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Transition-Metal-Promoted Reactions of Boron Hydrides. 3.[1] $(R_2C_2)Co_2(CO)_6$-Catalyzed Reactions of Alkynes and Small Carboranes: Synthesis of *B*-Alkenylcarboranes

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Complexes of the general formula $(RC_2R')Co_2(CO)_6$ (R, R′ = H, CH_3, or C_2H_5) have been found to catalyze the reaction of various alkynes (acetylene, 1-butyne, or 2-butyne) with small carboranes, including 1,5-$C_2B_3H_5$, 1,6-$C_2B_4H_6$, 2,4-$C_2B_5H_7$, and 2,3-$C_2B_4H_8$, to yield the corresponding boron-substituted alkenylcarboranes $(RHC{=}CR')_nC_2B_3H_{5-n}$, $(RHC{=}CR')_nC_2B_4H_{6-n}$, $(RHC{=}CR')_nC_2B_5H_{7-n}$, and $(RHC{=}CR')_nC_2B_4H_{8-n}$. The degree of substitution of the carborane can be controlled by varying the reaction conditions, and products have been obtained ranging from single substitution at only one boron site to complete substitution at all boron positions in the molecule. The overall reaction thus corresponds to a catalyzed BH addition of the carborane to the alkyne in a cis fashion, but in contrast to results normally expected for monometal-catalyzed addition reactions, it was found that when $(RC_2R')Co_2(CO)_6$ complexes are employed as catalysts, internal alkynes are more reactive than terminal and the reaction with 1-butyne proceeds to give predominantly Markovnikov addition.

Introduction

In a previous paper[1] we reported that acetylene complexes of the general formula $(RC_2R')Co_2(CO)_6$ promote, under mild conditions, the reactions of various alkynes with pentaborane(9) to yield the corresponding alkenylpentaborane derivatives. Furthermore, we noted that these complexes have reactivities and selectivities that are different from those normally observed for the addition reactions of unsaturated hydrocarbons catalyzed by monometal catalysts.[3] This work prompted us to further investigate the scope and applications of these catalysts for other boron cage systems. Of particular interest was the potential use of these catalysts for the synthesis of boron-substituted alkenylcarboranes, since the previously known carbon-substituted alkenylcarboranes have been[4] incorporated into polymers that exhibit high thermal stabilities and resistance to chemical degradation. Thus, boron-substituted alkenylcarboranes could prove to be even more versatile in polymer chemistry since the carbon atoms would be available for further functionality. The work described herein, therefore, is focused on the effects of these catalysts on the reactions of various alkynes with the small carboranes 1,5-$C_2B_3H_5$, 1,6-$C_2B_4H_6$, 2,4-$C_2B_5H_7$, and 2,3-$C_2B_4H_8$.

Experimental Section

Materials. Dicobalt octacarbonyl was purchased from Strem Chemicals and used as received. The acetylene complexes, $(RC_2R')Co_2(CO)_6$, were either synthesized[5] 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 1-butyne 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 a −110 °C trap. The carboranes 1,5-$C_2B_3H_5$, 1,6-$C_2B_4H_6$, and 2,4-$C_2B_5H_7$ were purchased from Chemical Systems Inc. 1,5-$C_2B_3H_5$ was freed of less volatile impurities by passing through a −95 °C trap on a high-vacuum line and then was passed into a −126 °C trap to remove any more volatile impurities. 1,6-$C_2B_4H_6$ was purified by passing through a −78 °C trap and into a −110 °C trap. 2,4-$C_2B_5H_7$ was purified by GLC on a 30% Apiezon-on-firebrick column. The carborane 2,3-$C_2B_4H_8$ was prepared by a literature method.[6] Reaction solvents either were Spectrograde quality and were used without further purification (pentane and hexanes) or were reagent grade and were purified by literature methods[7] and dried accordingly: benzene (P_2O_5); and tetrahydrofuran ($LiAlH_4$). All chromatographic solvents were reagent grade and were dried over molecular sieves (4A).

Physical Measurements and Chromatography. Boron-11 NMR spectra at 32.1 MHz were obtained on a JEOL PS-100 Fourier-transform spectrometer. 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 at the University of Pennsylvania. Proton decoupling was accomplished by irradiation at the proper frequency with a broad-band (2500 Hz) noise decoupler. All 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 100 MHz were recorded on the JEOL PS-100 Fourier-transform spectrometer. Boron-11 spin decoupling was accomplished by using double-resonance techniques with a broad-band noise decoupler. All proton chemical shifts were measured relative to internal residual solvent from the lock solvents utilized (99.5% C_6D_6, 99.8% $CDCl_3$, and 99.0% CD_2Cl_2) and then referenced to $(CH_3)_4Si = 0.00$ 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 either a Perkin-Elmer 521 or 337 grating infrared spectrophotometer. Elemental analyses were performed by Galbraith Laboratories Inc. All melting points are uncorrected. Preparative 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 0.25-mm (5 × 10 cm) silica gel F-254 plates (Merck). Column chromatography was conducted on silica gel, 0.05–0.2 (70–270 mesh) ASTM (MN-kieselgel). Gas–liquid chromatography (GLC) was conducted on a Varian Model 920 gas chromatograph equipped with either a 20 ft × 0.25 in. 6% tricresyl phosphate (TCP) on Chromosorb P (60–80 mesh) column or a 5 ft × 0.25 in. 1.5% OV-101 on Chromosorb G (100–120 mesh) column.

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 and solvent (if used) were charged into the tube under an inert atmosphere of N_2. The tube was attached to a high-vacuum line and evacuated, and measured amounts of alkyne and carborane 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 most cases, $Co_2(CO)_8$ served as the starting metal reagent, and therefore, prior to heating, the above mixtures were warmed to

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(2) Alfred P. Sloan Foundation Fellow.

(3) For general discussions of transition-metal-catalyzed addition reactions of unsaturated hydrocarbons, see for example: James, B. R. "Homogeneous Hydrogenation"; Wiley: New York, 1973. Speier, J. L. *Adv. Organomet. Chem.* **1979**, *17*, 407.

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Table I

carborane[a]	acetylene	overall conversion,[b] %	products obsd[c]	rel yields,[d] %	R_v[e]
$2,4\text{-}C_2B_5H_7$	2-butyne	100	1-(*cis*-2-but-2-enyl)-$2,4\text{-}C_2B_5H_6$, Ia	2.3	17.5^{1}
			5-(*cis*-2-but-2-enyl)-$2,4\text{-}C_2B_5H_6$, Ib	2.1	19.5^{1}
			3-(*cis*-2-but-2-enyl)-$2,4\text{-}C_2B_5H_6$, Ic	2.0	24.8^{1}
			5,6-(*cis*-2-but-2-enyl)$_2$-$2,4\text{-}C_2B_5H_5$, IIa	0.2	4.8^{4}
			1,5-(*cis*-2-but-2-enyl)$_2$-$2,4\text{-}C_2B_5H_5$, IIb	2.1	6.1^{4}
			1,3-(*cis*-2-but-2-enyl)$_2$-$2,4\text{-}C_2B_5H_5$, IIc	0.8	7.1^{4}
			1,7-(*cis*-2-but-2-enyl)$_2$-$2,4\text{-}C_2B_5H_5$, IId	0.2	7.5^{4}
			3,5-(*cis*-2-but-2-enyl)$_2$-$2,4\text{-}C_2B_5H_5$, IIe	0.7	10.3^{4}
			1,5,6-(*cis*-2-but-2-enyl)$_3$-$2,4\text{-}C_2B_5H_4$, IIIa	0.2	1.6^{2}
			1,5,7-(*cis*-2-but-2-enyl)$_3$-$2,4\text{-}C_2B_5H_4$, IIIb	1.7	2.1^{2}
			1,3,7-(*cis*-2-but-2-enyl)$_3$-$2,4\text{-}C_2B_5H_4$, IIIc	1.7	2.1^{2}
			1,3,5-(*cis*-2-but-2-enyl)$_3$-$2,4\text{-}C_2B_5H_4$, IIId	15.1	2.5^{2}
			3,5,6-(*cis*-2-but-2-enyl)$_3$-$2,4\text{-}C_2B_5H_4$, IIIe	1.7	2.7^{2}
			1,5,6,7-(*cis*-2-but-2-enyl)$_4$-$2,4\text{-}C_2B_5H_3$, IVa	4.4	5.9^{2}
			1,3,5,7-(*cis*-2-but-2-enyl)$_4$-$2,4\text{-}C_2B_5H_3$, IVb	41.8	$5.6\text{–}7.6^{2}$
			1,3,5,6-(*cis*-2-but-2-enyl)$_4$-$2,4\text{-}C_2B_5H_3$, IVc	11.4	$7.2\text{–}8.1^{2}$
			1,3,5,6,7-(*cis*-2-but-2-enyl)$_5$-$2,4\text{-}C_2B_5H_2$, V	11.5	$16.0\text{–}18.7^{2}$
$1,5\text{-}C_2B_3H_5$	2-butyne	77	2-(*cis*-2-but-2-enyl)-$1,5\text{-}C_2B_3H_4$, VI	4	1.0^{3}
			2,3,4-(*cis*-2-but-2-enyl)$_3$-$1,5\text{-}C_2B_3H_2$, VII	96	1.4^{2}
$1,5\text{-}C_2B_3H_5$	1-butyne	27	2-(2-but-1-enyl)-$1,5\text{-}C_2B_3H_4$, VIIIa	62	1.2^{3}
			2-(*trans*-1-but-1-enyl)-$1,5\text{-}C_2B_3H_4$, VIIIb	38	2.0^{3}
$1,5\text{-}C_2B_3H_5$	acetylene	5	2-(ethenyl)-$1,5\text{-}C_2B_3H_4$, IX	100	0.2^{3}
$1,6\text{-}C_2B_4H_6$	2-butyne	89	2-(*cis*-2-but-2-enyl)-$1,6\text{-}C_2B_4H_5$, X	5.7	5.3^{3}
			2,3-(*cis*-2-but-2-enyl)$_2$-$1,6\text{-}C_2B_4H_4$, XIa	3.5	0.25^{2}
			2,4-(*cis*-2-but-2-enyl)$_2$-$1,6\text{-}C_2B_4H_4$, XIb	1.1	0.35^{2}
			2,3,4-(*cis*-2-but-2-enyl)$_3$-$1,6\text{-}C_2B_4H_3$, XII	13.8	1.6^{2}
			2,3,4,5-(*cis*-2-but-2-enyl)$_4$-$1,6\text{-}C_2B_4H_2$, XIII	75.9	8.0^{2}
$2,3\text{-}C_2B_4H_8$	2-butyne	33	1-(*cis*-2-but-2-enyl)-$2,3\text{-}C_2B_4H_7$, XIVa	16.8	25.9^{1}
			5-(*cis*-2-but-2-enyl)-$2,3\text{-}C_2B_4H_7$, XIVb	18.0	36.0^{1}
			4-(*cis*-2-but-2-enyl)-$2,3\text{-}C_2B_4H_7$, XIVc	65.2	43.3^{1}

[a] For conditions of each reaction see text. Typically, reactions were run with a carborane:$(RC_2R')Co_2(CO)_6$ ratio of 10:1 and varying concentrations of alkyne at 75–100 °C for 1–2 h. [b] Based on starting amount of carborane. Yields based on consumed carboranes were ~100%. [c] Except for compound VII, which is a white crystalline solid, all products are liquids. [d] Determined from peak areas (uncorrected for response factor differences), which were determined by triangulation. [e] Key: (1) on TCP column at 80 °C; R_v(parent) 1.0; (2) on OV 101 column at 130 °C; R_v(hexamethylbenzene) 1.0; (3) on TCP column at 60 °C; R_v(benzene) 1.0; (4) on TCP column at 115 °C; R_v(Ia) 1.0.

room temperature to allow formation of the $(RC_2R')Co_2(CO)_6$ complex.[5] 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 each reaction are summarized in Tables I and V.

Various control reactions between alkynes and carboranes were also run in the absence of $(RC_2R')Co_2(CO)_6$ complexes; however, in each case no reaction was observed.

$2,4\text{-}C_2B_5H_7$ and 2-Butyne. The 5-mL tube was charged with 0.10 mmol of $[(CH_3)_2C_2]Co_2(CO)_6$, 1.0 mmol of $2,4\text{-}C_2B_5H_7$, 5.0 mmol of 2-butyne, and 1.0 mL of pentane. After this solution was heated at 100 °C for 2 h, the volatile material was fractionated through −22, −78, and −196 °C traps. The mono-*cis*-2-but-2-enyl derivatives of $2,4\text{-}C_2B_5H_7$ were retained in the −78 °C trap and were further separated by GLC on the TCP column to give compounds Ia–c listed in Table I. Anal. Calcd for Ia–c: C, 51.76; H, 9.41. Found for Ia: C, 51.63; H, 9.50. Found for Ib: C, 51.87; H, 9.51. Found for Ic: C, 51.91; H, 9.53. Exact mass: calcd for Ia–c 140.1483; found for Ia 140.1485, Ib 140.1488, Ic 140.1486. The di-*cis*-2-but-2-enyl derivatives of $2,4\text{-}C_2B_5H_7$ were found in the −22 °C trap and in the reaction tube with the higher alkenylated products. Generally, when higher alkenylated products were formed in substantial quantities, there was a tendency for the di-*cis*-2-but-2-enyl derivatives to remain in the reaction tube; otherwise, they slowly distilled into the −22 °C trap. Further separation of the di-*cis*-2-but-2-enyl derivatives was accomplished on the TCP column at 115 °C to give compounds IIa–e listed in Table I. Anal. Calcd for IIa–e: C, 62.13; H, 9.95. Found for IIb: C, 62.46; H, 9.95. Exact mass: calcd for IIa–e 194.1952; found for IIb 194.1967, IIc 194.1968, IIe 194.1963.

The residue in the reaction tube was extracted with methylene chloride and separated by TLC (pentane eluant) to give the tetracobalt complexes $Co_4(CO)_{12}$ (R_f 0.49) and $[(CH_3)_2C_2]Co_4(CO)_{10}$ (R_f 0.38) and one major colorless band (R_f 0.58, 310.6 mg). This band was further separated by GLC on the OV-101 column at 130 °C to give, in addition to residual amounts of di-*cis*-2-but-2-enyl derivatives, the tri-, tetra-, and penta-*cis*-2-but-2-enyl derivatives of $2,4\text{-}C_2B_5H_7$, compounds III–V shown in Table I, and hexamethylbenzene (30 mg, 0.19 mmol, R_v 1.0). Anal. Calcd for IIIa–e: C, 67.97; H, 10.18. Found for IIId: C, 67.77; H, 10.22. Calcd for IVa–c: C, 71.71; H, 10.36. Found for IVb: C, 71.81; H, 10.38. Calcd for V: C, 74.34; H, 10.49. Found: C, 74.34; H, 10.41. Exact mass: calcd for IIIa–e 248.2422; found for IIId 248.2432; calcd for IVa–c 302.2906; found for IVb 302.2941; calcd for V 356.3361; found 356.3390.

In addition to the above experiment, the reaction of $2,4\text{-}C_2B_5H_7$, 2-butyne, and $[(CH_3)_2C_2]Co_2(CO)_6$ under a variety of conditions (temperature, solvent, catalyst concentration, and reactant concentrations) was examined. The results of these investigations are summarized in Table V where overall conversion to alkenylated products and relative yield distributions of these products are listed for the various conditions. The quantity of $[(CH_3)_2C_2]Co_2(CO)_6$ recovered in these experiments varied considerably. For reactions where an excess of 2-butyne was maintained and the temperature was relatively low (i.e., 75 °C), all of the $[(CH_3)_2C_2]Co_2(CO)_6$ complex was recovered unchanged. However, as the concentration of 2-butyne approached zero, increasing amounts of $[(CH_3)_2C_2]Co_2(CO)_6$ were converted to $Co_4(CO)_{12}$ and $[(CH_3)_2C_2]Co_4(CO)_{10}$. Also, as the temperature was increased, there was a progressive decomposition of the $[(CH_3)_2C_2]Co_2(CO)_6$ complex and, in addition, an increase in the formation of hexamethylbenzene. The following amounts of hexamethylbenzene were obtained at the temperatures studied: undetectable amounts at 75 °C; 13 mg (9.6%) at 100 °C; 30 mg (22.5%) at 115 °C; 50 mg (43.2%) at 128 °C.

Finally, the direct reaction between $2,4\text{-}C_2B_5H_7$ and $[(CH_3)_2C_2]Co_2(CO)_6$ was examined. The reaction tube was charged with 30.0 mg (0.088 mmol) of $[(CH_3)_2C_2]Co_2(CO)_6$, 0.54 mmol of $2,4\text{-}C_2B_5H_7$, and 1.0 mL of pentane. The solution was heated at 100 °C for 1 h, after which time the contents were fractionated through −22, −78, and −196 °C traps. The −78 °C trap contained 5.8 mg (0.041 mmol) of the mono-*cis*-2-but-2-enyl derivatives of $2,4\text{-}C_2B_5H_7$. These were further separated by GLC on the TCP column at 80 °C to give compounds Ia, Ib, and Ic in a 1.18:1.04:1.00 ratio, respectively. The reaction tube contained 25.0 mg (0.044 mmol) of a mixture of

$Co_4(CO)_{12}$ and $[(CH_3)_2C_2]Co_4(CO)_{10}$.

1,5-$C_2B_3H_5$ and 2-Butyne. A 5-mL tube was charged with 0.10 mmol of $[(CH_3)_2C_2]Co_2(CO)_6$ (prepared in situ), 1.0 mmol of 1,5-$C_2B_3H_5$, 3.0 mmol of 2-butyne, and 1.0 mL of pentane. This solution was heated at 100 °C for 2 h, after which time the volatile materials were fractionated through −22, −78, and −196 °C traps. The −78 °C trap contained trace amounts of 2-(*cis*-2-but-2-enyl)-1,5-$C_2B_3H_4$ (VI), which was further purified on the TCP column. Exact mass: calcd for VI 116.1140; found 116.1139. The residue in the reaction tube was extracted with methylene chloride and evaporated onto ~10 g of silica gel, which was then added to a silica gel column and eluted with methylene chloride. This material was then separated by TLC using pentane eluant to give, in addition to small quantities of $Co_4(CO)_{12}$ and $[(CH_3)_2C_2]Co_4(CO)_{10}$, hexamethylbenzene ($R_f$ 0.50, trace) and 2,3,4-(*cis*-2-but-2-enyl)$_3$-1,5-$C_2B_3H_2$ (VII) (R_f 0.89, white crystalline solid, mp 50–51 °C). Anal. Calcd for VII: C, 75.15; H, 10.36. Found: C, 75.24; H, 10.44. Exact mass: calcd for VII 224.2079; found 224.2090.

1,5-$C_2B_3H_5$ and 1-Butyne. An experiment identical with the above except using 1-butyne and $[(CH_3CH_2)C_2H]Co_2(CO)_6$ in place of 2-butyne and $[(CH_3)_2C_2]Co_2(CO)_6$, respectively, was carried out. Examination of the volatile products and the residue in the reaction tube revealed the formation of the mono-2-(1-butenyl) derivatives of 1,5-$C_2B_3H_5$ (−78 °C trap) as the only boron-containing compounds. These were separated by GLC on the TCP column to give compounds VIIIa and VIIIb. Exact mass: calcd for VIIIa–b 116.1140; found VIIIa 116.1145, VIIIb 116.1141. No cobalt complexes were recovered; however, 55 mg of a liquid was retained in the −22 °C trap. This material was further separated by GLC on the OV-101 column at 90 °C to give several compounds. None of these contained any boron according to ^{11}B NMR spectra, and the predominent compound (68%) exhibited ^1H NMR and mass spectra that suggested it was 1,3,5-triethylbenzene.

1,5-$C_2B_3H_5$ and Acetylene. An experiment involving acetylene and $(H_2C_2)Co_2(CO)_6$ with 1,5-$C_2B_3H_5$ was performed in a manner similar to the above except that benzene was used as the solvent. Fractionation through −41, −78, −110, and −196 °C traps revealed a low yield of 2-(ethenyl)-1,5-$C_2B_3H_4$ (IX) in the −110 °C trap, which was further purified on the TCP column at 60 °C. More highly alkenylated products were not detected and no di- or tetracobalt complexes were recovered. Exact mass: calcd for IX 88.0827; found 88.0831.

1,6-$C_2B_4H_6$ and 2-Butyne. The 5-mL tube was charged with 0.10 mmol of $[(CH_3)_2C_2]Co_2(CO)_6$ (prepared in situ), 1.0 mmol of 1,6-$C_2B_4H_6$, 4.0 mmol of 2-butyne, and 1.0 mL of pentane. The solution was heated at 100 °C for 2 h, after which time all volatile material was fractionated through −22, −78, and −196 °C traps. The compound 2-(*cis*-2-but-2-enyl)-1,6-$C_2B_4H_5$ (X) was retained in the −78 °C trap, while the di-*cis*-2-but-2-enyl derivatives of 1,6-$C_2B_4H_6$ (XIa,b) were found in the −22 °C trap along with $[(CH_3)_2C_2]Co_2(CO)_6$. Little of the complex was recovered after the reaction, which was generally the case for experiments where a low alkyne concentration existed by the end of the reaction. Further separation and purification of the mono- and disubstituted derivatives were accomplished by GLC on TCP and OV-101 columns, respectively, as indicated in Table I. Anal. Calcd for X: C, 56.56; H, 9.49. Found: C, 55.23; H, 9.71. Calcd for XIa,b: C, 66.18; H, 10.00. Found for XIa: C, 67.72; H, 10.05. Exact mass: calcd for X 128.1311; found 128.1314; calcd for XIa,b 182.1781; found for XIa 182.1792, XIb 182.1786.

The residue remaining in the reaction tube was extracted with methylene chloride and separated on TLC plates (pentane eluant) to give, in addition to $Co_4(CO)_{12}$ and $[(CH_3)_2C_2]Co_4(CO)_{10}$, one major colorless band (R_f 0.62). Upon extraction and evaporation of solvent, this material was weighed (269.8 mg) and further separated by GLC on the OV-101 column at 130 °C to give, in addition to some residual disubstituted derivatives, the tri- and tetra-*cis*-2-but-2-enyl derivatives of 1,6-$C_2B_4H_6$, compounds XII and XIII listed in Table I, and hexamethylbenzene (40 mg, 0.25 mmol, R_v 1.0). Anal. Calcd for XII: C, 71.38; H, 10.27. Found: C, 71.20; H, 10.31. Calcd for XIII: C, 74.63; H, 10.44. Found: C, 74.26; H, 10.88. Exact mass: calcd for XII 236.2250; found 236.2253; calcd for XIII 290.2732; found 290.2751.

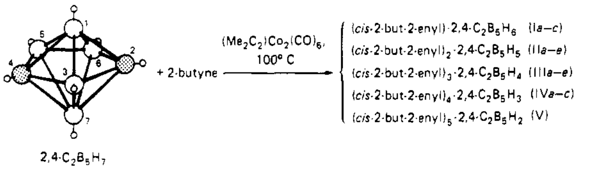
2,3-$C_2B_4H_8$ and 2-Butyne. Equimolar amounts (2.5 mmol) of 2,3-$C_2B_4H_8$ and 2-butyne were heated in the presence of 10 mol % $[(CH_3)_2C_2]Co_2(CO)_6$ at 100 °C for 2 h in 1.0 mL of pentane. Upon fractionation of the volatile material through −22, −78, and −196 °C traps, the three isomers of (*cis*-2-but-2-enyl)-2,3-$C_2B_4H_7$ were isolated in the −78 °C trap. These were further separated by GLC on the TCP column to give compounds XIVa–c listed in Table I. Much of the $[(CH_3)_2C_2]Co_2(CO)_6$ complex (~50%) was recovered in the −22 °C trap, and trace amounts of $Co_4(CO)_{12}$ and $[(CH_3)_2C_2]Co_2(CO)_6$ were left in the reaction tube. Exact mass: calcd for XIVa–c 130.1472; found for XIVa 130.1467, XIVb 130.1470, XIVc 130.1463.

Protonolysis Reactions. Onto 129.2 mg (0.58 mmol) of 2,3,4-(*cis*-2-but-2-enyl)$_3$-1,5-$C_2B_3H_2$ was charged 3.0 mL of glacial acetic acid. The mixture was stirred for 1 week 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 0.35 mmol (20% conversion) of 2-butene while acetic acid was retained in the −110 °C trap. The reaction vessel was extracted with pentane and filtered. Evaporation of the pentane extract gave 100.8 mg (0.45 mmol) of unreacted alkenylcarborane for a 92.3% yield of the 2-butene. 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]. The 2-butene was further identified by its mass spectrum and IR spectrum.

2,4-$C_2B_5H_7$ and 2-Butene. A 75-mL tube was charged with 0.10 mmol of $Co_2(CO)_8$, 1.0 mmol of 2,4-$C_2B_5H_7$, 5.0 mmol of 2-butene, and 2.0 mL of pentane. This solution was heated at 100 °C for 2 h, and then the volatile materials were fractionated through −22, −78, and −196 °C traps. Only unreacted starting reagents were found in the volatile materials, and no evidence for alkyl-substituted derivatives of 2,4-$C_2B_5H_7$ was obtained. A reaction similar to the above but replacing 2-butene with 2-butyne gave results analogous to those obtained for the reaction of 2,4-$C_2B_5H_7$ with 2-butyne in the presence of 10 mol % $[(CH_3)_2C_2]Co_2(CO)_6$.[8]

Results

2,4-$C_2B_5H_7$. In a typical reaction a 1.0:5.0:0.10 mixture of 2,4-$C_2B_5H_7$–2-butyne–$[(CH_3)_2C_2]Co_2(CO)_6$ was heated at 100 °C for 2 h in pentane and found to give a 100% conversion of the carborane into a mixture of its 17 possible boron-substituted 2-butenyl derivatives.



The mono-2-butenyl derivatives of 2,4-$C_2B_5H_7$ were isolated by vacuum-line fractionation and separated by GLC to give 1-(*cis*-2-but-2-enyl)-2,4-$C_2B_5H_6$ (Ia), 5-(*cis*-2-but-2-enyl)-2,4-$C_2B_5H_6$ (Ib), and 3-(*cis*-2-but-2-enyl)-2,4-$C_2B_5H_6$ (Ic) in a 1.15:1.05:1.00 ratio. The ^{11}B NMR spectra for these three compounds exhibit the proper resonances for the expected substitution and are identical,[10] except for slight differences in chemical shifts, with those of other similarly substituted derivatives of 2,4-$C_2B_5H_7$. Thus, singlets of intensity 1 that are observed at −10.4, 13.1, and 13.9 ppm are attributed to the substituted borons in compounds Ia, Ib, and Ic, respectively. The boron-decoupled proton NMR spectra are also consistent, showing expected resonances for the 2-butenyl group, cage CH protons, and all remaining BH groups. For example, the boron-decoupled proton NMR spectrum for 3-(*cis*-2-but-2-enyl)-2,4-$C_2B_5H_6$ (Ic) is shown in Figure 1 and is representative of these compounds. The cage proton resonances consist of two broad singlets of intensities 2:2 at 4.13 and 0.32 ppm, attributed to the hydrogens attached to borons

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(8) It has also been found that the analogous hydrosilation reactions of either 1-butene or 2-butene, which can be catalyzed by $Co_2(CO)_8$, are *not* catalyzed by $(R_2C_2)Co_2(CO)_6$ complexes.[22]

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

(10) (a) Grimes, R. N. *J. Am. Chem. Soc.* **1966**, *88*, 1895. (b) Dobbie, R. C.; Distefano, E. W.; Black, M.; Leach, J. B.; Onak, T. *J. Organomet. Chem.* **1976**, *114*, 233. (c) Plotkin, J. S.; Sneddon, L. G. *J. Am. Chem. Soc.* **1977**, *99*, 5194. (d) Plotkin, J. S.; Astheimer, R. J.; Sneddon, L. G. *Ibid.* **1979**, *101*, 4155.

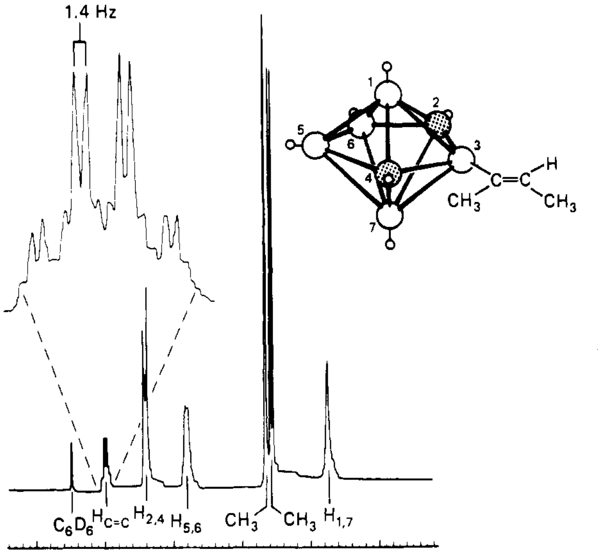


Figure 1. Boron-11 spin-decoupled ^{1}H NMR spectrum of 3-(*cis*-2-but-2-enyl)-2,4-$C_2B_5H_6$.

at positions 5,6 and 1,7, respectively, and a resonance of intensity 2 at 5.23 ppm assigned to the cage CH protons. This latter resonance exhibits fine structure that may result from coupling with either the adjacent 2-butenyl group or other cage protons. The resonances expected for the 2-butenyl group are also apparent in the spectrum, and the expansion of the vinylic hydrogen resonance (6.32 ppm; intensity 1) shows this resonance to consist of a quartet of quartets. The secondary coupling constant of 1.4 Hz is suggestive of the vinylic hydrogen being located trans to the methyl group on the α carbon.[9] This is consistent with the cis configuration of the butenyl substituent as previously found[1] for 2-(*cis*-2-but-2-enyl)-B_5H_8.

The remaining 2-butenyl derivatives of 2,4-$C_2B_5H_7$, compounds II–V, were extracted out of the reaction tube, separated from the tetracobalt complexes $Co_4(CO)_{12}$ and $[(CH_2)_2C_2]Co_4(CO)_{10}$ by TLC, and then separated from hexamethylbenzene and each other by GLC. All of these compounds are low volatile liquids, which slowly decompose upon exposure to air.

All five possible isomers of the di-*cis*-2-but-2-enyl boron-substituted derivatives (IIa–e) were observed in a 1.0:10.5:4.0:1.0:3.5 ratio along with the five triboron-substituted derivatives (IIIa–e) in a 1.0:8.5:8.5:75.5:8.5 ratio and the three tetraboron-substituted compounds (IVa–c) in a 1.0:9.5:2.7 ratio. Following extensive separations by TLC and GLC, compounds IIb, IIc, IIe, IIId, and IVb were obtained in sufficient quantities to allow collection of complete spectral data (Tables II, III, and IV), and their specific substitutions were assigned by using arguments similar to those outlined above for the monosubstituted derivatives. The remaining compounds were assigned the indicated substitutions from their boron-11 NMR spectra only, as indicated in Table II.

The pentasubstituted derivative, 1,3,5,6,7-(*cis*-2-but-2-enyl)$_5$-2,4-$C_2B_5H_2$ (V), exhibits a boron-11 NMR spectrum consisting of three singlets, of relative intensities 2:1:2, consistent with substitution of all borons in the molecule. Likewise, the boron-decoupled proton NMR spectrum does not show any resonances attributable to BH groups, while retaining the cage CH resonances of intensity 2 at 5.02 ppm. The butenyl resonances are apparent in this spectrum; however, these are too heavily overlapped to allow interpretation. Also in support of total boron substitution is the lack of any B–H stretching absorption in its infrared spectrum.

Table II. ^{11}B NMR Data for Alkenylcarboranes[a]

compd[b]	δ[c] (*J*, Hz; assignt)[d]	rel areas
Ia^{1}	8.5 (178; B3), 4.6 (178; B5, B6), −10.4 (s; B1), −26.8 (184; B7)	1:2:1:1
Ib^{1}	13.1 (s; B5), 7.4 (180; B3), 2.9 (189; B6), −19.7 (178; B1, B7)	1:1:1:2
Ic^{1}	13.9 (s; B3), 4.1 (173; B5, B6), −18.8 (178; B1, B7)	1:2:2
IIa^{1}	11.0 (s; B5, B6), 5.5 (173; B3), −19.3 (178; B1, B7)	2:1:2
IIb^{1}	11.9 (s; B5), 7.2 (178; B3), 1.5 (173; B6), 10.4 (s; B1), −25.9 (180; B7)	1:1:1:1:1
IIc^{1}	14.5 (s; B3), 4.3 (173; B5, B6), −9.2 (s; B1), −24.5 (178; B7)	1:2:1:1
IId^{1}	8.6 (160; B3), 4.1 (160; B5, B6), −17.2 (s; B1, B7)	1:2:2
IIe^{1}	11.7 (s; B3, B5), 0.2 (173; B6), −19.2 (176; B1, B7)	2:1:2
IIIa^{1}	9.1 (s; B5, B6), 6.5 (189; B3), −11.0 (s; B1), −26.1 (178; B7)	2:1:1:1
IIIb^{1}	11.7 (s; B5), 9.7 (178; B3), 2.1 (173; B6), −15.2 (s; B1, B7)	1:1:1:2
IIId^{1}	13.7 (s; B3, B5), 2.1 (173; B6), −8.4 (s; B1), −22.9 (178; B7)	2:1:1:1
IIIe^{1}	10.8 (s; B3, B5, B6), −17.0 (178; B1, B7)	3:2
IVa^{1}	13.7 (s; B5, B6), 2.1 (173; B3), −13.2 (s; B1, B7)	2:1:2
IVb^{1}	13.3 (s; B3, B5), 2.1 (167; B6), −13.8 (s; B1, B7)	2:1:2
IVc^{1}	10.5 (s; B3, B5, B6), −8.4 (s; B1), −22.5 (178; B7)	3:1:1
V^{1}	10.2 (s; B5, B6), 8.4 (s; B3), −22.5 (s; B1, B7)	2:1:2
VI^{2}	9.0 (190; B3, B4), 7.5 (s; B2)	2:1
VII^{1}	18.5 (s; B2, B3, B4)	1
VIIIa^{3}	8.0 (190; B3, B4), 6.8 (s; B2)	2:1
VIIIb^{3}	8.5 (181; B3, B4), 5.8 (s; B2)	2:1
IX^{2}	8.5 (172; B3, B4), 5.9 (s; B2)	2:1
X^{1}	−8.1 (s; B2), −17.2 (190; B3, B5), −23.9 (193; B4)	1:2:1
XIa^{1}	−7.1 (s; B2, B3), −21.3 (187; B4, B5)	1:1
XIb^{1}	−12.6 (s; B2, B4), −15.2 (176; B3, B5)	1:1
XII^{1}	−5.4 (s; B3), −10.7 (s; B2, B4), −18.8 (182; B5)	1:2:1
XIII^{1}	−11.0 (s; B2, B3, B4, B5)	1
XIVa^{2}	−1.0 (153; B4, B5, B6), −41.1 (s; B1)	3:1
XIVb^{2}	14.2 (s; B5), −3.4 (158; B4, B6), −51.9 (180; B1)	1:2:1
XIVc^{2}	9.7 (s; B4), −2.4 (158; B5, B6), −51.9 (180; B1)	1:2:1

[a] Spectra for compounds VI, VIIIa, VIIIb, and X were obtained at 115.5 MHz. All other spectra were obtained at 32.1 MHz. [b] Key: (1) run in CS_2 with C_6D_6 lock; (2) run in C_6D_6; (3) run in $CDCl_3$. [c] All chemical shifts are relative to external $BF_3\cdot O(C_2H_5)_2$; a negative sign indicates an upfield shift. [d] s = singlet.

The direct reaction of liquid 2,4-$C_2B_5H_7$ with $[(CH_3)_2C_2]Co_2(CO)_6$ at 100 °C was also examined, and it was found that under these conditions the dicobalt complex is quantitatively converted to $Co_4(CO)_{12}$ and $[(CH_3)_2C_2]Co_4(CO)_{10}$ according to

$$[(CH_3)_2C_2]Co_2(CO)_6 + 2,4\text{-}C_2B_5H_7 \xrightarrow{100\ ^\circ C} {}^{1}/_{2}[\text{Ia, Ib, Ic}] + {}^{1}/_{2}\{Co_4(CO)_{12}, [(CH_3)_2C_2]Co_4(CO)_{10}\} + \text{unreacted } 2,4\text{-}C_2B_5H_7$$

This result is consistent with our observation that the formation of the two tetracobalt complexes in the catalytic reactions is important only when the alkyne concentration is depleted in those reactions.

In an effort to determine ideal conditions for the catalyzed system and to possibly gain some insight into the mechanism of the reactions, 2-butyne and 2,4-$C_2B_5H_7$ were reacted in the presence of $[(CH_3)_2C_2]Co_2(CO)_6$ under varying conditions. The variables that were investigated included solvent, temperature, and catalyst and reactant proportions. The results of these investigations are presented in Table V.

Table III. ^{1}H NMR Data

2-Butenyl Derivatives

	δ^{b} (cage position)					
compd^{a}	vinyl α-CH_3^{c}	vinyl β-CH_3^{d}	vinyl H^{e}	cage CH	B-H^{f}	rel areas
Ia^{1}	1.28 (1)	1.47 (1)	5.25 (1)	5.54 (2,4)	4.95 (3), 4.24 (5,6), 0.08 (7)	3:3:1:2:1:2:1
Ib^{1}	1.93 (5)	1.76 (5)	6.07 (5)	5.28 (2,4)	4.84 (3), 4.05 (6), 0.32 (1,7)	3:3:1:2:1:1:2
Ic^{1}	1.96 (3)	1.80 (3)	6.32 (3)	5.23 (2,4)	4.13 (5,6), 0.32 (1,7)	3:3:1:2:2:2
IIa^{1}	1.92 (5,6)	1.80 (5,6)	5.92 (5,6)	5.05 (2,4)	4.75 (3), 0.57 (1,7)	6:6:2:2:1:2
IIb^{1}	2.04 (5), 1.32 (1)	1.82 (5), 1.45 (1)	6.15 (5), 5.35 (1)^{h}	5.35 (2,4)	4.89 (3), 4.13 (6), 0.28 (7)	3:3:3:3:1:3:1:1:1
IIc^{1}	2.02 (3), 1.29 (1)	1.87 (3), 1.47 (1)	6.35 (5), 5.34 (1)^{h}	5.34 (2,4)	4.20 (5,6), 0.28 (7)	3:3:3:3:1:3:2:1
IIe^{1}	2.03, 1.95 (3,5)	1.85, 1.77 (3,5)	6.35 (3), 6.09 (5)	5.18 (2,4)	3.89 (6), 0.39 (1,7)	3:3:3:3:1:1:2:1:2
IIId^{1}	2.07, 2.02 (3,5), 1.35 (1)	1.84 (3,5), 1.46 (1)	6.26 (3,5), 5.24 (1)^{h}	5.24 (2,4)	4.12 (6), 0.51 (7)	3:3:3:6:3:2:3:1:1
IVb^{1}	2.01 (3,5), 1.28 (1,7)	1.91 (3), 1.80 (5), 1.45 (1,7)	6.31 (3), 6.09 (5), 5.23 (1,7)^{h}	5.23 (2,4)	4.00 (6)	6:6:3:3:6:1:1:4:1
V^{1}	1.39 (1,7), 2.01-1.78 (3,5,6)^{g}	1.48 (1,7), 2.01-1.78 (3,5,6)	6.29 (3), 6.00 (5,6), 5.35 (1,7)	5.02 (2,4)		6:18:6:1:2:2:2
VI^{2}	1.71 (2)	1.63 (2)	6.09 (2)	5.24 (1,5)	4.48 (3,4)	3:3:1:2:2
VII^{1}	1.88 (2,3,4)	1.71 (2,3,4)	6.32 (2,3,4)	4.59 (1,5)		9:9:3:2
X^{1}	1.68 (2)	1.61 (2)	5.84 (2)	2.93 (1,6)	2.05 (3,5), 1.99 (4)	3:3:1:2:2:1
XIa^{1}	1.76 (2,3)	1.69 (2,3)	5.79 (2,3)	3.13 (1,6)	2.10 (4,5)	6:6:2:2:2
XIb^{1}	1.74 (2,4)	1.67 (2,4)	5.80 (2,4)	3.00 (1,6)	2.06 (3,5)	6:6:2:2:2
XII^{1}	1.80-1.69 (2,3,4)^{g}	1.80-1.69 (2,3,4)	5.86 (2,3,4)	3.14 (1,6)	2.22 (5)	18:3:2:1
XIII^{1}	1.73 (2,3,4,5)	1.70 (2,3,4,5)	5.77 (2,3,4,5)	3.18 (1,6)		12:12:4:2
XIVa^{2}	1.44 (1)	1.48 (1)	5.37 (1)	6.45 (2,3)	3.76 (4,5,6), −1.74 (BHB)	3:3:1:2:3:2
XIVb^{2}	1.85 (5)	1.62 (5)	6.04 (5)^{h}	6.04 (2,3)	3.72 (4,6), −0.52 (1), −1.01 (BHB)	3:3:3:2:1:2
XIVc^{2}	1.87 (4)	1.74 (4)	5.97 (4)^{h}	5.97 (2,3)	3.60 (5,6), −0.56 (1), −1.16 (BHB)	3:3:3:2:1:1
					−2.02 (BHB)	1

1-Butenyl Derivatives

	δ^{b} (J,^{i} Hz; assignt)				
compd^{a}	H_3C-CH_2-	vinyl H	cage CH	B-H^{f}	rel areas
VIIIa^{3}	2.16 (q, 7.3; CH_2), 0.96 (t, 7.3; CH_3)	5.51 (m; H_1 and H_2)	5.30 (t, 1.9)^{j}	4.21 (s; B3, B4)	2:3:2:2:2
VIIIb^{3}	2.14 (q, 7.3; CH_2), 0.99 (t, 7.3; CH_3)	6.50 (d of t, J_{1-2} = 17.5, J_{2-3} = 5.9; H_2), 5.64 (d of t, J_{1-2} = 17.5, J_{1-3} = 1.4; H_1)	5.22 (t, 1.9)^{j}	4.18 (s; B3, B4)	2:3:1:1:2:2

Ethenyl Derivatives

	δ^{b}		
compd^{a}	vinyl H	cage H (assignt)^{f}	rel areas
IX^{1}	5.90^{k}	5.25 (C1, C5), 4.37 (B3, B4)	3:2:2

[a] Key: (1) run in CS_2 with C_6D_6 lock; (2) run in C_6D_6; (3) run in $CDCl_3$. [b] All chemical shifts are relative to $(CH_3)_4Si$; negative sign indicates an upfield shift. [c] All resonances are singlets. [d] All resonances are doublets ($J \simeq 7.0$ Hz). [e] Unless heavily overlapped, these resonances appear as a quartet of quartets where primary coupling ($J_{\beta\text{-}CH_3\text{-}H}$) is ~7 Hz and secondary coupling ($J_{\alpha\text{-}CH_3\text{-}H}$) is ~2 Hz.

[f] Terminal and bridging BH resonances were observed as broad singlets with the appropriate ^{11}B spin decoupling. [g] Heavy overlap of methyl resonances. [h] Coincidental overlap of vinyl proton resonance with cage CH proton resonances in spectrum. [i] s = singlet; br s = broad singlet; d = doublet; t = triplet; q = quartet; m = multiplet. [j] Coupling due to terminal B-H protons. [k] Complex multiplet of which this resonance corresponds to the largest peak.

It is apparent from the data given in the table that both the rate of reaction and the degree of substitution can be controlled by the reaction conditions. Both the carborane and catalyst concentrations directly affected the rate of reaction, but the alkyne concentration (as long as it was not totally depleted) appeared to have no effect. It was also found that, until a maximum temperature of 115 °C was reached, an increase in temperature caused an increase in rate and the production of more highly substituted products. For example, at 75 °C only monosubstituted products are obtained at a low rate, while at 115 °C there was 100% conversion of the carborane in the 2-h reaction (~40 catalyst turnovers) with the products consisting of mostly more highly substituted products. It is also significant that at 75 °C the cobalt complex can be essentially completely recovered at the end of the reaction, while at higher temperatures some catalyst decomposition occurs, along with a progressive increase in the production of hexamethylbenzene. For example, at 128 °C 40% of the 2-butyne was cyclized, whereas at 115 °C only 20% was cyclized and at 100 °C below 10% was cyclized; at 75 °C no hexamethylbenzene was formed.

1,5-$C_2B_3H_5$. Heating a 1.0:3.0:0.10 mixture of 1,5-$C_2B_3H_5$–2-butyne–$[(CH_3)_2C_2]Co_2(CO)_6$ at 100 °C for 2 h in 1.0 mL of pentane resulted in a 77% conversion of this carborane into the two 2-butenyl derivatives 2-(*cis*-2-but-2-enyl)-1,5-$C_2B_3H_4$ (VI) and 2,3,4-(*cis*-2-but-2-enyl)$_3$-1,5-$C_2B_3H_2$ (VII) in a 4:96 ratio, respectively. This conversion and product distribution correspond to 22 turnovers for the catalyst in the 2-h period.

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

Ia[a,b,e]	3695 m, 2958 s, sh, 2915 s, 2855 s, 2615 vs, 1635 m, 1600 s, 1375 s, 1280 m, br, 1105 m, 1050 m, br, 970 w
Ib[a,b]	3695 m, 3090 w, 2970 m, sh, 2910 s, 2845 s, 2620 vs, 1630 s, 1600 m, 1530 m, 1380 m, 1345 m, 1295 s, 1165 w, 1110 m, 1048 m, br, 988 w, 965 w, 897 w, 866 w, 598 w, 537 w
Ic[a,b]	3695 m, 3085 w, 2975 m, sh, 2910 s, 2850 m, 2610 vs, 1710 w, 1635 s, 1605 m, 1445 w, sh, 1380 s, 1350 s, 1325 s, 1162 w, sh, 1138 w, 1050 m, br, 942 w, 902 w, 572 w
IIb[a,c]	3693 w, 3005 m, sh, 2915 s, 2860 s, 2618 vs, 1633 s, 1603 w, 1495 w, 1415 m, 1373 m, 1334 w, 1285 s, sh, 1177 vs, br, 1098 m, 1030 m, br, 985 w, 961 w, 917 w, 850 w, br, 685 vs, br, 663 vs, 650 vs, 624 s, sh, 575 w, 524 w
IIc[a,c]	3695 w, 2975 m, sh, 2910 s, 2855 s, 2609 vs, 2595 vs, sh, 1629 s, 1597 w, 1420 m, br, 1368 s, 1339 s, 1313 s, 1250 m, br, 1124 w, 1095 m, 1030 m, br, 925 m, 874 w, 621 s
IIe[a,c]	3007 m, sh, 2971 m, 2918 s, 2862 m, 2610 vs, 1634 s, 1437 m, 1375 m, 1346 s, 1321 s, 1287 w, 1155 m, 1105 w, 1045 s, 1000 w, sh, 845 w, sh, 819 m, 588 w
IIId[a,b]	3695 w, 2987 w, sh, 2914 s, 2855 s, 2610 s, 2327 m, 1630 s, 1605 w, sh, 1427 m, sh, 1376 s, 1347 s, 1327 s, 1102 m, 1035 m, br, 578 m, 559 w
IVb[a,c]	2913 s, 2880 s, sh, 2858 s, 2590 m, 2333 m, 1630 vs, 1600 w, sh, 1437 m, 1370 s, 1345 s, 1313 s, 1280 m, br, 1148 w, 1098 s, 1050 m, 988 w, 629 m, sh, 585 s, 567 m, sh
V[a,b]	3685 w, 2980 w, sh, 2949 m, sh, 2908 vs, 2850 s, 1850 w, 1635 s, 1600 w, sh, 1430 m, 1375 s, 1345 s, 1320 s, 1152 m, 1105 s, 1046 s, br, 974 m, br, 852 w, 805 w, 578 s
VI[c,d]	3025 m, 2975 m, 2930 s, 2872 m, 2605 vs, 1625 s, 1439 w, 1379 s, 1343 s, 1317 m, 1265 w, 1230 w, 1199 w, 1090 vs, 1057 m, sh, 1020 w, sh, 950 w, 888 m, 850 w, 800 w
VII[a,b]	2980 w, sh, 2910 vs, 2800 s, 1850 w, 1750 w, 1620 vs, 1435 m, sh, 1375 vs, 1340 vs, 1320 vs, 1250 s, br, 1129 vs, 1057 s, br, 1000 m, sh, 970 w, 940 w, 920 w, 780 w, br, 640 w, br, 456 w
VIIIa[c,d]	3072 m, 2980 vs, 2940 m, 2891 m, 2609 vs, 1880 w, 1613 m, 1445 m, 1406 s, 1342 s, 1315 w, sh, 1247 w, 1200 w, 1145 s, 1100 vs, 1050 w, sh, 957 m, sh, 933 s, 890 s, 854 m, 800 w, 780 w, sh
VIIIb[c,d]	3010 m, sh, 2980 s, 2947 m, sh, 2890 m, 2867 m, sh, 2607 vs, 1635 s, 1458 w, 1365 m, 1337 s, 1305 m, 1261 w, 1187 s, 1095 s, 1010 w, 977 m, 885 m, 855 w, 802 vw, 764 vw
IX[c,d]	3076 s, 3000 m, sh, 2975 s, 2935 w, sh, 2893 w, 2605 vs, 1967 w, 1615 m, sh, 1609 m, 1603 m, sh, 1423 vs, 1333 m, sh, 1310 s, 1264 s, 1195 vs, 1090 vs, 1043 w, 1027 m, 1020 m, 1000 m, 955 s, 891 s, 883 s, 875 m, sh, 855 m, 850 m, 802 w, sh, 794 w, 742, w, 684 w, 664 w
X[a,c]	2980 w, sh, 2902 s, 2848 s, 2630 vs, 1888 w, 1619 s, 1590 w, sh, 1422 s, br, 1360 s, 1330 s, 1300 s, 1118 s, 1088 s, 1048 w, 1000 w, 970 w, 885 w, 840 w, 806 w, 609 w, 480 m, sh, 447 s, 417 m, sh
XIa[a,c]	2950 m, sh, 2912 s, 2855 s, 2639 s, 1850 w, 1628 s, 1427 s, br, 1368 s, 1343 s, 1292 s, 1131 s, 1083 m, 1060 w, sh, 1006 w, 855 w, 810 w, 510 w, 435 m
XIb[a,c,e]	2955 m, sh, 2912 s, 2855 m, 2638 s, 1629 s, 1592 w, 1420 s, br, 1366 s, 1330 s, br, 1128 s, 1050 s, br
XII[a,b]	3690 w, 2985 w, sh, 2915 s, 2855 s, 2640 m, 1850 w, 1635 s, 1600 m, 1425 m, sh, 1377 s, 1353 s, 1328 s, 1300 m, 1145 s, 1065 m, br, 870 w, 808 w, br, 647 w, 536 w, 442 w
XIII[a,b]	3695 m, 2980 w, sh, 2940 s, sh, 2920 vs, 2850 s, 1805 w, 1630 s, 1600 s, 1410 m, sh, 1375 s, 1345 s, 1320 m, 1146 s, 1060 w, 800 w
XIVa[a,c]	2980 m, sh, 2965 m, 2914 s, 2858 m, 2583 vs, 1920 m, br, 1629 m, 1484 s, 1430 s, 1367 m, 1339 m, 1240 w, br, 1100 s, 1050 s, 1020 m, sh, 998 w, 968 w, 907 m, 885 m, 810 w
XIVb[a,c]	2970 m, sh, 2920 s, 2860 m, 2605 vs, sh, 2585 vs, 1960 m, br, 1633 s, 1428 s, br, 1367 m, 1335 w, sh, 1080 m, sh, 1043 s, br, 996 m, sh, 967 w, 920 w, br, 846 w, 606 m, 505 m
XIVc[a,c]	2970 m, 2930 s, sh, 2916 s, 2860 m, 2600 vs, 1900 w, 1866 w, 1625 s, 1592 w, 1482 s, 1467 m, sh, 1426 w, 1365 m, 1350 m, 1087 w, 1055 m, 968 m, 945 s, 932 m, sh, 880 m, 851 m, 812 w, 620 m, 602 m, 581 m, 506 m, 424 w

[a] Solution ($CHCl_3$); NaCl windows. [b] Run on Perkin-Elmer 337 grating infrared spectrophotometer. [c] Run on Perkin-Elmer 521 grating infrared spectrophotometer. [d] Gas sample; 10-cm length, 2-cm. o.d., NaCl windows. [e] Very weak spectrum.

The monosubstituted product, VI, was isolated by vacuum-line fractionation and purified by GLC to give a volatile liquid. The ^{11}B NMR spectrum (Table II) is characteristic[10a,b] of mono-B-substituted derivatives of 1,5-$C_2B_3H_5$. All expected cage hydrogens and protons associated with the 2-butenyl group are observed in the proton NMR and are assigned in Table III.

The trisubstituted derivative was extracted from the reaction tube along with the tetracobalt complexes, $Co_4(CO)_{12}$ and $[(CH_3)_2C_2]Co_4(CO)_{10}$, and minor quantities of hexamethylbenzene. These were separated on TLC plates to give VII as a white crystalline solid, which decomposes in air upon exposure for extended periods of time. Substitution of all three boron atoms is apparent from the ^{11}B NMR spectrum, which consists of a singlet at 18.5 ppm. The expected equivalency of the three 2-butenyl groups is supported by the boron-decoupled proton NMR spectrum (Table III), where a quartet of intensity 3, a singlet of intensity 9, and a doublet of intensity 9 are observed at 6.32, 1.88, and 1.71 ppm, respectively. Substitution of all three borons is also confirmed by the absence of any BH resonances and the observation of a sharp singlet of intensity 2 at 4.59 ppm attributable to the cage CH protons. Furthermore, the BH stretching band in the infrared spectrum (Table IV) of this compound is absent. Reaction of this compound with acetic acid generates 2-butene with a 98.6% cis purity.

Heating a 1.0:3.0:0.10 mixture of 1,5-$C_2B_3H_5$–1-butyne–$[(CH_3CH_2)C_2H]Co_2(CO)_6$ at 100 °C for 2 h in pentane gave a 27% conversion of 1,5-$C_2B_3H_5$ into an isomeric mixture of the monosubstituted 1-butenyl derivatives. This corresponded to a turnover frequency of less than 1.4 times/h for the $[(CH_3CH_2)C_2H]Co_2(CO)_6$ complex. The 1-butenyl derivatives were separated by vacuum-line fractionation and GLC to give 2-(2-but-1-enyl)-1,5-$C_2B_3H_4$ (VIIIa) and 2-(*trans*-1-but-1-enyl)-1,5-$C_2B_3H_4$ (VIIIb) in 62% and 38% relative yields, respectively.

Both compounds exhibit boron-11 NMR data similar to those of the mono-2-butenyl derivative of this carborane discussed above. The boron-11 spin-decoupled proton NMR spectra are also supportive of the proposed structures, where both the appropriate cage hydrogen resonances are observed, as well as the resonances associated with the butenyl group. For VIIIa, resonances at 2.16 (q; CH_2) and 0.96 ppm (t; CH_3) clearly define the ethyl group present in the 1-butenyl substituent and a single resonance at 5.51 ppm (m; 2 CH) is assignable to the 2 *gem* vinylic protons, which show small coupling. For VIIIb, the expected ethyl resonances, 2.14 (q;

Table V. Catalyzed Reaction of 2,4-$C_2B_5H_7$ with 2-Butyne under Various Conditions[a]

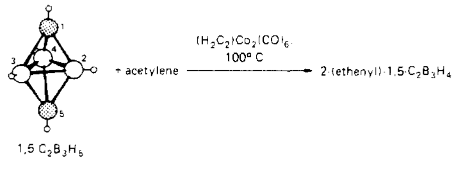
		rel yields,[c] %				
variable	conversion,[b] %	$RC_2B_5H_6$	R_2C_2-B_5H_5	R_3C_2-B_5H_4	R_4C_2-B_5H_3	R_5C_2-B_5H_2
mmol of 2,4-$C_2B_5H_7$						
0.5[d]	17	100	0	0	0	0
1.0[d]	17	100	0	0	0	0
mmol of 2-butyne						
0.5[e]	52	77	12	9	2	0
1.2	70	46	27	21	6	0
2.5	72	42	25	24	9	0
mol % catalyst[b]						
2	46	81	15	4	0	0
10	72	42	25	24	9	0
temp,[f] °C						
75[g]	17	100	0	0	0	0
100	72	42	25	24	9	0
115[e]	100	0	3	16	60	21
128[e]	98	10	21	29	34	6
solvent						
none[e]	77	20	28	32	19	1
pentane	72	42	25	24	9	0
hexane	91	27	28	29	15	1
THF	100	13	20	40	25	2
benzene	100	4	30	39	24	3

[a] Unless otherwise indicated the following conditions were employed: carborane, 0.5 mmol; alkyne, 2.5 mmol; $(CH_3)_2C_2Co_2(CO)_6$, 0.05 mmol; 1.0 mL of pentane at 100 °C for 2 h. [b] Based on carborane. Yields based on consumed 2,4-$C_2B_5H_7$ were 100%. [c] Determined from peak areas (uncorrected for response factor differences), which were determined by triangulation; monosubstituted derivatives were directly weighed after purification by vacuum-line fractionation. [d] Experiment run at 75 °C. [e] No $(CH_3)_2C_2Co_2(CO)_6$ remained; however, some $Co_4(CO)_{12}$ and $(CH_3)_2C_2Co_4(CO)_{10}$ were formed. [f] Hexamethylbenzene was formed accordingly: 75 °C, not detectable; 100 °C, 13 mg (0.08 mmol); 115 °C, 30 mg (0.19 mmol); 128 °C, 59 mg (0.36 mmol). [g] All $(CH_3)_2C_2Co_2(CO)_6$ was recovered. For other reactions not marked *e*, this complex was recovered in part and some of the tetracobalt complexes were formed.

CH_2) and 0.99 ppm (t; CH_3), are again observed, and resonances at 6.50 (d of t; CH) and 5.64 ppm (d of t; CH) are attributed to the trans vinylic protons, where the large primary coupling constants of 17.5 Hz indicate[9] trans location of these atoms in relation to each other.

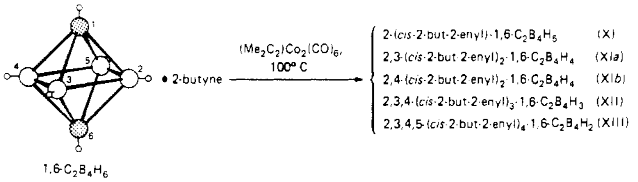
Also obtained from this reaction were substantial quantities of an organic liquid of low volatility, which consisted predominantly of 1,3,5-triethylbenzene (0.23 mmol; 23.1% conversion from 1-butyne). No $[(CH_3CH_2)C_2H]Co_2(CO)_6$ was recovered from this reaction, and no evidence for either $Co_4(CO)_{12}$ or $[(CH_3CH_2)C_2H]Co_4(CO)_{10}$ was obtained from the reaction tube; however, the tube did contain dark solids, which immediately decomposed on silica gel in air.

A reaction similar to the above was carried out when a 1.0:3.0:0.10 mixture of 1,5-$C_2B_3H_5$–acetylene–$(H_2C_2)Co_2(CO)_6$ in 1.0 mL of benzene was heated at 100 °C for 2 h. Fractionation of the volatile products revealed a 5% conversion of 1,5-$C_2B_3H_5$ into 2-(ethenyl)-1,5-$C_2B_3H_4$ (IX).



Compound IX was further purified by GLC to give a highly volatile liquid. The boron-11 NMR spectrum is identical with those of the other mono-B-substituted derivatives discussed above where substitution at the B2 position is evidenced by the observation of a singlet of intensity 1 at 5.9 ppm. The boron-decoupled proton NMR spectrum is also consistent with the above assignment where all expected cage protons are observed, and a multiplet of intensity 3 at 5.90 ppm is attributed to the ethenyl hydrogens. The splitting pattern of the latter resonance is similar to that observed for the ethenyl resonances of 2-(ethenyl)-B_5H_8 (I).[1]

1,6-$C_2B_4H_6$. Heating a 1.0:4.0:0.10 mixture of 1,6-$C_2B_4H_6$–2-butyne–$[(CH_3)_2C_2]Co_2(CO)_6$ at 100 °C for 2 h in 1.0 mL of pentane resulted in an 89% conversion of this carborane into a mixture of mono- through tetrasubstituted 2-butenyl derivatives:



Compound X accounted for 5.7% of this mixture and was isolated by vacuum-line fractionation and GLC as a liquid of moderate volatility. The boron-11 NMR spectrum is consistent with the proposed formula exhibiting doublets at −17.2 and −23.9 ppm and a singlet at −8.1 ppm of relative intensities 2:1:1, respectively. This spectrum is similar to other[10a,b] B-substituted derivatives of 1,6-$C_2B_4H_6$. Likewise, the boron-11 spin-decoupled proton NMR spectrum is compatible with the above assignment where resonances for the 2-butenyl group are observed at 5.84 (q; vinylic CH), 1.68 (s; CH_3), and 1.61 ppm (d; CH_3) and broad resonances at 2.05 (intensity 2) and 1.99 ppm (intensity 1) are assignable to the B3, B5 and to the B4 hydrogens, respectively. In addition, a singlet of intensity 2 at 2.93 ppm attributed to the cage CH groups confirms that substitution does not occur on the cage carbon atoms.

The di-*cis*-2-but-2-enyl derivatives XIa and XIb were isolated from the remaining products by vacuum-line fractionation and then further separated by GLC to give relative yields of 3.5% and 1.7%, respectively. The boron-11 spin-decoupled proton NMR spectra (Table III) for both compounds are identical. Each exhibits one set of resonances (quartet of intensity 2; doublet of intensity 6; singlet of intensity 6) for the two equivalent butenyl groups, one broad singlet of intensity 2 for the equivalent BH groups, and one singlet of intensity 2 for the equivalent CH hydrogens in each compound. Since chemical shifts of these resonances are similar, these compounds cannot be readily differentiated by proton NMR spectra. The ^{11}B NMR spectra for each compound are also similar where XIa exhibits a singlet of intensity 2 at −7.1 ppm and a doublet of intensity 2 at −21.3 ppm and XIb shows a singlet of intensity 2 at −12.6 ppm and a doublet of intensity 2 at −15.2 ppm. The specified structural assignments for XIa (2,3 isomer) and XIb (2,4 isomer) were made on the basis of chemical shift additivity relationships that have been proposed for this and other cage systems.[11]

The remaining products, 2,3,4-(*cis*-2-but-2-enyl)$_3$-1,6-$C_2B_4H_3$ (XII) and 2,3,4,5-(*cis*-2-but-2-enyl)$_4$-1,6-$C_2B_4H_2$ (XIII) (along with residual XIa and XIb), were extracted out of the reaction tube, separated from $Co_4(CO)_{12}$ and $[(CH_3)_2C_2]Co_4(CO)_{10}$ by TLC, and then further separated from hexamethylbenzene (0.25 mmol, 19% yield based on 2-butyne)

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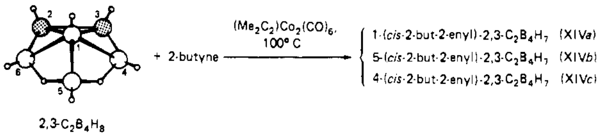
(11) (a) Takimot, C.; Siwapinyoyos, G.; Fuller, K.; Fung, A. P.; Liauw, L.; Jarvis, W.; Millhauser, G.; Onak, T. *Inorg. Chem.* **1980**, *19*, 107. (b) Ditter, J. F.; Klausman, E. B.; Williams, R. E.; Onak, T. *Ibid.* **1976**, *15*, 1063. (c) Onak, T.; Fung, A. P.; Siwapinyoyos, G.; Leach, J. B. *Ibid.* **1979**, *18*, 2878. (d) Tucker, P. M.; Onak, T.; Leach, J. B. *Ibid.* **1970**, *9*, 1430.

and each other by GLC to give liquids of low volatility in 13.8% and 75.9% relative yields, respectively. The spectral data for each compound are consistent with their formulations and are assigned in the tables.

Little $[(CH_3)_2C_2]Co_2(CO)_6$ is recovered from this reaction, which is consistent with the depletion of free alkyne and the formation of $Co_4(CO)_{12}$ and $[(CH_3)_2C_2]Co_4(CO)_{10}$. The overall conversion and product distribution for this reaction correspond to 32 turnovers for the catalyst during the 2-h reaction.

2,3-$C_2B_4H_8$. Heating equimolar amounts of 2-butyne and 2,3-$C_2B_4H_8$ at 100 °C for 1 h in the presence of 10 mol % $[(CH_3)_2C_2]Co_2(CO)_6$ gives a 33% conversion of this carborane into an isomeric mixture of boron-substituted 2-butenyl derivatives of 2,3-$C_2B_4H_8$ (XIVa–c). This conversion corresponds to 3.3 turnovers for the $[(CH_3)_2C_2]Co_2(CO)_6$ complex in the 1-h reaction time. The 2-butenyl derivatives of 2,3-$C_2B_4H_8$ were separated by vacuum-line fractionation and GLC to give 1-(*cis*-2-but-2-enyl)-2,3-$C_2B_4H_7$ (XIVa), 5-(*cis*-2-but-2-enyl)-2,3-$C_2B_4H_7$ (XIVb), and 4-(*cis*-2-but-2-enyl)-2,3-$C_2B_4H_7$ (XIVc) in a 1.00:1.07:3.88 ratio, respectively.



The ^{11}B NMR spectrum (Table II) for XIVa is characteristic[12,13] of apex-substituted 2,3-$C_2B_4H_8$ derivatives showing a singlet of intensity 1 at −41.1 ppm due to the substituted B1 position. The remainder of the spectrum consists of a doublet of intensity 3 at −1.0 ppm attributed to the 4,5,6 BH groups. The expected inequivalency of the B5 position compared to the B4, B6 groups is not evident in the spectrum; however, this coincidental overlap is also observed[13] for the parent carborane. Likewise, the boron-11 spin-decoupled proton NMR spectrum shows, in addition to the 2-butenyl resonances, one broad singlet at 3.76 ppm attributable to the 4,5,6 BH groups and a broad singlet at −1.74 ppm assignable to the two equivalent bridging protons. Also present is the expected cage CH resonance at 6.54 ppm. For this compound, the butenyl resonances are considerably shifted upfield when compared to the 2-butenyl resonances in the other isomers. An upfield shift is in agreement with predictions based on ring-current calculations[12] for the 2,3-$C_2B_4H_8$ cage. For example, the CH_3 resonance of 1-methyl-substituted 2,3-$C_2B_4H_8$[12] also appears considerably upfield in comparison to the 4- or 5-methyl-substituted compounds.

The remaining two isomers, XIVb and XIVc, exhibit similar resonances in the ^{11}B NMR spectra, where singlets of intensity 1 at 14.2 and 9.7 ppm for compounds XIVb and XIVc, respectively, indicate[12,13] substitution of the basal boron positions. These compounds are readily differentiated in their boron-decoupled proton NMR spectra by examination of the resonances associated with the bridging protons, which are assigned in Table III. For XIVb, this resonance appears as a broad singlet of intensity 2, which indicates that the plane of symmetry observed for the parent molecule is retained in this derivative. This is accomplished through attachment of the 2-butenyl group to the B5 position. For XIVc, the resonances due to bridge protons appear as two broad singlets each of intensity 1 indicating a destruction of the plane of symmetry, which is accomplished through attachment of the 2-butenyl group at the B4 position.

Discussion

The results presented above demonstrate that the μ-acetylene complexes $(RC_2R')Co_2(CO)_6$ catalyze the insertions of acetylenes into the boron–hydrogen bonds of various small carboranes to give the corresponding alkenylcarborane derivatives. Only one such small carborane compound, 2-(propenyl)-1,5-$C_2B_3H_5$, was previously known,[14] and it could be obtained in only low yields from the reaction (165 °C; 24 h) of propyne and 1,5-$C_2B_3H_5$. The metal-catalyzed syntheses reported herein are, therefore, the first general synthetic routes to these compounds to be reported.

The degree of substitution of the carborane can be controlled by varying the reaction conditions, and products can be obtained ranging from single substitution at only one boron site to complete substitution at all boron positions in the molecule. The effects of various reaction parameters (temperature, solvent, catalyst, and reactant proportions) on both the rate of reaction and the degree of substitution are presented in Table V for the reaction of 2-butyne with 2,4-$C_2B_5H_7$. It can be seen that, by careful manipulation of the conditions, reactions may be designed for the high-yield synthesis of alkenylcarboranes with the desired degrees of substitution. For example, high alkyne:carborane ratios in conjunction with higher temperatures (115 °C) favored the formation of the more highly substituted derivatives, while the use of lower temperatures (75 °C) and/or shorter times results in the formation of predominantly monosubstituted derivatives.

The reactivities and selectivities observed in these reactions are in agreement with the results obtained from the analogous reactions involving pentaborane(9), which were described elsewhere,[1] but are different from those generally observed for most monometal catalysts.[3] For example, these dicobalt catalysts were found to be most effective for internal rather than terminal alkynes. A typical illustration is the reaction of 1,5-$C_2B_3H_5$ with the alkynes 2-butyne, 1-butyne, and acetylene, which gave 78%, 27%, and 5% conversions, respectively, in 2 h. A similar behavior was observed for the other carboranes as well as with pentaborane(9).[1] It was also found that the catalysts examined here gave predominantly Markovnikov addition to the alkynes rather than the anti-Markovnikov addition, which is normally observed with monometal catalysts.[3] For example, the reaction of 1,5-$C_2B_3H_5$ with 1-butyne resulted in a 62% yield of the Markovnikov product, 2-(2-but-1-enyl)-1,5-$C_2B_3H_4$, and only a 38% yield of the anti-Markovnikov product, 2-(*trans*-1-but-1-enyl)-1,5-$C_2B_3H_4$.

Both the selectivities and reactivities observed in the carborane and pentaborane(9) reactions suggest a reaction sequence that is different from that normally proposed for monometal catalysts,[3] a mechanism that may involve interactions with both metal atoms. That the dicobalt unit, in fact, stays intact during the reaction is supported by the observation that the complex can be essentially completely recovered from reactions run at moderate temperatures. Furthermore, if these complexes were dissociating to give monometal fragments, then it would be expected that they should also catalyze the addition reactions of olefins, but this has not been observed.[8]

The $(RC_2R')Co_2(CO)_6$ complexes have been previously shown to function as alkyne trimerization catalysts[15] by a mechanism that involves, as an initial step, the dissociation of carbon monoxide. Such a step does not seem indicated in the addition reactions reported herein, since, as mentioned above, the complexes can be recovered intact in reactions run under mild conditions and no noncondensable gases were evolved.[16] Likewise, the observed temperature behavior of

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(12) Onak, T.; Marynick, D.; Mattschei, P.; Dunks, G. *Inorg. Chem.* **1968**, *7*, 1754.

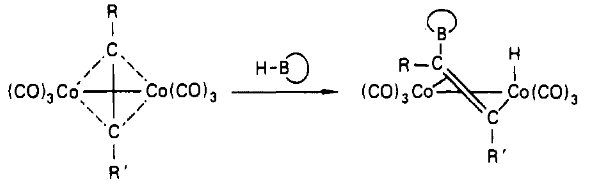
(13) Eaton, G. R.; Lipscomb, W. N. "NMR Studies of Boron Hydrides and Related Compounds"; W. A. Benjamin: New York, 1969.

(14) Burg, A. B.; Reilly, T. J. *Inorg. Chem.* **1972**, *11*, 1962.

(15) Hubel, W. "Organic Synthesis Via Metal Carbonyls"; Wender, I., Pino, P., Eds.; Interscience: New York, 1968; Vol. I, pp 273–371.

the carborane addition reactions supports the conclusion that carbon monoxide loss is not a step in the addition reactions. Thus, at temperatures at or below 115 °C the addition reactions proceed readily and the trimerization reaction is less important, but at higher temperatures the trimerization reaction becomes dominant due to the facilitated loss of carbon monoxide from the catalyst. These observations therefore suggest that these two competitive reactions proceed by different initial steps.

If the dicobalt–alkyne unit stays intact and carbon monoxide loss is not involved in the reaction sequence, then the initial step in the reaction must be a direct BH addition to the complex. This could, in principle, occur several ways. First, since all reactions gave cis addition to the alkyne, a direct addition across the coordinated carbon–carbon triple bond might be suggested. However, such an addition would resemble conventional uncatalyzed hydroborations of unsaturated hydrocarbons, which are well-known[17] to be highly specific for anti-Markovnikov additions, and would be opposite of the results observed here. Furthermore, Nicholas and Petit have shown[18] that the formation of an acetylene–dicobalt hexacarbonyl complex effectively renders the triple bond inert to electrophilic hydroborations; therefore, a direct addition to the carbon–carbon bond does not seem probable. A second possibility would be oxidative addition of the BH unit across the cobalt–cobalt bond. Such a step would necessitate the formation of monometal fragments and is therefore unlikely for the reasons discussed previously. A third possibility is the oxidative addition of the BH group at one metal, with the alkyne or a carbon monoxide being transferred to the second metal. A similar type of oxidative addition at a single metal of a bimetallic complex has been previously proposed,[19] for example, in the hydrogenations of olefins or acetylenes catalyzed by $\{HRh[P(O\text{-}i\text{-}C_3H_7)_3]\}_2$. For the reactions described herein, such intermediates can be formulated; however, it is difficult to rationalize why this mechanism would lead to Markovnikov addition products and in addition why these cobalt complexes do not catalyze the reactions with butene. A fourth possibility is the addition of the BH group across an acetylenic carbon–cobalt bond, which would result in an intermediate bridging vinyl species:



A similar direct-addition and transient bridging vinyl intermediate has been proposed by Muetterties[20] for the hydrogenation of a μ-acetylene-diiron hexacarbonyl complex, which gives the stoichiometric formation of olefin. In the present case, the more electropositive boron atom would be expected to preferentially attach to the acetylenic carbon while the hydrogen of the BH group would add to the cobalt. Consistent with this type of polarized transition state leading to the bridging vinyl intermediate is the observation that the order of BH addition for $2,4\text{-}C_2B_5H_7$ and $2,3\text{-}C_2B_4H_8$, as well as B_5H_9, appears to be related to the ground-state positive charges[21] on the cage boron atoms. For example, the three monosubstituted 2-butenyl derivatives of $2,4\text{-}C_2B_5H_7$ (Ia–c) and $2,3\text{-}C_2B_4H_8$ (XIVa–c) were not produced in a statistically random manner, but instead enhanced substitutions at the most positive borons were observed.

In the presence of excess acetylene, the bridging vinyl intermediate could undergo hydride transfer and replacement of the resulting olefin by a new acetylene molecule to regenerate the $(RC_2R')Co_2(CO)_6$ complex and a molecule of alkenylborane. In the absence of excess acetylene, the hydroboration produces a $Co_2(CO)_6$ species, which apparently can either dimerize or react with another molecule of $(RC_2R')Co_2(CO)_6$. This was demonstrated in the reactions of B_5H_9[1] or $2,4\text{-}C_2B_5H_7$ with $[(CH_3)_2C_2]Co_2(CO)_6$ by the formation of $Co_4(CO)_{12}$ and $[(CH_3)_2C_2]Co_4(CO)_{10}$.

If direct addition to the cobalt–carbon bond is involved in the mechanism, then for acetylenes such as 1-butyne BH addition would be expected to occur preferentially across the weaker cobalt–carbon bond in the corresponding $(RC_2R')Co_2(CO)_6$ complex. As the electron-withdrawing power of the substituents (R and R′) on the acetylenic carbon atoms is increased so are the acceptor properties of these carbon atoms increased toward back-donation. Therefore, it is reasonable that a BH group will more readily add across carbon–cobalt bonds that are destabilized by electron-releasing substituents (i.e., CH_3). The result would be predominantly Markovnikov addition to the 1-butyne as observed in the reactions discussed above.

Although a mechanistic step such as described above of addition of a B–H unit across the cobalt–carbon bond can be used to account for the selectivities observed in the reactions described herein, it is, as noted earlier, impossible at this time to distinguish between this mechanism and the alternative mechanism involving oxidative addition of the B–H group at one metal site. It should be noted, however, that although the exact mechanism of reaction of these catalysts is still unproven, we have recently demonstrated[22] that $(R_2C_2)Co_2(CO)_6$ complexes may be used to catalyze other types of acetylene-addition reactions with reactivities and selectivities similar to those observed for the carborane and borane reactions. The results of these studies, which are aimed at elucidating both the scope and mechanism of these catalysts, will be presented in future publications.

Finally, it is also significant that the use of these cobalt catalysts has now made possible the large-scale production of boron-substituted alkenylcarboranes, and we have, therefore, now undertaken an exploration of the potentially diverse chemistry and applications of these unusual compounds.

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Registry No. Ia, 79855-58-6; Ib, 79855-59-7; Ic, 79855-60-0; IIa, 79855-61-1; IIb, 79855-62-2; IIc, 79855-63-3; IId, 79855-64-4; IIe, 79872-82-5; IIIa, 79855-65-5; IIIb, 79855-66-6; IIIc, 79855-67-7; IIId, 79855-68-8; IIIe, 79855-69-9; IVa, 79855-70-2; IVb, 79855-71-3; IVc, 79855-72-4; V, 79855-73-5; VI, 79855-74-6; VII, 79872-83-6; VIIIa, 79855-75-7; VIIIb, 79855-76-8; IX, 79855-77-9; X, 79855-78-0; XIa, 79872-84-7; XIb, 79855-79-1; XII, 79855-80-4; XIII, 79855-81-5; XIVa, 79855-82-6; XIVb, 79855-83-7; XIVc, 79855-84-8; $2,4\text{-}C_2B_5H_7$, 20693-69-0; $1,5\text{-}C_2B_3H_5$, 20693-66-7; $1,6\text{-}C_2B_4H_6$, 20693-67-8; $2,3\text{-}C_2B_4H_8$, 18972-20-8; $[(CH_3)_2C_2]Co_2(CO)_6$, 37726-81-1; $[(CH_3CH_2)C_2H]Co_2(CO)_6$, 12264-15-2; $(H_2C_2)Co_2(CO)_6$, 12264-05-0; $Co_4(CO)_{12}$, 17786-31-1; $[(CH_3)_2C_2]Co_4(CO)_{10}$, 12564-37-3; 2-butyne, 503-17-3; 1-butyne, 107-00-6; acetylene, 74-86-2.

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(16) It has also been recently demonstrated that these cobalt complexes catalyze the hydrosilations of alkynes and that these reactions are not inhibited by added carbon monoxide.[22]

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