$(C_5H_5Co)_2C_2B_8H_{10}$: B, 23.46; C, 39.10; H, 5.47; Co, 31.97. Found: B, 26.31; C, 38.99; H, 5.65; Co. 28.89. Exact mass measurement calcd for $^{11}B_8{}^{12}C_{12}{}^{1}H_{20}{}^{59}Co_2{}^+$, 370.097305; found, 370.0985 ± 0.0014. Uv–visible [λ_{max}, nm (log ϵ)]: 230 (4.29), 315 (4.49), 426 (2.92), 598 (2.84). Ir (cm^{-1}): 2900 vs, 2560 s, 1460 s, 1420 w, 1370 s, 1130 w, 1120 w, 1110 w, 1050 m, 1020 w, 1010 w, 975 m, 930 w, 910 w, 870 w, 855 w, 835 s, 820 m, 755 w, 725 w. A reduction was observed at -1.32 V, an oxidation at $+1.03$ V.

(d) $C_5H_5CoC_2B_8H_9(C_2B_8H_9)$, VIII. Separated and isolated as described above was 0.182 g (0.5 mmol, 4%) of VIII.

(e) $C_5H_5CoC_2B_8H_{10}$, IX. Isolated as described above was 1.35 g (5.5 mmol, 44%) of IX.

(f) $(C_5H_5Co)_2C_2B_8H_{10}$, X. Isolated as described above was 9.2 mg (0.025 mmol, 0.2%) of X.

Cobalt Metallocarboranes from 2,3-$C_2B_9H_{11}$. 2,3-Dicarba-*closo*-undecaborane(11) (2.6 g, 19.6 mmol) was taken up in 80 ml of THF in a 500-ml flask identical with that used for 1,6-$C_2B_8H_{10}$, and Na (1.0 g, 40 mmol) was immediately added. The solution rapidly became yellow. After stirring overnight the solution was colorless and approximately half the Na had disappeared. $C_{10}H_8$ (0.2 g, 1.6 mmol) was added and the reaction continued for 3 days at which time no Na was visible. The reaction was cooled to 0°, and 60 mmol of NaC_5H_5 and 8.0 g (60 mmol) of $CoCl_2$ were added. After stirring overnight, air was bubbled through the reaction mixture, silica gel added, and the solvent removed. Two 5 × 30 cm columns of silica gel in hexane were used to separate the reaction mixture. The following products, listed in order of elution, were separated by techniques described above and characterized by tlc, ^1H nmr, and cyclic voltammetry: 3,10-$C_5H_5CoC_2B_7H_9$, VI (8 mg, 0.030 mmol, 0.15%); 2,9-$C_5H_5CoC_2B_9H_{11}$ (120 mg, 0.5 mmol, 2.5%); 1,6-$C_5H_5CoC_2B_7H_9$ (47 mg, 0.2 mmol, 1.0%); 2,4-$C_5H_5CoC_2B_9H_{11}$ (10 mg, 0.04 mmol, 0.2%); 2,3-$C_5H_5CoC_2B_8H_{10}$, IX (10 mg, 0.04 mmol, 0.2%); $(C_5H_5Co)_2C_2B_8H_{10}$, X (22 mg, 0.06 mmol, 0.3%); and $(C_5H_5)_2Co^+(7,9\text{-}C_2B_9H_{12})^-$ (19 mg, 0.06 mmol, 0.3%).

Acknowledgment. The authors wish to thank Dr. R. J. Wiersema for obtaining the 80.5-MHz ^{11}B and 250-MHz ^1H nmr spectra and the cyclic voltammetry data. This research was supported by the Office of Naval Research and the Army Research Office (Durham).

Organometallic Reactions of 1-Ethynyl-1,2-carborane

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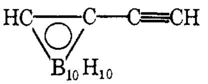
Received February 1, 1973

Abstract: Ethynylcarborane has been catalytically trimerized to 1,2,4-tris(1'-1',2'-carboranyl)benzene in high yield. The latter species failed to undergo electrophilic substitution on the aromatic ring. A normal substitution product was obtained from the reaction between $Co_2(CO)_8$ and ethynylcarborane. The interaction of ethynylcarborane with *trans*-$IrCl(CO)[P(C_6H_5)_3]_2$ afforded a novel octahedral complex containing σ-2-carboranylacetylide and σ-*trans*-2-carboranylvinyl substituents. Copper(II)-catalyzed oxidative coupling produced 1,4-di(1'-1',2'-carboranyl)butadiyne in good yield. The latter compound was resistant to addition reactions at the triple bonds.

The preparation of 1-ethynyl-1,2-carborane (I) was first reported by Dupont and Hawthorne in 1964.[1] These early investigations illustrated that reactions at the acetylenic CH bond with species such as Grignard reagents proceeded in a fashion similar to other substituted acetylenes. No additional studies on the chemical behavior of I have been reported, although its reactivity would be expected to be affected by its bulky, electron-withdrawing carboranyl substituent.



I

The recent development of an improved synthesis of I[2] has prompted a further study of its chemistry, and we wish to report its reactions with several transition metal species.

Results and Discussion

Catalytic Trimerization. Reaction of a benzene solution of I with a catalytic amount of the acetylene cyclotrimerization catalyst, bis(acrylonitrile)nickel(0),[3] followed by column chromatography, afforded an 85% yield of a product characterized as 1,2,4-tris(1'-1',2'-carboranyl)benzene (II). No evidence was found for the production of the 1,3,5 isomer or linear polymers although some dark colored material, which was not investigated further, was found to adhere to the top of the chromatographic column.

Compound II exhibited a mass spectral cutoff at *m/e* 510, corresponding to the $^{11}B_{30}{}^{12}C_{12}{}^{1}H_{36}{}^+$ ion. An osmometric molecular weight determination in benzene solution (calcd, 506; found, 503) further confirmed the formulation. The infrared spectrum of II (Table I) exhibited a strong B–H stretching absorption at 2600 cm^{-1}, and the C≡C and ≡C—H vibrations of the starting material were absent. Very weak absorptions in the 2000–1650-cm^{-1} range, in which phenyl overtones commonly occur,[4] were also observed. The 80.5-MHz ^{11}B nmr spectrum of II (Table II) showed severe overlap of resonances and gave no structural information. The ultraviolet–visible spectrum of II is presented in Table III.

The structure of II was assigned on the basis of its ^1H nmr spectrum (Table IV). In deuterioacetone solution at 60 MHz, II exhibited a multiplet of relative

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[1] J. A. Dupont and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **86**, 1643 (1964); U. S. Patents 3,228,986 and 3,228,987 (1966).

[2] T. E. Paxson, K. P. Callahan, and M. F. Hawthorne, *Inorg. Chem.*, 12, 708 (1973).

[3] G. N. Schrauzer, *J. Amer. Chem. Soc.*, **81**, 5310 (1959).

[4] L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," Wiley, New York, N. Y., 1958.

Table I. Infrared Spectra (cm^{-1}), Nujol Mulls

1,2,4-$(B_{10}C_2H_{11})_3C_6H_3$, II	3122 m, 3000 m, 2863 vs, 2698 w, 2630 vs, 1922 vw, 1845 vw, 1602 m, 1548 w, 1483 m, 1454 vs, 1388 s, 1354 m, 1342 w, 1305 w, 1257 w, 1120 m, 1095 m, sh, 1083 w, 1075 m, sh, 1070 s, 1015 s, 1000 m, 974 w, 926 w, 914 vw, 905 vw, 890 w, 880 vw, 872 vw, 859 w, 839 m, 807 w, 737 s, sh, 731 s, sh, 722 s, 694 m
$Co_2(CO)_6B_{10}C_4H_{12}$, III	3155 w, 2983 vs, 2918 vs, sh, 2768 vw, 2635 s, 2105 s, 2073 vs, 2040 vs, 2020 vs, sh, 1718 w, 1561 w, 1480 m, 1447 s, 1355 s, 1241 w, 1212 w, 1162 w, 1150 w, 1105 w, 1074 m, 1047 m, 1002 s, 992 w, 961 w, 922 w, 909 w, 874 s, 790 m, 723 s, 696 s
$IrCl(CO)[P(C_6H_5)_3]_2(B_{10}C_4H_{11})$-$(B_{10}C_4H_{13})$, IV	3060 m, 2918 vs, 2598 vs, 2337 vw, 2140 w, 2080 vs, 1570 w, 1478 m, 1458 vs, 1431 s, 1371 s, 1304 w, 1257 w, 1232 w, 1190 w, 1158 w, 1098 m, sh, 1092 s, 1064 m, 1029 m, 1016 m, 1002 m, 974 w, 926 w, 878 vw, 807 m, 747 m, 727 m, 707 s, 695 s
$B_{10}C_2H_{11}C{\equiv}CC{\equiv}CB_{10}C_2H_{11}$, VIII	3030 m, 2878 vs, 2599 vs, sh, 2562 vs, 2342 vw, 2175 vw, 1990 vw, 1923 vw, 1853 vw, 1449 vs, 1367 vs, 1298 vw, 1255 vw, 1220 w, 1163 w, sh, 1154 w, 1115 m, 1057 vs, 1047 w, 1008 vs, 997 m, 967 w, 927 w, 914 m, 903 w; sh, 874 w, 795 w, 780 m, 728 s, sh, 720 vs, 688 w

Figure 1. The 100-MHz ^1H nmr spectrum of II in CS_2 solution, δ 8–7: (a) normal spectrum, (b) spectrum upon irradiation of low-field doublet.

Table II. 80.5-MHz ^{11}B Nmr Spectra[a]

Compound	Feature	Chemical shifts, ppm (*J*, Hz)	Rel area
1,2,4-$(B_{10}C_2H_{11})_3C_8H_3$, II[b]	Overlapping doublets	+3.1 (138)	8.1
		+5.0 (147)	
	Overlapping doublets	+10.1 (137)	21.9
		+12.0 (150)	
$Co_2(CO)_6B_{10}C_4H_{12}$, III[c]	Overlapping doublets	+2.7 (137)	
		+5.7 (140)	
		+9.8 (161)	
		+12.7 (154)	
$IrCl(CO)[P(C_6H_5)_3]_2(B_{10}C_2H_{11})(B_{10}C_2H_{13})$, IV[b]	Overlapped doublet	+2.2 (123)	3.7
	Broad hump	+8.34 sh	16.3
		+10.06	
$B_{10}C_2H_{11}C{\equiv}C{-}C{\equiv}CB_{10}C_2H_{11}$, VIII[d]	Doublet	+2.9 (147)	4
	Overlapping doublets	+9.3 (134)	
		+11.0 (144)	16
		+12.9 (164)	

[a] Chemical shifts relative to $BF_3 \cdot O(C_2H_5)_2$ = 0.00 ppm. [b] Carbon disulfide solution. [c] Methanol solution. [d] Deuterioacetone solution.

Table III. Ultraviolet–Visible Spectra[a]

Compound	λ_{max}, mμ (ε)
1,2,4-$(B_{10}C_2H_{11})_3C_6H_3$, II	288 (2400), 283 sh (2200), 242 (12,800), 215 (26,500)
$Co_2(CO)_6B_{10}C_4H_{12}$, III	410 (1020), 354 (3970), 304 sh (6950), 252 (13,800)
$IrCl(CO)[P(C_6H_5)_3]_2(B_{10}C_4H_{11})$-$(B_{10}C_4H_{13})$, IV	277 sh (21,800), 270 (25,000), 230 (33,900), 215 (33,600)
$B_{10}C_2H_{11}C{\equiv}CC{\equiv}CB_{10}C_2H_{11}$, VIII	292 (425), 273 (670), 257 (882), 244 (841), 232 (628)

[a] Spectroquality acetonitrile solution.

intensity 3 in the aromatic region of the spectrum (δ 8–7) and two broad resonances of relative intensities 2:1 at higher field assigned to polyhedral CH groups. The spectrum was essentially unchanged at 100 MHz and the aromatic multiplet is shown in Figure 1a. Irradiation of the low field doublet of this multiplet resulted in the collapse of coupling of the two high field doublets, and this decoupled spectrum (Figure 1b) was confirmed to be an AB pattern. The normal spectrum of II was thus interpreted as an ABX pattern in which the hydrogen in position 3 acts as proton X (δ 8.27), and the protons at positions 5 and 6 (δ 8.09 and 7.76, respectively) are the AB units, with J_{AX} = 2.3, $J_{BX} \leq 1$, and J_{AB} = 9.2 Hz, conclusively establishing the 1,2,4-substitution pattern on the benzene ring. The observation of polyhedral CH resonances with relative intensities 2:1 is attributed to coincidental overlap; three equal-intensity resonances were observed in deuterioacetone solution at 250 MHz and in carbon disulfide solution at 60 MHz. The proposed structure of II is shown in Figure 2.

Table IV. ^{1}H Nmr Spectra

Compound	Chemical shift, δ (J, ppm) (rel intensity)	Assignment
1,2,4-$(B_{10}C_2H_{11})_3C_6H_3$[a]	8.27 d (2.3) (1)	H(3)
	8.09 d (9.2) (1)	H(5)
	7.76 dd (2.3, 9.2) (1)	H(6)
	5.18 brs (1)	
	4.89 brs (1)	Polyhedral CH protons
	4.09 brs (1)	
$Co_2(CO)_6B_{10}C_4H_{12}$, III[b]	6.02 s (1)	Acetylenic proton
	4.05 brs (1)	Polyhedral CH proton
$IrCl(CO)[P(C_6H_5)_3]_2(B_{10}C_4H_{13})(B_{10}C_4H_{11})$, IV[a]	7.52 m (30)	Phenyl protons
	6.80 dt (16, 2.2) (1)	Vinyl protons
	5.03 dt (16, 1.7) (1)	
	3.04 brs (1)	Polyhedral CH protons
	1.74 brs (1)	
$B_{10}C_2H_{11}C{\equiv}CC{\equiv}CB_{10}C_2H_{11}$, VIII[c]	5.14 brs	Polyhedral CH protons

[a] 100 MHz, carbon disulfide solution. [b] 60 MHz, carbon disulfide solution. [c] 60 MHz, deuterioacetone solution.

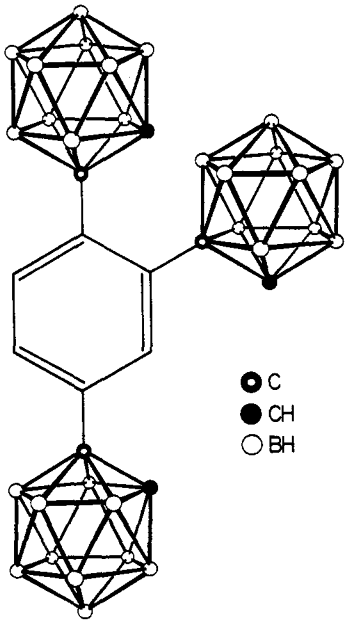

Figure 2. Proposed structure of II.

Because of the presence of three electronegative substituents on its aromatic ring, II would be expected to undergo electrophilic substitutions with difficulty. We have so far been unsuccessful in accomplishing electrophilic ring substitution of any type. Friedel–Crafts alkylation and acylation conditions only led to recovery of starting material, even under forcing conditions, as did attempted mixed acid nitration of II. We feel that this unusual lack of reactivity must be explained, for the most part, by electronic effects, for although the carborane substituents are large, scale models indicate sufficient room for substitution to occur at positions 5 and 6. Position 3 is partially blocked by the hydrogen atoms of the polyhedra at positions 2 and 4.

The lack of reactivity of the trisubstituted benzene ring was not paralleled by the polyhedral substituents, however. When methylation of the three carborane CH groups was attempted in ethereal solvents at room temperature, employing *n*-butyllithium to remove the protons, vividly colored solutions were produced, and after the addition of methyl iodide and normal work-up, no BH-containing species were detected in either organic or aqueous phases. The cyclic votammogram of II[5] showed an irreversible reduction wave at −1.03 V *vs.* sce, and this observation is consistent with reduction of II by *n*-butyllithium followed by decomposition.

The production of the more sterically hindered 1,2,4 isomer in the trimerization of I is attributed to catalytic specificity; other workers have observed that minor changes in catalyst profoundly affect the isomer ratio of the product.[6] We did not observe the incorporation of acrylonitrile into the product, as noted by Schrauzer,[7] and this may be ascribed to our lower catalyst concentration. The lack of production of linear polymers in substantial quantities was surprising, for observations with other catalysts showed a correlation between substituent size and the amount of linear polymer produced. The inability of $Mo(CO)_6$ to effect cyclotrimerization[8] was also unexpected.

Complexation with $Co_2(CO)_8$. Ethynylcarborane was found to react smoothly with a stoichiometric amount of dicobalt octacarbonyl in pentane at reflux in a nitrogen atmosphere. Column chromatography of the resultant reaction mixture afforded red needles of $Co_2(CO)_6(B_{10}C_2H_{11}C{\equiv}CH)$ (III) which were air-stable in the solid state but rapidly decomposed when its solutions were exposed to air.

The mass spectrum of III exhibited a cutoff at *m/e* 456, corresponding to the molecular ion $^{59}Co_2{}^{16}O_6{}^{12}C_{10}{}^{11}B_{10}{}^{1}H_{12}{}^{+}$, and successive loss of six carbonyl groups was indicated by envelope cutoffs at *m/e* 428, 400, 372, 344, 316, and 288. The infrared spectrum of a Nujol mull of II (Table I) showed several bands in the 2200–2000-cm^{-1} region, and at high resolution in cyclohexane solution five bands assigned as carbonyl stretching frequencies were observed at 2106, 2069, 2047, 2041, and 2027 cm^{-1}. The ^{1}H nmr spectrum of III at 60 MHz in carbon disulfide (Table IV) solution exhibited two resonances of equal intensity, a broad singlet at δ 4.05 and a sharp singlet at δ 6.02 which were assigned to the polyhedral CH group and the acetylenic proton, respectively. The 80.5-MHz ^{11}B nmr spectrum in the same solvent (Table II) exhibited severe overlap of resonances and was structurally un-

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(5) Measured in CH_3CN solution with 0.1 *M* $(C_2H_5)_4NClO_4$ supporting electrolyte.

(6) C. Hoogzand and W. Hübel in "Organic Syntheses via Metal Carbonyls," Vol. I, I. Wender and P. Pino, Ed., Interscience, New York, N. Y., 1968, p 343.

(7) G. N. Schrauzer, *Chem. Ber.*, **94**, 1403 (1961).

(8) W. Hübel and C. Hoogzand, *ibid.*, **93**, 103 (1960).

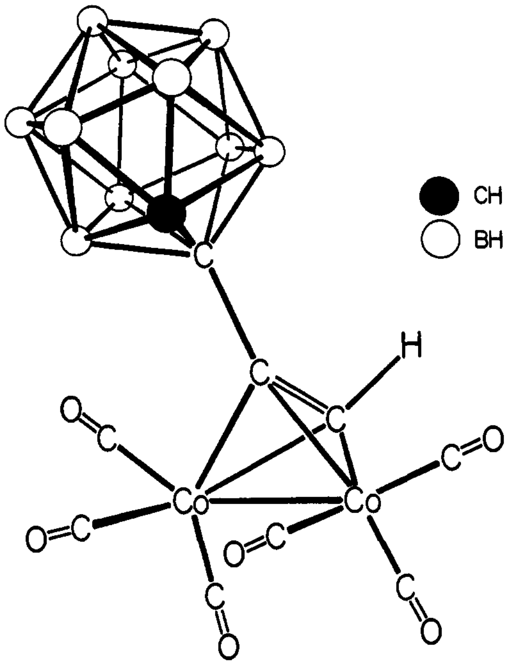

Figure 3. Proposed structure of III.

informative. The ultraviolet–visible spectrum of III is presented in Table III.

The above data are consistent with a μ-alkynehexacarbonyldicobalt structure similar to that found[9] for other compounds of the general formula $RC{\equiv}CRCo_2(CO)_6$, and the proposed structure of III is shown in Figure 3.

Reaction with Vaska's Complex. The oxidative addition reactions of mono- and disubstituted acetylenes with Vaska's complex, *trans*-$IrCl(CO)[P(C_6H_5)_3]_2$, have been shown to produce a variety of products of unusual structure.[10,11] To our knowledge, the only isolated product obtained from the interaction of a monosubstituted acetylene and Vaska's complex was shown[10] to be a six-coordinate hydridoacetylide compound which resulted from oxidative addition across the acetylenic CH bond.

Vaska's complex reacted with an excess of ethynylcarborane in benzene solution to afford as the major product (72%) a white crystalline solid IV which contained 2 equiv of ethynylcarborane per iridium atom, as shown by elemental analysis and osmometric molecular weight determination. The infrared spectrum of IV (Table I) contained a strong carbonyl stretch at 2080 cm^{-1} and a weak absorption at 2140 cm^{-1} which was tentatively assigned as an Ir–H stretching mode. Deuterated analogs of IV, prepared from ethynylcarborane deuterated solely on the polyhedral carbon atom and solely on the terminal acetylenic carbon, still exhibited the weak absorption at 2140 cm^{-1}, invalidating its assignment as ν(Ir–H); oxidative addition to a BH unit was considered unlikely.[12]

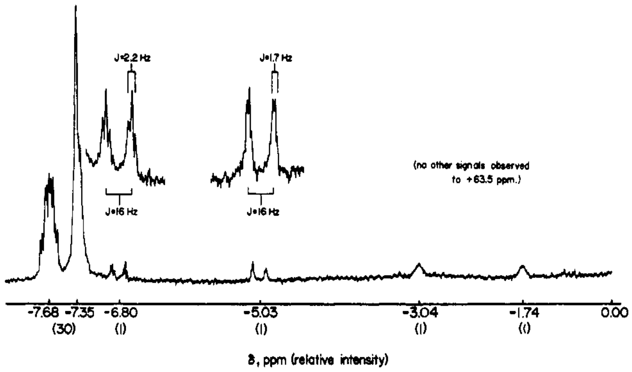

Figure 4. The 100-MHz ^1H nmr spectrum of IV in CS_2 solution.

The 100-MHz ^1H nmr spectrum of IV in CS_2 solution (Figure 4) exhibited two multiplets of combined relative intensity 30 centered at δ 7.52, assigned to the phenyl protons of the triphenylphosphine ligands; two doublets of triplets, each of relative intensity 1 centered at δ 6.80 and 5.03, the doublet coupling constant of both being 16 Hz (decoupling experiments confirmed the nature of this interaction), the triplet coupling constant of the former being 2.2 Hz and the latter 1.7 Hz; and two broad singlets, each of relative intensity 1, located at δ 3.04 and 1.74 and assigned to polyhedral CH resonances. No high field resonances attributable to Ir–H were observed. The doublets of triplets were therefore assumed to arise from the protons which, in the starting material, were acetylenic in nature. This assignment was confirmed by spectral examination of deuterated analogs of IV; the spectrum of the complex prepared from ethynylcarborane deuterated on the polyhedral carbon atom showed no broad resonances attributable to polyhedral CH groups, while the spectrum of the complex prepared from ethynylcarborane deuterated at the acetylenic carbon atom was devoid of the two doublets of triplets. The 80.5-MHz ^{11}B nmr spectrum of IV (Table II) was structurally uninformative. The ultraviolet–visible spectrum is presented in Table III.

The magnitude of the doublet coupling constant observed in the ^1H nmr (16 Hz) suggested a trans double bond environment for the two protons, and the slightly different triplet coupling constants indicated interaction with two phosphine ligands both cis to the ethylenic substituent. The presence of two hydrogen atoms on a C=C double bond made it evident that the other ethynylcarborane ligand must have no exopolyhedral protons, and indeed the presence of a σ-acetylide species is indicated by the weak infrared band at 2140 cm^{-1}, now assigned as a C≡C mode.

The structure of IV has been determined by an X-ray crystallographic study[13] and found to agree with the spectral interpretation discussed above. In this compound, Figure 5, the iridium atom is coordinated to two mutually trans triphenylphosphines (the stereochemistry generally observed in products derived from oxidative addition to Vaska's complex[14]) which are above and below the plane consisting of chloride, carbon monoxide, σ-2-carboranylacetylide, and σ-*trans*-2-carboranylvinyl ligands.

We envisaged that the production of IV might occur in two steps, the first of which involved the formation of a hydridoacetylide species, similar to that previously

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[9] W. G. Sly, *J. Amer. Chem. Soc.*, **81**, 18 (1959).

[10] J. P. Collman and J. W. Kang, *ibid.*, **89**, 844 (1967).

[11] J. P. Collman, J. W. Kang, W. F. Little, and M. F. Sullivan, *Inorg. Chem.*, 7, 1298 (1968).

[12] See, however, E. L. Hoel and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **95**, 2712 (1973).

[13] K. P. Callahan, C. E. Strouse, S. W. Layten and M. F. Hawthorne, *Chem. Commun.*, in press.

[14] J. P. Collman and C. T. Sears, *Inorg. Chem.*, 7, 27 (1968).

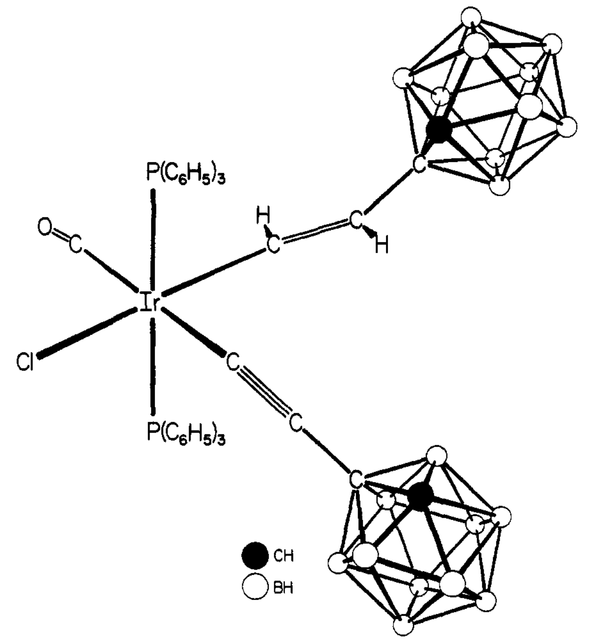
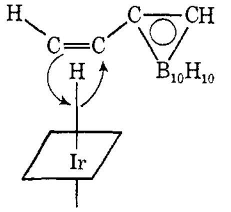


Figure 5. Structure of IV.

observed in the ethyl propiolate complex,[10] which then reacted with excess ethynylcarborane, accompanied by hydrogen transfer, to afford the observed product. Accordingly, we attempted to isolate the presumed intermediate species by allowing equimolar quantities of the starting reagents to react. Unchanged Vaska's complex was isolated from the reaction mixture (60.3% recovery), as was compound IV (75.3% based on Ir consumed), and small amounts of at least four other iridium-containing compounds which were too involatile for mass spectral analysis and too scarce to allow complete characterization. It thus appears that if a hydridoacetylide complex is first formed, it rapidly reacts with a second equivalent of ethynylcarborane to afford the observed product IV.

The stereospecific production of a trans C=C double bond in IV is most likely attributable to steric hindrance in the transition state since the bulk of the carborane substituent would prevent its close approach to the metal. It is reasonable to conceive of the formation of IV proceeding through an octahedral-wedge transition state, as depicted in V, although it must be emphasized that no experimental evidence supports this proposal.



V

Collman and coworkers[11] have observed the production of 2:1 complexes between disubstituted acetylenic esters and the N$_2$ analog of Vaska's complex and, on the basis of spectral measurements, assigned to them the "iridocycle" structure VI. These species reacted with additional ligands (CO or phosphines) to afford the hexacoordinate compounds VII. Collman's spectral data rule out the possibility that these complexes are actually structural analogs of IV, and this difference in product may reflect the inability of oxidative addition to occur across the C–C bond of the acetylenic ester.

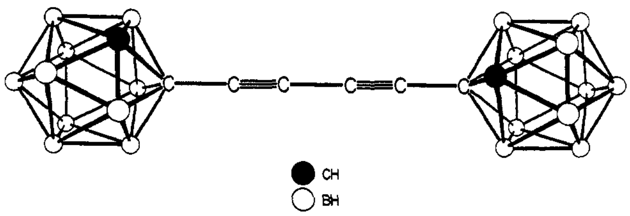
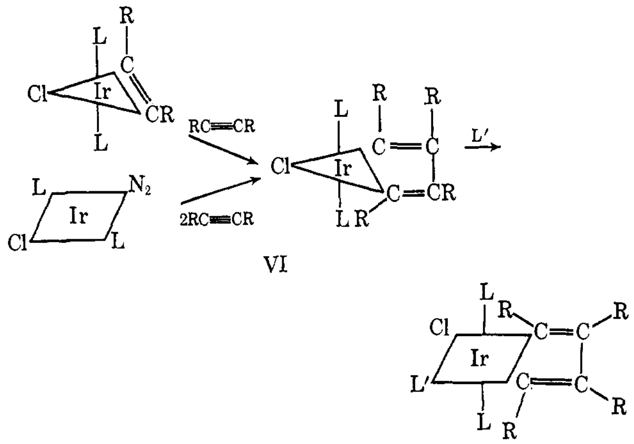


Figure 6. Proposed structure of VIII.



VI

VII

Oxidative Coupling. Ethynylcarborane was found to react with oxygen in the presence of a catalytic amount of cuprous chloride–*N*,*N*,*N*′,*N*′-tetramethylethylenediamine complex[15] to afford 1,4-di(1′-1′,2′-carboranyl)-butadiyne (VIII), Figure 6, in 50–60% yield. Compound VIII exhibited a mass spectral cutoff at m/e 338, corresponding to the molecular ion $^{11}B_{20}{}^{12}C_8{}^{1}H_{22}{}^+$. The major fragment ion observed in the mass spectrum was the product of symmetrical cleavage. The infrared spectrum (Table I) was relatively simple, in agreement with the proposed symmetrical structure, and no absorptions attributable to C≡C or acetylenic CH stretches were observed. A strong band observed in the Raman spectrum of a powdered sample of VIII at 2263 cm^{-1} was assigned as a C≡C stretching mode. The 80.5-MHz ^{11}B nmr spectrum (Table II) was structurally uninformative. The ultraviolet–visible spectrum of VIII is presented in Table III. The five absorptions separated by $\sim$2200 cm^{-1} appear to be due to vibrational coupling with ν(C≡C), as observed in diacetylene and other conjugated poly-ynes.[16] The ^{1}H nmr spectrum (Table IV) of VIII in deuterioacetone solution at 60 MHz exhibited one broad resonance at δ 5.14 assigned to the polyhedral CH units.

The presence of two carbon–carbon triple bonds in VIII immediately suggested the possibility of preparing the unknown molecule "tetracarborane" by reaction with 2 equiv of bis(ligand)decaborane. Unfortunately, both bis(acetonitrile)-[17] and bis(diethyl sulfide)decaborane[18] were found to be unreactive. A 21% re-

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(15) A. S. Hay, *J. Org. Chem.*, 27, 3320 (1962).

(16) J. Dale in "Chemistry of Acetylenes," H. G. Viehe, Ed., Marcel Dekker, New York, N. Y., 1969, p 59.

(17) R. O. Schaeffer, *J. Amer. Chem. Soc.*, 79, 1006 (1957).

(18) B. M. Graybill, J. K. Ruff, and M. F. Hawthorne, *ibid.*, **83**, 2669 (1961).

covery of VIII was obtained after it had been treated with excess $B_{10}H_{12}[S(C_2H_5)_2]_2$ at 80° for 96 hr, the remainder of the reaction mixture being polymeric. Attempted bromination of the triple bonds was equally unsuccessful; after 90 hr reaction with Br_2 in CH_2Cl_2 at room temperature with LiBr catalyst[19] in the dark, mass spectral analysis indicated that the product was a mixture of starting material and mono-, di-, tri- and tetrabrominated derivatives. The presence of mono- and tribrominated compounds indicated that some substitution had occurred on the polyhedron. No singlets could be observed in the 80.5-MHz ^{11}B nmr spectrum of this mixture, but the spectrum suffered from severe overlap of resonances and singlets may have been present. Separation of the product mixture was not achieved, and therefore we cannot determine whether any bromination at the triple bonds actually occurred.

The lack of reactivity of VIII may be rationalized on electronic grounds. Decreased reactivity has been previously noted for functional groups adjacent to a carborane cage,[20] and attributed to the electron-withdrawing power of the polyhedron.

Experimental Section

Physical Measurements. Infrared spectra were obtained on a Perkin-Elmer Model 137 spectrophotometer, and the carbonyl stretching region of compound III was measured on a Beckman IR 4 spectrophotometer. Proton nmr spectra were recorded at 60 MHz on a Varian Model A60-D spectrometer, at 100 MHz on a Varian HA-100, and at 250 MHz or an instrument constructed by Professor F. A. L. Anet of this department. Boron-11 nmr spectra were recorded at 80 MHz on the latter instrument. Ultraviolet-visible spectra were measured on a Beckman Model DB spectrophotometer at 25°. Raman spectra were obtained using a Cary 81 laser spectrophotometer. Controlled-potential cyclic voltammetry was carried out using an instrument based on the design of Lawless and Hawley.[21] Mass spectra were obtained with an Associated Electrical Industries Model MS-9 spectrometer. Elemental analyses and osmometric molecular weights were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Melting points are uncorrected.

Materials. Ethynylcarborane was prepared as previously described.[2] Bis(acrylonitrile)nickel was synthesized by the method of Schrauzer,[3] and *trans*-$IrCl(CO)[P(C_6H_5)_3]_2$ by the method of Collman, Sears, and Kubota.[22] Dicobalt octacarbonyl was purchased from Research Inorganic Chemical Co., *n*-butyllithium from Alfa Inorganics, deuterium oxide from Stohler Isotope Chemicals, cuprous chloride from J. T. Baker and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine from Eastman. Silica gel used in column chromatography was from J. T. Baker, 60–200 mesh. Benzene, hexane, and acetonitrile were reagent grade.

Preparation of 1,2,4-Tris(1′-1′,2′-carboranyl)benzene (II). A 100-ml round-bottomed Schlenk flask was charged with 0.1 g (0.61 mmol) of bis(acrylonitrile)nickel(0) in a drybox. In the laboratory under a stream of dry nitrogen, 50 ml of benzene, freshly distilled under nitrogen from CaH_2, and freshly sublimed ethynylcarborane (4.0 g, 23.8 mmol) were added, and the resulting solution was heated at reflux for 24 hr. The reaction mixture was cooled and evaporated to a dark viscous oil on a rotary evaporator and chromatographed on a 1 × 18 in. silica gel column prepared with hexane. Elution with hexane afforded the crude product, which was recrystallized from acetonitrile to afford white needles of 1,2,4-tris(1′-1′,2′-carboranyl)benzene, mp 290–291° (3.4 g, 85%), mol wt calcd, 505; found (osmometric in benzene), 503. *Anal.* Calcd for $B_{30}C_{12}H_{36}$: B, 64.33; C, 28.54; H, 7.13. Found: B, 63.66; C, 28.45; H, 7.54.

Preparation of $Co_2(CO)_6B_{10}C_2H_{11}C{\equiv}CH$ (III). In the drybox, dicobaltoctacarbonyl (2.0 g, 5.85, mmol) and ethynylcarborane (1.0 g, 5.95 mmol) were placed in a 100-ml round-bottomed Schlenk flask. The flask was stoppered and moved to the bench where, under dry nitrogen flow, 60 ml of degassed, freshly distilled pentane was added. The reaction mixture was stirred at room temperature for 5 hr, at which point no gas evolution was detectable. The mixture was filtered under nitrogen, evaporated to *ca.* one-fourth volume and chromatographed on a 1 × 10 in. silica gel column made up with N_2-saturated hexane. Hexane eluted a red band which was evaporated on a rotary evaporator to afford a red solid. Recrystallization from dry, N_2-saturated methanol afforded 1.0 g (2.20 mmol, 37%) of red needles, mp 70–70.5°. *Anal.* Calcd for $B_{10}C_{10}H_{12}Co_2O_6$: B, 23.83; C, 26.43; H, 2.64; Co, 25.94; O, 21.15. Found: B, 25.09; C, 26.55; H, 2.88; Co, 25.20.

Preparation of $IrCl(CO)[P(C_6H_5)_3]_2(B_{10}C_4H_{11})(B_{10}C_4H_{13})$ (IV). In a 100-ml round-bottomed Schlenk flask thoroughly purged with dry nitrogen were placed 1.0 g (1.28 mmol) of *trans*-$IrCl(CO)[P(C_6H_5)_3]_2$,[22] 3.0 g (17.8 mmol) of freshly sublimed ethynylcarborane, and 50 ml of benzene, freshly distilled from CaH_2 under nitrogen. The reaction mixture was heated to reflux with stirring under nitrogen for 24 hr, evaporated to a dark oil, and chromatographed on a 1 × 18 in. silical gel column made up with hexane. Unreacted ethynylcarborane was eluted with hexane, a small unidentified yellow band was removed with 50:50 hexane–benzene, and the major product IV was eluted with benzene to afford 1.03 g (0.92 mmol, 72%) of crude material which was recrystallized from ether–methanol, mol wt calcd, 1117; found (osmometric in benzene), 1121. *Anal.* Calcd for $C_{45}H_{54}B_{20}P_2IrClO$: C, 48.34; H, 4.83; B, 19.37; P, 5.55; Ir, 17.29; Cl, 3.17; O, 1.43. Found: C, 48.14; H, 4.77; B, 20.96; P, 5.16; Ir, 17.91; Cl, 2.56.

Preparation of Deuterated Ethynylcarboranes. (a) Dideuterioethynylcarborane. In a dry, nitrogen-filled 100-ml round-bottomed Schlenk flask was placed 1.55 g (9.2 mmol) of ethynylcarborane, which was dissolved in 40 ml of tetrahydrofuran, freshly distilled from $LiAlH_4$. To the stirring solution was added 13.5 ml of 1.6 *M* *n*-butyllithium in hexane, and the solution was heated to reflux for 3 hr. The reaction mixture was cooled to room temperature and quenched with 4 ml of D_2O. The mixture was filtered; the collected solids were washed with 2–25-ml portions of diethyl ether, and the combined organic fractions dried over anhydrous $MgSO_4$ and evaporated to dryness. The resulting solid was sublimed under high vacuum at room temperature to afford 1.15 g (6.07 mmol, 66%) of dideuterioethynylcarborane, ν(C–D) (polyhedral) 2290 cm^{-1}, ν(C–D) (acetylenic) 1995 cm^{-1}.

(b) Deuterioethynylcarborane (Polyhedral C–D). In a 100-ml round-bottomed Schlenk flask thoroughly purged with dry nitrogen were placed 1.50 g (8.8 mmol) of dideuterioethynylcarborane, 40 ml of freshly distilled tetrahydrofuran, and a Teflon-coated magnetic stirring bar. To the stirring solution was added 5.3 ml of a freshly prepared solution of 1.9 *M* C_2H_5MgBr in tetrahydrofuran. The solution was heated to reflux 4 hr, cooled, and quenched with 5 ml of H_2O. The mixture was extracted with pentane (2 × 50 ml), and the combined organic fractions were dried over anhydrous $MgSO_4$ and evaporated to a red oil which solidified on standing. Sublimation under high vacuum at room temperature to a Dry Ice cooled cold finger afforded 1.32 g (7.74 mmol, 88%) of product, ν(C–D) (polyhedral) 2290 cm^{-1}, ν(CH) (acetylenic) 3300 cm^{-1}.[23]

(c) Deuterioethynylcarborane (Acetylenic C–D). The reaction was carried out as in (b) above employing 1.5 g (8.8 mmol) of ethynylcarborane, 5.3 ml of 1.9 *M* C_2H_5MgBr and quenching with 4 ml of D_2O. The product was sublimed under high vacuum at room temperature to afford 1.37 g (8.05 mmol, 91.5%) of $B_{10}C_2H_{11}C{\equiv}CD$, ν(CH) (polyhedral) 3030 cm^{-1}, ν(CD) (acetylenic) 1995 cm^{-1}.[23]

Preparation of 1,4-Di(1′-1′,2′-carboranyl)butadiyne (VIII). To a stirring solution of 0.5 ml (3.9 mmol) of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine in 12.5 ml of acetone in a 50-ml erlenmeyer flask was added 1.0 g (10 mmol) of cuprous chloride, and stirring was continued for 1 min. The resulting blue-green solution was decanted, the remaining solid was washed once with 5 ml of acetone, and the combined acetone fractions were diluted with an additional

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[19] P. W. Robertson, W. E. Dasent, R. M. Milburn, and W. H. Oliver, *J. Chem. Soc.*, 1628 (1950).

[20] D. A. T. Young, T. E. Paxson, and M. F. Hawthorne, *Inorg. Chem.*, **10**, 786 (1971), and references therein.

[21] J. D. Lawless and M. D. Hawley, *J. Electroanal. Chem.*, **21**, 365 (1969).

[22] J. P. Collman, C. T. Sears, and M. Kubota, *Inorg. Syn.*, **11**, 101 (1968).

[23] The fact that $\nu(CH)/\nu(CD)$ for these vibrations is not exactly equal to $\sqrt{2}$ indicates that they are not pure C–H stretches, but are combinations. Nevertheless, these frequencies are useful in product characterization and have therefore been included.

10 ml of acetone and added to a 100-ml three-necked round-bottomed flask equipped with a Teflon stirring bar, reflux condenser, and a dropping funnel containing a solution of 2.14 g (12.7 mmol) of ethynylcarborane in 25 ml of acetone. A gas bubbler was connected to the flask and a rapid stream of O_2 was bubbled through the solution as the ethynylcarborane solution was added dropwise over a 30-min period. Oxygen was bubbled through the reaction mixture for an additional 2 hr, and then the contents of the flask was poured into 100 ml of ice-cold 3 *M* HCl and extracted with four 100-ml portions of pentane. The pentane extracts were combined, dried over anhydrous $MgSO_4$, and evaporated to dryness. The resulting brown solid was chromatographed on a 1 × 10 in. silica gel column and eluted with hexane to afford 1.10 g (3.29 mmol, 51.7%) of white product, mp 315–317° dec. *Anal.* Calcd for $B_{20}C_8H_{22}$: B, 64.69; C, 28.72; H, 6.58. Found: B, 64.84; C, 28.92; H, 6.24.

Acknowledgments. The authors are indebted to Dr. R. J. Wiersema for the 80.5-MHz ^{11}B nmr spectra and electrochemical measurements and to Professor M. Kubota for helpful discussions. This work was supported in part by the Office of Naval Research and the National Science Foundation under Grant GP-14372X1, to whom we express our thanks.

Resolution of the Accidental Degeneracy in the Spectrum of 2-[2′-Pentaboran(9)yl]pentaborane(9) by Application of Partially Relaxed Fourier Transform Boron-11 Nuclear Magnetic Resonance Spectroscopy[1]

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Abstract: The accidental degeneracy in the 70.6-MHz ^{11}B nmr spectrum of 2-[2′-pentaboran(9)yl]pentaborane(9) has been resolved by obtaining a series of partially relaxed Fourier transform (PRFT) spectra. The increased resolution reveals one singlet and three doublets, in accord with the predicted C_{2h} structure.

Structural studies using nmr are often hampered in the case of quadrupolar nuclei by overlap of the broad resoances. Line-narrowing techniques have been shown to be useful where significant chemical shift differences occur.[2] We describe here resolution of overlapping resonances in a case where little chemical shift difference is present.

The molecule chosen for study arises from slow decomposition of liquid pentaborane(9) at room temperature[3] or the hot–cold, flow-quench pyrolysis of gaseous B_5H_9 in the presence of diborane(6) at 140°.[4] The major product in both reactions is 2-[2′-pentaboran(9)-yl]pentaborane(9), 2,2′-$(B_5H_8)_2$.[5] Mass spectra and nmr studies suggest a structure comprised of two B_5H_8 units connected by a boron–boron bond (see Figure 1).

Our recently presented high-field pmr and ^{11}B nmr spectra of 2,2′-$(B_5H_8)_2$[6] support this structure based on the B_5H_9 model. However, neither spectrum displays the expected reduction in molecular symmetry from C_{4v} for B_5H_9 to C_{2h} for 2,2′-$(B_5H_8)_2$. The pmr spectrum of 2,2′-$(B_5H_8)_2$ nearly overlies that of B_5H_9; for the small range of proton chemical shifts, interference from ^{10}B–H septets and nuclear quadrapole broadening (^{11}B, $I = {}^3/_2$; ^{11}B, $I = 3$) cause accidental overlap of the ^{11}B–H quartets.[6] The high-field ^{11}B nmr spectrum of 2,2′-$(B_5H_8)_2$ closely resembles that of B_5H_9, but fails to show the splitting for the different types of basal boron atoms that has been reported for other 2-substituted B_5H_8 derivatives.[7]

Experimental Section

Details of the nmr apparatus,[8] the specific application of the PRFT technique[9] to ^{11}B nmr spectroscopy,[10] and the preparation and purification of 2,2′-$(B_5H_8)_2$[3,4] have been described elsewhere. Spectra were run on a 20% v/v solution in *n*-pentane.

Results and Discussion

Our previously reported high-field, continuous-wave ^{11}B nmr spectrum[6] of 2,2′-$(B_5H_8)_2$ is identical with that shown in Figure 2A. The high-field doublet of intensity 2 is easily assigned to the apical 1,1′ boron atoms by analogy to pentaborane(9). The low-field resonances of intensity 8 must be attributed to the accidental overlap of an expected B(2,2′) singlet ($I = 2$), a B-(3,3′,5,5′) doublet ($I = 4$), and a B(4,4′) doublet ($I = 2$). Attempts to improve the resolution by varying the solvent, concentration, or temperature failed. Noise-modulated proton decoupling and artificial line-narrowing experiments[2] were also unsuccessful.

Despite the small chemical shift differences for three

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(1) Studies of Boranes. XXXV; for paper XXXIV of this series, see R. R. Rietz and R. Schaeffer, *J. Amer. Chem. Soc.*, **95**, in press.

(2) A. O. Clouse, D. Moody, R. R. Rietz, T. Roseberry, and R. Schaeffer, *J. Amer. Chem. Soc.*, **95**, 2496 (1973).

(3) D. F. Gaines, T. V. Iorns, and E. N. Clevenger, *Inorg. Chem.*, **10**, 1096 (1971).

(4) J. Dobson, R. Maruca, and R. Schaeffer, *Inorg. Chem.*, **9**, 2161 (1970).

(5) Named and numbered under the new rules appearing in *Inorg. Chem.*, 7, 1945 (1968).

(6) R. R. Rietz, R. Schaeffer, and L. G. Sneddon, *Inorg. Chem.*, **11**, 1242 (1972).

(7) (a) T. Onak, G. B. Dunks, I. W. Searcy, and J. Spielman, *Inorg. Chem.*, **6**, 1465 (1967); (b) A. B. Burg, *J. Amer. Chem. Soc.*, **90**, 1407 (1968); (c) P. M. Tucker, T. Onak, and J. B. Leach, *Inorg. Chem.*, **9**, 1430 (1970).

(8) A. Allerhand, D. Doddrell, and R. Komoroski, *J. Chem. Phys.*, **55**, 189 (1971).

(9) R. L. Vold, J. S. Waugh, M. P. Klein, and D. E. Phelps, *J. Chem. Phys.*, **48**, 3831 (1968).

(10) A. Allerhand, A. O. Clouse, R. R. Rietz, T. Roseberry, and R. Schaeffer, *J. Amer. Chem. Soc.*, **94**, 2445 (1972).