Volume 18
Number 12
December 1979

Inorganic Chemistry

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Polyhedral Ferraboranes Derived from the $B_5H_8^-$ Ion. Analogues of Ferrocene, Hexaborane(10), and *nido*-$B_{11}H_{15}$

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Received April 3, 1979

The reaction of $B_5H_8^-$, Fe^{2+}, and $C_5H_5^-$ in THF at −78 °C followed by workup of the products in air gave violet 2-(η^5-C_5H_5)FeB_5H_{10}, yellow 2-(η^2-C_5H_5)$FeB_{10}H_{15}$, and ferrocene, plus traces of other ferraboranes. From ^{11}B and ^1H NMR spectra, 2-(η^5-C_5H_5)FeB_5H_{10} was assigned a pentagonal-pyramidal structure with iron in the base and five bridging hydrogen atoms (3 B–H–B and 2 Fe–H–B) on the open face. On being heated to 175–180 °C this compound rearranged to violet 1-(η^5-C_5H_5)FeB_5H_{10}, in which the iron atom is proposed to occupy the apex position. Both isomers are electronic analogues of B_6H_{10} and ferrocene, and the 1-isomer is a direct structural analogue of ferrocene which contains a cyclic $B_5H_{10}^-$ ligand, isoelectronic with $C_5H_5^-$. From NMR data the structure of 2-(η^5-C_5H_5)$FeB_{10}H_{15}$ was elucidated as an 11-vertex icosahedral fragment with iron in the equatorial belt adjacent to the apex boron, and five B–H–B bridges on the open face. A paramagnetic product formulated as $(C_5H_5)_2FeB_8H_8$ gave uninformative NMR spectra and was not structurally characterized.

Introduction

Studies of the reaction of $CoCl_2$, $C_5H_5^-$, and the $B_5H_8^-$ ion in this laboratory[1] have shown that a large number of crystalline, air-stable cobaltaboranes are produced, many having novel cage geometry or structural features of unusual interest. X-ray crystallographic analyses[2-7] of seven of the main species, which contain up to four cobalt atoms in the polyhedral cage, have established their geometries and confirmed the close relationship of these compounds to various metal cluster systems. In view of these findings, it was of interest to examine the reactions of $B_5H_8^-$ and $C_5H_5^-$ with other transition metal ions, particularly Fe^{2+} and Ni^{2+}. It was not entirely surprising to find that the isolable products of these reactions are markedly different from those of the cobalt system, and from each other. Preliminary findings on the iron reaction have been communicated earlier,[8] and the nickel system is described elsewhere.[20] In this paper we report the synthesis and structural characterization of several novel ferraboranes from the treatment of $B_5H_8^-$ ion with $FeCl_2$ and $C_5H_5^-$ in tetrahydrofuran (THF).

Results and Discussion

Reaction of $FeCl_2$ with $B_5H_8^-$ Ion and NaC_5H_5. In a single-stage procedure developed in earlier studies of the $CoCl_2$–$B_5H_8^-$–$C_5H_5^-$ reaction, $FeCl_2$ and B_5H_9 were added to a larger quantity of NaC_5H_5 in THF solution. The $C_5H_5^-$ ion plays a dual role,[1] deprotonating B_5H_9 to form the $B_5H_8^-$ ion and also serving as a capping ligand for Fe^{2+}. The reaction at room temperature produced largely ferrocene together with small quantities of several new ferraboranes which were isolated by column and thick-layer chromatography on silica. In all cases, the new products exhibited strong mass spectroscopic parent envelopes which are consistent with their established elemental compositions.

$$B_5H_9 + C_5H_5^- \rightarrow B_5H_8^- + C_5H_6$$

$$B_5H_8^- + FeCl_2 + C_5H_5^- \rightarrow (\eta^5\text{-}C_5H_5)_2Fe + 2\text{-}(\eta^5\text{-}C_5H_5)FeB_5H_{10} + (\eta^5\text{-}C_5H_5)FeB_{10}H_{15} + (C_5H_5)_2FeB_8H_8$$

Table I. 32.1-MHz ^{11}B FT NMR Data[a]

compd	δ[b] (*J*, Hz)	rel areas
2-(η^5-C_5H_5)FeB_5H_{10}	44.4 (145) B(3,6)–H	2
	8.2 (146) B(4,5)–H	2
	−53.0 (140) B(1)–H	1
1-(η^5-C_5H_5)FeB_5H_{10}	5.1 (145)	5
2-(η^5-C_5H_5)$FeB_{10}H_{15}$	27.0 (104)	2
	24.2 (102)	2
	13.4 (120)	3
	9.7 (141)	2
	−38.4 (152) B(1)–H	1
$(C_5H_5)_2FeB_8H_8$	−5.1 (s, br)	

[a] All spectra obtained in toluene-d_8 solution. [b] Chemical shifts relative to $BF_3\cdot O(C_2H_5)_2$ with positive values indicating deshielding.

Structural Characterization of 2-(η^5-C_5H_5)FeB_5H_{10}. The principal ferraborane product, 2-(η^5-C_5H_5)FeB_5H_{10}, was obtained as a violet, crystalline, moderately air-sensitive solid and characterized from its ^{11}B and ^1H NMR and unit- and high-resolution mass spectra (Tables I–III). The molecular structure shown in Figure 1A is in conformity with the spectroscopic data and with skeletal electron-count arguments;[9] the molecule has 16 skeletal valence electrons (1 from (C_5H_5)Fe, 1 from each bridging hydrogen, and 2 from each BH unit) and thus is a ($2n + 4$)-electron system for which one would expect a pentagonal-pyramidal nido cage structure. The ^{11}B NMR data reveal three types of boron environments in a 2:2:1 ratio, in which the low-field signal is assigned to B(3) and B(6) by virtue of their locations adjacent to iron.[10] The area 1 high-field resonance is attributed to the apex boron, B(1), and the intermediate signal to B(4) and B(5). In the undecoupled ^{11}B spectrum each signal appears as a B–H doublet which collapses to a fairly sharp singlet on proton decoupling.

The normal and ^{11}B-decoupled 100-MHz proton NMR spectra (Table II) exhibit the expected C_5H_5 singlet as well as separate quartets for the three types of terminal H–B proton, which appear in a 2:2:1 area ratio; each of these quartets

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Table II. 100-MHz ^1H FT NMR Data[a]

compd	δ[b]	multiplicity (J, Hz)	rel area	assignt
2-(η^5-C_5H_5)FeB_5H_{10}	4.04	singlet	5	C_5H_5
	6.96	quartet (147)	2	H_t–B
	3.86	quartet (153)	2	H_t–B
	−0.55	quartet (141)	1	H_t–B
	−1.70	broad singlet	2	B–H–B
	−2.33	broad singlet	1	B–H–B
	−15.99	quartet (70)	2	Fe–H–B
1-(η^5-C_5H_5)FeB_5H_{10}	4.23	singlet	1	C_5H_5
	3.50	singlet[c]	1	H_t–B
	−4.52	broad singlet	1	B–H–B
2-(η^5-C_5H_5)$FeB_{10}H_{15}$	5.10	singlet[c]	2	H_t–B
	4.92	singlet	5	C_5H_5
	4.30	singlet[c]	2	H_t–B
	3.54	singlet[c]	6	H_t–B
	−2.44	singlet[c]	2	B–H–B
	−2.64	singlet[c,d]	1	B–H–B
	−3.46	singlet[c]	2	B–H–B

[a] All spectra obtained in toluene-d_8 solution. [b] Parts per million relative to $BF\cdot O(C_2H_5)_2$, with positive sign indicating deshielding. [c] Measured from ^{11}B-decoupled spectrum. [d] Partially overlapped with peak at δ −2.44.

Table III. High-Resolution Mass Measurements

compd	ion	calcd	obsd
2-(η^5-C_5H_5)FeB_5H_{10}	$^{12}C_5{}^{11}B_5{}^1H_{16}{}^{56}Fe^+$[a]	187.1067	187.1062
2-(η^5-C_5H_5)$FeB_{10}H_{15}$	$^{12}C_5{}^{11}B_{10}{}^1H_{20}{}^{56}Fe^+$[b]	246.1845	246.1845
	$^{12}C_5{}^{11}B_{10}{}^1H_{21}{}^{56}Fe^+$[a]	247.1923	247.1917
$(C_5H_5)_2FeB_8H_8$	$^{12}C_{10}{}^{11}B_8{}^1H_{18}{}^{56}Fe^+$[b]	282.1502	282.1513
	$^{12}C_{10}{}^{11}B_8{}^1H_{19}{}^{56}Fe^+$[a]	283.1580	283.1572

[a] Mass of protonated parent ion obtained in methane under chemical ionizing conditions. [b] Mass of parent ion.

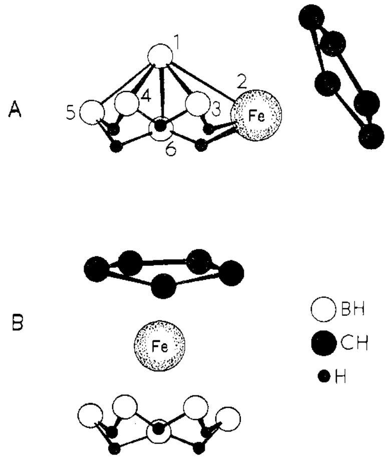

Figure 1. Proposed structures of 2-(η^5-C_5H_5)FeB_5H_{10} (top) and 1-(η^5-C_5H_5)FeB_5H_{10} (bottom). Fe–B connections are omitted in the lower drawing in order to emphasize the sandwich structure.

collapses to a sharp singlet on ^{11}B decoupling. In addition, the two types of B–H–B bridging protons are clearly distinguishable by broad singlets in a 2:1 area ratio, and the two equivalent Fe–H–B protons exhibit a characteristic high-field signal of area 2 centered nearly 16 ppm above $(CH_3)_4Si$. In the undecoupled spectrum this resonance appears as an approximate 1:3:3:1 quartet (J = 70 Hz); ^{11}B decoupling produces collapse of these lines to a sharp singlet, indicating that the quartet structure arises from coupling between the Fe–H–B protons and ^{11}B nuclei, with the Fe nucleus playing some as yet undefined role.

Since (η^5-C_5H_5)FeH is electronically equivalent to BH in the sense that each is a formal 2-electron donor to framework bonding,[9,11] 2-(η^5-C_5H_5)FeB_5H_{10} may be viewed as an analogue of hexaborane(10), B_6H_{10}. This complex is also an electronic and structural counterpart of the previously reported[12] species 2-$(CO)_3FeB_5H_9$, which has been shown to have a pentagonal-pyramidal geometry with iron in the base; indeed, it is interesting that the ^{11}B spectrum of the latter compound in CH_2Cl_2 contains basal resonances of 46.1 and 8.6 ppm and an apical signal at −47.2 ppm (new sign convention), remarkably close to the spectrum of 2-(η^5-C_5H_5)FeB_5H_{10}. (For comparison, we note that B_6H_{10} itself[13] exhibits basal and apical ^{11}B resonances at δ 15.0 and −51.2, respectively.)

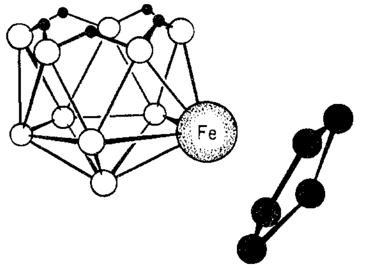

Figure 2. Proposed structure of (η^5-C_5H_5)$FeB_{10}H_{15}$.

Thermal Isomerization of 2- to 1-(η^5-C_5H_5)FeB_5H_{10}, "Pentaboraferrocene". The observation that 2-(η^5-C_5H_5)-FeB_5H_{10} is an electronic analogue not only of B_6H_{10} but also of $(\eta^5\text{-}C_5H_5)_2Fe$ (ferrocene) prompted us to attempt the conversion of it to the 1-isomer, in which iron occupies the apex position. It has previously been shown in our laboratory that the square-pyramidal cobalt complex 2-(η^5-C_5H_5)CoB_4H_8 undergoes thermal isomerization at 200 °C to 1-(η^5-C_5H_5)-CoB_4H_8, with cobalt moving from a basal to an apical location.[1,14] Accordingly, a sample of 2-(η^5-C_5H_5)FeB_5H_{10} was heated in vacuo at 175 °C without solvent, which produced partial isomerization accompanied by some decomposition. On further heating of the sample in toluene-d_8 for several days at 175 and 180 °C, the conversion to 1-(η^5-C_5H_5)FeB_5H_{10} was nearly complete as measured by ^1H NMR.

The proposed structure of the new isomer (Figure 1B) is based on the observation of a single ^{11}B NMR resonance and of lone terminal H–B and bridging B–H–B peaks in the ^1H NMR spectrum. The absences of a proton resonance in the high-field Fe–H region and of an ^{11}B signal in the δ −40 to −50 (apical BH) range are also significant since they point strongly to occupancy of the apex position by iron.

The product 1-(η^5-C_5H_5)FeB_5H_{10}, which like its isomer is a violet solid and somewhat air sensitive, contains the cyclic $B_5H_{10}^-$ ligand, isoelectronic with $C_5H_5^-$, and is the first complex of this ion to be reported. Several carborane analogues of planar $B_5H_{10}^-$, notably 2,3- and 2-4-$C_2B_3H_5^{4-}$ and 2,3-$C_2B_3H_7^{2-}$, have previously been observed by us as ligands in metallocarboranes, of which a number of crystal structures have been determined.[15] We have not as yet succeeded in obtaining crystals of 1-(η^5-C_5H_5)FeB_5H_{10} suitable for X-ray analysis.

Structural Characterization of (η^5-C_5H_5)$FeB_{10}H_{15}$. Electron-counting procedures[9,11] classify this molecule as a 26-electron, 11-vertex ($2n + 4$)-cage system for which one expects a nido structure; the obvious choice is an 11-vertex icosahedral fragment. Given this basic geometry, there are only three possible locations for the Fe(η^5-C_5H_5) group, i.e., in the 1 (apex), 2 (middle belt), or 7 (outer belt) vertices. The 1-isomer would have high (C_{5v}) symmetry with two boron environments in a 5:5 area ratio and is eliminated by the ^{11}B and ^1H NMR spectra. If the iron atom were located on the open face, one would expect an Fe–H–B resonance (δ < −5 relative to $(CH_3)_4Si$) in the ^1H NMR spectrum, and no such signal is observed. The placement of iron in the middle belt, as depicted in Figure 2, is entirely consistent with the ^{11}B and ^1H NMR data and is unambiguous. The high-field ^{11}B resonance at δ

−38.4 is assigned to the apex BH group and the four pairs of equivalent borons appear as signals of area 2, with the area 1 resonance from the unique B(9)–H group superimposed on one of the area 2 peaks. In the 100-MHz ^1H spectrum, the terminal H–B resonances are seen on ^{11}B decoupling as peaks of relative area 2:2:6, indicating some coincidental superposition, but the three kinds of B–H–B bridging protons exhibit distinguishable peaks in a 2:2:1 area ratio, as expected.

The $(\eta^5\text{-}C_5H_5)FeB_{10}H_{15}$ system is isoelectronic (in terms of skeletal electrons) with the $C_2B_9H_{11}^{2-}$ (dicarbollide) ions,[16] the hypothetical boranes $B_{11}H_{11}^{4-}$ and $B_{11}H_{15}$,[17] and the recently reported[18] tetracarbon metallocarborane $(\eta^5\text{-}C_5H_5)Co(CH_3)_4C_4B_6H_6$ isomers; each of these species is an 11-vertex, 26-electron cage and can be assigned an icosahedral-fragment nido structure. The FeB_{10} complex, however, differs from the others in having five B–H–B bridges on its open face. To our knowledge the only other known species with a planar B_5 face containing five hydrogen bridges are the $B_6H_{11}^+$ ion,[19] its 2-methyl derivative,[19] and 1-$(\eta^5\text{-}C_5H_5)FeB_5H_{10}$, described above.

$(\eta^5\text{-}C_5H_5)_2FeB_8H_8$. A violet solid trace product isolated from the original reaction was analyzed by low- and high-resolution mass spectroscopy, which established the composition as $C_{10}B_8FeH_{18}$. The NMR spectra are indicative of a paramagnetic species and yield no structurally interpretable information; the ^{11}B spectrum consists of a broad band ($w_{1/2} \approx 1500$ Hz) centered at δ −5.1 relative to $BF_3\cdot OEt_2$, and the proton spectrum contains no visible peaks between δ +100 and −90 relative to $(CH_3)_4Si$. A possible structure is $(\eta^5\text{-}C_5H_5)Fe^{III}H(C_3H_4)C_2B_8H_8$, which is envisioned as an 11-vertex *closo*-FeC_2B_8 cage whose carbon atoms are linked to an exopolyhedral $-CH_2CH{=}CH-$ chain; such a species could form via insertion of a $C_5H_5^-$ ion into a $(\eta^5\text{-}C_5H_5)FeHB_8H_x$ ferraborane cage. Precedent for structures of this type is found in (2,3)-1,3-C_3H_4-1,7,2,3-$(\eta^5\text{-}C_5H_5)_2CO_2C_2B_3H_3$,[1] which was shown crystallographically[5] to contain an "extra" C_5 ring, two of whose carbons are members of a *closo*-$Co_2C_2B_3$ skeleton.

Conclusions

We wish to make two points about this work. The first is that the reactions of first-row transition metal halides with $C_5H_5^-$ and $B_5H_8^-$ in THF give notably different results, at least as far as Co^{2+}, Ni^{2+}, and Fe^{2+} are concerned. In the case of cobalt,[1] metalloboranes containing one, two, three, and four skeletal metal atoms are isolated, the major product is $(\eta^5\text{-}C_5H_5)CoB_4H_8$, and *no* five-boron species are found. In the nickel reaction,[20] the only metalloboranes isolated are $(\eta^5\text{-}C_5H_5)_2Ni_2B_8H_8$ and $(\eta^5\text{-}C_5H_5)_2Ni_2B_{10}H_{10}$; again, no five-boron products have been detected (however, tetranickel four- and five-boron complexes are obtained when nickelocene is employed instead of nickel halides[20]). In contrast, the iron reaction described here generates no species containing more than one cage metal atom, and the main metalloborane product is in fact a five-boron system. Further reaction of 2-$(\eta^5\text{-}C_5H_5)FeB_5H_{10}$ with $B_5H_8^-$ probably yields the observed $(\eta^5\text{-}C_5H_5)FeB_{10}H_{15}$ species. These small borane–metal ion reactions thus differ, to a degree, from the formation of metallocarboranes[22] from carborane anions such as $C_2B_4H_7^-$, $C_2B_6H_8^{2-}$, and $C_2B_9H_{12}^-$ in the presence of metal ions and $C_5H_5^-$; the carborane ligands tend to form corresponding metal complexes in a relatively straightforward manner, generating few products, and in good yields (there are, however, exceptions such as $C_2B_5H_7^{2-}$, which is not stable and produces complex mixtures of cobaltacarboranes[10a] on treatment with $CoCl_2$ and $C_5H_5^-$). It should also be mentioned that large borane anions such as $B_9H_{12}^-$ and $B_{11}H_{13}^{2-}$ generally form B_9M and $B_{10}M$ metal complexes without extensive degradation,[23,24] as does the $B_3H_8^-$ ion.[25] The $B_5H_8^-$ ion, in contrast, is more reactive, degrades easily in reactions with transition metal reagents, and tends to generate structurally novel species in low individual yields.[27]

The second point is that the synthesis in this work of two isomers of $(\eta^5\text{-}C_5H_5)FeB_5H_{10}$, which are direct structural and electronic analogues of both hexaborane(10) and ferrocene, illustrates emphatically the central role of metalloboranes in tying together such different areas as metallocenes and boron hydrides. The basic validity of the electron-counting arguments first advanced by Wade[9] is also supported by synthetic findings such as these. Indeed, one can now usefully regard all types of "electron-deficient" clusters—boron cages, metal clusters, organometallic clusters, metallocenes, pyramidal carbocations, and others—as different molecular manifestations of a common set of structural and bonding principles. To be sure, there are plenty of local variations in the structural patterns exhibited by different cluster types (violations of Wade's rules[26]) which underline the need for continuing synthetic and structural investigations of cluster chemistry.

Experimental Section

Materials. Pentaborane(9) from laboratory stock was purified by trap-to-trap distillation in vacuo. Cyclopentadiene was distilled from dicyclopentadiene (Aldrich) under a nitrogen atmosphere. Sodium hydride was obtained as a 50% dispersion in mineral oil (Alfa) and used as received. All other reagents and solvents were reagent grade, and tetrahydroguran (THF) was dried over lithium aluminum hydride before use.

Spectra. Boron-11 NMR spectra at 32.1 MHz and proton NMR spectra at 100 MHz were obtained on a JEOL-100P pulse Fourier transform spectrometer interfaced to a JEOL-Texas Instruments EC-100 computer system. Unit resolution mass spectra were obtained on a Hitachi Perkin-Elmer RMU-6E mass spectrometer; all compounds reported herein exhibited intense parent groupings and profiles consistent with their indicated formulas. High-resolution mass measurements were conducted on an AEI-902 double-focusing instrument equipped with an SRI chemical ionization source and were obtained under chemical ionizing conditions.

General Procedure. Except where otherwise indicated, all reactions were run in high vacuum systems or in an inert atmosphere. Thin-layer and preparative-layer chromatographies were conducted in air on precoated plates of silica gel F-254 purchased from Brinckmann Instruments, Inc.

Reaction of $FeCl_2$, $Na^+B_5H_8^-$, and $Na^+C_5H_5^-$. Ferrous chloride (1.544 g, 12.24 mmol) and pentaborane(9) (10.1 mmol) were added at −78 °C to a solution of $Na^+C_5H_5^-$ which had been prepared from 24.4 mmol of cyclopentadiene and 21.0 mmol of sodium hydride in THF. This mixture was warmed to ca. ~ −20 °C to effect solution and was then recooled to −78 °C and maintained at that temperature for 17 h. As there was no evidence of reaction, the mixture was slowly warmed to room temperature and held there for 3 h. The solvent was then removed by distillation in vacuo and dry nitrogen at 1 atm was introduced. The remainder of the workup was conducted on the laboratory bench in air.

The solids remaining in the reaction vessel were extracted with methylene chloride, and the resulting solution was chromatographed on a silica gel column with successively pure *n*-hexane, hexane–benzene mixtures, pure benzene, and finally methylene chloride. Pure hexane eluted violet 2-$(\eta^5\text{-}C_5H_5)FeB_5H_{10}$, 46.3 mg (2.5% yield based on B_5H_9), and orange $(\eta^5\text{-}C_5H_5)_2Fe$ (ferrocene) identified from its ^1H NMR and mass spectra; the remainder of the ferrocene appeared in the 10% benzene/90% hexane fraction, for a total ferrocene yield of 782.6 mg (34.4% based on $FeCl_2$). Elution with 20% benzene/80% hexane gave a fraction which was further developed on a TLC plate in 25% benzene/75% hexane to give 3.3 mg of yellow 2-$(\eta^5\text{-}C_5H_5)FeB_{10}H_{15}$. Elution with 100% benzene followed by development in 50% benzene/hexane on a TLC plate gave 1 mg of pink-violet, paramagnetic $(C_5H_5)_2FeB_8H_8$. Traces of other species were detected mass spectroscopically but were not characterized.

Isomerization of 2- to 1-$(\eta^5\text{-}C_5H_5)FeB_5H_{10}$. A 20-mg sample of the 2-isomer was heated under vacuum in a sealed tube at 175 °C for 20.5 h, at which point significant decomposition was evident from accumulated solids (elemental iron) on the reaction walls. The volatiles were sublimed out of the reactor and washed with toluene-d_8 into an NMR tube which was then sealed. The ^{11}B and ^1H FT NMR spectra indicated a 2:1 mixture of the 2- and 1-isomers. The heating was continued at 175 °C for 70 h followed by 5 h at 180 °C, after which the ^{1}H and ^{11}B NMR spectra showed the isomerization to be essentially complete. Again, the presence of undissolved solid residues and of ferrocene (identified from its mass spectrum) indicated that some decomposition had occurred during the isomerization. The rearranged isomer [1-(η^5-C_5H_5)FeB_5H_{10}], a dark violet air-sensitive solid, was characterized from its ^{11}B and ^{1}H NMR and mass spectra.

Acknowledgment. This work was supported in part by the Office of Naval Research. The pulse Fourier transform NMR equipment was obtained in part via a departmental instrument grant from the National Science Foundation.

Registry No. 2-(η^5-C_5H_5)FeB_5H_{10}, 71661-61-5; 1-(η^5-C_5H_5)-FeB_5H_{10}, 65188-99-0; 2-(η^5-C_5H_5)$FeB_{10}H_{15}$, 71661-62-6; (η^5-C_5H_5)$_2$Fe, 102-54-5; pentaborane(9), 19624-22-7.

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Improved Synthetic Routes to Small Carboranes. Bench-Scale Preparation of *nido*-2,3-$C_2B_4H_8$ Derivatives from B_5H_9 and from $B_3H_8^-$ Salts

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Received April 17, 1979

A method has been developed for producing the *C,C'*-dimethyl and *C*-phenyl derivatives of 2,3-$C_2B_4H_8$ in gram quantities and in yields of >50% without the use of heat, solvent, or large-volume gas bulb reactions. This approach involves formation of a B_5H_9·2L adduct (L = triethylamine or dimethyl sulfide) which reacts with 2-butyne or phenylacetylene in situ, at or below room temperature, to give the corresponding $RR'C_2B_4H_6$ carborane. The carborane product is easily isolated in high purity by vacuum fractionation. The most satisfactory results are obtained with triethylamine, with B_5H_9 maintained in excess, and with simultaneous incremental addition of the amine and alkyne to the borane. The use of dimethyl sulfide in place of triethylamine gives slightly higher carborane yields but results in a much slower reaction. The triethylamine method has been combined with a previously reported synthesis of B_5H_9 from $B_3H_8^-$ salts, to generate $C_2B_4H_8$ derivatives from $B_3H_8^-$ in a "one-pot" synthesis, thereby eliminating the isolation or handling of B_5H_9 and other volatile boranes. Since $B_3H_8^-$ salts are readily prepared from $NaBH_4$, this method offers a safe and relatively inexpensive route to lower carboranes.

Studies of the smaller carboranes and their metal-containing derivatives have been hampered by the absence of efficient, convenient, and safe preparative routes to the lower carborane starting materials. The commonly used preparative methods for these compounds utilize reactions of alkynes with volatile boranes, usually at elevated temperatures in the gas phase;[1,2] in most cases the products are obtained as complex mixtures of carboranes and organoboranes, which require gas chromatographic separation, together with solid waste materials. Since these reactions are conducted in the gas phase, considerations of safety and practicality normally restrict such preparations to a scale of a few millimoles or less. Obviously, bench-scale methods that operate under mild conditions and generate easily separable carborane products would be desirable. Especially useful would be a means of producing carboranes directly from the inexpensive bulk chemical sodium borohydride ($NaBH_4$) or from salts of $B_3H_8^-$, which are easily prepared from that compound.[3]

A small carborane of particular importance in synthetic work is *nido*-2,3-$C_2B_4H_8$ [dicarbahexaborane(8)]. This com-

0020-1669/79/1318-3294$01.00/0