It is quite clear that the bridging pyrazine ligand has in this case proved to be ineffective in coupling the magnetic moments of the two $Ru_2(chp)_4^+$ ions. We are somewhat surprised and disappointed by this. In view of the fact that the $Ru_2(chp)_4^+$ unit has two of its three unpaired electrons present in π^* orbitals, we had hoped that, by overlap of these with the π or π^* orbitals of the pyrazine ring, significant interaction would be facilitated.

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Supplementary Material Available: Tables of anisotropic thermal parameters, bond length and angle data, and least-squares planes for $1{\cdot}4CH_2Cl_2$ and **2**, tables of crystal data, atomic positional parameters, anisotropic thermal parameters, bond length and angle data, and least-squares planes and an ORTEP diagram for $1{\cdot}2CH_2Cl_2{\cdot}2pyz$, figures showing IR spectra of **1** and **2**, and tables of variable-temperature magnetic susceptibility data for **1** and **2** (30 pages); listings of observed and calculated structure factors for $1{\cdot}4CH_2Cl_2$, $1{\cdot}2CH_2Cl_2{\cdot}2pyz$, and **2** (73 pages). Ordering information is given on any current masthead page.

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Small Heteroborane Cluster Systems. 5. Factors Affecting the 2D $^{11}B-^{11}B$ COSY NMR Spectra of Terminal- and Bridge-Substituted Pentaborane Cluster Systems[1]

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The $^{11}B-^{11}B$ correlation NMR spectra (2D $^{11}B-^{11}B$ COSY NMR) and T_1 relaxation times for pentaborane(9), B_5H_9, and 10 terminal- and bridge-substituted pentaborane clusters, including phosphinopentaboranes, silylpentaboranes, and metal pentaborane complexes, have been measured. Both J_{PB} and "long-range" $^2J_{PBB}$ couplings, observed the first time in boranes, were measured for the (μ-phosphino)pentaborane compounds. The long-range $^2J_{PBB}$ couplings were not directly observable in the normal 1D spectra but were clearly resolved in the cross peaks of the 2D spectra. The magnitudes of these J_{PB} and $^2J_{PBB}$ coupling constants were related to the calculated MO cage bonding scheme for the clusters. A direct relationship between the MNDO-calculated boron-boron bond orders and the intensity of the developed cross peaks in the 2D $^{11}B-^{11}B$ COSY NMR spectra for adjacent cage boron atoms was observed which relates the calculated electron density localized in bonding interactions to observed NMR parameters in the clusters. The relationship among the MNDO-calculated bond order, T_1 relaxation time, and the appearance of cross peaks in COSY spectra has been evaluated. The first double-quantum $^{11}B-^{11}B$ correlation NMR experiment for the framework cage elucidation of a borane cluster is reported.

Introduction

Since 1982 homonuclear $^{11}B-^{11}B$ correlation NMR ($^{11}B-^{11}B$ COSY NMR) spectroscopy has been widely used for the elucidation of the structural features and the assignment of NMR spectral resonances for new boron cluster compounds.[2] Since then, the technique has been extended to include other quadrupolar nuclei such as ^{51}V ($I = {}^7/_2$).[3] Over the last 9 years, however, relatively little has been done to quantify the parameters associated with the development of a cross peak between coupled boron atoms.[2,4]

In the 2D NMR experiment, cross peaks (off-diagonal peaks) reveal spin-spin coupling interactions between the correlated nuclei.[5,6] In $^{11}B-^{11}B$ homonuclear COSY NMR spectra, the presence or absence of these cross peaks has been used effectively in the assignment of framework connectivities in unknown cage structures.[2] The systematic absence of a cross peak where one would normally be expected to develop has caused, in some cases, significant assignment difficulties, resulting in structural ambiguity for these new cages. This problem has been especially pronounced for the heteroborane and metallaborane clusters. It is therefore of importance to address the underlying chemical reasons for cross peak absences in 2D $^{11}B-^{11}B$ NMR spectra in order to improve the applicability of this powerful method toward making reliable cage framework assignments.

The two most important factors governing cross peak evolution in the 2D spectrum are the amount of electron density localized between the boron atoms in question and the relaxation times for these nuclei.[2b,5,6] In this paper, we address these parameters quantitatively by calculating boron-boron bond orders using semiempirical theoretical techniques and by measuring the 2D spectra and T_1 values for the cage boron atoms in a variety of substituted pentaborane cluster compounds. Since the presence of a cross peak in the 2D experiment requires the localization of significant electron density between correlated nuclei, because scalar coupling is propagated primarily through the bonding electrons, it should be possible to obtain a correlation between the calculated boron-boron bond order and the development of a cross peak in the 2D spectrum, assuming that the corresponding T_1 values are sufficiently long. This expectation is supported by the qualitative relationship observed between the expected bonding

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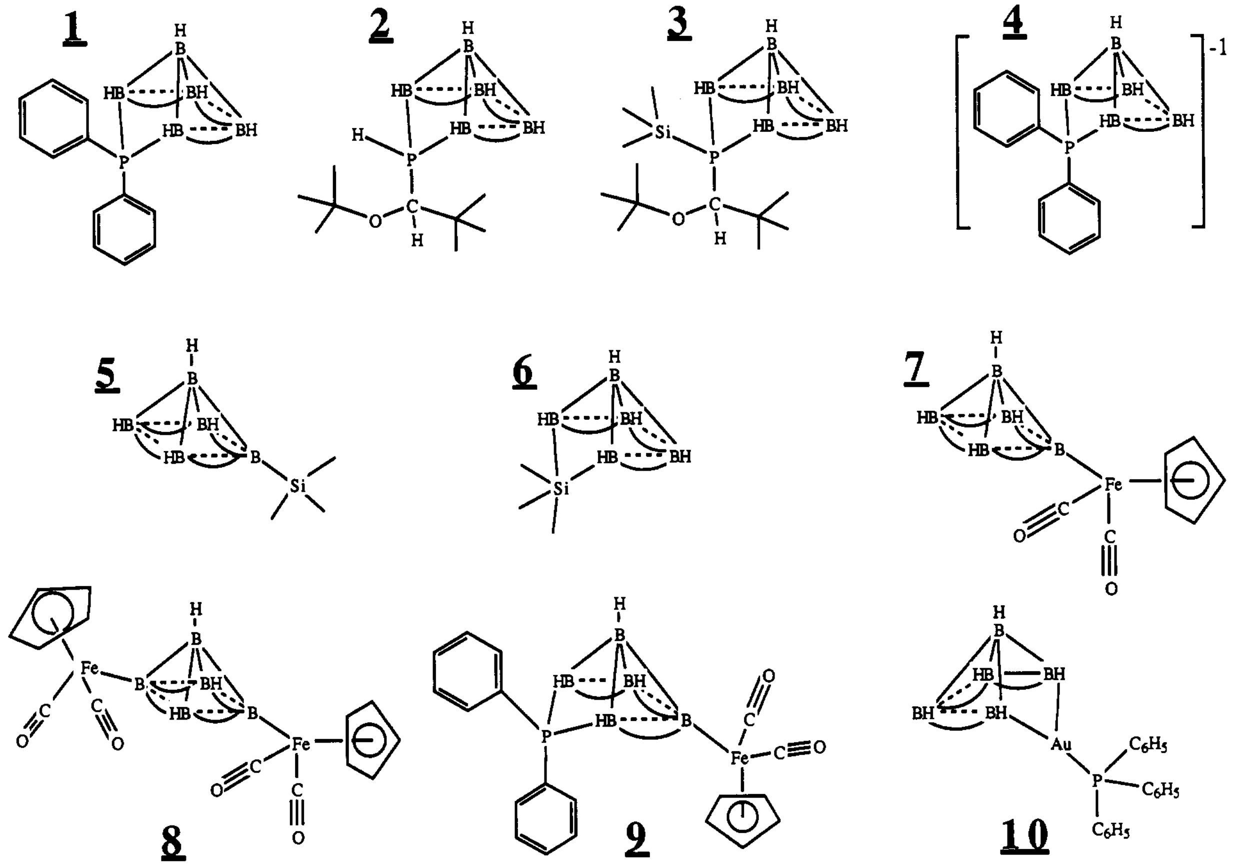
Chart I. Structures of Substituted Pentaboranes **1**–**10**[a]



[a] An arc indicates a bridging hydrogen.

electron density between correlated nuclei in the cage framework[7] and the difficulty in observing the corresponding cross peak in the 2D spectrum. In general, boron–boron 2-center-2-electron (2c–2e) bonds have been observed to provide strong cross peaks, while cross peaks arising from coupling through B–H–B 3-center-2-electron (3c–2e) bonds give either weak or, more rarely, missing cross peaks.[2] In this paper, we report a direct correlation between the measured cross peak intensity (integral) and the calculated boron–boron bond order for the coupled boron atoms. The second factor affecting the development of cross peaks in the 2D spectrum relates to the T_1 values for the coupled nuclei. The cross peak intensity is, in general, attenuated when T_1 values are very small with respect to the reciprocal of J_{BB} (i.e., when $T_1 \ll (2\pi J)^{-1}$).[2b,8] In this paper, T_1 relaxation times for cage boron atoms in a variety of bonding situations are measured and the effect of very short T_1 times on the appearance of the 2D ^{11}B–^{11}B COSY NMR spectrum has been investigated. In addition, the T_1 times measured for the cage boron atoms should provide a sensitive probe of the bonding scheme displayed in the cage-substituent interaction. Thus, insights gained from these calculational relationships and quantitative NMR measurements on a close structurally related series of boron clusters should facilitate the structural assignments and interpretation of bonding interactions for new compounds directly from ^{11}B–^{11}B COSY NMR spectra, particularly in cases where cross peaks either are of low intensity or are absent entirely.

In 2D ^{11}B–^{11}B COSY NMR spectra, cross peaks resulting from the spin–spin coupling interactions between adjacent boron atoms are readily observed in spite of the fact that ^{11}B–^{11}B coupling is rarely observed in the normal 1D spectrum for boron cluster compounds.[2] The successful measurement of routine ^{11}B–^{11}B 2D COSY spectra thus shows that the 2D experiment is capable of resolving normally obscured spin–spin coupling information. It was, therefore, of interest to determine if the ^{11}B–^{11}B 2D COSY NMR experiment could be used to resolve small couplings between boron nuclei and bonded magnetically active heteroatoms in borane clusters that had previously not been observed. In addition, it appears that spin–spin ^{11}B–^{11}B coupling information observed in the 2D spectrum for boranes has been restricted to one-bond coupling, either through direct B–B bonding or in some instances through B–H–B or B–B–B 3-center-2-electron (3c–2e) interactions. A study of bridged and terminally substituted pentaborane clusters based on the closely related *nido*-B_5H_9 and *arachno*-B_5H_{11} parent structures, including the phosphinopentaborane, silylpentaborane, and metal pentaborane compounds, provides a convenient series of compounds to investigate the resolution and range of potential boron–heteroatom coupling. This family of pentaborane-derived compounds also provides a unique series for which a deeper understanding may be gained concerning the role localized bonding electron density and T_1 factors play in the development of cross peaks in 2D ^{11}B–^{11}B COSY spectra.

Finally, the use of the double-quantum correlation experiment[5,6] to provide additional cross peak and coupling information relative to the 2D ^{11}B–^{11}B COSY NMR experiment for boron-containing compounds has not been explored. This experiment has proven to be a very powerful tool for the structural assignment of unknown organic and bioorganic compounds by ^{13}C–^{13}C (INADEQUATE) NMR studies.[6] The technique provides important structural information frequently obscured in the 2D COSY experiment by removing interferences caused by the overlap of intense diagonal peaks with the cross peaks and by providing a separation of the peaks which is twice as large as that observed in the COSY spectrum. In this paper, we present the first ^{11}B–^{11}B double-quantum correlation experimental data for a borane cluster.

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Experimental Section

Materials. The compounds $[(\mu\text{-P}(C_6H_5)_2)B_5H_8]$ (**1**),[9] $[(\mu\text{-P}(H)(CH(OSiMe_3)(^tBu)))B_5H_8]$ (**2**),[10] $[(\mu\text{-P}(SiMe_3)(CH(OSiMe_3)(^tBu)))B_5H_8]$ (**3**),[10] $Na[(\mu\text{-P}(C_6H_5)_2)B_5H_7]$ (Na(**4**)),[23] $[2\text{-}(Si(CH_3)_3)B_5H_8]$ (**5**),[11] $[(\mu\text{-Si}(CH_3)_3)B_5H_8]$ (**6**),[11] $[2\text{-}(Fe(\eta^5\text{-}C_5H_5)(CO)_2)B_5H_8]$ (**7**),[13] $[2,4\text{-}(Fe(\eta^5\text{-}C_5H_5)(CO)_2)_2B_5H_7]$ (**8**),[13] $[4\text{-}(Fe(\eta^5\text{-}C_5H_5)(CO)_2)B_5H_7(\mu\text{-}2,3\text{-P}(C_6H_5)_2)]$ (**9**),[9] and $[(\mu\text{-}2,3\text{-}(C_6H_5)_3PAu)B_5H_8]$ (**10**),[14] shown in Chart I, were prepared and purified according to known literature methods. Pentaborane(9), B_5H_9, was from our laboratory stock. All compounds were prepared and manipulated using standard vacuum-line techniques.[15] All solvents used in the syntheses were of reagent grade or better and were distilled from the appropriate drying agents under a dry nitrogen atmosphere prior to use: THF (Na), pentane (Na), and diethyl ether (Na). Organic solvents, after drying, were degassed by repeated freeze–thaw cycles and finally stored in vacuo prior to use. Deuterated solvents were used as received and were stored over 4-Å molecular sieves prior to use. Analytical thin-layer chromatography was conducted on 2.5 × 7.5 cm silica gel strips (1B-F, Baker), and conventional column chromatography was conducted using 2.5 × 30 cm columns packed with 230–400-mesh (ASTM) silica gel (EM Science).

Physical Measurements. Boron (^{11}B) NMR spectra were recorded on either a Cryomagnetics CM-250 or a General Electric QE-500 spectrometer operating at 80.26 or 160.45 MHz, respectively. Spectra were recorded in 5-mm (o.d.) tubes in both the coupled and decoupled modes and were externally referenced to BBr_3 at +40.0 ppm (positive chemical shifts indicate downfield resonances). All 2D ^{11}B–^{11}B COSY NMR and T_1 measurements were recorded in the ^1H-decoupled mode. For the 2D ^{11}B–^{11}B COSY NMR spectra, samples were prepared in a nitrogen atmosphere and referenced to $BF_3{\cdot}Et_2O$ from the previously determined chemical shifts of the compounds. The Cryomagnetics spectrometer required a pulse width of ~12 μs, while th QE-500 spectrometer required ~24 μs in order to produce a 90° pulse. All of the COSY experiments were performed using the previously described pulse sequence[2a,b] such that T_w–$(\pi/2)$–T_i–$(\pi/2)$–acquisition with data collected in a 128 × 256 $t_1 \times t_2$ data matrix (where T_w is the postacquisition delay and T_i is the incremental delay time). Data processing was carried out using NMR2[16] software programs on a SUN computer system. Data processing involved the application of baseline correction, sine bell apodization, zero-fill processing (twice in t_1 and once in t_2), Fourier transformation, magnitude calculation, and diagonal symmetrization to give a 512 × 512 $f_1 \times f_2$ 2D ^{11}B–^{11}B COSY NMR spectrum. The T_1 measurements were made using the inversion-recovery method in which $y = A(1 - (1 + w(1 - e^{-k/T}))e^{-x/T}$ where A = amplitude, $T = T_1$ (in seconds), $k = D_2 + D_5$ in the pulse sequence, and $w = -(A \text{ at } x = 0)/A$.[17,18] No less than 10 data points were fit to this function for each measurement. The double-quantum experiments were performed as previously reported.[5,6]

Theoretical Calculations. The bond orders for the compounds studied here were calculated using the MNDO semiempirical method found in MOPAC5.0[19] on the VAX 2280 computer of the Syracuse University Academic Computing Center. Parametrizations for the atoms were those reported in the literature.[20] The bond orders for $[(\mu\text{-P}(C_6H_5)_2)B_5H_8]$ (**1**), $[(\mu\text{-P}(H)(CH(OSiMe_3)(^tBu)))B_5H_8]$ (**2**), and $[(\mu\text{-P}(SiMe_3)(CH(OSiMe_3)(^tBu)))B_5H_8]$ (**3**) were calculated from the fixed atom positions of the minimized structures previously reported.[21] The calculations to find the minimum-energy geometry and bond orders for $Na[(\mu\text{-P}(C_6H_5)_2)B_5H_7]$ (Na(**4**)), $[2\text{-}(Si(CH_3)_3)B_5H_8]$ (**5**), and $[(\mu\text{-Si}(CH_3)_3)B_5H_8]$ (**6**) followed standard procedures similar to those previously used for the determination of the MNDO-optimized structures for the phosphinopentaborane clusters.[21] These calculations were run with the PRECISE[20e] option employed and were allowed to freely vary with only the constrains of an overall C_s molecular symmetry applied to locate the stationary point on the potential energy surface. No difficulties were encountered in the calculations.

Results and Discussion

The structurally related series of substituted pentaborane clusters studied in this paper, compounds **1**–**10**, provides an informative set of compounds by which the relative importance of several structural and NMR parameters to the appearance and interpretation of complex spectra can be studied. Of particular interest are the 2D homonuclear ^{11}B–^{11}B COSY NMR and related experiments which have recently found increased use in the structural elucidation of complex cluster species. The members of a structurally related class of clusters were required in which the effect of various substitutions and bonding patterns on NMR parameters could be investigated to order to render complex NMR experiments more readily useful in providing valuable structural and bonding information. Such a series of compounds is readily available in the bridged and terminally substituted pentaborane cluster series. The 2D ^{11}B–^{11}B COSY NMR spectra and T_1 values for these species were measured using simple modifications of relatively standard techniques.[2a] In addition, other NMR experiments, such as the double-quantum experiment,[5,6] should be directly applicable to these cluster systems to gain further structural and bonding information on the cage. Accurate theoretical tools, the final component required for this study, have been well developed for the study of these boron clusters and have been shown to be valuable in the exploration of the fundamental bonding nature of these species. The MNDO (modified neglect of differential overlap) semiempirical method of Dewar[20] has been extensively employed in calculations for these systems and has been shown to provide superior structural and thermodynamic data for boron hydride and heteroborane systems.[10,21,22] Recent calculational studies on phosphorus-substituted borane clusters have shown that the MNDO method is very successful in duplicating important structural and electronic features of these clusters.[21,22e] The MNDO-calculated geometries for all the structurally characterized phosphaborane systems provided exceptionally good agreement between the calculated and the experimentally determined parameters.[21] Recently, the MNDO calculations for the phosphaborane $1,2\text{-}PCB_{10}H_{11}$ were reported and the results of these calculations compared to the compound's gas-phase photoelectron spectrum.[22e] The experimental data agreed remarkably well with the data obtained from the MNDO calculation. Thus, for the substituted pentaborane family of clusters, the experimental and theoretical techniques were available for the investigation of the relationships between these important structural, bonding, and NMR spectroscopic parameters.

For this study, 10 substituted pentaborane clusters with structures based upon either the *nido*-B_5H_9 or *arachno*-B_5H_{11} parent compounds were selected (Chart I). The ^{11}B chemical shifts and coupling constants for these compounds are presented in Table I, the 2D ^{11}B–^{11}B COSY NMR data for this series of compounds are summarized in Table II, and the ^{11}B NMR T_1 spin-lattice relaxation times, the measured spectral line widths, and the calculated natural line widths are given in Table III. Selected

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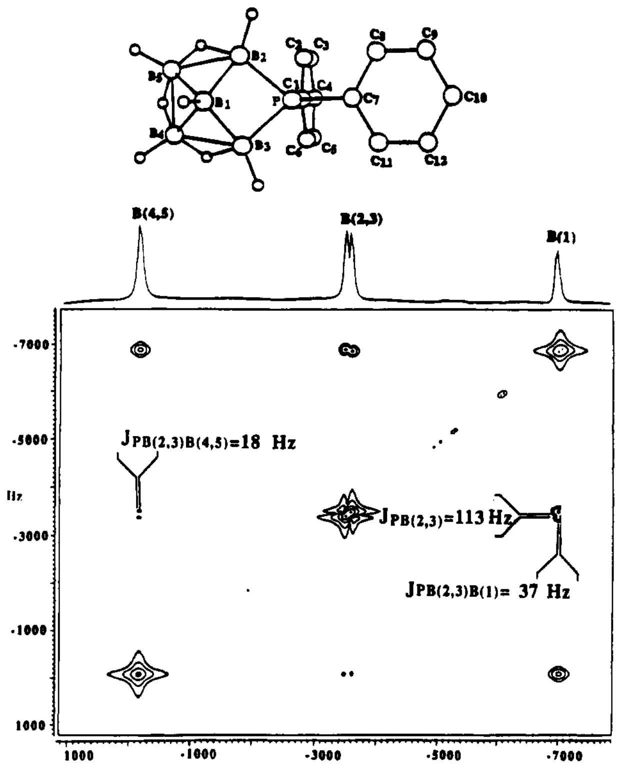

Figure 1. 160.45-MHz 2D ^{11}B–^{11}B COSY NMR spectrum at 25 °C in $CDCl_3$ for [(μ-$P(C_6H_5)_2)B_5H_8$] (1). The MNDO-calculated minimum-energy structure and the atomic numbering scheme are shown above the spectrum. The view is normal to the basal B_4 plane with the apical boron projecting above the basal plane. The hydrogen atoms on the exopolyhedral groups have been omitted for clarity. Phopshorus–boron coupling constants which are unresolved in the 1D spectrum are indicated on the appropriate cross peaks in the 2D spectrum.

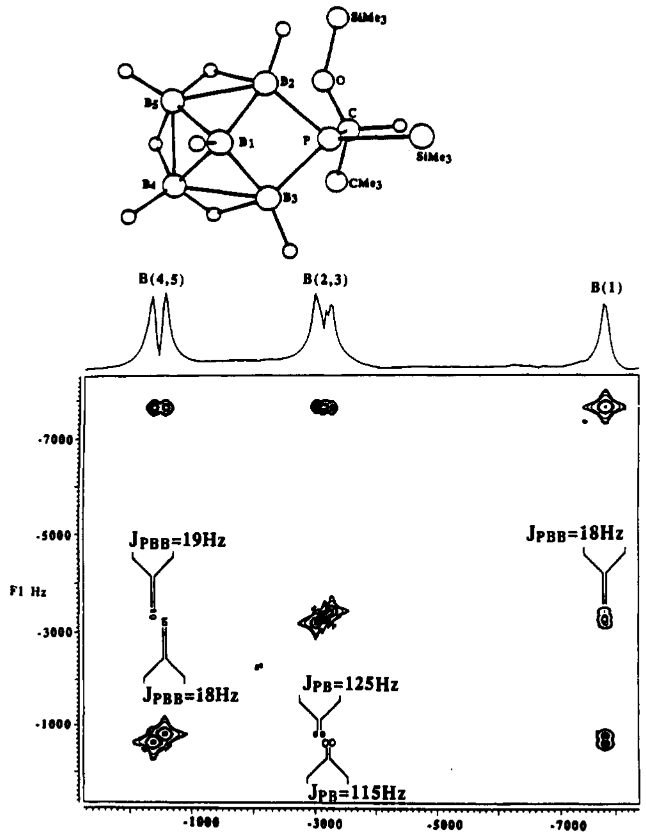

Figure 2. 160.45-MHz 2D ^{11}B–^{11}B COSY NMR spectrum at 25 °C in $CDCl_3$ for [(μ-$P(SiMe_3)(CH(OSiMe_3)(^tBu)))B_5H_8$] (3). The MNDO-calculated minimum-energy structure and the atomic numbering scheme are shown above the spectrum. The view is normal to the basal B_4 plane with the apical boron projecting above the basal plane. The hydrogen atoms on the exopolyhedral groups have been omitted for clarity. Phopshorus–boron coupling constants which are unresolved in the 1D spectra are indicated on the appropriate cross peaks in the 2D spectra.

spectra, along with the appropriate MNDO-calculated minimum-energy structures, are shown in Figures 1–8. The general theory for the interpretation of 2D ^{11}B–^{11}B COSY NMR spectra has been presented previously and will not be discussed in this paper.[2,5,6]

The structures of the phosphinopentaborane cluster compounds **1**–**4** consist of a modified pentaborane framework in which one of the bridging hydrogen atoms has been formally replaced by a bridging phosphino group. Since the phosphino group is a 3-electron donor[1] and thus forms two 2-center–2-electron bonds to the cage boron atoms, in contrast to the hydrogen atom's 1-electron donation in a 3-center–2-electron scheme, the basal B–B distance bridged by the phosphino group is significantly lengthened.[9,23] The general structure of these clusters has recently been confirmed by a crystal structure analysis of the $Fe(\eta^5\text{-}C_5H_5)(CO)_2$ basally substituted derivative of **1**.[23]

The 1D ^{11}B spectrum of **1** (μ-diphenylphosphino)pentaborane, shows three peaks in a 2:2:1 ratio comprising the two pairs of basal borons and the single apical boron atom, respectively.[9,10,23] In Figure 1 is shown the 1D and 2D ^{11}B–^{11}B COSY NMR spectra and the MNDO-calculated minimum-energy geometry for compound **1**. In the 2D spectrum, expected cross peaks between all of the resonances involving B–B and B–H–B bonding arrangements are clearly resolved. In addition, the one- and two-bonded phosphorus–boron couplings between the bridged phosphorus atom and all of the sets of boron nuclei are observed for the first time as phosphorus-split 2D cross peaks. These J_{PB} and $^2J_{PBB}$ coupling interactions appear as asymmetric doublets for the cross peaks between boron atoms B(1) and B(2,3) and also for the B(2,3) and B(4,5) pair. These "long-range" $^2J_{PBB}$ couplings are not directly observable in the 1D spectra presumably due to the fact that these resonances are broad due to the presence of J_{BH}, J_{BB}, J_{PB}, and $^2J_{PBB}$ couplings as well as quadrupolar interactions.[9,10a,b] The resolution of J_{PB} and $^2J_{PBB}$ couplings in the cross peaks of the 2D NMR spectra is a general feature for all the phosphinopentaborane compounds studied. Comound **2**, in which the two phenyl groups attached to the phosphorus atom have been replaced with a proton and a $CH(OSiMe_3)(^tBu)$ group, displays a spectrum very similar to that observed for **1** with no expected cross peaks missing.

The ^{11}B NMR spectra data reported previously[10a,b] for compound **3** consisted of three resonances corresponding to the two sets of equivalent basal borons and one unique apical boron in 2:2:1 relative intensity. The B–H(terminal) couplings for the two sets of basal boron resonances were not resolved, and the resonances were observed as relatively broad, featureless peaks in both the ^1H-coupled and ^1H-decoupled 1D ^{11}B spectra. The lack of resolution in these basal boron resonances was unusual when compared with the spectra of other known phosphinopentaboranes and was attributed to three possible causes: (1) the presence of endo–exo isomers seprated by relatively large barriers to interconversion, due to the bulky substituents on the phosphorus, which were not independently resolved in the spectrum, (2) the possibility that the compound exhibited similar values for B–H(terminal) and B–P(bridging) couplings which, when superimposed in the spectrum, resulted in the observed broadness, and (3) the unresolved overlap of the four inequivalent basal boron resonances. This latter inequivalence of all of the basal boron atoms arises from the presence of a chiral exopolyhedral group, $CH(OSiMe_3)(^tBu)$, attached to the phosphorus center. Data from 160.45-MHz 1D and 2D ^{11}B–^{11}B COSY NMR experiments reported here can be readily used to provide an explanation for this lack of peak resolution. The broad featureless resonance for the B(2,3) nuclei bonded to the bridged phosphorus atom in the

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[23] Goodreau, B. H.; Ostrander, R. L.; Spencer, J. T. *Inorg. Chem.* **1991**, *30*, 2066.

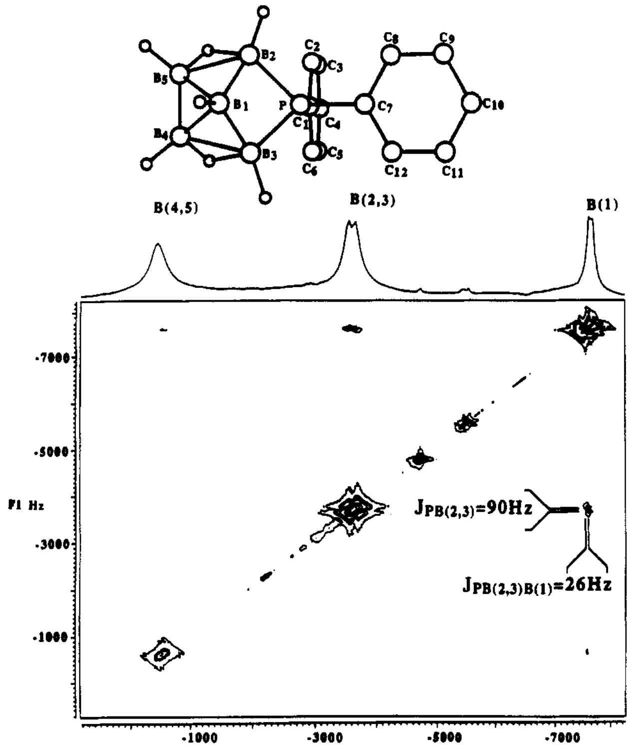

Figure 3. 160.45-MHz 2D ^{11}B–^{11}B COSY NMR spectrum at 25 °C in $CDCl_3$ for $Na[(\mu\text{-}P(C_6H_5)_2)B_5H_7]$ (Na(4)). The MNDO-calculated minimum-energy structure and the atomic numbering scheme are shown above the spectrum. The view is normal at the basal B_4 plane with the apical boron projecting above the basal plane. The hydrogen atoms on the exopolyhedral groups have been omitted for clarity.

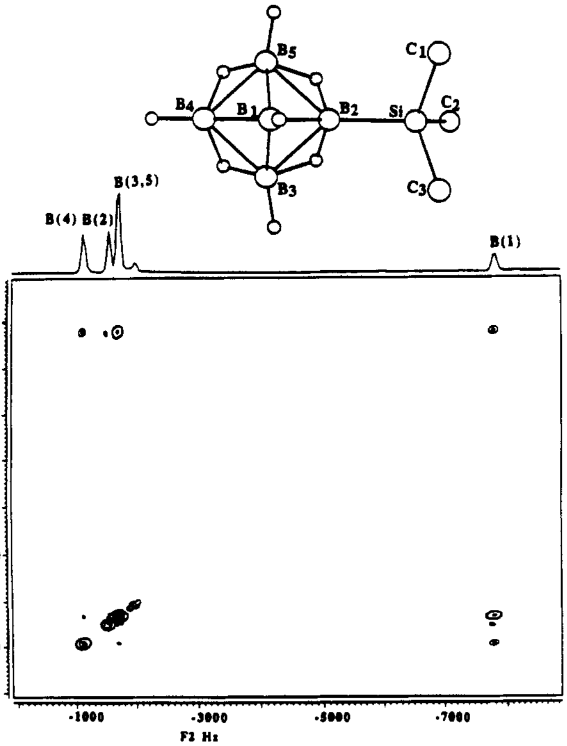

Figure 4. 160.45-MHz 2D ^{11}B–^{11}B COSY NMR spectrum at 25 °C in $CDCl_3$ for $[2\text{-}(Si(CH_3)_3)B_5H_8]$ (5). The MNDO-calculated minimum-energy structure and the atomic numbering scheme are shown above the spectrum. The view is normal to the basal B_4 plane with the apical boron projecting above the basal plane. The hydrogen atoms on the exopolyhedral groups have been omitted for clarity.

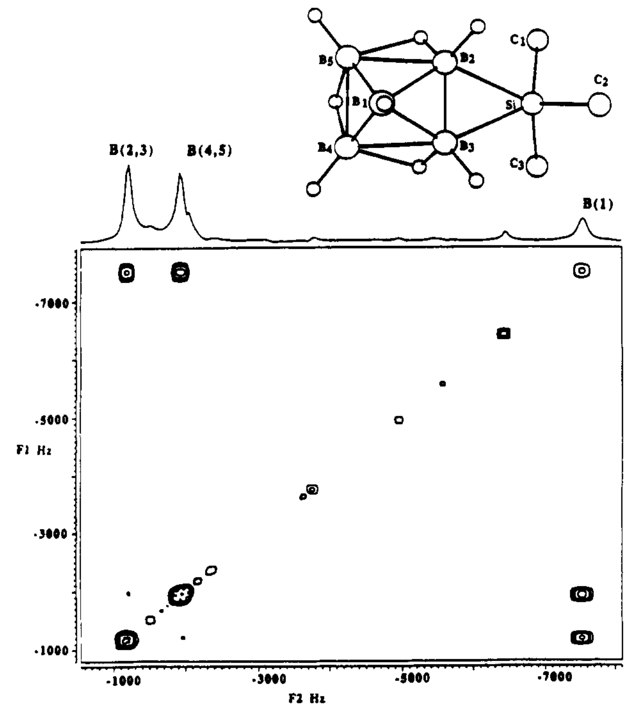

Figure 5. 160.45-MHz 2D ^{11}B–^{11}B COSY NMR spectrum at 25 °C in $CDCl_3$ for $[(\mu\text{-}Si(CH_3)_3)B_5H_8]$ (6). The MNDO-calculated minimum-energy structure and the atomic numbering scheme are shown above the spectrum. The view is normal to the basal B_4 plane with the apical boron projecting above the basal plane. The hydrogen atoms on the exopolyhedral groups have been omitted for clarity.

80.26-MHz spectrum is resolved into two resonances in the 160.45-MHz ^1H-decoupled ^{11}B spectrum shown in Figure 2. The J_{BP} coupling (125 and 115 Hz) is clearly resolved in the cross peaks in the 2D spectrum. The resonance for the "back" basal boron atoms, B(4) and B(5), is similarly resolved into two peaks with $^2J_{PBB}$ coupling values of 18 and 19 Hz measured in the 2D NMR cross peaks. These data indicate that the primary reason for the broadness of the peaks in the 80.26-MHz spectrum is the inequivalence of all the boron atoms in the basal plane due to chiral inductive effects of the exopolyhedral group. Further complication arises, however, in the resonances for the B(2) and B(3) nuclei, since the J_{PB} coupling approaches the magnitude of the expected, but unobserved, J_{BH} coupling.

The reaction of compound **1** with NaH results in the deprotonation of the cage at a bridge hydrogen position and the formation of its anion, **4**. The 2D NMR spectrum for **4**, shown in Figure 3, again showed the expected cross peaks and J_{PB} splittings except that the cross peaks between pairs of basal boron atoms B(2,3) and B(4,5) were not observed.

As described above, the primary factors governing cross peak evolution in the 2D spectrum are the amount of electron density localized between the boron atoms in question and the relaxation times for these nuclei. In order to quantitatively probe the reasons for the missing cross peaks in the 2D NMR spectrum for **4**, T_1 values and MNDO-calculated bond orders for the phosphinopentaborane clusters were determined. The calculated bond order for the interaction between pairs of basal boron atoms B(2,3) and B(4,5) in **4**, shown in Table II, was found to be typical for this interaction relative to other phosphinopentaboranes in which cross peaks were observed in the 2D spectrum. In the case of **4**, however, the missing cross peak can be traced directly to two extremely short T_1 spin–lattice relaxation values for the B(2,3) and B(4,5) sets of nuclei (3.83 and 1.64 ms, respectively). When the condition $T_1 \ll (2\pi J_{BB})^{-1}$ occurs, a significant loss of cross peak intensity can be expected.[8a,24] Using this relationship between T_1 and J_{BB} with the measured T_1 value of 1.64 ms for **4**, the minimum required J_{BB} coupling constant necessary for the observation of a cross peak in the 2D NMR spectrum was calculated. This calculated minimum J_{BB} value, shown in Table IV, was 97 Hz for the B(4,5)–B(2,3) interaction. It seems very likely that the B(2,3)–B(4,5) coupling in **4** is well below this value, on the basis of previous experiments which estimate a J_{BB} of <2 Hz for this

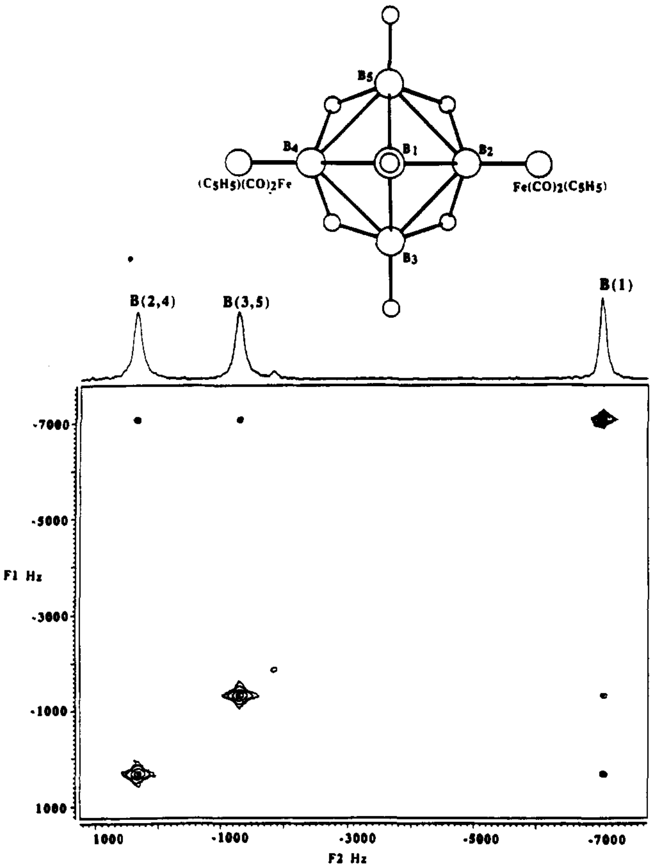

Figure 6. 160.45-MHz 2D $^{11}B-^{11}B$ COSY NMR spectrum at 25 °C in $CDCl_3$ for $[2,4-(Fe(\eta^5-C_5H_5)(CO)_2)_2B_5H_7]$ (**8**). The molecular structure and the atomic numbering scheme are shown above the spectrum. The view is normal to the basal B_4 plane with the apical boron projecting above the basal plane. The hydrogen atoms on the exopolyhedral groups have been omitted for clarity.

interaction in the parent *arachno*-B_5H_{11} structure.[8b]

For each of the phosphinopentaborane clusters, the magnitudes of the P–B couplings were found, in general, to decrease in the series ${}^1J_{PB(2,3)} > {}^2J_{PB(2,3)B(1)} > {}^2J_{PB(2,3)B(4,5)}$ with average values for the four clusters of 110, 29, and 23 Hz, respectively. This ordering is fully consistent with MO considerations for the clusters in which the one-bond coupling for the P–B(2,3) bond involving only 2c–2e interactions[9,10,21] is the largest, followed by the two-bond P–B(2,3)–B(1) interaction involving no B–H–B bonds and finally ending with the two-bond P–B(2,3)–H–B(4,5) interaction observed as the weakest (smallest J value), primarily due to the presence of the B–H–B 3c–2e multicenter bond between the basal boron atoms.

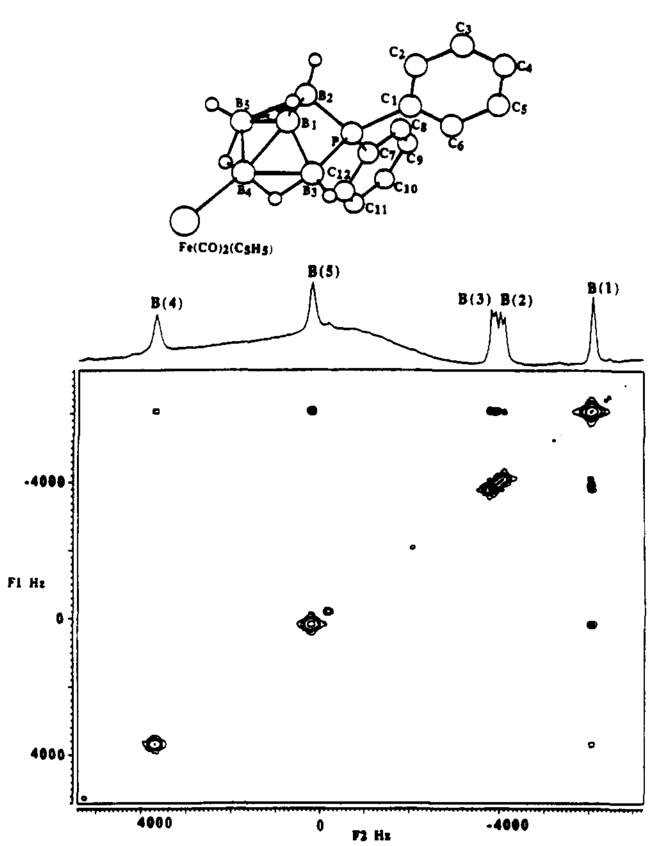

Figure 7. 160.45-MHz 2D $^{11}B-^{11}B$ COSY NMR spectrum at 25 °C in $CDCl_3$ for $[4-(Fe(\eta^5-C_5H_5)(CO)_2)B_5H_7(\mu-2,3-P(C_6H_5)_2)]$ (**9**). The molecular structure and the atomic numbering scheme are shown above the spectrum. The view is from approximately 45° above the basal B_4 plane with the apical boron shown above the plane. The hydrogen atoms on the exopolyhedral groups have been omitted for clarity.

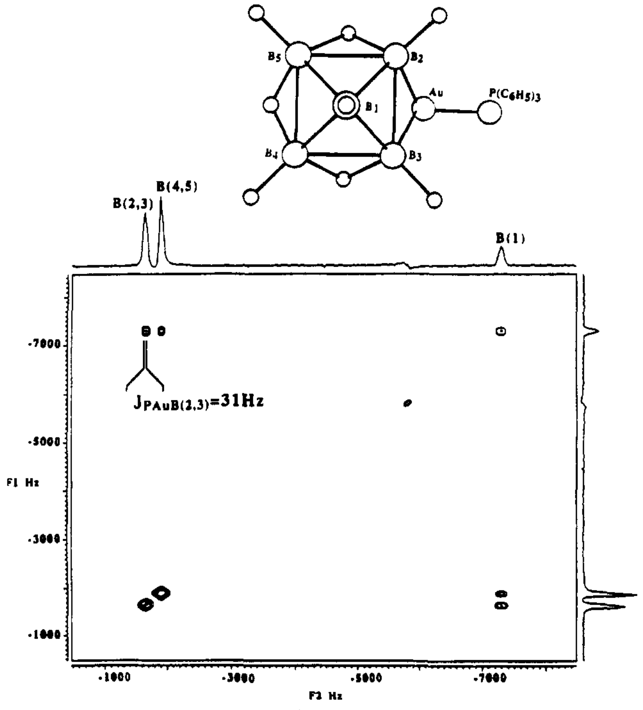

Figure 8. 160.45-MHz 2D $^{11}B-^{11}B$ COSY NMR spectrum at 25 °C in $CDCl_3$ for $[((C_6H_5)_3PAu)B_5H_8]$ (**10**). The molecular structure and the atomic numbering scheme are shown above the spectrum. The view is normal to the basal B_4 plane with the apical boron projecting above the basal plane. The hydrogen atoms on the exopolyhedral groups have been omitted for clarity.

Several trends were observed in the bond order and T_1 data for the (μ-phosphino)pentaborane compounds. The MNDO calculations show a decrease in bond order of B(1)–B(2,3) > B(1)–B(4,5) > B(2,3)–B(4,5) for all of the compounds studied. This trend is directly reflected in the observed cross peak intensity (peak volume) for the corresponding NMR 2D resonances. A plot of peak volume (calculated from the unapodized spectrum) versus bond order for compounds **1**–**3** is shown in Figure 9.[25] The intensities of cross peaks in $^{11}B-^{11}B$ COSY spectra correlate reasonably well with the calculated bond order of the coupled

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(24) Farrar, T. C.; Becker, E. D. *Pulse and Fourier Transform NMR*; Academic Press: New York, 1971.

(25) The silylpentaboranes were not included in this correlation because full relaxation was not achieved during the postacquisition delay and hence peak integrals do not accurately reflect the full strength of the coupling. The metallaboranes were also excluded from the plot because the T_1 attenuation, from very short T_1 times, for these compounds results in missing cross peaks. The largest peak in each spectrum was normalized to 1.

(26) (a) Eaton, G. R.; Lipscomb, W. N. *NMR Studies of Boron Hydrides and Related Compounds*; Benjamin: New York, 1969. (b) Todd, L. J.; Siedle, A. R. *Prog. Nucl. Magn. Reson. Spectrosc.* **1979**, *13*, 87. (c) Siedle, A. R. *Annu. Rep. NMR Spectrosc.* **1982**, *12*, 77.

Table I. ^{11}B NMR Data for Substituted Pentaborane Systems

		coupling, Hz		
compound	δ^a	B–H	P–B	ref[b]
B_5H_9	−51.8 (s, 1 B, B(1))	$J_{B(1)H} = 174$		17[c,d]
	−12.5 (s, 4 B, B(2–5))	$J_{B(2-5)H} = 161$		
B_5H_{11}	−53.5 (s, 1 B, B(1))	$J_{B(1)H} = 168$		19[c,e]
	7.7 (s, 2 B, B(2,5))	$J_{B(2,5)H} = 132$		
	0.7 (s, 2 B, B(3,4))	$J_{B(3,4)H} = 168$		
$B_5H_9P(CH_3)_3$	−52.6 (s, 1 B, B(1))	$J_{BB} = 20$	$J_{PB(1)} = 139$	18[c,f]
	−4.2 (s, 4 B, B(2–5))	$J_{B(2-5)H} = 120$		
$[(\mu\text{-}P(C_6H_5)_2)B_5H_8]$ (**1**)[g]	−45.6 (s, 1 B, B(1))	$J_{B(1)H} = 153$	$J_{PB(2,3)B(1)} = 37$	this work
	−22.5 (d, 2 B, B(2,3))	$J_{B(2,3)H} = 110$	$J_{PB(2,3)} = 113$	
	−0.8 (s, 2 B, B(4,5))	$J_{B(4,5)H} = 164$	$J_{PB(2,3)B(4,5)} = 18$	
$[(\mu\text{-}P(H)(CH(OSiMe_3)(^t\mathrm{Bu})))B_5H_8]$ (**2**)[g]	−47.5 (s, 1 B, B(1))	$J_{B(1)H} = 152$	$J_{PB(2,3)B(1)} = 36$	this work
	−22.3 (d, 2 B, B(2/3))	$J_{B(2/3)H} = 80$	$J_{PB(2,3)} = 108$	
	−1.7 (s, 2 B, B(4/5))	$J_{B(4/5)H} = 156$	$J_{PB(2,3)B(4,5)} = 36$	
$[(\mu\text{-}P(SiMe_3)(CH(OSiMe_3)(^t\mathrm{Bu})))B_5H_8]$ (**3**)[g]	−48.8 (s, 1 B, B(1))	$J_{B(1)H} = 152$	$J_{PBB} = 18$	this work
	−20.4 (d, 1 B, B(2/3))	$J_{B(2/3)H}$ = unres	$J_{PB} = 125$	
	−19.4 (d, 1 B, B(2/3))	$J_{B(2/3)H}$ = unres	$J_{PB} = 115$	
	−3.6 (s, 1 B, B(4/5))	$J_{B(4/5)H}$ = unres	$J_{PBB} = 18$	
	−2.2 (s, 1 B, B(4/5))	$J_{B(4/5)H}$ = unres	$J_{PBB} = 19$	
$Na[(\mu\text{-}P(C_6H_5)_2)B_5H_7]$ (Na(**4**))[h]	−48.0 (s, 1 B, B(1))	$J_{B(1)H} = 172$	$J_{PB(2,3)B(1)} = 26$	this work
	−23.5 (d, 2 B, B(2,3))	$J_{B(2,3)} = 134$	$J_{PB(2,3)} = 90$	
	−3.1 (s, 2 B, B(4,5))	$J_{B(4,5)H} = 185$		
$[2\text{-}(Si(CH_3)_3)B_5H_8]$ (**5**)[g]	−50.4 (s, 1 B, B(1))	$J_{B(1)H} = 174$		this work[i]
	−7.2 (s, 1 B, B(2))			
	−11.1 (s, 2 B, B(3,5))	$J_{B(3,5)H} = 150$		
	−9.7 (s, 1 B, B(4))	$J_{B(4)H} = 162$		
$[(\mu\text{-}Si(CH_3)_3)B_5H_8]$ (**6**)[g]	−46.6 (s, 1 B, B(1))	$J_{B(1)H} = 171$		this work[i]
	−7.0 (s, 2 B, B(2,3))	$J_{B(2,3)H} = 149$		
	−11.7 (s, 2 B, B(4,5))	$J_{B(4,5)H} = 159$		
$[2\text{-}(Fe(\eta^5\text{-}C_5H_5)(CO)_2)B_5H_8]$ (**7**)[g,i,j]	−47.9 (s, 1 B, B(1))	$J_{B(1)H} = 170$		this work[k]
	−8.7 (s, 1 B, B(2))			
	−9.9 (s, 2 B, B(3,4))	$J_{B(3,4)H} = 150$		
	−13.6 (s, 1 B, B(5))	$J_{B(5)H} = 160$		
$[2,4\text{-}(Fe(\eta^5\text{-}C_5H_5)(CO)_2)_2B_5H_7]$ (**8**)[g]	−44.0 (s, 1 B, B(1))	$J_{B(1)H} = 168$		this work[k]
	−8.2 (s, 2 B, B(2,4))			
	2.0 (s, 2 B, B(3,5))	$J_{B(3,5)H} = 127$		
$[4\text{-}(Fe(\eta^5\text{-}C_5H_5)(CO)_2)B_5H_7(\mu\text{-}2,3\text{-}P(C_6H_5)_2)]$ (**9**)[g]	−37.6 (s, 1 B, B(1))	$J_{B(1)H} = 155$		this work
	−24.9 (d, 1 B, B(2))	$J_{B(2)H}$ = unres	$J_{PB(2)} = 106$	
	−23.6 (d, 1 B, B(3))	$J_{B(3)H}$ = unres	$J_{PB(3)} = 126$	
	23.1 (s, 1 B, B(4))			
	1.5 (s, 1 B, B(5))	$J_{B(5)H} = 166$		
$[((C_6H_5)_3PAu)B_5H_8]$ (**10**)[g]	−45.5 (s, 1 B, B(1))	$J_{B(1)H} = 169$		this work
	−10.5 (s, 2 B, B(2,3))	$J_{B(2,3)H} = 145$	$J_{PAuB} = 31$	
	−11.9 (s, 2 B, B(4,5))	$J_{B(4,5)H} = 143$		

[a] Relative to BBr_3 (40.0 ppm). Abbreviations for the ^{11}B spectra: s = singlet, d = doublet, unres = unresolved coupling. Sine multiplication resolution enhancement applied to the FID in the ^{11}B NMR analysis. [b] References listed are for the 2D ^{11}B–^{11}B COSY spectra and the J_{PB} data. [c] Reference indicates the reported ^{11}B NMR data. [d] Reference 26. [e] Reference 27. [f] Reference 28. [g] In $CDCl_3$. [h] In d_8-THF. [i] The NMR data for this compound were originally reported in ref 11. The data shown here, however, are from our measurements. [j] The numbering scheme used has the $[Fe(\eta^5\text{-}C_5H_5)(CO)_2]$ unit attached to the B_5 cage at B(2). [k] The NMR data for this compound were originally reported in ref 13. The data shown here, however, are from our measurements.

atoms, considering the level of the calculations and the accuracy of the peak volume measurements. As the bond order is extrapolated to zero, the anticipated cross peak intensity also approaches zero, as expected. The relationship between the calculated bond order and cross peak integral displayed in the plot was only expected to provide a general correlation, since cross peak intensity is not solely affected by J values but is also related to the efficiency of magnetization transfer between coupled spins and relaxation effects.[5] Compound **1** has the lowest bond order for which a 2D cross peak is observed for any of the compounds where calculations are available to us (bond order = 0.27 for the B(2,3)–B(4,5) interaction). Cross peaks should be detectable at even lower bond orders, but their intensities will approach the noise level of the spectrum and will, therefore, be difficult to observe either without significant reductions in the spectral noise. The T_1 relaxation times for the phosphinopentaborane compounds decrease in the order B(1) > B(2,3) > B(4,5). These general trends allow for the prediction of the relative order of intensities expected for the 2D cross peaks for a unknown compound.

Additional correlation and J-coupling information for cluster systems may be gained through the application of the double-quantum correlation experiment to borane cluster systems, similar to the INADEQUATE experiment for ^{13}C–^{13}C systems.[6] In the typical double-quantum experiment, frequency responses are obtained only from homonuclear coupled spins through the use of multiple-quantum coherences (MQC). The resulting double-quantum experiment displays the normal chemical shifts along the f_2 axis and displays the double-quantum frequencies along the f_1 axis. Therefore, a double-quantum peak will develop in f_1 from two coupled signals at a frequency of $\nu_1 + \nu_2$. In a typical double-quantum correlation spectrum, the diagonal peaks of the COSY spectrum are absent due to phase cycling. Pairs of peaks in the f_1 domain appear which correspond to nuclei that are spin coupled. From a known starting point in the spectrum, it is therefore usually possible to quickly determine unambiguously the framework of the molecule. The double-quantum correlation spectrum for compound **1** showed all of the expected correlations for the known cage framework as paired signals in the double-quantum spec-

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(27) (a) Kameda, M.; Kodama, G. *Inorg. Chem.* **1982**, *21*, 1267. (b) Savory, C. G.; Wallbridge, M. G. H. *J. Chem. Soc., Dalton Trans.* **1973**, 179. (c) Fratini, A. V.; Sullivan, G. W.; Denniston, M. L.; Hertz, R. K.; Shore, S. G. *J. Am. Chem. Soc.* **1974**, *96*, 3013.

(28) Williams, R. E.; Gerhart, F. J.; Pier, E. *Inorg. Chem.* **1965**, *4*, 1239.

Table II. 2D ^{11}B–^{11}B COSY Data and MNDO-Calculated Parameters for Substituted Pentaborane Systems

compound	cross peak correlation[a]	cross peak obsd[b]	MNDO-calcd bond order[c]	MNDO-calcd bond length[d]
B_5H_9	B(1)–B(2–5)	Y	0.65	1.72
$[(\mu\text{-}P(C_6H_5)_2)B_5H_8]$ (**1**)	B(1)–B(2,3)	Y	0.83	1.63
	B(1)–B(4,5)	Y	0.48	1.81
	B(2,3)–B(4,5)	Y	0.27	1.98
$[(\mu\text{-}P(H)(CH(OSiMe_3)(^tBu)))B_5H_8]$ (**2**)	B(1)–B(2,3)	Y	0.83	1.64
	B(1)–B(4,5)	Y	0.48	1.80
	B(2,3)–B(4,5)	Y	0.28	1.97
$[(\mu\text{-}P(SiMe_3)(CH(OSiMe_3)(^tBu)))B_5H_8]$ (**3**)	B(1)–B(2,3)	Y	0.82	1.63
	B(1)–B(4,5)	Y	0.49	1.80
	B(2,3)–B(4,5)	Y	0.28	2.03
$Na[(\mu\text{-}P(C_6H_5)_2)B_5H_7]$ (Na(**4**))	B(1)–B(2,3)	Y	0.92	1.60
	B(1)–B(4,5)	Y	0.41	1.80
	B(2,3)–B(4,5)	N	0.30	1.96
$[2\text{-}(Si(CH_3)_3)B_5H_8]$ (**5**)	B(1)–B(2)	Y	0.61	1.72
	B(1)–B(3,5)	Y	0.58	1.77
	B(1)–B(4)	Y	0.87	1.58
	B(2)–B(3,5)	Y	0.39	1.90
	B(4)–B(3,5)	Y	0.35	1.92
$[(\mu\text{-}Si(CH_3)_3)B_5H_8]$ (**6**)	B(1)–B(2,3)	Y	0.45	1.82
	B(1)–B(4,5)	Y	0.80	1.63
	B(2,3)–B(4,5)	Y	0.34	1.95
$[2\text{-}(Fe(\eta^5\text{-}C_5H_5)(CO)_2)B_5H_8]$ (**7**)	B(1)–B(2–5)	Y		
$[2,4\text{-}(Fe(\eta^5\text{-}C_5H_5)(CO)_2)_2B_5H_7]$ (**8**)	B(1)–B(2–5)	Y		
$[4\text{-}(Fe(\eta_5\text{-}C_5H_5)(CO)_2)B_5H_7(\mu\text{-}2,3\text{-}P(C_6H_5)_2)]$ (**9**)	B(1)–B(2–5)	Y		
$[((C_6H_5)_3PAu)B_5H_8]$ (**10**)	B(1)–B(2–5)	Y		

[a] Assignments made onthe basis of the data presented in Table I. [b] Y = cross peak observed; N = cross peak absent. [c] The standard procedures for the determination of the MNDO-optimized structures for phosphapentaboranes have been reported previously and were followed in the work reported here.[21] [d] Average values in angstroms.

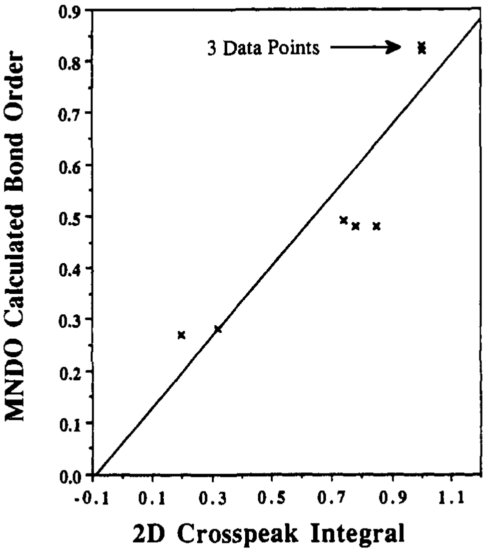

Figure 9. Plot of the calculated MNDO bond order versus the observed 2D ^{11}B–^{11}B COSY NMR cross peak integrals for (μ-2,3-phosphino)pentaborane cluster compounds, **1**–**3**.[25]

trum.[6,29] While not necessary for the complete spectral interpretation for compound **1**, the double-quantum experiment allows for the direct matching of coupled signals since the midpoints of lines connecting coupled pairs lie on the spectral diagonal with a slope of 2. This feature, along with the removal of interferences from the diagonal peaks and a twice as large separation of the peaks in the COSY spectrum, allows for the straightforward interpretation of complex and poorly resolved spectra. This latter feature, larger peak separation in the multiple-quantum experiment, should be very useful in interpreting the spectra of the larger, more complex cage systems by greatly eliminating much of the spectral congestion frequently encountered in the normal 2D spectrum. Further studies involving this technique are currently in progress in our laboratory. The accumulation of the double-quantum spectrum, however, took approximately 8 times longer than that for a typical 2D ^{11}B–^{11}B COSY NMR experiment for compound **1**.

The structures of the (trimethylsilyl)pentaborane compounds, both terminal (**5**) and bridged (**6**), are based on a substituted *nido*-pentaborane(9) parent structure.[11] In these compounds, a cage hydrogen atom, either terminal or bridged, has been replaced by an $SiMe_3$ group. Since the $SiMe_3$ unit is isoelectronic and isolobal with the hydrogen atom with respect to cage bonding,[7e] the cage structure of the *nido*-B_5H_9 framework remains intact, with no further opening of the cluster as was observed for the (μ-phosphino)pentaboranes. Terminal and bridged silylpentaboranes are related chemically by a Lewis base induced shift of the $SiMe_3$ group from a bridged to a terminal position on the cage.[11] The ^{11}B–^{11}B NMR 2D correlation spectra and calculated structures for these compounds are shown in Figures 4 and 5. Of interest was the potential cross peak for the B(2)–B(3,5) interaction in compound **5**, $[2\text{-}(Si(CH_3)_3)B_5H_8]$ (Figure 4), since these resonances are poorly resolved in the 1D spectrum. In order to determine if the cross peak observed for this interaction was from correlated nuclei or from the overlap of tailing diagonal peaks, an appropriate apodization function which emphasized this coupling was applied to the FID prior to Fourier transformation. Analysis of the spectrum showed that the observed cross peak was indeed real. The B(4)–B(3,5) basal boron interactions showed the expected cross peak, while none was observed between the B(2) and B(4) nuclei, as expected. Coupling through all B–B and B–H–B bonds was indicated by the appearance of cross peaks in the 2D spectrum. The expected cross peaks were also observed for the silyl-bridged compound **6**, in which the $SiMe_3$ group is bound to the two adjacent basal boron atoms through a 3c–2e bond. Both compounds thus exhibit B–B coupling between nearest neighbor boron atoms through both 2c–2e and 3c–2e bonds.

The apparent difference in the bonding between the bridged silyl compound as compared with the bridged phosphino compounds was reflected in their measured T_1 values (Table III). A comparison of the T_1 values for compounds **1**, $[(\mu\text{-}P(C_6H_5)_2)B_5H_8]$, and **6**, $[(\mu\text{-}Si(CH_3)_3)B_5H_8]$, shows that, while the T_1 values for compound **6** are approximately half the T_1 values observed for pentaborane(9), they are also an order of magnitude greater than those found for compound **1**. This is consistent with the 3c–2e bonding of the silyl group in **6** compared with the electron-precise two 2c–2e bonding scheme of the (μ-phosphi-

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Table III. T_1 and Spectral Half-Width ^{11}B NMR Data for Substituted Pentaborane Systems

compound	assignt[a]	T_1,[b] ms	$\nu_{1/2}$, Hz	natural line width,[c] Hz
B_5H_9[d]	B(1)	484 (6)	133	0.6
	B(2–5)	56.6 (6)	67	5.6
B_5H_{11}[e]	B(1)	54.9	65.0	5.7
	B(2,5)	7.5	47.0	42.0
	B(3,4)	20.7	61.0	15.2
$[(\mu\text{-P}(C_6H_5)_2)B_5H_8]$ (**1**)[d]	B(1)	14.4 (2)	97	22.1
	B(2,3)	5.46 (7)	74[f]	58.3
	B(4,5)	3.10 (4)	105	103.7
$[(\mu\text{-P(H)(CH(OSiMe}_3)(^t\text{Bu})))B_5H_8]$ (**2**)[d]	B(1)	33.4 (9)	117.6	9.5
	B(2,3)	13.4 (5)	60[f]	23.7
	B(4,5)	6.96 (5)	121	45.7
$[(\mu\text{-P(SiMe}_3)(\text{CH(OSiMe}_3)(^t\text{Bu})))B_5H_8]$ (**3**)[d]	B(1)	19 (1)	110	16.7
	B(2,3)	4.09 (7)	unres	77.8
	B(4,5)	3.26 (5)	unres	97.6
$\text{Na}[(\mu\text{-P}(C_6H_5)_2)B_5H_7]$ (Na(**4**))[g]	B(1)	23.6 (3)	147	13.5
	B(2,3)	3.83 (1)	243	83.1
	B(4,5)	1.64 (4)	273	194.1
$[2\text{-(Si(CH}_3)_3)B_5H_8]$ (**5**)[d]	B(1)	223 (2)	101	1.4
	B(2)	12.6 (3)	unres	25.3
	B(3,5)	20.00 (5)	unres	15.9
	B(4)	12.6 (2)	84	25.3
$[(\mu\text{-Si(CH}_3)_3)B_5H_8]$ (**6**)[d]	B(1)	143 (4)	112	2.2
	B(2,3)	15.9 (2)	80	20.0
	B(4,5)	20.1 (2)	92	15.6
$[2\text{-(Fe(}\eta^5\text{-}C_5H_5)(CO)_2)B_5H_8]$ (**7**)[d,h]	B(1)	149 (6)	118	2.1
	B(2)	7.2 (5)	88	44.2
	B(3,5)	9.0 (2)	92	35.4
	B(4)	7.3 (2)	84	43.6
$[2,4\text{-(Fe(}\eta^5\text{-}C_5H_5)(CO)_2)_2B_5H_7]$ (**8**)[d]	B(1)	117 (5)	97	2.7
	B(2,4)	2.7 (5)	161	117.9
	B(3,5)	3.2 (4)	146	99.5
$[4\text{-(Fe(}\eta^5\text{-}C_5H_5)(CO)_2)B_5H_7(\mu_3\text{-2,3-P}(C_6H_5)_2)]$ (**9**)[d]	B(1)	14.4 (7)	201	22.1
	B(2)	6 (1)	unres	22.1
	B(3)	6 (1)	unres	53.0
	B(4)	1.8 (5)	210	176.8
	B(5)	9 (2)	252	28.3
$[((C_6H_5)_3\text{PAu})B_5H_8]$ (**10**)[d]	B(1)	106 (5)	105	3.0
	B(2,3)	7.0 (2)	105	45.5
	B(4,5)	15.6 (8)	84	20.4

[a] Spectral assignments were based on the data presented in Table I. [b] T_1 values were measured by the inversion-recovery method using composite pulses. Estimated standard deviations in the least significant figure are given in parentheses. [c] $(\pi T_1)^{-1}$. [d] In $CDCl_3$. [e] Values shown are those reported in ref 8a. [f] The reported value ($\nu_{1/2(\text{corr})}$,[d] corrected for J_{PB}) is $\nu_{1/2(\text{corr})} = \nu_{1/2} - J_{PB}$. [g] In d_8-THF. [h] The numbering scheme used has the $[\text{Fe}(\eta^5\text{-}C_5H_5)(CO)_2]$ unit attached to the B_5 cage at B(2).

Table IV. Calculated Boron–Boron Coupling Constant (J_{BB}) Required for Cross Peak Disappearance in 2D ^{11}B–^{11}B COSY NMR Spectra

compound	calcd J_{BB} for cross peak collapse,[a] Hz
$\text{Na}[(\mu\text{-P}(C_6H_5)_2)B_5H_7]$ (Na(**4**))	97
$[2,4\text{-(Fe(}\eta^5\text{-}C_5H_5)(CO)_2)_2B_5H_7]$ (**8**)	59
$[4\text{-(Fe(}\eta^5\text{-}C_5H_5)(CO)_2)B_5H_7(\mu\text{-2,3-P}(C_6H_5)_2)]$ (**9**)	88
$[((C_6H_5)_3\text{PAu})B_5H_8]$ (**10**)	23

[a] $1/2\pi T_1 = J_{BB}$.

no)pentaborane clusters. Thus the spin–lattice relaxation is most pronounced for the phosphorus systems in which greater electron density is located between the cage and the bridged heteroatom.

In the spectra of the substituted pentaborane clusters presented above, only **4** failed to show an expected cross peak in the 2D spectrum. This feature was ascribed principally to the very short T_1 spin–lattice relaxation times for the coupled nuclei. In order to explore this relationship further for cluster compounds, the T_1 values and 2D ^{11}B–^{11}B COSY spectra of several σ-terminally and μ-bridged bound metal pentaborane and metal phosphinopentaborane complexes were studied to explore the effect of metal substitution on these NMR parameters. The 2D ^{11}B–^{11}B COSY spectra for $[2,4\text{-(Fe(}\eta^5\text{-}C_5H_5)(CO)_2)_2B_5H_7]$ (**8**), $[4\text{-(Fe(}\eta^5\text{-}C_5H_5)(CO)_2)B_5H_7(\mu\text{-2,3-P}(C_6H_5)_2)]$ (**9**), and $[(\mu\text{-2,3-}(C_6H_5)_3\text{PAu})B_5H_8]$ (**10**) are shown in Figures 6–8, respectively.

In the 2D spectrum for compound **8** (Figure 6), cross peaks between the apical and basal boron atoms were observed, while no cross peaks were found between B(2,3) and B(4,5) atoms. Compound **9** (Figure 7) also exhibits correlations between the apical boron and all basal borons, however, with an unusually low intensity correlation for B(1)–B(4) couple arising from the effect of the σ-bound organoiron fragment substituted on B(4). No correlations were observed between the basal boron atom couples. The spectrum for compound **10** (Figure 8) displays similar cross peak patterns.

The missing cross peaks in each of these three spectra are between boron atoms which are bridged by a hydrogen atom. The cross peak intensities arising from B–H–B interactions are expected to be low due to the reduction of electron density localized between these basal boron atoms,[2] although these cross peaks were observable in the related silyl- and phosphinopentaborane compounds. MNDO calculations are not possible for iron and gold compounds, but the basal boron–basal boron bond orders are likely to be nearly the same as those observed for the parent structures, since the chemical shifts, BH coupling constants, and crystal structure data for compounds **9** and **10** show that the bonding environment of the cage boron atoms in these metal pentaborane complexes is similar to that observed for the parent structures.[8b,14,23] The absence of a basal–basal cross peak in the 2D spectra for these metal pentaborane complexes therefore presumably arises from very short spin–lattice relaxaton times and is not principally due to the lack of appreciable electron density localized between the boron atoms.

The upper limit of the boron–boron coupling necessary for decoupling of the boron nuclei by fast relaxation times and hence cross peak disappearance can be calculated using the measured T_1 values and the expression $(2\pi J_{BB})T_1 = 1$.[8a,24] These calculated J_{BB} values for selected compounds are given in Table IV. In all cases, the actual J_{BB} values for the metallaborane clusters are likely to be much less than the calculated $(2\pi T_1)^{-1} = J_{BB}$ values, since the B(apical)–B(basal) coupling constant is 17 Hz in *arachno*-B_5H_{11}[8b] and 19.4 Hz in *nido*-B_5H_9.[8a,b] In addition, the B(basal)–B(basal) coupling must be significantly lower than the B(apical)–B(basal) coupling, since less electron density resides on the vector between the boron atoms in a B–H–B bond of the B(basal)–B(basal) interaction as compared with a B–B bond in the B(apical)–B(basal) interaction.[8a,b] Thus, assuming that the B(basal)–B(basal) coupling constant is far less than those shown in Table IV and assuming that the calculated theoretical relationship between T_1 and J_{BB} is valid, it is clear that, for the compounds presented in Table IV, no B(basal)–B(basal) coupling would be observed in the 2D spectrum. The absence of cross peaks in the 2D spectrum may also be partly due to short transverse (T_2) relaxations which can also cause peak attenuation by signal decay. For boranes, T_2 is generally equal to or less than T_1 so that T_2 decoupling cannot be entirely eliminated. Our data, however, do provide strong support that decoupling by fast T_1 relaxation is at least a major factor in the observed decoupling.

A lower limit of T_1 for which a cross peak develops varies from compound to compound, depending on the J_{BB} values for the correlation in question. The shortest T_1 value, however, which gave rise to a cross peak in the 2D spectrum for the compounds reported here was 3.1 μs for compound **1**, while a T_1 of 1.64 μs for the closely related cluster **4** did not show a cross peak. It is therefore necessary to measure both the 2D COSY NMR spectrum and the T_1 values for the nuclei to determine whether a cross peak is missing due to a lack of electron density localized between the boron atoms under consideration (i.e., as for nonadjacent atoms) or due to short T_1 relaxation times. The line widths for each boron resonance of all the compounds studied in this work have been measured, and the natural line widths have been calculated on the basis of T_1 values, assuming $T_1 = T_2$. The data are given in Table III. In most cases, the observed line widths are significantly larger than those calculated, providing further support for the presence of unresolved coupling in the 1D spectrum.[2b]

As a final note on ^{11}B–^{11}B cross peak intensities, the detection of correlations for B–H–B 3c–2e bonds requires the collection of a large amount of spectral data, while correlations for 2c–2e bonds require significantly fewer data (typically, 8 scans versus 128 scans, respectively, for **1**). This is undoubtedly because small couplings require a long evolution time such that a higher signal to noise ratio is necessary for their detection.[5]

In summary, 2D ^{11}B–^{11}B COSY NMR correlations are typically observable for structures where the electron density between coupled boron atoms is relatively low (small J_{BB} values), at least down to an MNDO-calculated bond order of 0.27. No 2D correlations were observed in the spectra with calculated bond orders below this value in the closely related series of compounds studied here. There is, as qualitatively expected, a direct correlation between the localized electron density between coupled nuclei and the intensity of the corresponding cross peak in the 2D spectrum. Expected cross peaks may, however, be absent due to very short T_1 relaxation times, as described previously.[2] Thus, the structural elucidation of cluster frameworks, especially heteroatom or metal fragment substituted clusters, requires both 2D ^{11}B–^{11}B COSY spectra and T_1 measurements to assign the connectivities accurately. Assistance in these assignments for boron clusters may be readily gained, however, through the use of multiple-quantum correlation experiments. These measurements provide a clearer picture of the framework bonding and electron distribution within a cluster molecule through the application of readily available and convenient experimental and theoretical techniques.

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Supplementary Material Available: Archive files for the MNDO calculations for **1**–**6** (14 pages). Ordering information is given on any current masthead page.