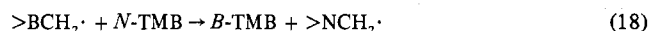


for the formation of *N*-TMB from HMB.

Photolysis of *B*-TMB + *N*-TMB mixtures led to a solid product identified as DMBE. The *N*-TMB was completely consumed in the reaction, but most of the *B*-TMB was recovered unchanged, except for some hydrogen-methyl exchange. To account for this behavior it appears that the radical formed from *B*-TMB reacts with *N*-TMB



Equation 18 implies that $>\text{NCH}_2\cdot$ is thermodynamically more stable than $>\text{BCH}_2\cdot$.

Acknowledgment. We are grateful for support of this work by the National Science Foundation (Grant GH 33637) through the Material Science Center, Cornell University, and Grant No. CHE76-02477.

Registry No. *N*-MB, 21127-94-6; *N*-DMB, 23208-28-8; *N*-TMB, 1004-35-9; *N*-TEB, 7360-03-4; *B*-TMB, 5314-85-2; $[\text{H}_3\text{B}_3\text{N}_3\text{H}_2\text{-CH}_2]_2$, 60607-08-1; $[\text{H}_3\text{B}_3\text{N}_3\text{HCH}_3\text{CH}_2]_2$, 60607-09-2; $[\text{H}_3\text{B}_3\text{-N}_3(\text{CH}_3)_2\text{CH}_2]_2$, 54517-76-9; $[\text{H}_3\text{B}_3\text{N}_3(\text{CH}_2\text{CH}_3)_2\text{CHCH}_3]_2$, 60607-10-5; $[\text{CH}_2(\text{CH}_3)_2\text{B}_3\text{N}_3\text{H}_3]_2$, 60607-11-6.

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Proton-Proton Spin Coupling in Metallocarboranes.

Triple-Resonance Nuclear Magnetic Resonance Spectroscopy as a Structural Probe for Boron Compounds¹

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Three-bond proton-proton spin coupling in 2,4- $\text{C}_2\text{B}_5\text{H}_7$ and a number of metallocarboranes have been examined in detail via triple-resonance NMR spectroscopy, in which ^{11}B and selective ^1H decouplings are conducted simultaneously while observing the proton NMR spectrum. Spin-spin coupling constants were obtained by direct measurement or by computer simulation of line spectra. The ranges were 10–20 Hz for H–C–C–H, 1–10 Hz for H–C–B–H, and 0–4 Hz for H–B–B–H. In the closo seven-atom cages, equatorial–equatorial proton interactions are stronger than those between equatorial and apical nuclei. The triple-resonance technique is shown to be a useful tool for investigating structure, frequently removing uncertainties in the interpretation of conventional NMR spectra and allowing unequivocal assignments of resonances.

Introduction

Proton nuclear magnetic resonance, in contrast to its overriding importance to organic chemists, has been a tool of only secondary interest to workers in the field of cage boron compounds. In the usual proton NMR spectrum of a borane or carborane, the resonances of hydrogen atoms bound to a ^{11}B atom (80% natural abundance, spin $3/2$) appear as broad, widely spaced quartets ($J \approx 180$ Hz) which are difficult to detect and often disappear entirely into the baseline noise.² Even when the H–B quartets can be identified, they rarely add significantly to the structural insights which are gleaned from the ^{11}B NMR spectrum of the same compound.

Recently, however, it has become clear that the proton spectra of carboranes contain inherently a wealth of information which is relevant to electronic and geometric structure, to a degree comparable to that seen in organic compounds. Several years ago we observed that certain metallocarboranes exhibit proton NMR spectra (uncoupled) in which the cage H–C resonances appear as multiplets instead of the usual broad singlets, and we postulated H–C–B–H proton-proton coupling as the cause of the observed fine structure.^{3–7} With the aid of ^{11}B decoupling, Onak and Wan⁸ have found similar three-bond proton-proton interactions in small carboranes; long-range coupling has also been reported

in some of the lower boron hydrides.⁹ We became interested in the systematic exploitation of proton-proton coupling as a structural tool in boron chemistry and initiated the present study which utilized a "triple-resonance" technique in which both ^{11}B decoupling and selective ^1H decoupling are simultaneously employed during observation of the 100-MHz proton NMR spectrum. The compounds examined included some whose structures are established and others of less well-defined geometry in which the ^1H – ^1H coupling patterns could be used to remove structural ambiguities.

Experimental Section

Materials. The metallocarboranes studied were prepared by previously described methods as cited in the text; *closo*-dicarbaheptaborane(7) ($\text{C}_2\text{B}_5\text{H}_7$) was purchased from Chemical Systems, Inc., and used as received. Solvents were reagent grade and used as received.

Spectra. All metallocarboranes were examined in CDCl_3 solution in capped 5-mm tubes, while the $\text{C}_2\text{B}_5\text{H}_7$ spectra were obtained in acetone- d_6 solution in a sealed 5-mm tube under vacuum. Spectra were recorded in the pulse Fourier transform mode on a JEOL PS-100 P/EC spectrometer, using a deuterium lock.

Double-resonance experiments involving decoupling of ^1H and ^{11}B were conducted with the standard JEOL accessories JNM-OA-1M and JNM-SD-HC, respectively. The only modification required for triple-resonance experiments (decoupling ^{11}B and ^1H nuclei si-

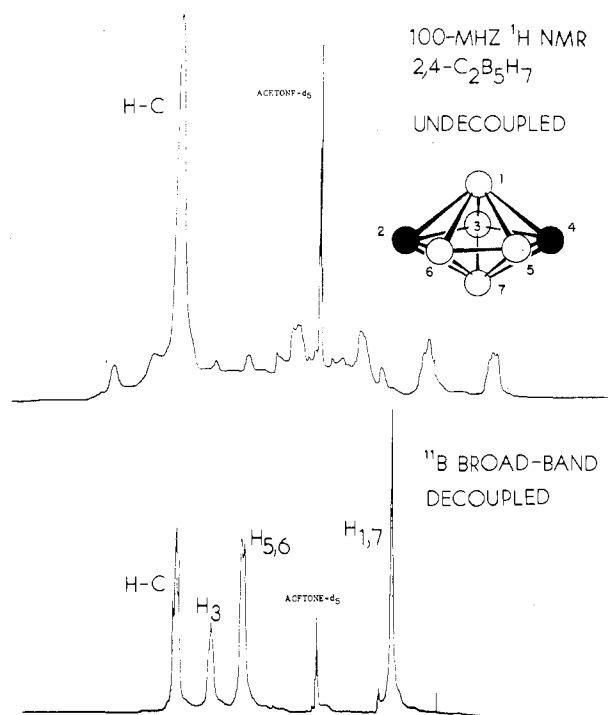


Figure 1. Undecoupled and ^{11}B -decoupled ^1H NMR spectra of $2,4\text{-C}_2\text{B}_5\text{H}_7$.

multaneously) was the addition of a power supply for the hetero-decoupling oscillator; this was provided by a standard JEOL RF unit identical with that supplied for the observing frequency (100 or 94 MHz) of the PS-100 continuous-wave instrument.

Computer Simulation of Spectra. Simulated line spectra were generated by a modified version of computer program LAOCN3, given in ref 18. We are grateful to Professor Ekk Sinn for providing the modified program.

Results and Discussion

$2,4\text{-C}_2\text{B}_5\text{H}_7$. Although this paper is concerned primarily with metallocarboranes, the small carborane *closo*-dicarboheptaborane(7) illustrates the use of the method. Figure 1 (top) depicts the undecoupled proton spectrum, which contains an H-C singlet and several overlapping H-B quartets. Shown below is the ^{11}B -decoupled spectrum in which the H-B resonances appear as intense peaks, some of which have fine structure as does the H-C resonance. In Figure 2, the top line shows these proton resonances with a 20-fold horizontal scale expansion which clearly reveals the individual line shapes. An interpretation of these spectra given earlier by Onak⁸ attributes the main features to H-C-B-H coupling between H_4 (or H_2) and H_3 and between H_4 and H_5 (or H_2 and H_6); the 1,7 resonance is a sharp singlet, suggesting little or no apical-equatorial proton coupling. The spectra in the top line of Figure 2 are similar to that reported earlier,⁸ except that additional fine structure is visible in the H_3 and $\text{H}_{5,6}$ resonances. It was possible to explore these latter observations as well as to confirm the postulated H-H interactions by decoupling selected protons while maintaining the ^{11}B decoupling as shown in the remainder of Figure 2. Irradiation at the resonance frequency of the H-C ($2,4$) protons collapses both the H_3 and $\text{H}_{5,6}$ peaks to singlets; similarly, decoupling either H_3 or $\text{H}_{5,6}$ drastically alters the appearance of the H-C resonance. Thus, H_3 and $\text{H}_{5,6}$ are both clearly coupled to H-C, and the magnitudes of the coupling constants (J) can be determined by direct measurement or from computer-simulated spectra (direct measurement of $J_{5,6}$ is not possible from this second-order spectrum). Decoupling $\text{H}_{1,7}$ does not have a noticeable effect on the $\text{H}_{2,4}$ or $\text{H}_{5,6}$ resonances but it does eliminate the secondary "triplet-of-triplets" effect in

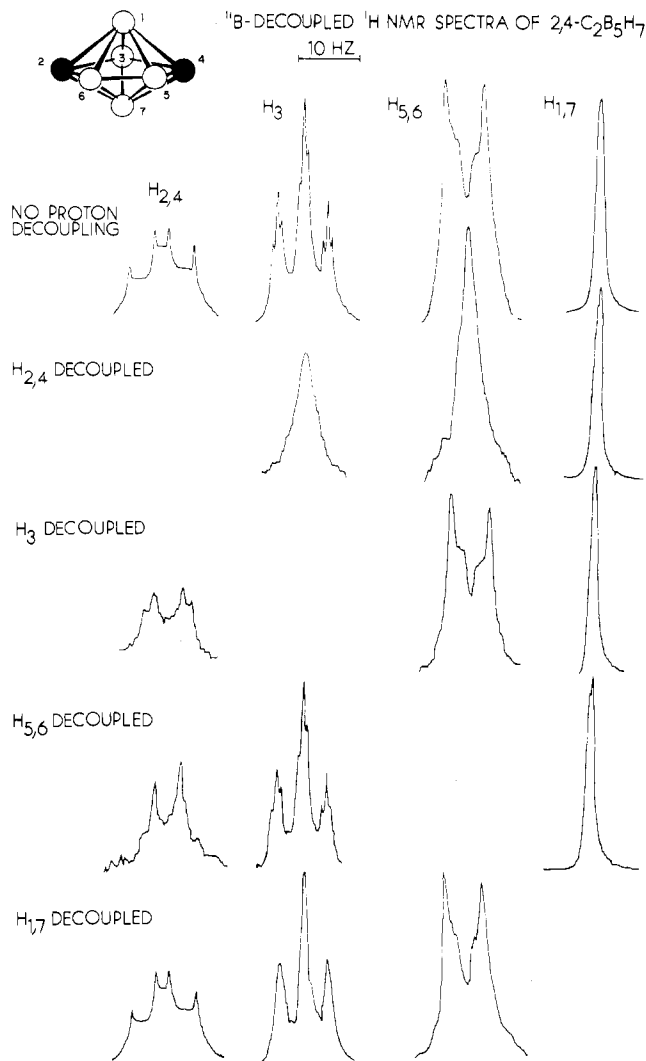


Figure 2. ^{11}B -Decoupled proton resonances of $2,4\text{-C}_2\text{B}_5\text{H}_7$, with the decoupling frequency adjusted in each case to produce maximum resolution. In the top line, only boron is decoupled; in the remaining spectra, the boron nuclei and selected protons are decoupled simultaneously (triple resonance).

H_3 (Figure 2, bottom line) thus demonstrating slight (~ 1 Hz) coupling between the apex protons and H_3 . Finally, simulated spectra indicate that the asymmetry in the $\text{H}_{5,6}$ doublet arises from coupling between H_5 and H_6 ($J \approx 2$ Hz). All possible nearest-neighbor equatorial H-H couplings are thus shown to occur, with apical interactions not observed except for $\text{H}_{1,7}\text{-H}_3$.

Although the structure of $2,4\text{-C}_2\text{B}_5\text{H}_7$ is well defined from microwave studies,¹⁰ it is worth noting that the proton-proton coupling patterns described above allow one to conclusively differentiate between the 2,4 and 2,3 (adjacent-carbon) isomers. The latter compound has been reported only in trace quantity¹¹ and was unavailable to us, but it is clear from metallocarborane studies described below that the presence of adjacent equatorial CH groups in a pentagonal-bipyramidal $\text{C}_2\text{B}_5\text{H}_7$ molecule will produce quite different H-H couplings, including a characteristically large H-C-C-H interaction. No such clear distinction between 2,3- and $2,4\text{-C}_2\text{B}_5\text{H}_7$ is possible from ^{11}B or ^1H NMR peak area ratios and chemical shifts alone, inasmuch as these species are symmetrically equivalent (C_{2v} point group).¹² Thus, proton-proton spin couplings can provide an additional "handle" on structure which augments the commonly determined NMR parameters in a highly useful way. This is particularly evident in the metallocarborane area,

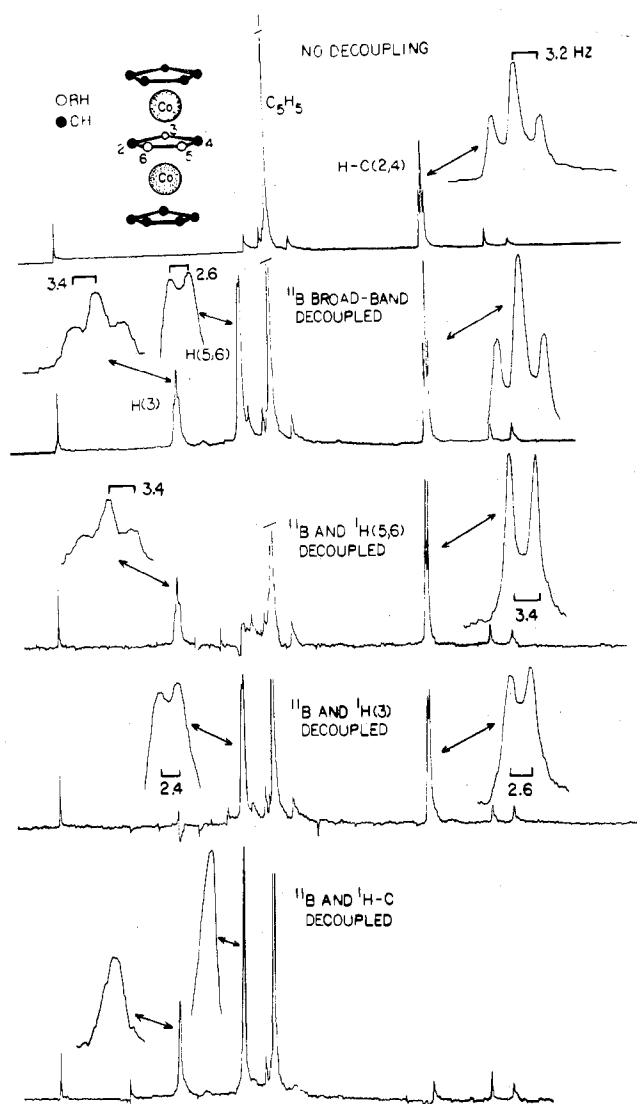


Figure 3. Triple-resonance proton NMR of 1,7,2,4-(η^5 -C₅H₅)₂-Co₂C₂B₃H₅. Individual H-C and H-B resonances are shown with a horizontal scale expanded by 10X compared to the original spectrum.

as illustrated by the following examples.

1,7,2,4-(η^5 -C₅H₅)₂Co₂C₂B₃H₅.¹³ The triple-decker sandwich geometry (Figure 3), analogous to that of 2,4-C₂B₅H₇ with the apex BH groups replaced by (C₅H₅)Co units, has been confirmed in an x-ray diffraction study¹⁴ and the effects of substituents on the ¹H and ¹¹B NMR spectra have been examined in some detail.¹⁵ In Figure 3 are shown the undecoupled-proton NMR spectrum, the ¹¹B-decoupled (double-resonance) spectrum, and several ¹¹B-, ¹H-decoupled (triple-resonance) spectra. From the observed patterns it is clear that the H-C protons (H_{2,4}) are coupled both to H₅ and to H₃; in addition, computer analysis indicates that H₅ and H₆ (which are chemically but *not* magnetically equivalent) are weakly coupled to each other with $J \approx 1$ Hz. The observed and calculated J values for these and all other H-H interactions in this study are listed in Table I. The 2-methyl derivative exhibits slightly different coupling constants but has the same pattern of interactions as the parent compound.

1,7,2,3-(η^5 -C₅H₅)₂Co₂C₂B₃H₅.⁶ The isomeric triple-decker species has also been structurally confirmed by a crystal structure analysis,³ and studies of substituent NMR effects in our laboratory¹⁵ support the presence of a localized carbon-carbon double bond in the central ring. The spectrum is second-order and the individual peaks (Figure 4) are less

Table I. ¹H NMR Chemical Shifts and Coupling Constants in CDCl₃

Compd	Chem shift, Hz ^a (assignment)	J , Hz ^b	H-H interactn
2,4-C ₂ B ₅ H ₇ ^c	5.89 (H _{2,4})	6.7 ^d	H ₂ -H ₃
	0.03 (H _{1,7})	10.0 ^d	H ₂ -H ₆
	4.05 (H _{5,6})	≤ 1	H ₁ -H ₂
	4.93 (H ₃)	2	H ₅ -H ₆
		1.2 ^d	H ₁ -H ₃
		≤ 1	H ₁ -H ₅
1,2,3-(C ₅ H ₅)CoC ₂ B ₄ H ₆	5.76 (H _{2,3})	10	H ₂ -H ₃
	3.70 (H _{4,6})	3.7 ^d	H ₂ -H ₆
	4.15 (H ₅)	4.3 ^d	H ₄ -H ₅
	1.15 (H ₇)	≤ 1	H ₂ -H ₇
	4.88 (C ₅ H ₅)	≤ 1	H ₄ -H ₇
1,2,4-(C ₅ H ₅)CoC ₂ B ₄ H ₆	3.97 (H _{2,4})	5	H ₂ -H ₃
	4.77 (H ₃)	6	H ₂ -H ₆
	4.08 (H _{5,6})	2	H ₅ -H ₆
	1.10 (H ₇)	≤ 1	H ₃ -H ₇
	4.87 (C ₅ H ₅)	≤ 1	H ₅ -H ₇
		≤ 1	H ₂ -H ₇
3-C ₁₀ H ₇ -1,2,4-(C ₅ H ₅)CoC ₂ B ₄ H ₅	4.33 (H _{2,4})	5.8 ^d	H ₂ -H ₆
	4.31 (H _{5,6})	≤ 1	H ₅ -H ₇
	1.47 (H ₇)		
	4.81 (C ₅ H ₅)		
	7.61 ^e (naphthyl)		
	8.04 ^e (naphthyl)		
	8.55 (naphthyl)		
1,7,2,3-(C ₅ H ₅) ₂ Co ₂ C ₂ B ₃ H ₅	5.62 (H _{2,3})	≥ 10	H ₂ -H ₃
	3.49 (H _{4,6})	3	H ₂ -H ₆
	6.21 (H ₅)	2.0 ^d	H ₄ -H ₅
	4.49 (C ₅ H ₅)		
1,7,2,4-(C ₅ H ₅) ₂ Co ₂ C ₂ B ₃ H ₅	2.38 (H _{2,4})	3.4 ^d	H ₂ -H ₃
	5.68 (H ₃)	2.6 ^d	H ₂ -H ₆
	4.84 (H _{5,6})	1	H ₅ -H ₆
	4.44 (C ₅ H ₅)		
2-CH ₃ -1,7,2,4-(C ₅ H ₅) ₂ Co ₂ C ₂ B ₃ H ₄	2.38 (H ₄)	2.9 ^d	H ₃ -H ₄
	5.57 (H ₃)	2.9 ^d	H ₄ -H ₅
	4.73 (H _{5,6})	≤ 1	H ₅ -H ₆
	1.96 (CH ₃)		
	4.43 (C ₅ H ₅)		
1,2,4,5-(C ₅ H ₅) ₂ Co ₂ C ₂ B ₃ H ₅	5.19 (H _{4,5})	≥ 20	H ₄ -H ₅
	6.79 (H _{3,6})	6.0 ^d	H ₃ -H ₄
	1.86 (H ₇)	1	H ₄ -H ₇
	4.56 (C ₅ H ₅)	1	H ₃ -H ₇
	4.90 (C ₅ H ₅)		
1,2,3,5-(C ₅ H ₅) ₂ Co ₂ C ₂ B ₃ H ₅	8.30 (H ₃)	5	H ₃ -H ₄
	4.52 (H ₄)	4	H ₄ -H ₅
	3.74 (H ₂)	6	H ₄ -H ₆
	7.20 (H ₆)	≤ 1	H ₃ -H ₇
	1.72 (H ₇)	≤ 1	H ₄ -H ₇
	4.57 (C ₅ H ₅)	≤ 1	H ₆ -H ₇
	5.06 (C ₅ H ₅)	3	H ₃ -H ₅
1,8,5,6-(C ₅ H ₅) ₂ Co ₂ C ₂ B ₃ H ₇	13.11 (H ₄)	4.4 ^d	H ₂ -H ₅
	0.11 (H _{2,7})	3	H ₃ -H ₅
	4.21 (H _{3,6})	3	H ₂ -H ₆
	3.91 (H _{5,8})	≤ 1	H ₂ -H ₃
	4.82 (C ₅ H ₅)	≤ 1	H ₂ -H ₄
1,7,5,6-(C ₅ H ₅) ₂ Co ₂ C ₂ B ₃ H ₇	9.57 (H ₄)	4	H ₂ -H ₅
	1.63 (H _{2,8})	3	H ₃ -H ₅
	3.10 (H _{3,6})	3	H ₃ -H ₆
	2.86 (H ₅)	2	H ₂ -H ₃ or H ₃ -H ₄
	8.63 (H ₇)		
	4.71 (C ₅ H ₅)		

^a Ppm relative to tetramethylsilane; positive values denote shift to lower field. Peak area ratios are in all cases in agreement with assignments. ^b Estimated uncertainties are ≤ 1 Hz except where otherwise indicated. ^c Acetone-*d*₆ solvent. ^d Estimated uncertainty is < 0.5 Hz. ^e Most intense peak of multiplet.

well resolved than in the spectrum of the 1,7,2,4 isomer. However, J values were obtained (Table I) for all nearest-neighbor H-H couplings in the carborane ring, the largest of which was ≥ 10 Hz for H-C-C-H. Once again the obser-

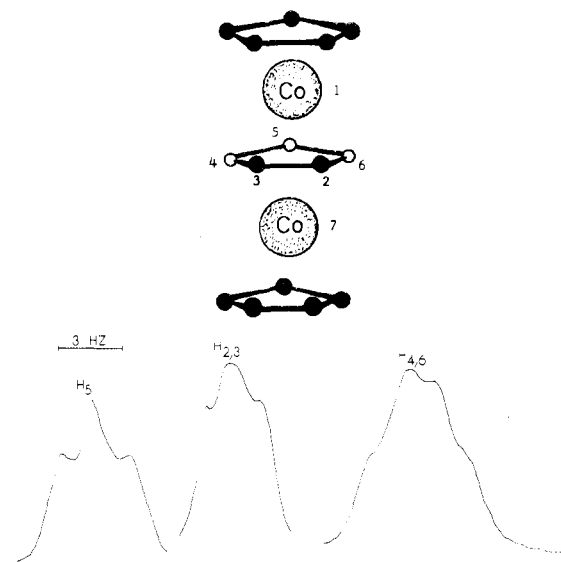


Figure 4. Proton NMR resonances of 1,7,2,3-(η^5 -C₅H₅)₂Co₂C₂-B₃H₅, ¹¹B decoupled with the frequency adjusted to produce maximum resolution.

vation of H-H coupling patterns provides structural information (i.e., adjacent CH groups) which could not be obtained from conventional ¹¹B and ¹H NMR spectra, in this case distinguishing between the symmetry-equivalent (η^5 -C₅H₅)₂Co₂C₂B₃H₅ isomers.

1,2,3-(η^5 -C₅H₅)CoC₂B₄H₆.⁶ Formal replacement of an apex BH unit by a (C₅H₅)Co group in 2,3- and 2,4-C₂B₅H₇ (or, equivalently, substitution of BH for one (C₅H₅)Co in the 1,7,2,3- and 1,7,2,4-(C₅H₅)₂Co₂C₂B₃H₅ species discussed above) generates the respective (C₅H₅)CoC₂B₄H₆ isomers (the actual synthesis from C₂B₄H₇⁻ ion, CoCl₂, and Na⁺C₅H₅⁻ is described in ref 6). The 1,2,3 species exhibits a proton NMR spectrum similar to that of 1,7,2,3-(C₅H₅)₂Co₂C₂B₃H₅, with H_{2,3} appearing as a distorted triplet, H₅ as a resolved triplet, and H_{4,6} as a broad resonance with triplet structure; the apical H₇ resonance (identified from its high-field chemical shift) is a singlet ($w_{1/2}$ = 4 Hz) with no fine structure. Direct measurement together with computer simulation yielded the *J* values given in Table I. Again, the patterns of strong equatorial H-C-C-H, intermediate equatorial H-B-C-H and H-B-B-H, and weak apical-equatorial couplings are followed.

1,2,4-(η^5 -C₅H₅)CoC₂B₄H₆. In the undecoupled spectrum the H-C (H_{2,4}) resonance is a triplet, which on ¹¹B decoupling changes to a multiplet (Figure 5A). In order to assign these peaks it was necessary to employ partial relaxation in concert with ¹¹B and ¹H decoupling. In Figure 5B the high-field portion of the ¹¹B-decoupled spectrum has been nearly nulled out by a 180°- τ -90° pulse sequence, and in Figure 5C the same conditions prevail except that H₃ has been decoupled; clearly the homodecoupling has little effect. In Figure 5D the low-field area of the spectrum has been almost nulled by adjustment of the 180°- τ -90° sequence (spectra D and E are obtained as negative peaks and are inverted here for ease of comparison with A-C). When ¹H decoupling of H₃ is applied under these conditions, the triplet in D collapses to a rough doublet (Figure 5E) which appears as the reverse of the doublet in spectrum B; this is precisely what one would expect for a second-order spectrum. Thus, the H-C protons (H_{2,4}) are coupled to H₃ and to H_{5,6} with *J* = 5 and 6 Hz, respectively. From computer-simulated spectra it can be shown that the H₅-H₆ coupling is approximately 2 Hz.

3-C₁₀H₇-1,2,4-(η^5 -C₅H₅)CoC₂B₄H₅. The 3-naphthyl derivative of the 1,2,4 isomer discussed in the preceding paragraph provided an interesting case. The undecoupled ¹H

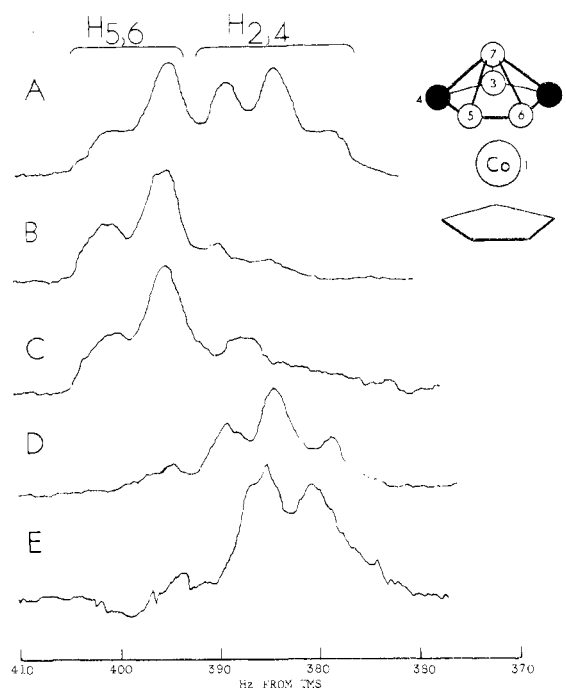


Figure 5. Cage H-C region of the proton NMR spectrum of 1,2,4-(η^5 -C₅H₅)CoC₂B₄H₆, showing overlapping H-C and H-B_{5,6} resonances: A, ¹¹B decoupled. B, ¹¹B decoupled and partially relaxed via a 180°- τ -90° pulse sequence to nearly null out the high-field portion; C, same as B except that H₃ is decoupled; D, ¹¹B decoupled and partially relaxed to almost null out the low-field peaks; E, same as D but with H₃ decoupled. D and E appeared as negative peaks but are shown here inverted for ease of comparison.

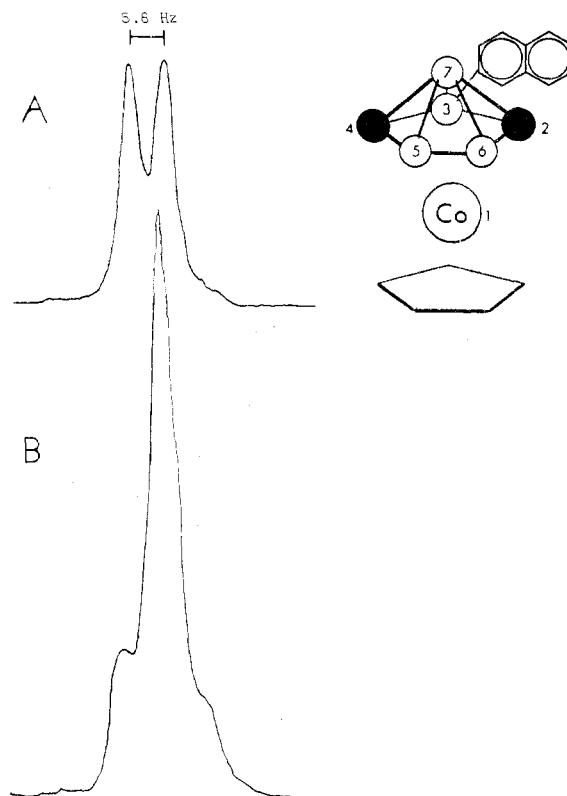


Figure 6. Cage H-C region of the proton NMR spectrum of 3-naph-1,2,4-(η^5 -C₅H₅)CoC₂B₄H₅, showing the effect of ¹¹B heteronuclear decoupling: A, undecoupled; B, ¹¹B decoupled. Relative intensities and peak positions are on comparable scales.

NMR spectrum contains an H-C (H_{2,4}) doublet with *J* = 5.8 Hz (Figure 6A), readily attributed to coupling of H₂₍₄₎ with

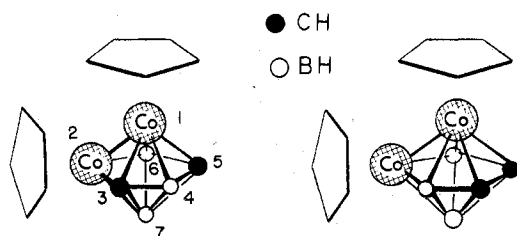


Figure 7. Structures of 1,2,3,5- and 1,2,4,5-(η^5 -C₅H₅)₂Co₂C₂B₃H₅.

H₆₍₅₎. However, on ¹¹B decoupling the H-C region contains a singlet of enhanced intensity with shoulders on either side (Figure 6B), as well as a singlet at 1.47 Hz which is assigned to H₇ from its high-field chemical shift. No separate peak assignable to H_{5,6} can be seen, but from area integrations and the fact that partially relaxed spectra show that the C₅H₅ resonance does not obscure an H-B peak, it is clear that the H_{5,6} resonance falls under the H-C peak. The strange appearance of the signals in Figure 6B is explained by computer simulations which demonstrate that in a strongly coupled system, effects such as that shown can be produced by reducing a large coupling constant (e.g., $J_{H-B} \approx 150$ Hz) to zero, as is done in ¹¹B decoupling. Treating the system as AA'BB'XX' with AA' = H_{5,6}, BB' = H_{2,4}, and XX' = B_{5,6} and employing a spin of 1/2 for ¹¹B (due to the inability of the program to handle spin 3/2 nuclei, a factor which would not be expected to significantly affect the region of the spectrum of interest here), one can simulate the doublet in Figure 6A by assuming a value of 150 Hz for J_{H-B} . When this constant is changed to zero, the appearance of the computed second-order spectrum approximates that in Figure 6B.

Attempts to study further effects of the various parameters in the simulated spectrum were inconclusive due to the complexity of the system.

1,2,3,5- and 1,2,4,5-(η^5 -C₅H₅)₂Co₂C₂B₃H₅.^{5,13} These metallocarboranes are isomeric with the 1,7,2,3 and 1,7,2,4 triple-decker species dealt with earlier in this paper and indeed are intermediates in the thermal rearrangement of the 1,7,2,3 to the 1,7,2,4 system.¹³ In contrast to the latter species, the structures of the 1,2,3,5 and 1,2,4,5 isomers have not been crystallographically established; the geometries shown in Figure 7 were based on ¹¹B and ¹H chemical shifts^{5,13} and the assumption that no more than one cobalt atom may occupy an equatorial vertex in a pentagonal bipyramid. In the case of the 1,2,4,5 isomer, the alternative 1,2,3,6 structure (which also contains a mirror plane) could not be ruled out on this basis. Thus, these species furnished an excellent opportunity to utilize proton-proton spin coupling in gaining more confident structural characterizations. The ¹¹B-decoupled proton spectrum of the 1,2,3,5 isomer exhibits all five cage proton resonances as well as the two C₅H₅ peaks. The low-field H-C (H₃) signal is a doublet of doublets, which changes to a doublet when either the middle H-B (H₄) or the high-field H-C (H₅) is decoupled; thus, H₃ is coupled to both H₄ and H₅. The H₃-H₅ interaction ($J = 3$ Hz) is the only example of four-bond (H-C-B-C-H) coupling detected in this study; all previously reported cases of such very long-range coupling⁸ in carboranes occur between trans nuclei, e.g., the H-C protons in 1,5-C₂B₃H₅.

The H₄ peak is nearly obscured by a C₅H₅ resonance but was observed by partial relaxation of the latter. Although it has no apparent fine structure, H₄ is clearly coupled to both H₃ and H₅, as shown by the collapse of the H₃ resonance to a doublet and the loss of fine structure by the H₅ signal, when H₄ is decoupled. The high-field H-C (H₅) resonance exhibits a five-line multiplet which results from coupling to three other protons with similar J values, identified as H₄, H₆, and H₃.

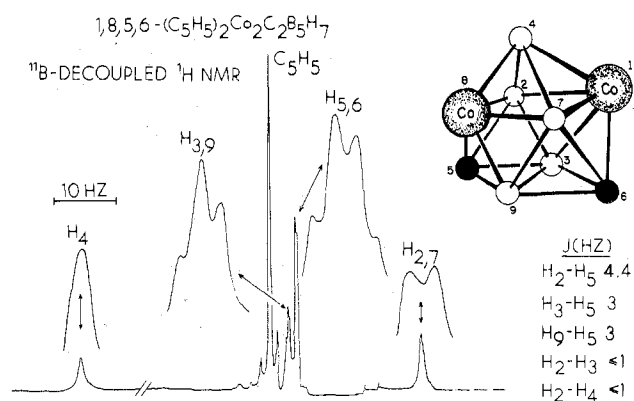


Figure 8. Proton NMR spectrum of 1,8,5,6-(η^5 -C₅H₅)₂Co₂C₂B₅H₇. Individual resonances are shown with 20-fold scale expansion and with ¹¹B decoupling adjusted in each case to produce maximum resolution.

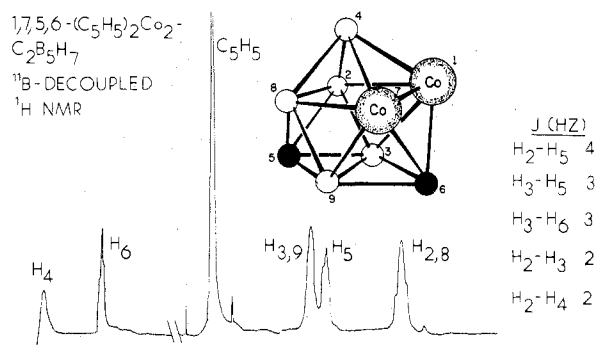


Figure 9. Proton NMR spectrum of 1,7,5,6-(η^5 -C₅H₅)₂Co₂C₂B₅H₇, with ¹¹B broad-band decoupling only.

Finally, the high-field H-B, assigned to H₇ from its chemical shift, appears as a poorly resolved doublet arising from weak coupling ($J < 1$ Hz) to H₄, as demonstrated by conversion of the H₇ signal to a singlet on homonuclear decoupling of the latter resonance. All of the above assignments are in accord with the structure originally postulated (Figure 7).

The more highly symmetrical (C_s) 1,2,4,5 isomer (Figure 7) displays a simple ¹¹B-decoupled proton spectrum, consisting of a cage H-C (H_{4,5}) resonance, two H-B peaks in a 2:1 area ratio, and two C₅H₅ singlets. The high-field H₇ resonance is a very poorly resolved triplet which collapses on decoupling H_{4,5}. The H_{4,5} and H_{3,6} signals are apparent triplets, each of which becomes a singlet on decoupling the other. From computer simulations it is clear that the H-C protons are strongly coupled to each other with a J value of at least 20 Hz. Thus, the 1,2,4,5 structure with adjacent equatorial carbon atoms is supported by these findings, and alternate possibilities such as the 1,2,3,6 geometry can be effectively discounted.

1,8,5,6- and 1,7,5,6-(η^5 -C₅H₅)₂Co₂C₂B₅H₇.^{4,5} In comparison with the smaller seven-vertex cage systems discussed up to this point, the spectra of many larger heteroboranes are apt to present formidable difficulties in unraveling all of the proton-proton interactions. However, the nine-vertex (η^5 -C₅H₅)₂Co₂C₂B₅H₇ isomers (Figures 8 and 9) are structurally well characterized from x-ray studies¹⁶ and appeared worthwhile candidates for investigation. Complete interpretation of the spectra was not possible due to the number of protons involved and other factors, but certain relations were obvious, and from these other couplings could be deduced. In the ¹¹B-decoupled spectrum of the 1,8,5,6 isomer (Figure 8) the low-field H-B of area 1 (H₄) does not appear to be significantly coupled to any other protons. The high-field H-B of area 2 is a doublet which collapses to a singlet on irradiation

of the H-C ($H_{5,6}$) resonance and hence is assigned to $H_{2,7}$; the remaining area 2 H-B signal must then be due to the $H_{3,9}$ protons. Furthermore, the H-C and $H_{3,9}$ multiplets are clearly coupled to each other, as shown by homonuclear ^1H -decoupling experiments, in accord with their nearest-neighbor relationship in the molecule.

In the 1,7,5,6 isomer (Figure 9) the area 1 H-B resonance is again readily assigned to the unique (H_4) proton. The low-field H-C resonance is attributed to H_6 due to its proximity to the cobalt atoms, an assignment supported by the proton-proton coupling patterns in the molecule. From homonuclear decoupling it is shown that H_6 is split into a triplet by the low-field area 2 BH, which is consequently assigned to $H_{3,9}$ (the nearest pair of equivalent H-B protons); in turn, the $H_{3,9}$ resonance is split into a doublet by H_6 . As expected, the $H_{3,9}$ protons are also coupled to the other H-C proton, H_5 . The H_5 resonance is split into a triplet by the remaining pair of H-B protons $H_{2,8}$; the latter nuclei are also coupled to another proton that could not be identified but may be H_4 .

Conclusions

The existence of proton-proton coupling in carboranes and metallocarboranes is not in itself surprising, but the extent to which it was found to occur in this study was not anticipated. These results lead us to suggest the following generalizations:

1. All three-bond couplings (H-C-B-H, H-B-B-H, H-C-C-H) can be expected to occur, with four-bond coupling rarely observed except for protons in trans locations.

2. The magnitudes of these interactions are strongly and characteristically influenced by the nature of the attached atoms (i.e., boron vs. carbon) and by the coordination number of the occupied vertex. The ranges of observed J values are 10–20 Hz for H-C-C-H, 1–10 Hz for H-C-B-H, and 0–4 Hz for H-B-B-H. In pentagonal-bipyramidal cages, equatorial protons are more strongly coupled to each other than to apical protons; apical-equatorial interactions are usually small ($J < 1$ Hz) and are frequently not directly observed.

3. H-B and H-C resonances are inherently sharp, with natural line widths of ~ 1 –2 Hz (as determined from T_1 measurements¹⁷). The broad H-B and H-C peaks observed in uncoupled spectra are, as suggested by Onak,⁸ due primarily to unresolved coupling which can be removed with ^{11}B and ^1H decoupling. From this work as well as from extensive T_1 measurements in this laboratory,¹⁷ it is clear that although ^{11}B quadrupolar relaxation contributes broadness to ^{11}B NMR spectral lines, it is not a significant factor in ^1H

NMR line broadening. This fact is important to recognize, since it means that with appropriate decoupling the ^1H spectra of many boron compounds can be analyzed in detail in much the same manner as those of organic compounds, with ^1H NMR thereby assuming the role of a major structural tool.

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Registry No. 2,4- $\text{C}_2\text{B}_5\text{H}_7$, 20693-69-0; 1,2,3-(C_5H_5) $\text{CoC}_2\text{B}_4\text{H}_6$, 50860-25-8; 1,2,4-(C_5H_5) $\text{CoC}_2\text{B}_4\text{H}_6$, 41660-23-5; 3- C_{10}H_7 -1,2,4-(C_5H_5) $\text{CoC}_2\text{B}_4\text{H}_5$, 41660-25-7; 1,7,2,3-(C_5H_5) $_2\text{Co}_2\text{C}_2\text{B}_3\text{H}_5$, 39388-45-9; 1,7,2,4-(C_5H_5) $_2\text{Co}_2\text{C}_2\text{B}_3\text{H}_5$, 39388-44-8; 2- CH_3 -1,7,2,4-(C_5H_5) $_2\text{Co}_2\text{C}_2\text{B}_3\text{H}_4$, 56679-06-2; 1,2,4,5-(C_5H_5) $_2\text{Co}_2\text{C}_2\text{B}_3\text{H}_5$, 56669-15-9; 1,2,3,5-(C_5H_5) $_2\text{Co}_2\text{C}_2\text{B}_3\text{H}_5$, 53421-57-1; 1,8,5,6-(C_5H_5) $_2\text{Co}_2\text{C}_2\text{B}_5\text{H}_7$, 41636-82-2; 1,7,5,6-(C_5H_5) $_2\text{Co}_2\text{C}_2\text{B}_5\text{H}_7$, 53452-50-9; ^{11}B , 14798-13-1.

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Ultraviolet Spectroscopy Study of Intramolecular Charge Transfer in $(\text{C}_6\text{H}_5)_3\text{M}$ Compounds ($\text{M} = \text{B}, \text{Ga}, \text{In}$) and Effects of Ring Substitution in Triaryl Gallium Systems

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The near-ultraviolet spectra of $(\text{C}_6\text{H}_5)_3\text{B}$, $(\text{C}_6\text{H}_5)_3\text{Ga}$, and $(\text{C}_6\text{H}_5)_3\text{In}$ are recorded in methylcyclohexane to locate the charge-transfer bands and to determine their periodic trend. The charge-transfer excited states fall in the energy series of $\text{B} \ll \text{Ga} < \text{In}$. The charge-transfer energy trend compares favorably to the ^{13}C chemical shift of the carbon atom para to the central atom in the pseudoisoelectronic series $(\text{C}_6\text{H}_5)_3\text{M}$, $\text{M} = \text{C}^+, \text{B}, \text{Ga}, \text{In}$. Ring substitution by CH_3 , CH_3CH_2 , $(\text{CH}_3)_2\text{C}$, CH_3O , F , Cl , and Br in the para position of triphenylgallium causes E_{CT} to vary according to the ionization potential of the monosubstituted benzene. Meta and ortho substitution causes E_{CT} to behave as though the gallium atom, perhaps through steric effects, has been removed from any active participation in the electronic changes occurring in the phenyl ring.

Introduction

The group 3A elements react in a variety of ways in an effort to obtain a coordinately saturated valence shell. The dramatic

behavior of boron and aluminum are, of course, well known.¹ For the heavier elements, gallium and indium, less unusual bonding patterns occur but the desire of these elements to