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Two-Dimensional ^{11}B - ^{11}B NMR Spectroscopy: Coupling through Bridging Hydrogen Atoms

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Application of ^{11}B - ^{11}B two-dimensional correlated spectroscopy (COSY) to a variety of boranes and substituted boranes has shown coupling between ^{11}B nuclei linked by bridging hydrogen atoms to be more common than previously observed. Coupling between the hydrogen-bridged boron nuclei in decaborane(14), 2-(CH_3) $_2\text{B}_5\text{H}_8$, B_4H_{10} , (Me_2N) $_2\text{B}_4\text{H}_8$, (μ - Me_2NCH_2) $_2\text{B}_5\text{H}_8$, and (μ - $\text{Me}_3\text{CCH}=\text{N}$) $_2\text{B}_5\text{H}_8$ are reported. The factors that contribute to the detection of coupling between hydrogen-bridged boron atoms are discussed.

Introduction

Two-dimensional ^{11}B - ^{11}B nuclear magnetic resonance (2-D NMR) has become a powerful probe for determining the structures of a variety of boron cage species. Several investigators¹⁻¹⁴ have used the COSY (correlated spectroscopy) pulse sequence to produce contour spectra, the x and y axes of which represent ^{11}B chemical shift values while the z direction represents resonance intensities in the form of contours. The contour peaks lying on the diagonal of the 2-D spectrum are identical with those of a normal (1-D) NMR spectrum while the off-diagonal peaks, called cross peaks, indicate the presence of J -coupling connectivities between adjacent ^{11}B cluster nuclei.

Although the technique has been applied with a good deal of success, interpretation of the spectra has not always been straightforward. For example, a general feature of ^{11}B - ^{11}B COSY experiments to date has been the absence of coupling between boron nuclei linked by bridging hydrogen atoms in three-center-two-electron B-H-B bonds. A growing number of boron cluster compounds, however, including five carboranes or metallaboranes (*nido*-1,2,3- $[\text{C}_6(\text{CH}_3)_6]\text{Fe}(\text{C}_2\text{H}_5)_2\text{C}_2\text{B}_3\text{H}_5$,^{1b} 2-(C_5H_5) CoB_4H_8 ,^{1b} 5,6- $\text{C}_2\text{B}_6\text{H}_{12}$,⁹ CB_8H_{14} ,⁸ and $\text{CB}_8\text{H}_{13}^{-8}$), have been reported to show correlations between hydrogen-bridged boron atoms. Grimes' pioneering work^{1b} demonstrated that the apparent absence of a correlation between two boron atoms known to be adjacent does not necessarily indicate the presence of a B-H-B bridge. We are presently aware of four compounds ((CH_3) $_4\text{C}_4\text{B}_7\text{H}_9$,^{1b} (CH_3) $_2\text{SB}_9\text{H}_{13}$,³ $\text{B}_{12}\text{H}_{16}$,^{6b} and 5,6- $\text{C}_2\text{B}_6\text{H}_{12}$)⁹ that illustrate this point. Each contain adjacent boron atoms that do not exhibit correlation.

Definitive explanations for the absence of cross peaks mentioned above have not yet been possible, but such absences can be ra-

Table I. Selected Acquisition and Processing Parameters for Two-Dimensional ^{11}B - ^{11}B NMR Experiments

compd	angle for mixing pulse, deg	$t_1 \times t_2$	apodization function ^a
$\text{B}_{10}\text{H}_{14}$	45	256 × 1K	G (LB = -350, GB = 0.3)
2-(CH_3) $_2\text{B}_5\text{H}_8$	45	128 × 512	S
B_4H_{10}	90	512 × 2K	S
(Me_2N) $_2\text{B}_4\text{H}_8$	90	128 × 512	Q
(μ - Me_2NCH_2) $_2\text{B}_5\text{H}_8$	45	128 × 512	S
(μ - $\text{Me}_3\text{CCH}=\text{N}$) $_2\text{B}_5\text{H}_8$	90	128 × 512	S

^aLegend: G = Gaussian function; S = unshifted sine-bell function; Q = unshifted sine-bell-squared function.

tionalized in several ways. In some cases there may be insufficient electron density between the nuclei to permit scalar coupling. In other cases the ^{11}B relaxation rate may exceed the coupling constant to such an extent that no correlation is seen. The observation of correlations in a COSY experiment can also be quite sensitive to the accumulation and processing parameters.¹⁵ Fontaine et al.¹² have made mention of the fact that "with an appropriate choice of conditions" the correlation between the hydrogen-bridged borons in decaborane can be observed. Decaborane had previously been reported not to show this correlation.^{1b,3}

In our laboratories, we have also observed the correlation between the hydrogen-bridged borons in decaborane; in this paper we discuss the conditions that allowed its detection. We also describe the results of our recent COSY experiments on seven other boranes. In all but two of these compounds coupling between boron atoms linked by bridging hydrogen atoms has been observed. We trust that these results will be helpful in ultimately arriving at a clearer understanding of the bonding and coupling networks in boron hydrides.

Experimental Section

Decaborane was purchased from Dexcel Corp., Hamden, CT 06514. 2-(CH_3) $_2\text{B}_5\text{H}_8$,¹⁶ B_4H_{10} ,¹⁷ (Me_2N) $_2\text{B}_4\text{H}_8$,¹⁸ (μ - Me_2NCH_2) $_2\text{B}_5\text{H}_8$,¹⁹ and (μ - $\text{Me}_3\text{CCH}=\text{N}$) $_2\text{B}_5\text{H}_8$ ²⁰ were prepared as described in the cited references.

Spectra were obtained on Bruker Instruments Corp. AM 500 and AM 360 spectrometers equipped with a pulse programmer and a process controller, respectively.

The NMR samples were prepared in 5 mm o.d. NMR tubes, and lock was achieved with deuterated solvents. NMR data were collected at ambient temperature and referenced externally to $\text{BF}_3\text{-OEt}_2$ with positive chemical shifts downfield.

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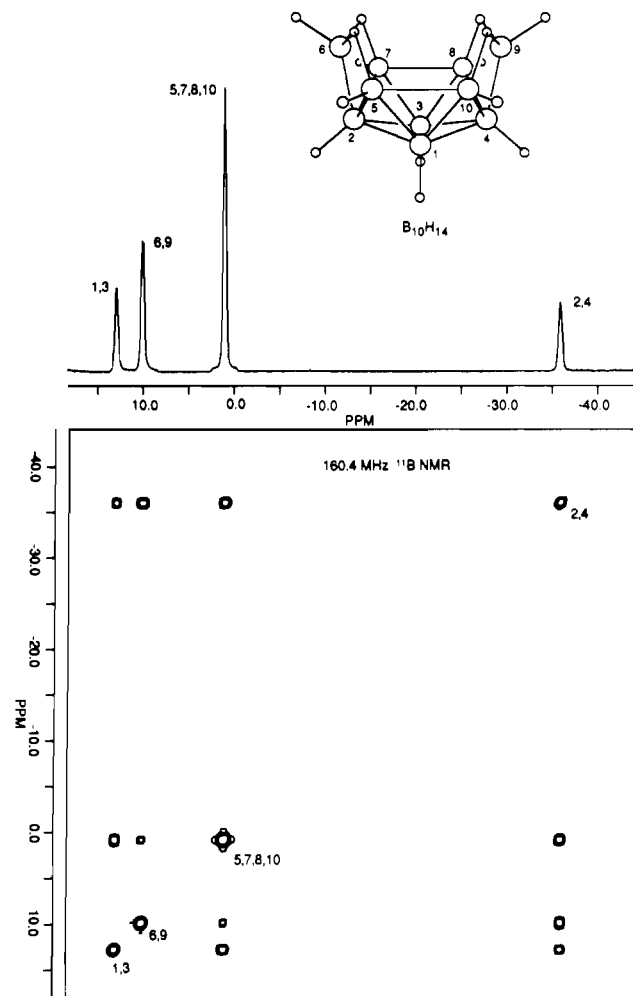


Figure 1. 160.46-MHz $^{11}\text{B}\{^1\text{H}\}$ 1-D and 2-D spectra of a saturated pentane solution of $\text{B}_{10}\text{H}_{14}$. The cross peak between the B(6,9) and B(5,7,8,10) signals indicates spin-spin coupling between these hydrogen-bridged boron atoms.

For individual COSY experiments the ^{11}B mixing pulse angle, the size of the τ_1, τ_2 data matrix, and the particular apodization function used are shown in Table I. Use of 45° , rather than 90° , ^{11}B mixing pulses reduces the intensity of peaks on the diagonal, which is especially helpful when the reliability of a cross peak between two closely spaced resonances is in question. Processing of the two-dimensional data matrix involved apodization, zero-filling once in τ_1 , Fourier transformation, and symmetrization. The noise level in the resulting absolute value contour spectra was in all cases less than or equal 0.5% of the tallest diagonal peak.

Results and Discussion

$\text{B}_{10}\text{H}_{14}$. The 160.4-MHz 1-D $^{11}\text{B}\{^1\text{H}\}$ and $^{11}\text{B}-^{11}\text{B}$ COSY spectra of $\text{B}_{10}\text{H}_{14}$ are shown in Figure 1. In initial COSY experiments in our laboratories we were able to duplicate the previously reported spectra of $\text{B}_{10}\text{H}_{14}$.^{1b,3} After becoming more familiar with the technique and noting the presence of correlations between hydrogen-bridged borons in other boranes (vide infra), we reinvestigated the COSY spectrum of $\text{B}_{10}\text{H}_{14}$. We found that by the use of carefully chosen acquisition and processing parameters we could observe a cross peak between the B(5,7,8,10) and B(6,9) resonances indicating coupling between these hydrogen-bridged boron nuclei.

Several factors are responsible for the detection of this cross peak. First, since considerable signal remained in the free induction decay after 512 data points were acquired, final acquisition was increased to 1K words. Second, the solvent chosen produces a large chemical shift difference between the B(1,3) and B(6,9) signals in $\text{B}_{10}\text{H}_{14}$.²¹ Third, the time-domain signals were mul-

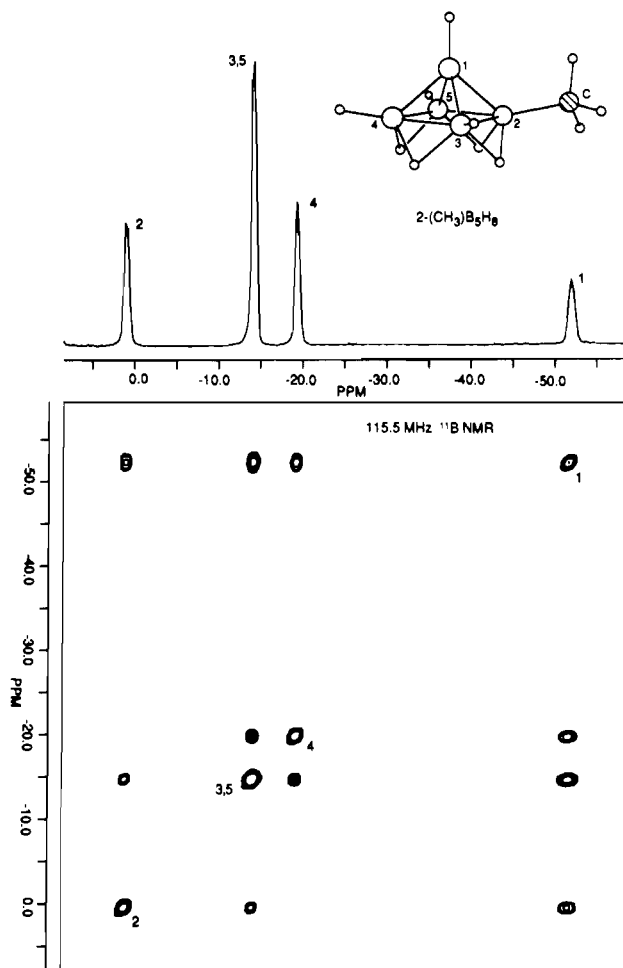


Figure 2. 115.5-MHz $^{11}\text{B}\{^1\text{H}\}$ 1-D and 2-D spectra of $2\text{-(CH}_3)_5\text{B}_8$ in C_6D_6 . The cross peaks between the B(3,5) signal and the B(2) and B(4) signals indicate $^{11}\text{B}-^{11}\text{B}$ coupling between these hydrogen-bridged boron atoms.

tiplied by a shaping function that converts them into "pseudoechoes". Bax and Freeman¹⁵ have described how such shaping functions increase the intensity of cross peaks relative to that of diagonal peaks. These functions also eliminate dispersion-mode line-shape components, producing more circular intensity contours for the peaks on the diagonal. This solves the problem of overlapping ridges from strong diagonal peaks and permits lower levels of the contour spectrum to be viewed. In the case of $\text{B}_{10}\text{H}_{14}$, the best results were obtained when a Gaussian function with $\text{LB} = -350$ and $\text{GB} = 0.3$ was applied to both dimensions. The cross peak between the B(5,7,8,10) and the B(6,9) resonances is small but real, having an intensity nearly 6 times greater than the noise level. Further evidence for the real nature of this cross peak was obtained from COSY experiments with different fixed delays before and after the mixing pulse. A longer mixing time produced a more intense cross peak, as is expected for two nuclei coupled by a small coupling constant.¹⁵

$2\text{-(CH}_3)_5\text{B}_8$. The 115.5-MHz 1-D $^{11}\text{B}\{^1\text{H}\}$ and $^{11}\text{B}-^{11}\text{B}$ COSY spectra of $2\text{-(CH}_3)_5\text{B}_8$ are shown in Figure 2. Assignment of the resonances follows from the proton-coupled 1-D spectrum. The low-field singlet resonance arises from the alkylated boron B(2). All basal boron resonances show cross peaks to the apical boron B(1). Cross peaks are also observed between the B(3,5) resonance and both B(2) and B(4), indicating $^{11}\text{B}-^{11}\text{B}$ coupling between inequivalent basal borons that are linked by bridging hydrogen atoms.

B_4H_{10} . The 115.5-MHz 1-D $^{11}\text{B}\{^1\text{H}\}$ and $^{11}\text{B}-^{11}\text{B}$ COSY spectra of B_4H_{10} are shown in Figure 3. A cross peak between B(1,3) and B(2,4) indicates the presence of coupling between boron atoms connected by bridging hydrogen atoms. The narrow line widths cause the contour peaks to appear small, but the cross peak is 10%

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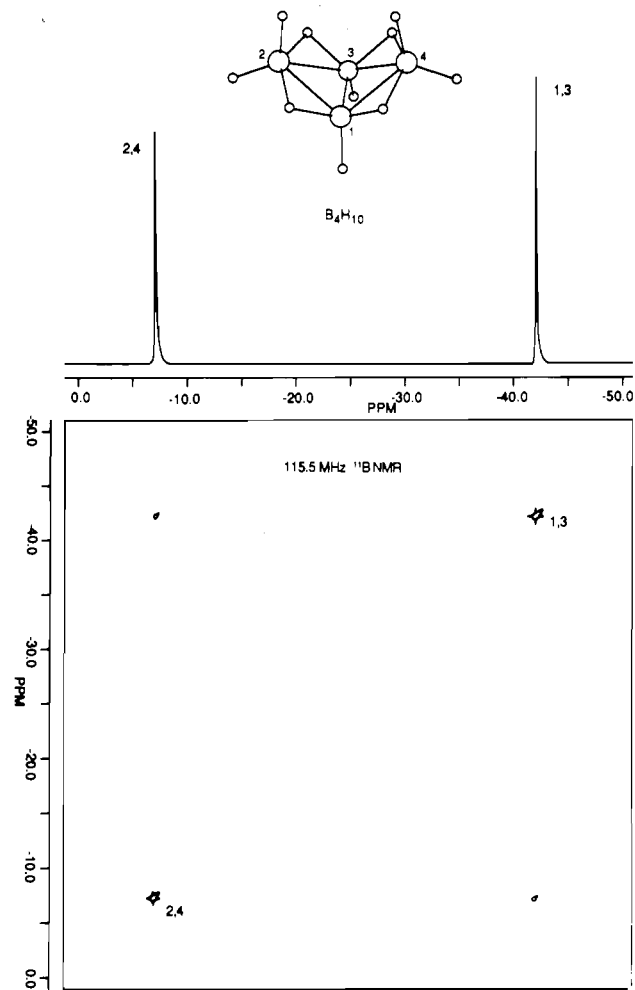


Figure 3. 115.5-MHz ¹¹B{¹H} 1-D and 2-D spectra of B₄H₁₀ in C₆D₆. The cross peak between the B(1,3) and B(2,4) signals indicates ¹¹B–¹¹B coupling between these boron atoms, which are linked by bridging hydrogen atoms only.

as intense as the tallest peak on the diagonal and 100 times more intense than the noise level.

(Me₂N)₂B₄H₈. The 160.4-MHz 1-D ¹¹B{¹H} and ¹¹B–¹¹B COSY spectra of (Me₂N)₂B₄H₈ are shown in Figure 4. Its proposed structure is similar to that of B₄H₁₀, with two dimethylamino groups in bridging positions. In the ¹¹B proton-coupled spectrum the low-field peak of intensity 1 is a triplet with *J* = 110 Hz. The central peak of intensity 2 at –7.49 ppm is resolved on line narrowing to a septet with *J* = 34 Hz. The broad high-field peak of intensity 1 shows no resolvable coupling even upon substantial line narrowing. Along with the ¹H NMR spectrum, these data could also support a structure in which the dimethylamino groups are in terminal positions on B(2). This alternative structure would require a reassignment of the low-field triplet from B(2) to B(4), the only boron remaining able to produce a triplet with *J* = 110 Hz. The proposed structure is favored on the basis of comparisons of the 1-D spectrum with those of aminoboranes of known structure.

The COSY spectrum provides more conclusive evidence for the proposed structure. A strong cross peak is observed between the two high-field peaks while no correlations are observed for the low-field peak. If the proposed structure is correct, this would indicate coupling between the hydrogen-bridged B(1,3) and B(4) nuclei and no coupling between the nitrogen-bridged B(1,3) and B(2) nuclei. Boron atoms should not be expected to exhibit observable coupling through bridging nitrogen atoms, considering the quadrupole moment of ¹⁴N and its generally poor directly observable coupling to boron. If the alternative structure is correct, an explanation must be found for the fact that B(1,3), linked to both B(NMe)₂ and BH₂ moieties by bridging hydrogens, shows

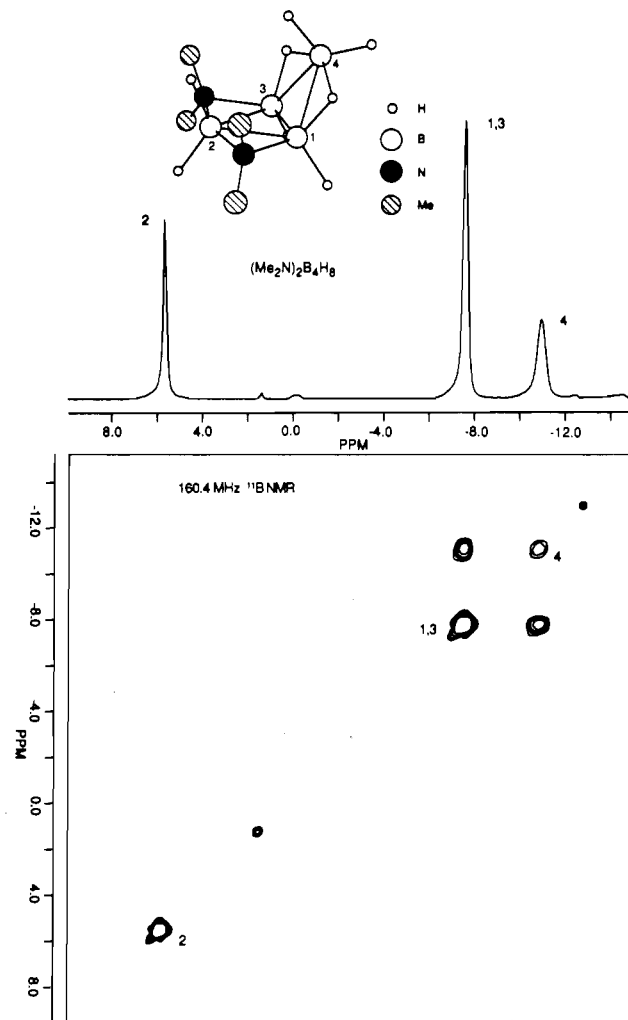


Figure 4. 160.46-MHz ¹¹B{¹H} 1-D and 2-D spectra of (Me₂N)₂B₄H₈ in CD₂Cl₂. A cross peak between the B(1,3) and B(4) signals indicates ¹¹B–¹¹B coupling between these hydrogen-bridged boron atoms.

coupling to the former and not to the latter. Regardless of which structure is correct, the COSY spectrum clearly shows coupling between boron atoms that are linked by bridging hydrogen atoms. It is of interest that the cross peak in this spectrum is more intense than one of the resonances on the diagonal that gives rise to it.

(μ-Me₂NCH₂)B₅H₈. The 115.5-MHz 1-D ¹¹B{¹H} and ¹¹B–¹¹B COSY spectra of *arachno*-(μ-Me₂NCH₂)B₅H₈ are shown in Figure 5. The high-field resonance is assigned to the apical boron atom. The resonances at +16.3 and –0.7 ppm have been tentatively assigned to B(3) and B(2), respectively, on the basis of ¹¹B–¹H coupling constants and line widths. It is not possible to assign the two remaining resonances on the basis of the 1-D spectrum. The cross peaks observed in the COSY spectrum, however, allow unambiguous assignment of all the spectral resonances, assuming only that the broad low-field resonance is due to the boron bonded to nitrogen, B(3).

The COSY spectrum shows that B(3) is coupled to B(1) and to the resonance at –4.0 ppm, which is therefore identified as B(4). The B(4) resonance in turn shows coupling to B(1) and B(3) and to the resonance at +3.76 ppm, which is identified as B(5). The remaining resonance at –0.7 ppm, due to B(2), shows coupling to B(1) and B(5) only, as expected.

It should be noted that the cross peaks that made possible the assignment described above resulted from coupling through bridging hydrogen atoms.

(μ-Me₃CCH=N)B₅H₈. Figure 6 shows the 115.5-MHz 1-D and 2-D ¹¹B–¹¹B COSY spectra of (μ-Me₃CCH=N)B₅H₈ and the proposed structure of this bridge-substituted imino-pentaborane derivative. The high-field resonance is assigned to the apical boron atom, B(1). The two overlapping low-field resonances

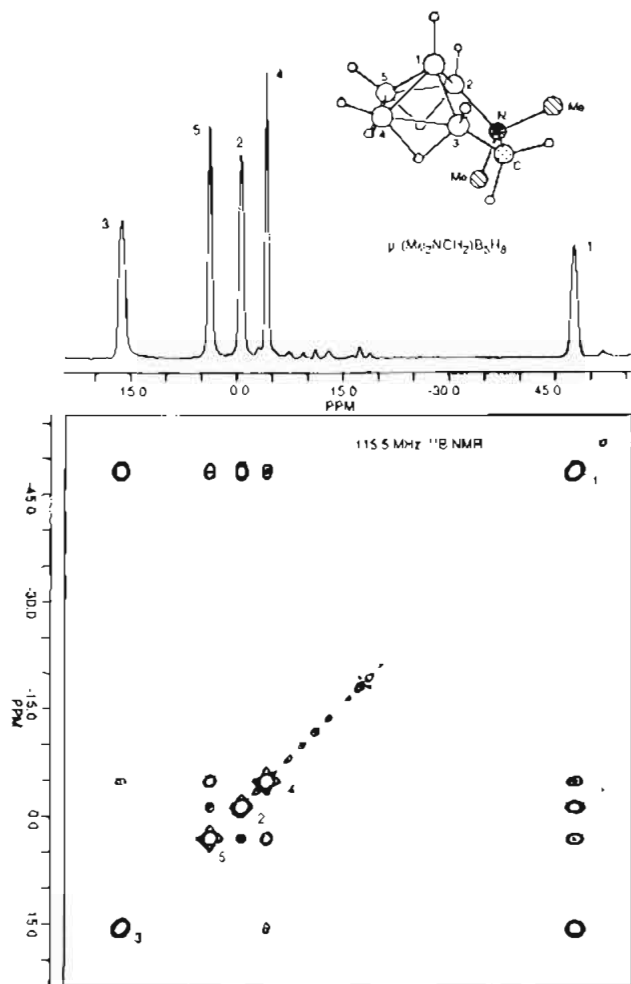


Figure 5. 115.5-MHz $^{11}\text{B}\{^1\text{H}\}$ 1-D and 2-D spectra of $(\mu\text{-Me}_2\text{NCH}_2)\text{B}_3\text{H}_8$ in C_6D_6 . Cross peaks are observed between all adjacent basal boron atoms, indicating $^{11}\text{B}\text{-}^{11}\text{B}$ coupling through bridging hydrogens.

are assigned to B(2) and B(3) on the basis of their smaller ^{11}B -terminal proton coupling constants. The remaining peak of intensity 2 is assigned to B(4) and B(5), which though inequivalent are presumed to be overlapping.

Two cross peaks are evident between the basal resonances, indicating coupling between B(3) and B(4) and between B(5) and B(2). The chemical shifts of these cross peaks are -13.75 and -14.26 ppm, while that of the peak on the diagonal is -14.0 ppm. This chemical shift difference indicates that B(4) and B(5) are indeed magnetically inequivalent. Thus the cross peaks in the COSY spectrum have allowed resolution of two boron resonances that appear as a single resonance in the corresponding 1-D spectrum. On the basis of the COSY spectrum, the order of the boron resonances from low to high field is either 2,3,5,4,1 or 3,2,4,5,1, depending on whether B(2) or B(3) is assigned to the low-field resonance.

Further Observations. Two compounds that do not exhibit $^{11}\text{B}\text{-}^{11}\text{B}$ coupling through bridging hydrogens are $(\text{CO})_3\text{ReB}_3\text{H}_8$ and $(\text{CO})_3\text{MnB}_3\text{H}_8$. The NMR-determined structure of these metallaboranes are pentagonal pyramids in which the metal atom occupies a basal vertex. Three hydrogen atoms occupy bridging positions between the basal boron atoms. Our initial experiments appeared to show weak cross peaks between the basal boron atoms. Their reliability, however, was called into question when we noticed that they were only slightly more intense than several artifacts in the F_1, F_2 submatrix file. The artifacts were cross peaks that

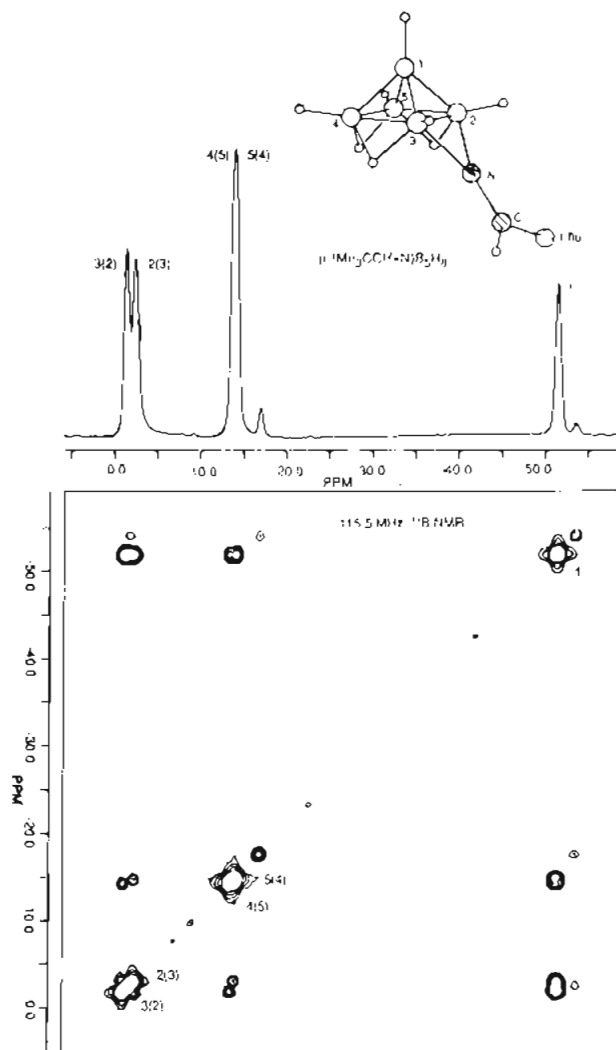


Figure 6. 115.5-MHz $^{11}\text{B}\{^1\text{H}\}$ 1-D and 2-D spectra of $(\mu\text{-Me}_3\text{CCH}=\text{N})\text{B}_3\text{H}_8$ in C_6D_6 . Two cross peaks are observed between the B(3) and B(4) signals and the B(5) and B(2) signals, indicating $^{11}\text{B}\text{-}^{11}\text{B}$ coupling through bridging hydrogens. These cross peaks allow resolution of the B(4) and B(5) resonances, which are unresolved in the corresponding 1-D spectrum. The order of the boron resonances depends on whether B(2) or B(3) is assigned to the low-field resonance.

appeared between all of the boron resonances and a sharp spike located at the spectrometer offset frequency on the diagonal. In addition, these spurious cross peaks were more intense than the spike on the diagonal. There is as yet no satisfactory explanation for this observation.

We also investigated the COSY spectrum of $\text{Et}_2\text{SB}_3\text{H}_{13}$ and duplicated the results of a previous investigation³ that found no coupling between the boron atoms linked by bridging hydrogen atoms in the corresponding Me_2S derivative.

Conclusion

One condition necessary for observation of a cross peak in a 2-D spectrum is sufficient electron density between the nuclei to permit scalar coupling. Our findings indicate that the amount and distribution of electron density in three-center-two-electron B-H-B bonds are often sufficient to permit the observation of coupling between boron atoms linked in this manner, provided that optimum acquisition and processing parameters are chosen.

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