)_8$ with the appropriate alkyne at room temperature and purified by column chromatography. The 2-butyne and propyne were purchased from the Farchan Division of the Story Chemical Corp. and vacuum fractionated through a −78 °C trap before use. Acetylene was purchased from Matheson Gas Products and purified by vacuum fractionation three times through −110 and −196 °C traps. Pentaborane(9) was obtained from laboratory stock. All chromatographic solvents were reagent grade and dried over molecular sieves (4A).

Physical Measurements and Chromatography. Boron-11 NMR spectra at 32.1 MHz and proton NMR spectra at 100 MHz were recorded on a JEOL PS-100 Fourier transform spectrometer. Boron-11 or proton spin decoupling was accomplished by irradiation at the proper frequency with a broad-band noise decoupler. The 115.5-MHz boron-11 spectra were obtained on a Bruker WH-360 Fourier transform spectrometer located in the Mid-Atlantic Regional NMR Facility. Boron-11 chemical shifts were referenced to BF_3·

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Table I[a]

acetylene	catalyst	% conversion[b] (time)	products	rel[c,d] yield (%)
acetylene	$Ir(CO)Cl(PPh_3)_2$	5 (4 h)	2-(ethenyl)-B_5H_8 (I)	100
propyne	$Ir(CO)Cl(PPh_3)_2$	8 (4 h)	2-(2-propenyl)-B_5H_8 (IIa)	5
			2-(*trans*-1-propenyl)-B_5H_8 (IIb)	95
2-butyne	$Ir(CO)Cl(PPh_3)_2$	<1 (4 h)	2-(*cis*-2-but-2-enyl)-B_5H_8 (III)	100
acetylene	$(RC_2R')Co_2(CO)_6$	(1 h)	. . .	0
propyne	$(RC_2R')Co_2(CO)_6$	7 (15 min)	IIa	75
			IIb	25
2-butyne	$(RC_2R')Co_2(CO)_6$	27 (1 h)	III	100

[a] See text for exact reaction conditions. [b] Based on B_5H_9. [c] Determined from peak areas in GLC (uncorrected for response factor differences) which were determined by triangulation. [d] Yields based on consumed B_5H_9 were usually near 75%.

Table II. ^{11}B NMR Data

compd[a]	δ[b] (*J* (Hz) assignt)[c]	rel areas
	Alkenyl Boranes	
I[d]	−0.7 (s, B2), −13.8 (147, B3, 5), −17.9 (144, B4), −50.9 (176, B1)	1:2:1:1
IIa[d]	0.4 (s, B2), −15.2 (153, B3, 5), −18.4 (138, B4), −51.1 (173, B1)	1:2:1:1
IIb[d]	0.0 (s, B2), −14.2 (156, B3, 5), −18.7 (153, B4), −51.2 (176, B1)	1:2:1:1
III[d]	3.2 (s, B2), −14.4 (160, B3, 5), −18.6 (167, B4), −50.9 (174, B1)	1:2:1:1
	Alkyl Derivatives of 2-CB_5H_9	
V[d]	24.0 (s, B3), 15.2 (156, B6), −6.8 (156, B4, 5), −48.4 (156, B1)	1:1:2:1
VII[d]	13.7 (141, B3, 6), 11.7 (s, B4), −4.9 (172, B5), −48.4 (156, B1)	2:1:1:1
IX[d]	14.2 (171, B3, 6), 9.0 (s, B4), −4.7 (160, B5), −47.8 (162, B1)	2:1:1:1
X[e]	28.4 (s, B3), 16.6 (158, B6), −5.0 (140, B4 or 5), −6.2 (153, B4 or 5), −49.9 (169, B1)	1:1:1:1:1
XI[d]	14.9 (160, B3, 6), 12.2 (s, B4), −4.1 (149, B5), −51.2 (167, B1)	2:1:1:1

[a] All spectra obtained in C_6D_6. [b] Chemical shifts are relative to external $BF_3{\cdot}O(C_2H_5)_2$ with a negative sign indicating an upfield shift. [c] s = singlet. [d] 32.1 MHz. [e] 115.5 MHz.

$O(C_2H_5)_2$ = 0.0 ppm with a negative sign indicating an upfield shift. All proton chemical shifts were measured relative to internal residual solvent from the lock solvent, (99.5% C_6D_6) and then referenced to Me_4Si = 0.00 ppm with a positive value indicating a downfield shift. High- and low-resolution mass spectra were obtained on a Perkin-Elmer Hitachi RMH-2 mass spectrometer interfaced to a Kratos DS50-S data system. Infrared spectra were recorded on Perkin-Elmer 521 grating infrared spectrophotometer. Elemental analyses were performed by Schwarzkopf. Thin-layer chromatography (TLC) was conducted on 0.5-mm (20 × 20 cm) silica gel F-254 plates (Merck), and analytical thin-layer chromatography was conducted on silica gel, 0.05–0.2 (70–270 mesh). Gas liquid chromatography (GLC) was conducted on a Varian Model 920 gas chromatograph equipped with a 20 ft. × 0.25 in. 6% tricresyl phosphate (TCP) on chromosorb P (60–80 mesh) column.

Reactions with Chlorocarbonylbis(triphenylphosphine)iridium(I). General Procedure. All reactions were run in a cylindrical, Pyrex glass tube (5-mL volume) equipped with a greaseless Teflon stopcock. For each reaction, the tube was charged with 0.01 mmol of $Ir(CO)Cl[P(C_6H_5)_3]_2$ and evacuated on a high-vacuum line. Exactly 3.0 mmol each of alkyne and borane were then condensed into the tube. This mixture was first warmed to room temperature and then heated in an oven at 75 °C for 4 h. The reaction of pentaborane(9) with three separate acetylenes (acetylene, propyne, 2-butyne) was examined. The results of these reactions are summarized in Table I and described below.

B_5H_9 and Acetylene. Following the reaction of B_5H_9 with acetylene in the presence of $Ir(CO)Cl[P(C_6H_5)_3]_2$, the tube was opened to the vacuum line and the volatile material was fractionated through −41, −78, −110, and −196 °C traps. Unreacted B_5H_9 and acetylene were found in the −110 and −196 °C traps, respectively, while relatively pure 2-(ethenyl)-B_5H_8 (I) was retained in the −78 °C trap. This alkenylborane was further purified by GLC on the TCP column (80 °C, R_v = 4.3, (R_v(B_5H_9) = 1.0)). Exact mass for $^{12}C_2{}^{11}B_5{}^1H_{11}$: calcd, 90.1328; found, 90.1325. No $Ir(CO)Cl[P(C_6H_5)_3]_2$ was detected (analytical TLC) in the reaction tube following the experiment; however, red-purple solids remained which could not be readily dissolved.

B_5H_9 and Propyne. The volatile products from the reaction of B_5H_9 with propyne were subjected to vacuum line fractionation which yielded an isomeric mixture of propenylpentaboranes retained in the −78 °C trap. This mixture was then purified by GLC on the TCP column (80 °C) to yield 2-(2-propenyl)-B_5H_8 (IIa) (R_v = 8.5) and 2-(*trans*-1-propenyl)-B_5H_8 (IIb) (R_v = 11.9). Exact mass for $^{12}C_3{}^1H_{13}{}^{11}B_5$: calcd, 104.1485; found, IIa 104.1488, IIb 104.1481. Yellow, air-sensitive solids remained in the reaction tube which did not contain any detectable amounts of $Ir(CO)Cl[P(C_6H_5)_3]_2$. These solids were contaminated with small quantities of a low volatile liquid, and their characterization was not investigated. Addition of new pentaborane(9) and propyne to these solids and heating for another 4 h at 75 °C produced small amounts of propenyl-B_5H_8 (2.0% conversion).

Reactions of pentaborane(9) and propyne in the presence of only triphenylphosphine were also investigated but were found not to yield any alkenylborane products.

B_5H_9 and Butyne. The reaction of B_5H_9 with 2-butyne was examined, and the volatile products were fractionated through −22, −78, and −196 °C traps. The product, 2-(*cis*-2-but-2-enyl)-B_5H_8 (III), was retained in the −78 °C trap and was further purified on the TCP column (80 °C; R_v = 17.6). Exact mass for $^{12}C_4{}^1H_{15}{}^{11}B_5$: calcd, 118.1643; found, 118.1650. Also formed were significant quantities (~25 mg) of a low volatile liquid which was slowly distilled from the reaction tube and retained in the −22 °C trap. GLC of this liquid on the TCP column at 110 °C gave two major peaks; but, the ^{11}B and ^1H NMR spectra for these compounds indicated that they were organic materials without any boron, and they were not further investigated.

Reactions with μ-Acetylene-dicobalt Hexacarbonyl Complexes. General Procedure. All reactions were run in a cylindrical, Pyrex glass tube (5-mL or 75-mL volume) equipped with a greaseless Teflon stopcock. For each reaction, the appropriate metal reagent was charged into the tube under an inert atmosphere of N_2 and then the tube was attached to a high-vacuum line and evacuated, and measured amounts of alkyne and pentaborane(9) were condensed into the tube. This mixture was warmed to room temperature and then heated in an oven at the appropriate temperature for a specified amount of time. In several cases for reactions involving $(RC_2R')Co_2(CO)_6$ complexes, $Co_2(CO)_8$ served as the starting metal reagent, and, therefore, prior to heating, the above mixtures were warmed to room temperature to allow the formation of the $(RC_2R')Co_2(CO)_6$ complex.[9] When bubbling due to carbon monoxide liberation had terminated, the resultant red solutions were frozen to −196 °C and the CO was removed from the tube before heating. Reactions employing $(RC_2R')Co_2(CO)_6$ complexes, directly, gave results identical with those starting with $Co_2(CO)_8$. The results for representative reactions are summarized in Table I.

B_5H_9 and 2-Butyne. Equimolar amounts (2.5 mmol) of pentaborane(9) and 2-butyne were heated in the 5-mL tube in the presence of 10 mol % $[(CH_3)_2C_2]Co_2(CO)_6$ at 75 °C for 1 h. The reaction tube was then opened to the vacuum line and the volatile material fractionated through −22, −78, and −196 °C traps. Unreacted B_5H_9 and 2-butyne were found in the −196 °C trap (further separated by GLC on a 30% Apiezon on firebrick column at 60 °C) while relatively pure 2-(*cis*-2-but-2-enyl)-B_5H_8 (III) was retained in the −78 °C trap. This latter compound was again further purified on the TCP column.

Table III. ^{1}H NMR Data[a]

compd	δ (assignt)[b]	rel areas
	Alkenylboranes	
I	5.68 (m, CH and CH_2), 2.54 (BH3, 4, 5), 1.13 (BH1), −1.49 (BHB), −2.49 (BHB)	3:3:1:2:2
IIa	5.35 (s, CH_A or CH_B), 5.23 (s, CH_A or CH_B), 2.51 (BH3, 4, 5), 1.86 (s, CH_3), 1.12 (BH1), −1.45 (BHB), −2.48 (BHB)	1:1:3:3:1:2:2
IIb	5.92 (d of q, $J_{H_A-H_B} = 17.5$, $J_{CH_3-H_B} = 5.9$, CH_B), 5.44 (d of q, $J_{H_A-H_B} = 17.5$, $J_{CH_3-H_A} = 1.4$, CH_A), 2.52 (BH3, 4, 5), 1.66 (d, $J_{CH_3-H_B} = 5.9$, CH_3), 1.12 (BH1), −1.45 (BHB), −2.51 (BHB)	1:1:3:3:1:2:2
III	5.67 (q of q, $J_{\beta CH_3-H} = 6.8$, $J_{\alpha CH_3-H} = 1.4$, CH), 2.52 (BH3, 5), 2.32 (BH4), 1.71 (d, $J_{\alpha CH_3-H} = 1.4$), 1.61 (d, $J_{\beta CH_3-H} = 6.8$), 1.03 (BH1), −1.33 (BHB), −2.52 (BHB)	1:2:1:3:3:1:2:2
	Alkyl Derivatives of 2-CB_5H_9	
V	4.46 (BH6), 3.12 (BH4, 5), 2.33 (q, $J = 6.9$, CH_2), 1.25 (t, $J = 6.9$, CH_3), 0.74 (s, CH_3), −0.75 (BH1 and BHB), −1.87 (BHB), −2.44 (BHB)	1:2:2:3:3:2:1:1
VII	4.34 (BH3, 6), 3.25 (BH5), 2.23 (s, CH_3), 1.08 (s, CH_2CH_3), −0.43 (B1H and and BHB), −1.70 (BHB), −2.14 (BHB)	2:1:3:5:2:1:1
IX	4.32 (BH3, 6), 3.24 (B5H), 2.21 (s, CH_3), 0.51 (s, CH_3), −0.42 (B1H and BHB), −1.77 (BHB), −2.14 (BHB)	2:1:3:3:2:1:1
X	5.02 (s, CH), 4.65 (B6H), 3.19 (BH, 4, 5), 1.29 (m, CH_2CH_3), −0.70 (B1H and BHB), −1.91 (BHB), −2.40 (BHB)	1:1:2:5:2:1:1
XI	5.36 (s, CH), 4.52 (BH3, 6), 3.30 (BH5), 1.07 (s, CH_2CH_3), −0.28 (B1H), −0.66 (BHB), −1.75 (BHB), −2.20 (BHB)	1:2:1:5:1:1:1:1

[a] All spectra run in C_6D_6 at 100 MHz. [b] Key: s = singlet, t = triplet, q = quartet, and m = multiplet. All *J* values are given in hertz. Terminal and bridging B–H resonances were observed as broad singlets with the aid of ^{11}B spin decoupling.

Table IV. Infrared Spectra (cm^{-1})

I[a]	3080 m, 3000 w, 2980 w, 2605 vs, 1820 m, br, 1600 w, br, 1400 s, br, 1300 w, 1148 m, 1105 w, 1020 m, 1000 w, 985 w, 945 m, 883 s, 842 w, 700 m, 640 s
IIa[a]	3080 m, 2980 m, 2940 sh, 2900 w, 2610 vs, 1920 m, br, 1630 w, br, 1450 s, 1395 s, 1060 m, 1018 w, 910 s, 890 s, 850 w, 795 w, 638 s
IIb[a]	3010 sh, 2975 w, 2938 m, 2880 w, 2610 vs, 1800 w, br, 1642 m, 1445 m, 1393 s, 1320 w, 1260 w, 1150 w, 1020 m, 975 m, 890 s, 845 w, 790 w, 690 w, 635 s
III[b]	3000 m, sh, 2977 m, 2920 m, 2600 vs, 1810 m, br, 1636 s, 1600 w, br, 1433 vs, 1380 vs, 1325 m, sh, 1230 m, 1135 w, sh, 1112 m, 1085 w, sh, 1032 s, 1010 m, sh, 980 w, 950 w, 895 s, 835 w, 680 m, 640 s, 605 m, 575 w, 498 m
V[a]	2988 s, 2950 sh, 2893 m, 2590 vs, 1920 w, br, 1590 w, br, 1470 s, 1410 m, 1328 s, 1255 w, 1090 m, 1000 m, 923 m, 880 m, 800 w, 695 m, 630 m
VII[a]	2975 s, 2940 s, 2890 m, 2590 sh, 2580 vs, 1900 w, br, 1500 s, 1460 s, 1250 w, 1105 m, 995 m, 940 m, 860 w, 830 vw, 795 w, 695 w
IX[a]	2975 s, 2944 s, 2890 m, 2580 vs, 1905 w, br, 1495 s, 1445 s, 1320 m, 1250 m, 1110 m, 1025 m, 965 m, 915 m, 870 w, 825 w, 790 w
X[a]	2975 s, 2935 m, 2900 m, 2600 vs, 1930 m, br, 1588 w, 1470 s, 1415 s, 1320 m, 1255 m, 1140 sh, 1130 w, 1080 m, 1020 m, 990 sh, w, 935 w, 888 s, 790 w, 710 w, br
XI[a]	2990 s, 2935 m, 2900 m, 2600 vs, 1910 w, br, 1510 s, 1468 s, 1250 m, 1125 sh, 1108 s, 1150 w, 995 m, 945 w, 905 m, 850 m, 800 m, 745 w, 715 w

[a] Gas samples; 10-cm length; 2-cm. o.d.; NaCl windows. [b] Solution $CHCl_3$ vs. $CHCl_3$; NaCl windows.

Much of the $[(CH_3)_2C_2]Co_2(CO)_6$ (~50%) was recovered in the −22 °C trap and identified by its infrared spectrum.

The residue remaining in the reaction tube was extracted with methylene chloride, filtered, and evaporated onto ~10 g of silica gel which was added to a silica gel column and eluted with methylene chloride. This material was then separated by TLC with use of pentane as eluant to give two previously known compounds $Co_4(CO)_{12}$ (R_f 0.49) and $[(CH_3)_2C_2]Co_4(CO)_{10}$ (R_f 0.38). Both complexes were isolated in trace quantities and identified by comparison of their color, R_f values, and infrared spectra with authentic samples. Similar reactions as above run at 100 °C resulted in lower conversions (~15%) to the alkenylborane.

A direct reaction between B_5H_9 and $[(CH_3)_2C_2]Co_2(CO)_6$ was also examined. The 5-mL reaction tube was charged with 325.1 mg (0.95 mmol) of the dicobalt complex and 3.22 mmol of B_5H_9. This solution was heated at 80 °C for 1 h, and upon workup of the volatile material there was obtained 31.0 mg (0.26 mmol, 44% yield based on consumed B_5H_9) of 2-(*cis*-2-but-2-enyl)-B_5H_8, and no $[(CH_3)_2C_2]Co_2(CO)_6$ was recovered. The reaction tube contained 278.6 mg of CH_2Cl_2-soluble dark solids. TLC on an analytical plate (pentane as eluant) indicated that this solid was a mixture of $Co_4(CO)_{12}$ and $[(CH_3)_2C_2]Co_4(CO)_{10}$. Preparative TLC caused significant decomposition of these complexes so that quantitative yields could not be obtained.

B_5H_9 and Propyne. A similar reaction as above was carried out for B_5H_9 and propyne in the presence of 10 mol % $[(CH_3)C_2H]Co_2(CO)_6$. Upon fractionation through −41, −78, and −196 °C traps, a low conversion (2% based on B_5H_9) of propenylpentaboranes was isolated in the −78 °C trap. This material was further separated by GLC on the TCP column to give compounds IIa and IIb. In addition, 36 mg of a liquid were retained in the −41 °C trap. This material exhibited a ^{1}H NMR and mass spectrum which indicated that it was a mixture of trimethylbenzene isomers (36 mg, 0.30 mmol, 36% yield based on propyne). No di- or tetracobalt complexes were recovered from either the −41 °C trap or the reaction tube.

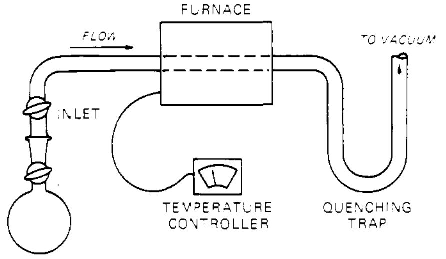

Figure 1. Thermolysis reactor.

So that the trimerization reaction in the above experiment could be suppressed, another reaction was performed where B_5H_9 was used in excess: a 75-mL tube was charged with 1.5 mmol of $[(CH_3)C_2H]Co_2(CO)_6$ (prepared in situ), 20.0 mmol of B_5H_9, and 7.5 mmol of propyne. This solution was heated at 75 °C for 15 min. Fractionation of the volatile material indicated a 7% conversion of pentaborane(9) into propenylpentaborane with only trace amounts of trimethylbenzene being detected.

B_5H_9 and Acetylene. An experiment involving acetylene and $[H_2C_2]Co_2(CO)_6$ with B_5H_9 was performed in a similar manner as above except that benzene was used as a solvent. Upon fractionation, no alkenylpentaborane was detected among the volatile products.

Protonolysis Reactions. Onto 148.4 mg (1.26 mmol) of 2-(*cis*-2-but-2-enyl)-B_5H_8 (III) (produced in the $[(CH_3)_2C_2]Co_2(CO)_6$-catalyzed reaction) was charged 0.5 mL of glacial acetic acid. The mixture was stirred for 1 day at room temperature in vacuo after which time the volatile material was fractionated through −110 and −196 °C traps. The material passing the −110 °C trap proved to be 0.33 mmol (25% conversion) of 2-butene while acetic acid was retained in the 110 °C trap. GLC analysis of the butene on a Durapak Phenyl Isocyanate (on Poracil C; 80–100 mesh; 35 °C) column indicated a cis:trans ratio of 97.2:2.8 [R_v(trans) = 1.00; R_v(cis) = 1.25]. For 2-(*cis*-2-but-2-enyl)-B_5H_8 (III), obtained from the $Ir(CO)Cl[P(C_6H_5)_3]_2$-catalyzed reaction, the similarly derived 2-butene displayed a cis:trans ratio of 98.6:1.4.

Thermal Reactions of Alkenylpentaboranes. General Procedure. The high-temperature, low-pressure pyrolysis of a given alkenyl boron

Table V. Thermal Reactions of Alkenylpentaboranes

borane (t, °C)[a]	% overall conversion	products	% yield	R_v[f]
2-(*cis*-2-butenyl)-B_5H_8 (III) (0)	85	1-C_2H_5-2-CH_3-2-CB_5H_7 (IV)[b]	3[e]	0.28
		2-C_2H_5-3-CH_3-2-CB_5H_7 (V)[b]	4[e]	0.32
		2-CH_3-3-C_2H_5-2-CB_5H_7 (VI)[b]	36[e]	0.39
		2-CH_3-4-C_2H_5-2-CB_5H_7 (VII)[b]	39[e]	0.41
		1,5-$(CH_3)_2$-1,5-$C_2B_3H_3$[d]	3	
2-(2-propenyl)-B_5H_8 (IIa) (−22)	67	2-CH_3-3-CH_3-2-CB_5H_7 (VIII)[b]	28[e]	0.45
		2-CH_3-4-CH_3-2-CB_5H_7 (IX)[b]	18[e]	0.50
		3-C_2H_5-2-CB_5H_8 (X)[b]	4[e]	0.62
		4-C_2H_5-2-CB_5H_8 (XI)[b]	2[e]	0.72
		1-CH_3-1,5-$C_2B_3H_4$[d]	13	
2-(1-*trans*-1-propenyl)-B_5H_8 (IIb) (−22)	72	2-CH_3-3-CH_3-2-CB_5H_7 (VIII)[b]	8[e]	0.34
		2-CH_3-4-CH_3-2-CB_5H_7 (IX)[b]	9[e]	0.39
		3-C_2H_5-2-CB_5H_8 (X)[b]	26[e]	0.47
		4-C_2H_5-2-CB_5H_8 (XI)[b]	16[e]	0.55
		1-CH_3-1,5-$C_2B_3H_4$[d]	13	
2-(ethenyl)-B_5H_8 (I) (−41)	70	1-CH_3-2-CB_5H_8 (XII)[c]	4[e]	0.31
		2-CH_3-2-CB_5H_8 (XIII)[c]	15[e]	0.43
		3-CH_3-2-CB_5H_8 (XIV)[c]	23[e]	0.48
		4-CH_3-2-CB_5H_8 (XV)[c]	13[e]	0.64
		$CH_3CB_5H_6$ (isomeric mixture)[c]	15	

[a] Temperature at which inlet vessel in Figure 4 was maintained. [b] Retained in −78 °C trap during fractionation. [c] Retained in −95 °C trap during fractionation. [d] Retained in −196 °C trap during fractionation. [e] Determined from peak areas (uncorrected for response factor differences) which were determined by triangulation. [f] Relative to starting alkenylpentaborane.

hydride was performed in a quartz reaction apparatus shown schematically in Figure 1. The furnace used was a 115 V, 515 W cylindrical furnace, Electro-Applications Inc., Houston, PA. Since the quartz reaction tube did not fit snugly into the heating cavity of the furnace, glass wool was wound around the tube at the exit parts of the furnace to minimize heat loss.

The inlet vessel was kept at a low enough temperature such that the vapor pressure of the reactant was only 1–5 torr. This allowed the reactant to be bled very slowly into the high-temperature section (355 °C) while pumping with a high-vacuum system at the opposite end of the apparatus. The pressure recorded at the exit end of the quenching trap (−196 °C) was usually about 0.1 torr which was largely due to the production of noncondensable gases. The conditions and results for representative reactions are summarized in Table V.

The thermolysis reactions were run on various scales, but in a typical reaction approximately 15–20 min were required to pass 222 mg of 2-(*cis*-2-but-2-enyl)-B_5H_8 (III) through the reaction tube. This yielded 182 mg of volatile material which was then found to consist of the carborane products listed in the table in the indicated proportions.

The temperature of 355 °C for the reaction zone was selected as a result of three separate experiments performed for 2-(*cis*-2-but-2-enyl)-B_5H_8. At a lower temperature of 325 °C, a substantial portion (~50%) of the starting material was recovered unchanged. By 355 °C all of the alkenyl borane had reacted, and therefore this was considered an optimum minimum temperature for the conversion. An experiment carried out at a higher temperature of 400 °C noticeably lowered the yield (~60% overall) of carboranes.

Upon complete passage of the alkenylpentaboranes through the furnace, the material retained in the quenching trap was fractionated through −22, −78, (−95 °C for products from ethenyl-B_5H_8), and −196 °C traps, with the majority of products being retained in the −78 °C (−95 °C) trap. Separation of this latter material by GLC revealed (Table V) it to consist of a mixture of alkyl derivatives of the monocarbon carborane, 2-CB_5H_9. Many of these compounds, IV, VI, VIII, XII, XIII, XIV and XV, were previously known[10] and were identified by comparison of their mass spectra and ^{11}B and ^1H NMR spectra with literature values. The new derivatives each gave exact mass measurements on their parent ions which were consistent with their proposed formulations (V and VII, calcd 118.1643; obsd V 118.1641, VII 118.1643; IX, X, and XI, calcd 104.1485; obsd IX 104.1480, X 104.1479, and XI 104.1477. Calcd for VII: B, 46.11. Found: B, 46.12). Their structural assignments were deduced from the spectroscopic data presented in the tables.

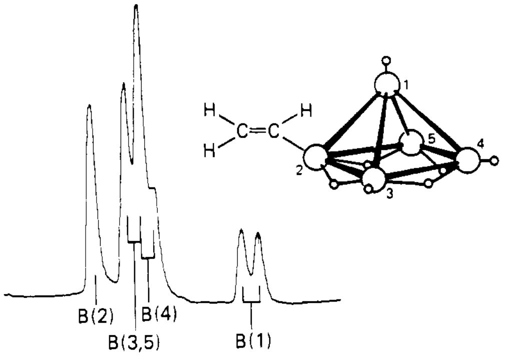

Figure 2. 32.1-MHz boron-11 NMR spectrum of 2-(ethenyl)-B_5H_8 (I) in C_6D_6.

The −196 °C trap from the above fractionation generally contained only minor amounts of material and was found to consist mainly of methyl derivatives of 1,5-$C_2B_3H_5$.

Thermal Stabilities. In separate experiments, the compounds 2-CH_3-3-C_2H_5-2-CB_5H_7 (VI) and 2-CH_3-4-C_2H_5-2-CB_5H_7 (VII) were passed through the reaction tube at 355 °C. Both compounds were fully recovered with only slight (~1%) conversion into the other isomers.

Results

Reactions with Chlorocarbonylbis(triphenylphosphine)iridium(I). All reactions were conducted in the liquid phase in a 5-mL evacuated tube. Typically, reactions were performed with a borane:acetylene:$Ir(CO)Cl[P(C_6H_5)_3]_2$ mole ratio of 1:1:0.003 and were run for 4 hours at 75 °C. Larger amounts of $Ir(CO)Cl[P(C_6H_5)_3]_2$ could not be used due to its limited solubility.

Initial reactions involved heating pentaborane(9) and acetylene in the presence of $Ir(CO)Cl[P(C_6H_5)_3]_2$. Vacuum line fractionation of the reaction products revealed a 5% conversion of the pentaborane(9) into a compound characterized as 2-(ethenyl)-B_5H_8 (I) (eq 1). This new derivative

$$B_5H_9 + \text{acetylene} \xrightarrow[75\ °C]{Ir(CO)Cl[P(C_6H_5)_3]_2} \text{2-(ethenyl)-}B_5H_8\ (I) \qquad (1)$$

of pentaborane(9), which has not been detected in uncatalyzed experiments, can then be further purified by GLC to give an air-sensitive liquid which slowly decomposes to polymeric material under vacuum.

The ^{11}B NMR spectrum of I (Figure 2) consists of three doublets and a singlet with relative intensities of 2:1:1:1, confirming substitution at the B2 position.[11] Likewise, the ^{11}B spin-decoupled proton NMR spectrum (Figure 3) is in agreement with this formulation, showing broad resonances from the protons bound to the boron cage, as well as the resonances expected from the ethenyl group centered at 5.68 ppm. The complex coupling pattern for the ethenyl resonances is similar to that observed[12] for other ABC systems such as monosubstituted ethylene molecules. The infrared spectrum is also compatible with the proposed structure containing characteristic absorptions at 3080 cm^{-1} for geminal CH

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(10) (a) G. B. Dunks and M. F. Hawthorne, *Inorg. Chem.*, **8**, 2667 (1969); (b) T. P. Onak, G. B. Dunks, J. R. Spielman, F. J. Gerhart, and R. E. Williams, *J. Am. Chem. Soc.*, **88**, 2061 (1966).

(11) For boron-11 NMR data of other 2-substituted pentaborane(9) derivatives see: G. R. Eaton and W. N. Libscomb, "NMR Studies of Boron Hydrides and Related Compounds", W. A. Benjamin, New York, 1969.

(12) F. A. Bovey, "Nuclear Magnetic Resonance Spectroscopy", Academic Press, New York, 1969.

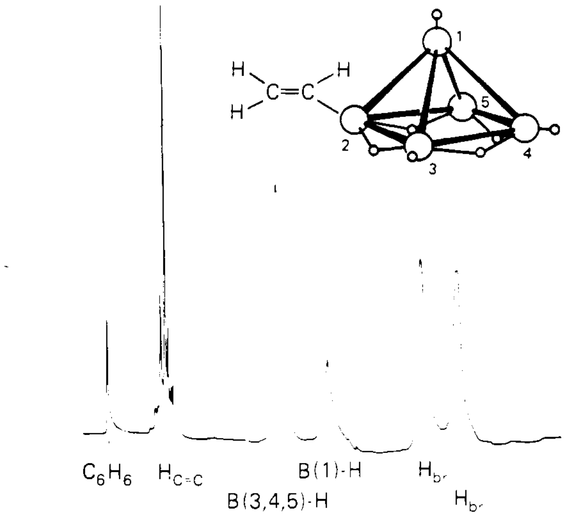


Figure 3. Boron-11 spin-decoupled 100-MHz ^{1}H NMR spectrum of 2-(ethenyl)-B_5H_8 (I) in C_6D_6.

stretching, 3000 and 2980 cm^{-1} for olefinic CH stretching, 2605 cm^{-1} for terminal BH stretching, 1820 cm^{-1} for bridging BHB bonding, and 1600 cm^{-1} for carbon–carbon double-bond stretching.

Although the iridium catalyst had turned over 15 times during the 4-h reaction period, by the end of the reaction it had altered its composition as evidenced by the appearance of purplish, intractable solids in the solution. Following removal of the volatile products in vacuo, no Ir(CO)Cl[P(C_6H_5)$_3$]$_2$ was detected among the remaining solids.

The above reaction was then expanded to include other acetylenes. Experiments using propyne in place of acetylene resulted in 8% conversion of pentaborane(9) into an isomeric mixture of propenylpentaborane(9). These were separated by vacuum line fractionation and GLC to give 2-(2-propenyl)-B_5H_8 (IIa) and 2-(*trans*-1-propenyl)-B_5H_8 (IIb) in a 5:95 ratio (eq 2).

$$B_5H_9 + \text{propyne} \xrightarrow[75\ ^\circ\text{C}]{\text{Ir(CO)Cl[P}(C_6H_5)_3]_2} \text{2-(2-propenyl)-}B_5H_8 \text{ (IIa)} + \text{2-(}\textit{trans}\text{-1-propenyl)-}B_5H_8 \text{ (IIb)} \quad (2)$$

The proposed structures for IIa and IIb are also in agreement with their spectral data. Thus, substitution at the 2-position of a pentaborane(9) cage is again indicated for both compounds by their ^{11}B NMR spectra which are similar to that of compound I. The attachment of the propenyl substituents are unambiguously determined from the proton NMR spectra (Figure 4). For IIa the resonances observed at 5.35 (s, vinylic CH), 5.23 (s, vinylic CH), and 1.86 ppm (s, CH_3) are characteristic of a 2-substituted propene molecule. The latter resonance appears as an apparent singlet which shows fine coupling upon expansion. For the resonances associated with the vinylic hydrogens, the combination of the coupling due to the geminal hydrogens (1–3 Hz) with that resulting from a long range effect of the methyl group (1–3 Hz) gives the appearance of broadened singlets. For IIb, the resonances observed at 5.92 (d of q, vinylic CH), 5.44 (d of q, vinylic CH), and 1.66 ppm (d, CH_3) are characteristic of a 1-substituted propene molecule. The primary coupling constants for the vinylic hydrogens (17.5 Hz) are indicative[12] of their trans location to each other (cis 6–12 Hz). Infrared spectral data also readily differentiate these two isomers where compound IIa exhibits a sharp absorption for geminal CH stretching (3080 cm^{-1}) which is absent in the spectrum for compound IIb.

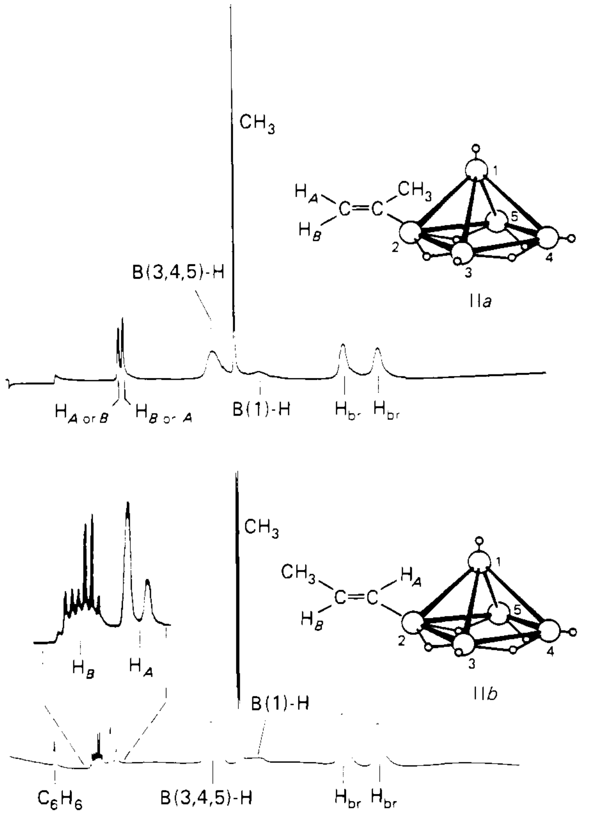


Figure 4. Boron-11 spin-decoupled 100-MHz ^{1}H NMR spectrum of 2-(2-propenyl)-B_5H_8 (IIa) and 2-(*trans*-1-propenyl)-B_5H_8 (IIb).

In this reaction the iridium catalyst underwent 24 turnovers in the 4-h reaction period. Although no Ir(CO)Cl[P(C_6H_5)$_3$]$_2$ was again detected among the materials remaining in the reaction tube, a yellow air-sensitive solid was left which was not characterized due to the presence of minor amounts of a contaminating oily byproduct. Addition of fresh amounts of B_5H_9 and propyne followed by reaction at 75 °C for 4 more h resulted in the formation of more propenylpentaborane(9); however, the conversion rate (2% in 4 h) was substantially lower than before.

The reaction of propyne with pentaborane(9) in the presence of only triphenylphosphine was also examined with the use of similar conditions as above in order to determine what effect, if any, free P(C_6H_5)$_3$ may have in the above reaction, but it was found that no alkenylborane products were produced.

The reaction of 2-butyne with B_5H_9 in the presence of Ir(CO)Cl[P(C_6H_5)$_3$]$_2$ was also investigated and found to yield 2-(*cis*-2-but-2-enyl)-B_5H_8 (III) (eq 3). It should be noted,

$$B_5H_9 + \text{2-butyne} \xrightarrow[75\ ^\circ\text{C}]{\text{Ir(CO)Cl[P}(C_6H_5)_3]_2} \text{2-(}\textit{cis}\text{-2-but-2-enyl)-}B_5H_8 \text{ (III)} \quad (3)$$

however, that this reaction gave substantially lower conversions (<1%) than the previous reactions with terminal acetylenes. Furthermore, large amounts of unidentified organic side products were found which necessitated the extensive use of GLC for separation and purification.

The spectral data for III are again consistent with the proposed structure. Thus, the ^{11}B NMR spectrum exhibits the proper resonances including the singlet of intensity one attributed to the substituted boron. In the boron-11 spin-decoupled proton NMR the resonances for the 2-butenyl group at 5.76 (q, 1 H), 1.71 (s, 3 H), and 1.61 ppm (d, 3 H) are assignable to the vinylic and methyl protons, respectively. These resonances clearly signify the presence of a 2-substituted 2-butene molecule. A cis configuration of the 2-butenyl group was confirmed by the reaction of III with excess glacial acetic acid and analysis of the resulting 2-butene to give a cis:trans ratio of 97.2:2.8.

Reactions with μ-Acetylene-dicobalt Hexacarbonyl Complexes. All reactions were conducted in the liquid phase without solvent in evacuated tubes. Typically, reactions were performed with a borane:metal reagent ratio of 10:1 and varying concentrations of alkyne.

Vacuum line fractionation of the products resulting from heating (75 °C) equimolar amounts of pentaborane(9) and 2-butyne for 1 h in the presence of $[(CH_3)_2C_2]Co_2(CO)_6$ revealed a 27% conversion of pentaborane(9) into 2-(*cis*-2-but-2-enyl)-B_5H_8 (III) and a partial recovery (~50%) of the $[(CH_3)_2C_2]Co_2(CO)_6$ complex (eq 4). This conversion corresponds to 2.7 turnovers for the catalyst. Compound III was identified by comparison of its spectral data with that of the sample obtained in the $Ir(CO)Cl[P(C_6H_5)_3]_2$-catalyzed reaction, and a cis configuration of the 2-butenyl group was again confirmed by reaction with acetic acid followed by 2-butene analysis (cis:trans = 98.6:1.4). Also obtained in trace quantities from this reaction were the four cobalt complexes, $Co_4(CO)_{12}$, and $[(CH_3)_2C_2]Co_4(CO)_{10}$. These were extracted from the reaction tube, separated on TLC plates, and identified by color and comparison of their infrared spectra and R_f values with those of authentic samples.

$$B_5H_9 + \text{2-butyne} \xrightarrow[75\ ^\circ C]{[(CH_3)_2C_2]Co_2(CO)_6} \text{2-(}\textit{cis}\text{-2-but-2-enyl)-}B_5H_8\ \text{(III)} \quad (4)$$

So that insight could be gained into the formation of the tetracobalt complexes, the direct reaction of liquid pentaborane(9) with $[(CH_3)_2C_2]Co_2(CO)_6$ at 75 °C was examined. This was found to react according to eq 5. As indicated below, quantitative yields of a mixture of the tetracobalt complexes, $Co_4(CO)_{12}$, and $[(CH_3)_2C_2]Co_4(CO)_{10}$ were obtained. As a result of the thermal instability exhibited by III, yields of this compound based on consumed B_5H_9 were less than 100%. Therefore, the exact stoichiometry of this product was not determined.

$$[(CH_3)_2C_2]Co_2(CO)_6 + B_5H_9 \xrightarrow{75\ ^\circ C} \text{2-(}\textit{cis}\text{-2-but-2-enyl)-}B_5H_8\ \text{(III)} + {}^1/_2[Co_4(CO)_{12} + [(CH_3)_2C_2]Co_4(CO)_{10}] \quad (5)$$

Heating equimolar amounts of B_5H_9 and propyne at 75 °C for 1 h in the presence of 10 mol % $[(CH_3)C_2H]Co_2(CO)_6$ (prepared in situ) resulted in 2% conversion of pentaborane(9) into an isomeric mixture of the propenylpentaborane(9) compounds IIa and IIb, previously isolated in the $Ir(CO)Cl[P(C_6H_5)_3]_2$-catalyzed reaction. In contrast to the results with $Ir(CO)Cl[P(C_6H_5)_3]_2$, compound IIa predominates over IIb in a 75:25 ratio (eq 6). Both compounds were identified by comparison of their spectral data with those of the previously obtained spectra. In addition to these products, larger quantities of trisubstituted methylbenzenes, identified by mass spectra and proton NMR spectra, were formed but none of the complexes, $[(CH_3)C_2H]Co_2(CO)_6$, $Co_4(CO)_{12}$, or $[(CH_3)C_2H]Co_4(CO)_{10}$, were recovered.

$$B_5H_9 + \text{propyne} \xrightarrow[75\ ^\circ C]{[(CH_3)C_2H]Co_2(CO)_6} \underset{75\%}{\text{2-(2-propenyl)-}B_5H_8\ \text{(IIa)}} + \underset{25\%}{\text{2-(}\textit{trans}\text{-1-propenyl)-}B_5H_8\ \text{(IIb)}} \quad (6)$$

Although the formation of IIa and IIb in the above experiment was metal promoted, the overall reaction appeared to be noncatalytic. In an attempt to increase the conversion to IIa and IIb by suppressing the trimerization reaction, an experiment involving larger excesses of B_5H_9 was examined. This resulted in higher yields (7%) of IIa and IIb; however, the reaction still appeared to be noncatalytic.

Similar reactions as above involving heated mixtures of acetylene and B_5H_9 in the presence of $[H_2C_2]Co_2(CO)_6$ did not result in any detectable amounts of vinyl-B_5H_8 among the volatile products.

Thermolysis of Alkenylpentaboranes. All thermolysis reactions were conducted by slow passage of the alkenylpentaborane through a heated tube (355 °C) in vacuo, using the apparatus described in the Experimental Section. The results of these reactions are presented in Table V.

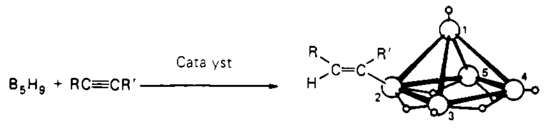
Initially, the reaction of 2-(*cis*-2-but-2-enyl)-B_5H_8 (III) was examined and found to give an 85% yield of carborane compounds. These were separated by vacuum line fractionation and GLC to give as major products the carboranes 2-CH_3-3-C_2H_5-2-C_5H_7 (VI) and 2-CH_3-4-C_2H_5-2-CB_5H_7 (VII) along with smaller amounts of 1-C_2H_5-2-CH_3-2-CB_5H_7 (IV) 2-C_2H_5-3-CH_3-2-CB_5H_7 (V), and 1,5-$(CH_3)_2$-1,5-$C_2B_3H_3$. Several pyrolyses were executed at various reaction temperatures for 2-(*cis*-2-but-2-enyl)-B_5H_8. At temperatures somewhat lower than 355 °C (at 325 °C), substantial amounts of starting material could be recovered unchanged. At 355 °C, all of the alkenylborane had reacted and high conversion to carborane products was observed. At higher temperatures (400 °C), the overall yield of carborane products had diminished. All thermolysis reactions were subsequently carried out at 355 °C.

The thermolysis reactions of the isomers 2-(2-propenyl)-B_5H_8 (IIa) and 2-(1-*trans*-propenyl)-B_5H_8 (IIb) were then individually investigated. Both compounds gave the same five carborane products, consisting of four alkyl derivatives of 2-CB_5H_9 and 1-CH_3-1,5-$C_2B_3H_4$ in comparable overall yields. The relative yields of the individual products, however, differed substantially. For IIa, the major products are 2,3-$(CH_3)_2$-2-CB_5H_7 (VIII) and 2,4-$(CH_3)_2$-2-CB_5H_7 (IX) whereas for IIb the major products are 3-C_2H_5-2-CB_5H_8 (X) and 4-C_2H_5-2-CB_5H_8 (XI).

Finally, the thermolysis of 2-ethenyl-B_5H_8 (I) was investigated and found to give results consistent with the products observed above. Thus, thermolysis of I yields as major products the four possible monomethyl derivatives of 2-CB_5H_9 along with an isomeric mixture (not separated) of several monomethyl derivatives of CB_5H_7. These compounds were identified by comparison of their NMR and mass spectra with literature values.[10b,13]

Discussion

The effects of two different types of potential catalysts, $Ir(CO)Cl[P(C_6H_5)_3]_2$ and $(RC_2R')Co_2(CO)_6$ complexes, on the reaction of pentaborane(9) and alkynes were examined and were each found to catalyze these reactions under mild conditions to yield previously unreported alkenylpentaboranes: eq 7.



(7)

The iridium complex has previously been shown to catalyze the addition reactions of acetylenes,[8a] and although mechanistic studies were not performed in the present investigation, the

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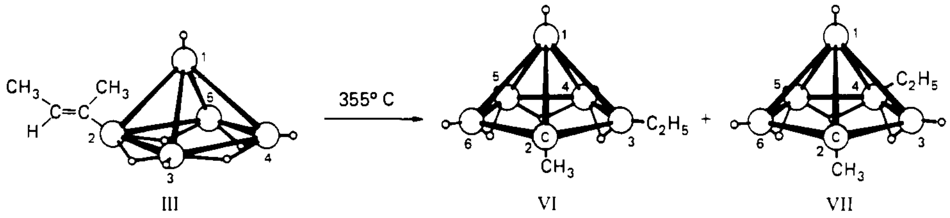
(13) E. Groszek, J. B. Leach, G. T. E. Wong, C. Ungermann, and T. P. Onak, *Inorg. Chem.*, **10**, 2770 (1971); T. P. Onak, R. P. Drake, and G. B. Dunks, *J. Am. Chem. Soc.*, **87**, 2505 (1965); S. R. Prince and R. Schaeffer, *Chem. Commun.*, 451 (1968); T. P. Onak, P. Mattschei and E. Groszek, *J. Chem. Soc. A*, 1990 (1969).



(8)

results obtained for the pentaborane(9) reactions are consistent with the mechanism proposed[14] for the analogous hydrogenation reactions catalyzed by $Ir(CO)Cl[P(C_6H_5)_3]_2$. Thus, this would involve the substitution of a triphenylphosphine ligand by an acetylene molecule, followed by oxidative addition at the metal of a B–H unit of pentaborane(9). This last step is further supported by the report[15] that pentaborane(9) will oxidatively add to *trans*-$Ir(CO)Cl[P(CH_3)_3]_2$ to yield the metallaborane 2-$[IrH(CO)Cl[P(CH_3)_3]_2]$-B_5H_8. In that complex the metal is bound to a basal boron position of the pentaborane(9), which is consistent with the observed selective formation of only 2-alkenyl pentaborane compounds in the reactions reported herein. Following oxidative addition, subsequent insertions of the alkyne into the Ir–H and Ir–B bonds would lead to the alkenylborane products and regeneration of the catalytic species.

Also in agreement with the reported hydrogenation reactions catalyzed by $Ir(CO)Cl[P(C_6H_5)_3]_2$ is the observation that the pentaborane(9) reaction is most effective with terminal rather than internal acetylenes. Furthermore, the reactions of acetylenes such as propyne with pentaborane(9) in the presence of this catalyst give predominately cis anti-Markownikoff addition as expected.

The relatively low conversion rates observed with $Ir(CO)Cl[P(C_6H_5)_3]_2$ may be attributed to its low solubility and a gradual reduction in catalytic activity of the complex during the reactions. This loss of activity was revealed in the acetylene reaction by the appearance of purplish insoluble solids as the reaction progressed. Similar intractable solids have been obtained following catalyzed trimerization reactions using derivatives of $Ir(CO)Cl[P(C_6H_5)_3]_2$.[16] For the propyne reaction, yellow solids remained after an initial 4-h reaction which did not contain any $Ir(CO)Cl[P(C_6H_5)_3]_2$. These solids did promote further reaction of freshly added B_5H_9 and propyne but with substantially lower conversion rates than the initial reaction.

The bimetallic compounds, $(RC_2R')Co_2(CO)_6$, also promoted the pentaborane(9)–alkyne reactions to yield alkenylpentaboranes. As in the iridium-catalyzed reactions, cis addition was again observed, but, importantly, these cobalt complexes exhibited significantly different types of reactivities than those shown by the iridium catalyst. For example, it was found that these catalysts promoted the reaction of pentaborane(9) more effectively with internal rather than terminal acetylenes, in contrast to what was observed with $Ir(CO)Cl[P(C_6H_5)_3]_2$. Likewise, it was also found that the reaction of pentaborane(9) and propyne promoted by $(CH_3C_2H)Co_2(CO)_6$ did not lead to the anti-Markownikoff addition products normally expected, but instead gave predominately Markownikoff addition.

This reactivity and regiospecificity is opposite that observed for conventional electrophilic hydroboration reactions,[17] as well as that found[8] for most transition-metal (monometal) catalyzed addition reactions such as hydrosilations of unsaturated hydrocarbons. These results suggest that the $(RC_2R')Co_2(CO)_6$-catalyzed reactions occur by a mechanism which is substantially different than, for example, that which is outlined for the iridium complex above. Furthermore, it should also be noted that similar reactivities and selectivities have now been observed[18] for the reactions of alkynes with other boron cage systems such as small carboranes catalyzed by these cobalt complexes. These results and their corresponding mechanistic implications will be discussed in a future publication.[18]

It is clear from the above discussions that various transition-metal reagents can be used to activate the pentaborane(9)–alkyne reaction to yield the corresponding alkenylpentaborane derivatives. Since alkenylpentaboranes have been proposed[4c,7] to be intermediates in thermally induced small carborane syntheses, it was expected that these compounds could be readily converted into carboranes. The thermolysis reactions of the alkenylpentaboranes were therefore investigated, and it was found that the quick passage of any of these compounds through a heated tube resulted in a high yield conversion to monocarbon carborane products. Furthermore, all of the major carborane products were based on the same cage system, the 2-CB_5H_9 carborane. For example, pyrolysis of 2-(*cis*-2-but-2-enyl)pentaborane(9) (III) gives an 85% conversion to monocarbon carborane products which consist mainly of the two isomers 2-CH_3-3-C_2H_5-2-CB_5H_7 (VI) (36%) and 2-CH_3-4-C_2H_5-2-CB_5H_7 (VII) (39%) as indicated in eq 8.

Previously, 2-CB_5H_9 and its alkyl derivatives could be obtained as only minor products of the thermal reaction of pentaborane(9) and acetylenes[4c] or from the reaction of 2,6-$C_2B_6H_8$ with tetramethylammonium borohydride.[10a] Thus, the development of the metal-promoted synthesis of the alkenylpentaborane(9) compounds combined with their thermolysis reactions provides an important new large scale synthetic route to the alkyl derivatives of 2-CB_5H_9, thereby enabling extensive chemical investigations of this unusual monocarbon carborane.

The major products observed in all of the alkenylpentaborane(9) thermolysis reactions (Table V) are consistent with the reaction mechanism originally proposed[4c,7] by Williams to account for the formation of 2-CB_5H_9 alkyl derivatives as minor products in the thermal reaction (215 °C) of alkynes with pentaborane(9). A plausible reaction sequence based on this mechanism which allows the conversion of the alkenylpentaborane(9) compounds to the observed monocarbon carboranes is depicted in Figure 5. The first step can be envisioned as an internal hydroboration of the alkenyl substituent by an adjacent B–H group (boron positions 1 or 3) with the boron adding to the α-carbon and the hydrogen to the β-carbon. Thus the α-carbon is incorporated into the cage while the β-carbon becomes part of an alkyl group which migrates to adjacent boron positions 1 or 3. In the case of 2-but-2-enyl-pentaborane(9) (III), this sequence would generate both 2-CH_3-3-C_2H_5-2-CB_5H_7 (VI) and 1-C_2H_5-2-CH_3-2-CB_5H_7 (IV). The latter compound was, in fact, isolated

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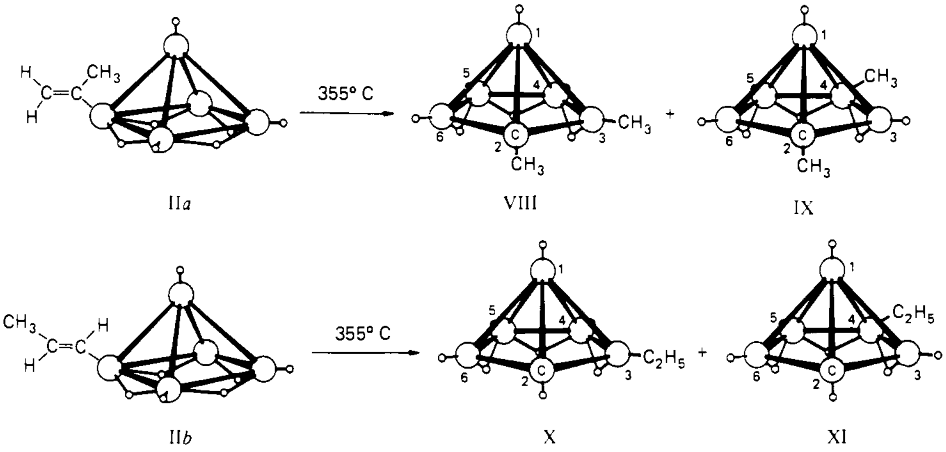

(9)

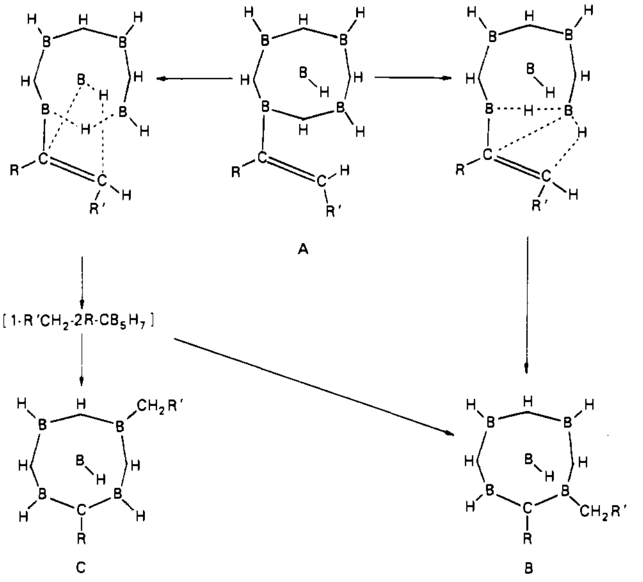

Figure 5. Proposed mechanism for the conversion of alkenylpentaboranes into monocarbon carboranes.

in only small amounts from the reaction, but this was not unexpected since IV would be predicted to readily rearrange under the reaction conditions employed to yield both basal substituted isomers VI and 2-CH_3-4-C_2H_5-2-CB_5H_7 (VII). Similar facile apex to basal alkyl migrations have been observed[19] for 1-alkylpentaboranes. This conclusion concerning the formation of isomer VII is also supported by the observation (see Experimental Section) that neither of these basal isomers will isomerize at these temperatures, thereby eliminating compound VI as a precursor to VII.

The mechanism outlined in Figure 5 is also strongly supported by the results from the thermolysis reactions of the two isomeric propenylpentaboranes, IIa and IIb. Thus, if this mechanism is correct, upon thermolysis these two compounds should yield different carborane isomers. Since IIa contains a methyl group on the α-carbon, it should form carboranes which are methyl substituted at the carbon cage position and also methyl substituted at either the 3 or 4 boron positions. Compound IIb, on the other hand, has the methyl group on the β-carbon and should, therefore, yield carboranes containing no alkyl substituent on the cage carbon position but instead having an ethyl group at either the 3 or 4 boron position. In both cases, monocarbon carborane products are obtained in good yields with the major products, as indicated in eq 9, consistent with these predictions.

In addition to the monocarbon carborane products which were formed as the major products of the thermolysis reactions of IIa, IIb, and III, minor amounts of the methyl derivatives of 1,5-$C_2B_3H_5$ were also isolated. These probably resulted from the thermal decomposition of the 2-CB_5H_9 derivatives, as has been previously reported.[20] Similarly, in reactions involving compound I, small quantities of the methyl derivatives of the monocarbon closo carborane CB_5H_7 were also detected. These may also have been produced from the 2-CB_5H_9 derivatives by loss of H_2.[13a]

In summary, the development described above of a transition-metal-catalyzed synthesis of alkenylpentaboranes is important since it illustrates that transition-metal reagents may be employed to induce reactions, involving boron hydrides, which could previously be carried out only under relatively severe conditions. Thus, with the lower temperatures allowed, both higher yield and selectivity of reaction are possible. In addition, compounds such as the alkenylpentaboranes, which have been postulated intermediates in the thermal reactions but never actually observed, can now be isolated, thereby allowing a more detailed understanding of the mechanisms of these reactions. We therefore feel that the use of transition-metal reagents for both stoichiometric[21] and catalytic transformations in boron hydride chemistry will be an important, expanding research area of the future.

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Registry No. I, 78837-91-9; IIa, 78837-92-0; IIb, 78837-93-1; III, 73910-58-4; IV, 24286-01-9; V, 78856-99-2; VI, 24286-02-0; VII, 78857-00-8; VIII, 24286-00-8; IX, 78857-01-9; X, 78857-02-0; XI, 78857-03-1; XII, 24285-96-9; XIII, 24285-97-0; XIV, 23087-40-3; XV, 32070-37-4; 1,5-$(CH_3)_2$-1,5-$C_2B_3H_3$, 78837-94-2; 1-CH_3-1,5-$C_2B_3H_4$, 78837-95-3; acetylene, 74-86-2; propyne, 74-99-7; 2-butyne, 503-17-3; B_5H_9, 16624-22-7; $Ir(CO)Cl[P(C_6H_5)_3]_2$, 15318-31-7; $[(CH_3)_2C_2]Co_2(CO)_6$, 37726-81-1.

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