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Photoinsertion of Alkynes into a Ferraborane. Preparation and Characterization of a Novel Tetracarbon Carborane

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Abstract: The photolysis of the nido ferraborane, $B_4H_8Fe(CO)_3$, in the presence of an alkyne, RCCR, produces a good yield of the tetracarbon carborane, $R_4C_4B_4H_4$. The *C*-tetramethyl derivative of this new carborane has been characterized primarily by mass and NMR spectroscopy. An intermediate in the formation of this carborane, $(CH_3)_4C_4B_4H_4Fe(CO)_3$, has been isolated and partially characterized. Evidence is also presented for the formation of six- and eight-carbon carboranes in this system. Finally, the photolytic behavior of the ferraborane is contrasted with that of the isoelectronic organometallic compound, $C_4H_4Fe(CO)_3$.

The ability to synthetically modify the size and atom content of heteroborane cages has been a key development behind much of the progress in this area in the last decade.[1] The synthetic methods used have not, in general, included photolysis, although there are some examples of the effective use of photolytic techniques.[2,3] In the work reported below we demonstrate that an iron tricarbonyl fragment in a borane cage constitutes a functional group that, when activated by visible light, facilitates the insertion of alkynes into the borane cage, thereby producing unusual carboranes.[4]

The relationship between boranes and metalloboranes has been explored in detail in recent years.[5] Pertinent to this work is the fact that in many compounds the $Fe(CO)_3$ fragment behaves as a B–H fragment insofar as the geometry of the metalloborane cage is concerned. On the other hand, there are some large differences between boranes and ferraboranes, not the least of which is that the latter absorb in the visible. In fact ferraboranes are light sensitive,[6] suggesting that these compounds may exhibit some useful photochemistry.

As we have previously noted similarities between the filled MO structure of $B_4H_8Fe(CO)_3$ and that of $C_4H_4Fe(CO)_3$[7] and as the latter compound exhibits some interesting photochemistry,[8] we have chosen to first examine the behavior of $B_4H_8Fe(CO)_3$. Pettit and co-workers have demonstrated that the photolysis of cyclobutadieneiron tricarbonyl in the presence of alkynes yields substituted benzenes.[8] Thus, we felt that photolysis of the ferraborane under similar conditions might well yield carboranes. As detailed below, a variety of ferracarboranes and carboranes are produced, although reaction conditions and workup can be chosen such that a single novel tetracarbon carborane can be produced in good yield.

Results and Discussion

Photoactivation of Ferraboranes. The basic features of the electronic structure of ferraboranes as revealed by photoelectron spectroscopy have been discussed previously.[7] Recently, the MO properties of $B_4H_8Fe(CO)_3$ have been explored using SCF Xα scattered wave calculations.[9] The nature (energy and atomic composition) of the highest filled MOs of $B_4H_8Fe(CO)_3$ is given in Figure 1 and compared with the highest filled MOs of B_5H_9, the borane analogue of the ferraborane.[10] This comparison emphasizes the fact that the highest lying orbitals in $B_4H_8Fe(CO)_3$ have no counterpart in B_5H_9, are composed mainly of iron 3d atomic functions, and are essentially nonbonding with respect to the cage.[11] The UV–visible spectrum of a methyl derivative of $B_4H_8Fe(CO)_3$ is shown in Figure 2 and the lowest energy absorption is schematically indicated in Figure 1, where it is also compared to that for B_5H_9. As noted in Table I, a variety of ferraboranes and ferracarboranes have lowest energy absorptions in the same energy range and, in all cases, the difference between measured lowest ionization potential and excitation energy is roughly the same. Thus, we suggest that the LUMO in these compounds is also associated with the $Fe(CO)_3$ fragment and irradiation of $B_4H_8Fe(CO)_3$ at 3.1 eV will mainly perturb the $Fe(CO)_3$ fragment. It is well established by work on metal carbonyl systems in general[12] that the absorption of a photon by the metal carbonyl moiety leads to the dissociation of a CO ligand, thereby producing an unsaturated metal center. In the presence of other ligands, this leads to substitution. In the case of $B_4H_8Fe(CO)_2$, ligands such as alkynes may bind to the iron where they are in a potentially reactive position with respect

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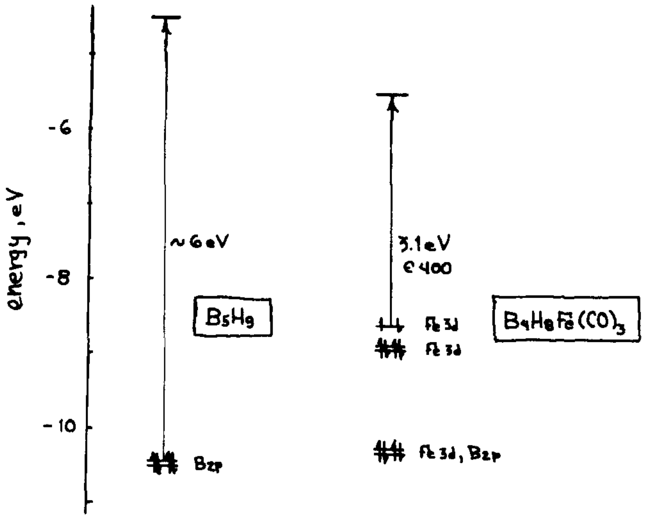


Figure 1. A schematic representation of the HOMO and LUMO structure of B_5H_9 and B_4H_8Fe $(CO)_3$ from photoelectron spectroscopy.

Table I. Lowest Electronic Transitions in Ferraboranes and Ferracarboranes

compd	band max, eV	IP-E, eV
1,2,4-$(CO)_3FeC_2B_3H_5$	3.3	5.3
1-$(CO)_3FeB_4H_8$	3.1	5.5
1-$(CO)_3FeB_4H_6(CH_3)_2$[a]	3.1	
2-$(CO)_3FeB_5H_9$	2.8	5.6
1-$(CO)_3FeB_5H_3(CO)_2$[b]	2.6	5.4

[a] Positions of methyl groups not known. [b] Locations of terminal CO's are either 2,3 or 2,4.

to insertion into the boron fragment. These qualitative considerations are confirmed by the products resulting from the photolysis of $B_4H_8Fe(CO)_3$ in the presence of alkynes.

Characterization of the Primary Stable Product. In terms of boron only, the photolysis of a solution of $B_4H_8Fe(CO)_3$ under conditions detailed in the Experimental Section is described by the equation

$$B_4H_8Fe(CO)_3 + CH_3C{\equiv}CCH_3 \rightarrow (CH_3)_4C_4B_4H_4 \quad (1)$$

The molecular formula of the single major product indicated in eq 1 was established mass spectrometrically. On a 1-mmol scale or less, the isolated yield of carborane product is 60%. The conversion of $B_4H_8Fe(CO)_3$ to the carborane as a function of photolysis time is shown in Figure 3. Within experimental error, the amount of ferraborane lost at any time is directly proportional to the amount of carborane formed. As no other product containing boron was observed by NMR, the relative ^{11}B signal intensities suggest that the actual yield of the reaction is probably higher than 60%. In most reactions $B_5H_9Fe(CO)_3$ was an impurity. Thus, as a control, the photolysis of this compound as a function of time in the presence and absence of the alkyne is reported in Figure 4. Clearly, there is a photoreaction between $B_5H_9Fe(CO)_3$ and the alkyne and the reaction is even more efficient than that with $B_4H_8Fe(CO)_3$. However, the only product found under these conditions is an insoluble, nonvolatile solid, demonstrating that $B_5H_9Fe(CO)_3$ is not responsible for the observed carborane product. A dark reaction with $B_4H_8Fe(CO)_3$, carried out under similar conditions, showed no evidence of reaction. Finally, the photolysis of $B_4H_8Fe(CO)_3$ with diphenylacetylene gave the tetraphenyl product, demonstrating that the reaction is not restricted to 2-butyne as the alkyne.

The NMR data on the major product are given in Table II. The ^1H and ^{13}C data show that there is one type of methyl group;[13] the ^1H and ^{11}B data indicate that there are two pairs of different BH groups; the residual coupling (Figure 5) of the $^1H\{^{11}B\}$ resonance at δ 2.52 (1.6 Hz), attributed to three-bond proton-proton spin coupling, shows that each of this pair of BH's is adjacent to the other two equivalent BH's. A static structure consistent with the NMR data that conforms to the electron-counting rules[5] is shown in Figure 6a. This structure is generated by removing a four-coordinate vertex from a tricapped trigonal prism and corresponds to a nido cage. The data do not rule out the other possible nido structure (Figure 6b), derived by removing a five-coordinate vertex, as the molecule may exhibit fluxional behavior. To test this possibility (see also below) the methyl resonance was observed down to −80 °C. It remains sharp, broadening no more than the solvent resonance. As the chemical-shift difference between the methyl groups in structure b may be small, this negative evidence does not rule out fluxional behavior.

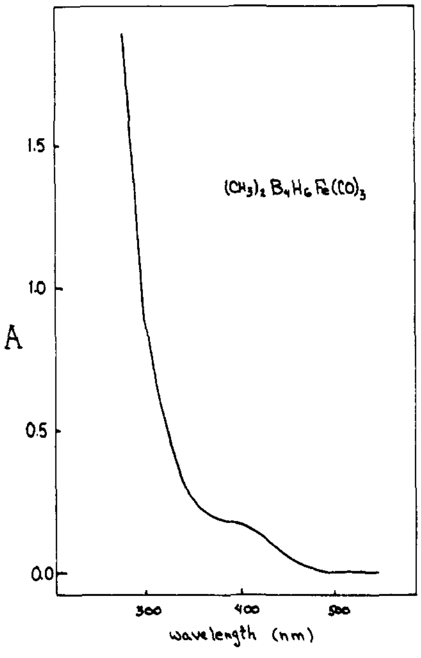
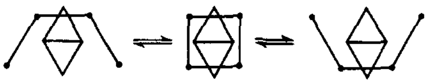


Figure 2. The UV-visible spectrum of $(CH_3)_2B_4H_6Fe(CO)_3$ in pentane.

The $^{11}B\{^1H\}$ spectrum is somewhat unusual (Figure 7) in that the upfield resonance is considerably broader than the downfield resonance. This cannot be explained by ^{11}B-^{11}B coupling as an A_2B_2 system must be symmetrical about the midpoint of the spectrum.[14] It is unlikely that the broadening is due to slightly inequivalent borons as the ratios of the fwhm peak widths are the same at 25.2 and 32.1 MHz. The broadness could be due to some sort of relaxation phenomenon; however, the ratios of peak widths are the same in both the $^1H\{^{11}B\}$ and $^{11}B\{^1H\}$ spectra (Table II). Lastly, the broadness might be ascribed to a kinetic process affecting one pair of borons more than the other. In fact, as indicated below, structure b (Figure 6) can undergo a fluxional process giving an average structure equivalent to (a) without losing one plane of symmetry. Unfortunately, the relative broadness of the $^{11}B\{^1H\}$ resonances did not change from −80 to 80 °C. Thus, the source of the inequivalence in the two resonances remains unexplained and structure a best summarizes the solution structural data.



The same carborane skeleton has recently been prepared in good yield by an entirely different route by El-Essawi and Siebert.[15] The derivative reported has ethyl substituents on the

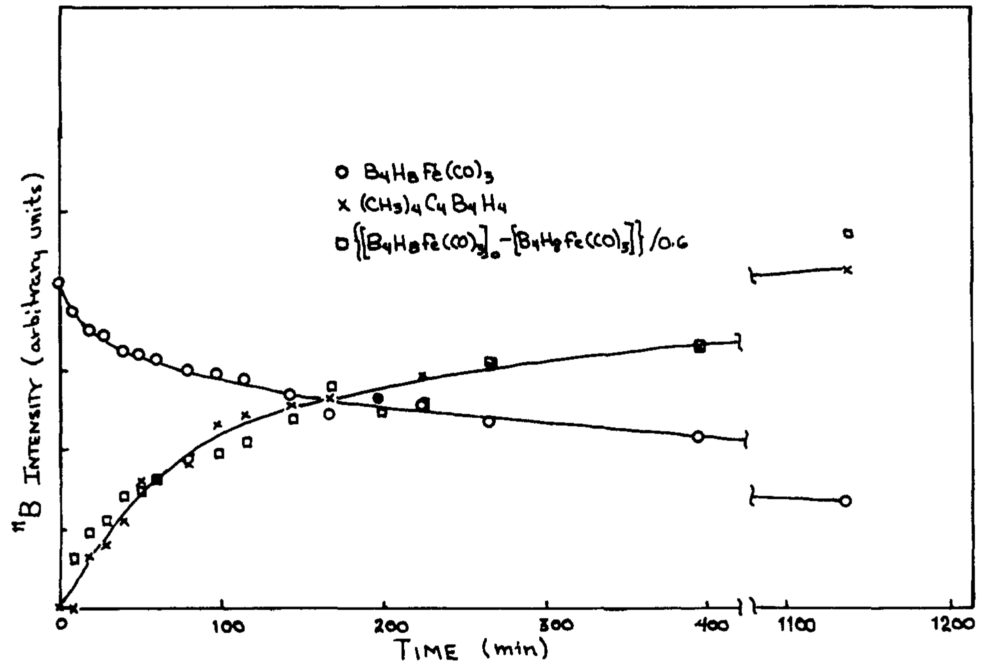


Figure 3. The photolysis of $B_4H_8Fe(CO)_3$ in the presence of CH_3CCCH_3 in pentane at 20 °C with 360-nm light. The reaction was carried out in a Pyrex NMR tube and the $^{11}B\{^1H\}$ signal intensities were used to monitor reaction progress. The time axis is not directly proportional to number of photons as the solution gradually darkened.

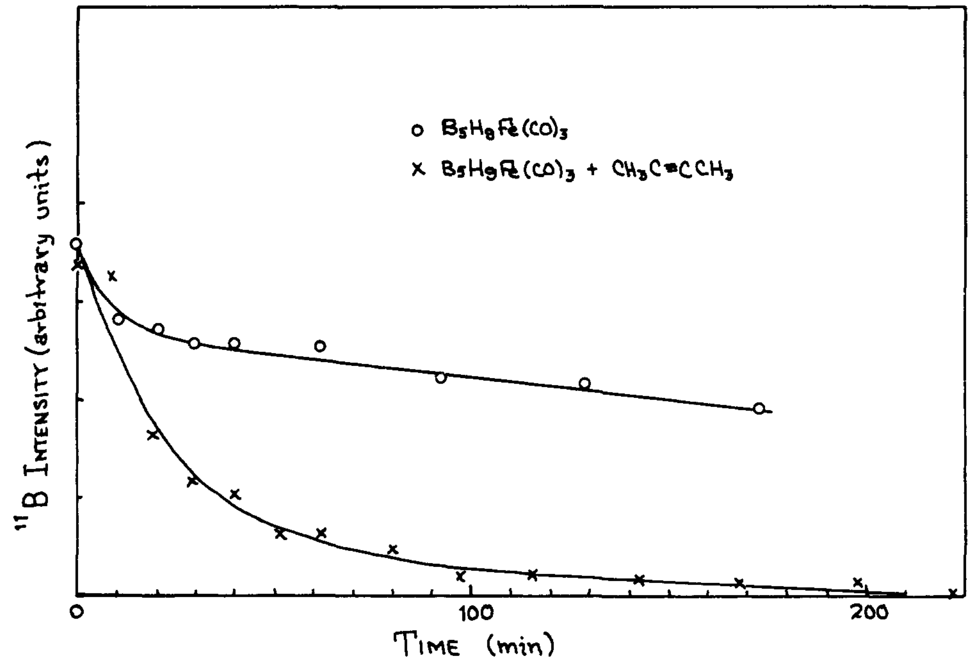


Figure 4. The photolysis of $B_5H_9Fe(CO)_3$ with and without the presence of CH_3CCCH_3 in pentane at 20 °C with 360-nm light. The reaction was carried out in a Pyrex NMR tube and the $^{11}B\{^1H\}$ signal intensities were used to monitor reaction progress.

carbons and methyl substituents on the borons. Here the presence of two different ethyl groups in the NMR clearly suggests the nonfluxional nido structure of Figure 6b. At face value the data show that substituents either freeze out the fluxional behavior or change the cage structure.

Consideration of the structures of eight-atom cages and four-carbon carboranes show that this is not as surprising as it seems. The two four-carbon, four-boron carboranes are derivatives of $C_4B_4H_8$, which is isoelectronic with the known compounds B_8H_{12} and $C_2B_6H_{10}$. The former is known to have an arachno structure in the solid state[16] despite a nido electron count. An arachno structure is also suggested for the latter compound,[17] although the data do not completely rule out a nido structure. Note that an arachno structure is also possible for $(CH_3)_4C_4B_4H_4$.[4] An equilibrated dodecahedral structure is proposed for the three-carbon carborane, $C_3B_5H_7$, with presumably 18 skeletal electrons.[18] Others have commented on the variety of structures exhibited by $B_8H_8^{2-}$ depending on conditions and note was taken of the fact that the barriers to structural interconversion for this eight-atom, closo system are low and depend on many factors including the heteroatom content of the cage.[19] Finally, another four-carbon carborane, $(CH_3)_4C_4B_8H_8$, exists in two readily interconvertible forms having different structures.[20] All these observations strongly suggest that the eight-atom cage system does not possess an overwhelmingly favored cage geometry. Thus, the observation

Table II. NMR Data of Products

compd	nuc obsd	nuc decoupled	chem^a shift	multiplicity^b	J, Hz	rel area	fwhm, Hz
$(CH_3)_4C_4B_4H_4$	^1H		2.52	q	134		
			2.02	s			
			1.14	q	172		
	^1H	^{11}B	2.52	t	1.6	1	5
			2.02	s		6	
			1.14	s		1	8
	^{11}B		−12.4	d	138		
			−14.0	d	170		
	^{11}B	^1H	−12.4	s		1	20
			−14.0	s		1	42
	^{13}C	^1H	34.5	s			
$(CH_3)_4C_4B_4H_4Fe(CO)_3$^{c}	^1H		2.05	s			
	^1H	^{11}B	2.70	s		1	
			2.55	s		1	
			2.05	s		6	
	^{11}B^{d}		−5	m			

[a] ^1H in δ, ^{11}B in parts per million relative to $BF_3{\cdot}(C_2H_5)_2O = 0$, downfield shifts positive, ^{13}C in parts per million relative to $Me_4Si = 0$. [b] s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. [c] Contaminated with $(CH_3)_4C_4B_4H_4$. [d] FT at 25.2 MHz unlocked.

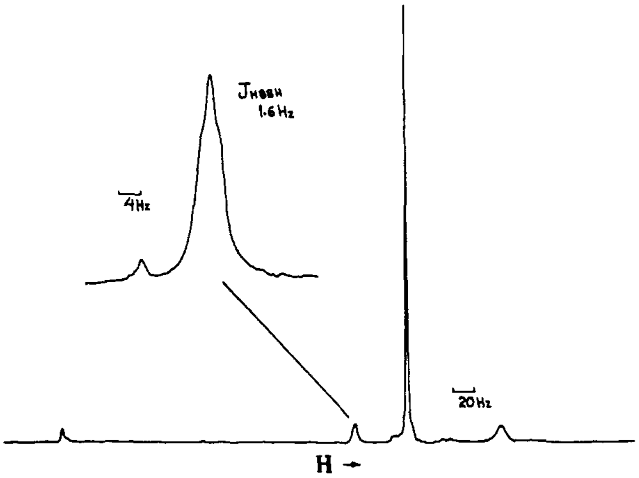


Figure 5. The 100-MHz $^1H\{^{11}B\}$ FT NMR spectrum of $(CH_3)_4C_4B_4H_4$.

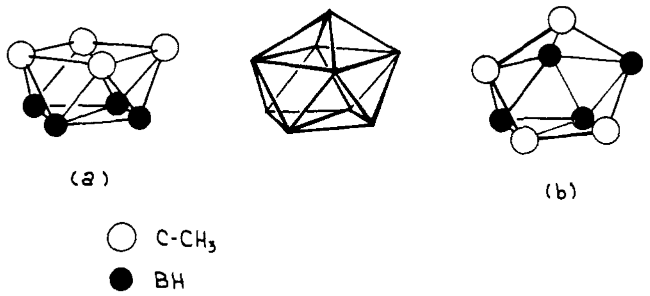


Figure 6. Possible nido structures for $(CH_3)_4C_4B_4H_4$ based on the tricapped trigonal prism.

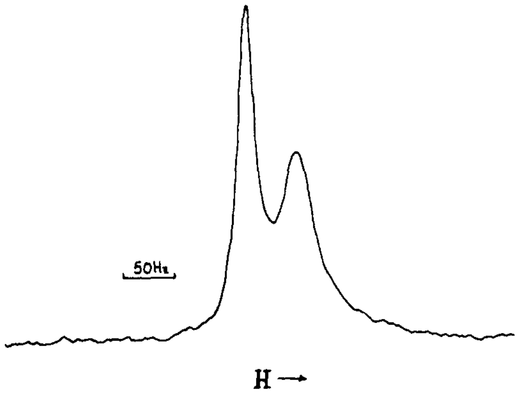


Figure 7. The 32.1-MHz $^{11}B\{^1H\}$ FT NMR spectrum of $(CH_3)_4C_4B_4H_4$.

that in the $C_4B_4H_8$ system exopolyhedral substituents either change barriers to interconversion or change cage structure is consistent with this suggestion.

A Ferracarborane Intermediate. To investigate the reaction system in more detail, a preparative photolysis was carried out with low photon intensity and frequent product removal. Under these conditions reaction corresponding to the equation

$$B_4H_8Fe(CO)_3 + CH_3C{\equiv}CCH_3 \rightarrow (CH_3)_4C_4B_4H_4Fe(CO)_3 \quad (2)$$

was observed. The ferracarborane indicated as a product decomposed slowly but continuously and could not be isolated free of the decompositon product, $(CH_3)_4C_4B_4H_4$, by vacuum-line fractionation. It was, however, "isolated" using the GC/MS technique, being characterized by a unique retention time and mass spectrum. The new ferracarborane is a deep red liquid that has been partially characterized by NMR (Table II). The ^1H and ^{11}B resonances are qualitatively similar to those of $(CH_3)_4C_4B_4H_4$ but shifted downfield. The tricapped prismatic structure shown in Figure 8 accommodates the available data. However, this compound has a nido electron count (22 electrons) and the structure would be predicted to be a bicapped Archimedian antiprism with a vacant vertex. Thus, Figure 8 may only express a possible average structure of the ferracarborane and, if so, even the relative positions of B, C, and Fe in the cage are not defined. Both the 22-electron $Cp_3Ni_3CB_5H_6$ and $Cp_4Ni_4B_5H_5$ have nido cage geometry in the solid state.[21,22] On the other hand, there is precedence for nine-atom systems with geometries other than the one predicted by the electron counting rules. The compound $L_2PtC_2B_6H_6R_2$ is a 9-atom, 20 skeletal electron metallocarborane that exhibits both a nido and a closo isomer in the solid state as well as in solution.[21] Despite the uncertainty concerning its structure, the isolation of the ferracarborane is circumstantial evidence that the alkyne molecules are inserted into the borane fragment via the iron atom.

Minor Products and Byproducts. In a number of experiments a more thorough examination of the reaction mixture was carried out. Figure 9 compares the mass spectra and retention times for two more new carboranes with that for the primary product discussed above. These new compounds constitute examples of rather unusual carboranes in that no other examples of six- and eight-carbon carboranes have been reported.

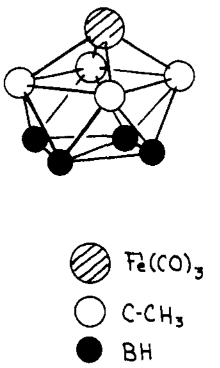
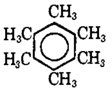
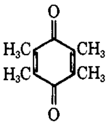
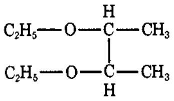


Figure 8. The proposed average solution structure of $(CH_3)_4C_4B_4H_4Fe(CO)_3$.

Table III. Other Products Observed

compd	rel yield[a]	conditions, if specific
H_2	not measd	
CO	not measd	
	trace[b]	
	7%[b]	neat $(CH_3C)_2$
 $C_2H_5-O-CH(CH_3)-CH(CH_3)-O-C_2H_5$	300%	$(C_2H_5)_2O$, 254 nm, 40 °C, $(C_6H_5C)_2$
C_4H_8	not measd	

[a] Based on $B_4H_8Fe(CO)_3$. [b] Minimized at 20 °C.

The six-carbon carborane has been isolated in very small amounts as a white, crystalline, sublimable solid. Although the mass spectra demonstrate a structural relationship between the three compounds, the structures shown in Figure 9 are speculative and the possibility that these compounds are alkylated four-carbon carboranes cannot be completely eliminated at this point. Small quantities of $(CH_3)_2C_2B_4H_4Fe(CO)_3$, a known compound,[24] were also observed by the GC/MS technique.

Depending on reaction conditions a host of products containing no boron were observed. Table III lists those definitely identified. Generally, these products can be accounted for on the basis of known reactions of alkynes in systems containing iron carbonyls.[25] For example, butene is observed and it is known that photolysis of $Fe(CO)_5$ can cause hydrogenation.[12] Hexamethylbenzene and duroquinone were also found and, again, examples of their production in metal carbonyl systems are known.[25] One unusual product formed with ether as the solvent is $[C_2H_5O(H)\ (CH_3)C-]_2$. As it was produced in greater than 100% yield, it is clearly the net consequence of some type of radical reaction. The richness of this reaction system is typical of alkyne-metal carbonyl systems in general.[26] However, by choosing solvent, temperature, and light frequency properly these products can be minimized and a relatively clean conversion of the ferraborane to tetracarbon carborane can be accomplished.

Mechanism. Although insufficient information exists to define a complete mechanism, Scheme I summarizes the observations in a self-consistent fashion. All species, except those in brackets, have been observed in this work. This mechanism is very similar to that proposed for the photoinsertion of alkynes into $C_4H_4Fe(CO)_3$. The major difference is that the key intermediate for the ferraborane apparently has sufficient lifetime to react with either CO or another alkyne. This may well be due to the fact that $[(CH_3)_2C_2]_2B_4H_4Fe(CO)_2$ can theoretically exist in a closo structure with a saturated iron atom or in a nido structure with an unsaturated iron atom. Hence it seems that the multiple insertion of alkyne observed for the ferraborane is a natural consequence of its borane nature.

Direct hydroboration of the ferraborane by the alkyne does not occur under the reaction conditions. This is reasonable in

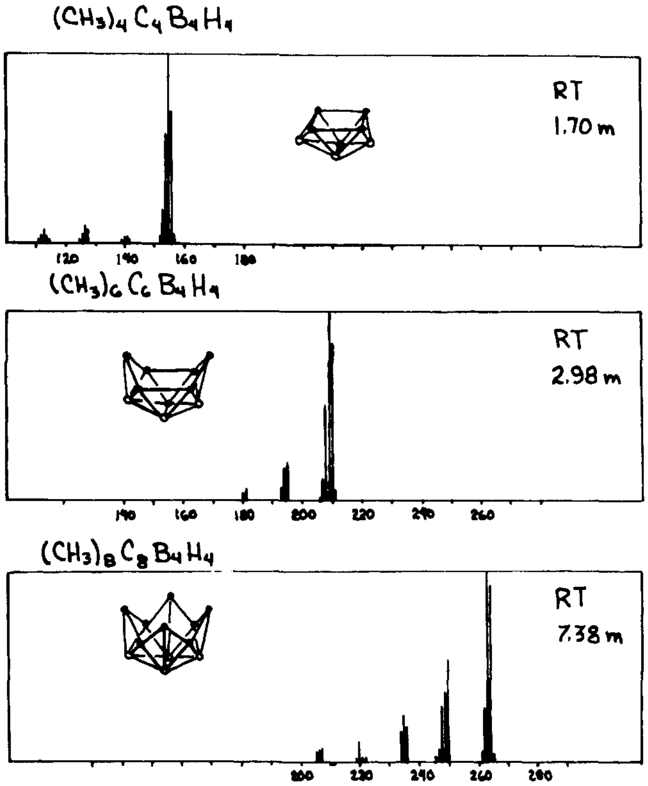


Figure 9. Mass spectra and retention times of $(CH_3)_4C_4B_4H_4$, $(CH_3)_6C_6B_4H_4$, and $(CH_3)_8C_8B_4H_4$ with possible structures.

Scheme I

$$\begin{tikzcd}
B_4H_8Fe(CO)_3 \arrow[d, "h\nu"] & \\
{[B_4H_8Fe(CO)_2]} \arrow[d, "{+R_2C_2,\ -2H_2}"] & \\
{[R_2C_2B_4H_4Fe(CO)_2]} \arrow[r, "+CO"] \arrow[d, "+R_2C_2"] & R_2C_2B_4H_4Fe(CO)_3 \\
{[R_4C_4B_4H_4Fe(CO)_2]} \arrow[r, "+CO"] \arrow[d, "+R_2C_2"] \arrow[dr, "-Fe(CO)_2"] & R_4C_4B_4H_4Fe(CO)_3 \arrow[d, "-Fe(CO)_3"] \\
{[R_6C_6B_4H_4Fe(CO)_2]} \arrow[d, "+R_2C_2"] \arrow[dr, "-Fe(CO)_2"] & R_4C_4B_4H_4 \\
{[R_8C_8B_4H_4Fe(CO)_2]} \arrow[dr, "-Fe(CO)_2"] & R_6C_6B_4H_4 \\
 & R_8C_8B_4H_4
\end{tikzcd}$$

that the thermal insertion of an alkyne into a similar metalloborane (2-$CpCoB_4H_8$), presumably via an alkenylborane, requires a temperature of 175 °C.[27] On the other hand, a mechanism in which the absorption of a photon activates the cage toward hydroboration or direct insertion rather than CO dissociation cannot be eliminated. However, in the absence of any direct evidence for photoactivation of the cage, the mechanism presented above is favored.

The question of mechanism does not obscure the fact that the type of reaction observed here constitutes a new, rational route for the insertion of carbon atoms into the borane cage. Superficially, it is related to the method of Grimes and coworkers[1] in which the oxidative properties of the metal in metallocarboranes are utilized to fuse carborane and metallocarborane cages into larger cages. Clearly, metalloboranes and metalloheteroboranes can serve as useful synthetic intermediates.

Finally, the photoactivated reaction of $B_4H_8Fe(CO)_3$ with alkynes has a curious relationship to the Reppe process for the cyclic polymerization of acetylene to cyclooctatetraene and some benzene.[28] (Cyclobutadiene, if formed, would not be observed.) The three carboranes observed (Figure 9) might be viewed as the B_4H_4 "adducts" of cyclobutadiene, benzene, and cyclooctatetraene. If, as suggested in the proposed mechanism, the metal is the center upon which the carborane is assembled, then, considering the proposed mechanisms for the cyclic polymerization of acetylene,[29] the similarity between the two systems is not all that surprising.

Experimental Section

Diethyl ether and pentane were distilled in vacuo at room temperature from lithium aluminum hydride immediately prior to use. Methylene chloride was dried over P_2O_5 before distillation. The 2-butyne was obtained from K&K Laboratories and was also distilled in vacuo before use. $B_4H_8Fe(CO)_3$ and $B_5H_9Fe(CO)_3$ were prepared as previously described.[6,30] Diphenylacetylene was purchased from K&K Laboratories and was sublimed before use.

The FT NMR spectra were obtained on a Varian XL-100 spectrometer controlled by a Transform Technology TT-100 computer and operating at 100.1 (^{1}H), 32.1 (^{11}B locked), or 25.2 MHz (^{11}**B** unlocked). Mass spectra were obtained on an AEI-MS9 mass spectrometer. Unless indicated otherwise irradiations were carried out in a Rayonet reactor at either 254 or 360 nm. The UV-visible spectra were measured on a Cary 15 spectrophotometer. GC/MS were obtained on a Du Pont DP-1 system.

Standard high-vacuum techniques were employed[31] and reactions were carried out in vacuo in Pyrex reaction flasks equipped with a high-volume Teflon stopcock. The irradiations at 254 nm were carried out in quartz bulbs. In a typical reaction the flask was attached to the vacuum line and evacuated. After immersion in liquid nitrogen, the ferraborane, alkyne, and solvent were sequentially distilled in vacuo into the flask. The flask was then warmed to room temperature and the reactants were mixed before photolysis was initiated. Temperatures below ambient (about 40 °C) in the photolytic reaction were achieved by using a special bulb incorporating a water-cooled finger in contact with the ferraborane solution. After the reaction was complete, the volatile reaction products were transferred to the vacuum line and separated by trap-to-trap fractionations. The nonvolatile residue was separated using thin layer and column chromatography in air.

$(CH_3)_4C_4B_4H_4$. This compound was observed under all conditions examined, i.e., diethyl ether, pentane, or no solvents, 20–40 °C, 254–400-nm irradiation. The best conditions were found to be dry pentane as solvent, 20 °C, and irradiation at 360 nm. Under these conditions, the irradiation of 0.3 mmol of $B_4H_8Fe(CO)_3$ with 1.7 mL (~30 mmol) of CH_3CCCH_3 in 4.4 mL of pentane for 18 h yielded 0.2 mmol (60%) of the carborane. The product which is retained by a −30 °C trap is a clear, colorless, viscous liquid at room temperature. The compound is only slightly less volatile than $B_4H_8Fe(CO)_3$ but traces of the latter may be removed by exposure to air. Alternatively, the product may be isolated using GLC (5-ft Chromosorb G, 70–80, 5% SE-30, column at 80 °C, t_R = 6.3 min). The mass spectrum consists of a parent envelope with an intensity distribution consistent with a molecule containing four borons. Very little fragmentation is observed (see Figure 9). Precise mass measurement of the parent ion yields the molecular formula $^{11}B_4{}^{12}C_8{}^{1}H_{16}^+$ (156.162 calcd, 156.161 measd).

$(CH_3)_4C_4B_4H_4Fe(CO)_3$. A solution of 0.8 mmol of $B_4H_8Fe(CO)_3$ and about 40 mmol of CH_3CCCH_3 in pentane was irradiated for 100 h with an Oriel 150-W Xe lamp through a Corning 4.97 filter (360–600 nm). After each 20 h the solution was fractionated, the products less volatile than $B_4H_8Fe(CO)_3$ were removed, and the unreacted material was irradiated again. In this fashion a significant amount of an unstable, deep red, slightly volatile material stopping in a 0 °C trap was obtained. The mass spectrum clearly showed the loss of 2 CO molecules from the *m/e* 268 ion ($^{56}Fe^{11}B_4{}^{12}C_{10}{}^{1}H_{16}{}^{16}O_2^+$, 268.087 calcd, 268.091 measd). The presence of a parent ion at *m/e* 296 was determined by observing a leak-dependent peak at *m/e* 296.082 and by observing a small *m/e* 296 ion peak in the GC/mass spectrum. Despite the fact that $(CH_3)_4C_4B_4H_4$ slowly passes a 0 °C trap, this carborane could not be removed from the ferracarborane. The best purity achieved was 40% carborane–60% ferracarborane. The ferracarborane continuously decomposed yielding carborane and was only "isolated" in the GC/MS experiments ($t_R((CH_3)_4C_4B_4H_4Fe(CO)_3) = 6.0$ min; under the same conditions $t_R((CH_3)_6C_6B_4H_4) = 5.6$ min).

$(CH_3)_6C_6B_4H_4$. Only small amounts of this carborane have been isolated and its characterization remains incomplete. It was observed mass spectrometrically (see Figure 9) in all the reactions and was isolated as a white, sublimable solid (stopping at 0 °C) in the larger scale reactions. Sufficient amounts have not been obtained so that unambiguous NMR spectra could be obtained. The molecular formula was measured by precise mass measurement: $^{11}B_4{}^{12}C_{12}{}^{1}H_{22}^+$ (210.210 calcd, 210.208 measd).

$(C_6H_5)_4C_4B_4H_4$. This derivative was prepared in the same manner as the methyl compound using $(C_6H_5)CC(C_6H_5)$. Small amounts of the product were isolated by thin layer chromatography (R_f 0.4 in 5% $(C_2H_5)_2O$ in hexane) and identified mass spectrometrically.

Organic Products. Under certain conditions (Table III) duroquinone, $C_{10}H_{12}O_2$, was isolated by TLC in small yield. This light yellow, solid compound was identified from its mass spectrum, exact parent ion mass (164.084 calcd, 164.083 measd), IR spectrum, and ^{1}H and ^{13}C NMR spectra. Very small amounts of hexamethylbenzene were also observed (mass spectrum, exact mass, 162.141 calcd, 162.127 measd, and ^{1}H NMR). It was extremely difficult to separate $(CH_3)_6C_6B_4H_4$ from these two organics without losing most of the carborane.

Butene and H_2 were identified as products via volatility and ion fragmentation patterns. CO was identified as a product by exact mass measurements on the nonvolatile products.

In one reaction a curious product derived from the solvent was isolated. This is the "dimer" of diethyl ether, $C_2H_5OC(H)(CH_3)$-$C(H)(CH_3)OC_2H_5$ (Table III). It is a fairly volatile (stopping in a −63 °C trap), clear liquid with a mass spectrum characteristic of a dimer (cleavage resulting in $C_4H_9O^+$ is predominant). Exact mass measurement on the parent yields 146.131 calcd, 146.132 measd, ^{1}H NMR exhibits complex multiplets at δ 1.0 and 3.4 with relative areas of 2:1, and the IR shows bands characteristic of ROR′.

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Electron-Diffraction Investigations of the Molecular Structures of *cis*- and *trans*-1,2-Dimethyldiborane

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Abstract: The structures of *cis*- and *trans*-1,2-dimethyldiborane have been investigated at room temperature by gas-phase electron diffraction. The more important distances (r_a/Å), angles (∠/deg), and amplitudes of vibrations (l/Å), with uncertainties estimated at 2σ, are as follows: r(B–B) = 1.798 (7) (cis), 1.799 (8) (trans); r(B–C) = 1.579 (2), 1.581 (3); $r(\mathrm{B{-}H}_b)$ = 1.358 (6), 1.365 (8); $r(\mathrm{B{-}H}_t)$ = 1.239 (8), 1.241 (10); r(C–H) = 1.108 (2), 1.110 (3); ∠BBC = 122.6 (5), 121.8 (6); $\angle\mathrm{BBH}_t$ = 117.0 (assumed), 118.5 (27); ∠BHC = 113.3 (2.1), 112.5 (2.6); l(B–B) = l(B–C) + 0.0100 = 0.0726 (32), 0.0721 (33); $l(\mathrm{B{-}H}_b) = l(\mathrm{B{-}H}_t) + 0.0140 = l(\mathrm{C{-}H}) + 0.0600$ = 0.0865 (40), 0.0891 (44). The contribution of H distances dependent on methyl torsion was described in terms of cosinusoidal one-methyl potential functions, both threefold and sixfold for the cis (V_3 = 1.5 kcal/mol, lowest for CH_3 staggered to $\mathrm{B(H}_b)_2\mathrm{H}_t$; V_6 = −0.5 kcal/mol) but only threefold for the trans (V_3 = 2.0 kcal/mol). The distance and angle values generally lie between those of diborane and tetramethyldiborane, and it seems that there is appreciable methyl–methyl repulsion in the cis compound.

The isolation and characterization of the two stereoisomers of 1,2-dimethyldiborane(6)[2] (DMDB) afforded the opportunity to establish the molecular structures quantitatively and to make comparisons with diborane(6)[3] and some of its other derivatives. The indications were of little change in dimensions in the remnant of the parent molecule[4] except on extensive substitution to tetramethyldiborane(6) (TeMDB), which considerably lengthens the B–B distances.[5a] The B–C distance, however, remains nearly the same in TeMDB, and even in trimethylborane,[5b] as it is in monomethyldiborane(6)[4a] (MMDB).

Experimental Section

Samples of *trans*-1,2-DMDB (93%, mp −102 °C) and *cis*-DMDB (96%, mp −132.5 °C) were purified at the University of Washington and transported at −196 °C to Oregon State University in sealed Pyrex tubes. For the diffraction experiments they were warmed to −70 to −65 °C to provide vapor pressures of about 15 Torr. About 3 mmol of each was used. The remainder of each sample was reassayed, and no detectable change in purity was found in either.

Diffraction photographs were made in the Oregon State apparatus, with an r^3 sector and 8 × 10 in. Kodak projector slide (medium) plates at nominal nozzle-to-plate distances of 70 and 30 cm (long and intermediate cameras). Other experimental conditions: nozzle tip at room temperature for trans and at −27 °C for cis; beam currents, 0.4–0.5 μA; exposure times, 1.5–3.0 min; ambient apparatus pressure during exposures, 0.6–2.0 × 10^{-5} Torr; plate development, 10 min in D-19 diluted 1:1; electron wavelengths about 0.057 Å determined by a voltage measurement, calibrated in separate experiments with gaseous CO_2 (r_a(C=O) = 1.164 Å and r_a(O···O) = 2.3244 Å).

The plates (cis, three long camera and four intermediate camera; trans, three long and two intermediate) were handled as described previously[6] to obtain scattered intensity data. Calculated, smooth backgrounds[7] containing contributions from theoretical elastic[8] and inelastic[9] electron scattering amplitudes were subtracted to give the molecular intensity distributions (Figure 1), for these molecules adequately represented by

$$sI_m(s) = k \sum_{i,j} A_i A_j r_{ij}^{-1} \exp(-l_{ij}^2 s^2/2) \cos(\eta_i - \eta_j) \sin r_{ij}s \qquad (1)$$

The ranges of the data from the long and intermediate camera distances were $2.00 \leqslant s \leqslant 12.75$ Å^{-1} and $7.00 \leqslant s \leqslant 31.00$ Å^{-1} for cis and $1.00 \leqslant s \leqslant 12.75$ Å^{-1} and $7.00 \leqslant s \leqslant 31.50$ Å^{-1} for trans; the data interval was Δs = 0.25 Å^{-1}. The reduced data, calculated backgrounds, and molecular intensity averages are available as supplementary material.

The least-squares structure refinements[10] were based on eq 1 with A's and η's derived[11] from tables.[8] The observed intensity data were