^{11}B NMR SOLUTION STUDIES OF THE INTERACTIONS BETWEEN SmI_2(TETRAHYDROFURAN)$_x$ AND NIDO-PENTABORANE(9) COMPOUNDS

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Abstract

The nature of the interactions between samarium(II) and the *nido*-octahydropentaborate anion, NaB_5H_8, and neutral *nido*-pentaborane(9), B_5H_9, in THF solutions were investigated by ^{11}B NMR spectroscopy. In these studies, chemical shifts, ^{11}B-^{1}H$_t$ coupling constants, spectral line widths and variable temperature data for the apical and basal $[B_5H_8]^{-1}$ resonances indicate that significant interactions occur between the paramagnetic samarium center and the $[B_5H_8]^{-1}$ cluster with significantly weaker interactions observed between the samarium(II) and the neutral *nido*-pentaborane(9) cage. The ^{11}B NMR spectral data for both pentaborane clusters were observed to depend linearly and solely on the Sm(II) concentration in solution. A mechanism is proposed to account for these observations.

Introduction

The reactive square pyramidal *nido*-octahydropentaborate anion, $[B_5H_8]^{-1}$, has been successfully employed as an organometallic ligand in forming a variety of metallaborane cluster compounds.[1] The discovery that the *nido*-$[B_5H_8]^{-1}$ anion is readily obtained by the removal of a bridging proton from the parent *nido*-pentaborane(9) cluster,[2] which itself is easily handled in solution in relatively large quantities,[3] has contributed to the widespread use of this versatile ligand. The organometallic chemistry of this cluster has not, however, been extended to the 4f-block lanthanide metals. In the past few years, the isolation of a number of lanthanide metal complexes of larger carborane and borane clusters has been reported.[4-7] In several of these instances, the lanthanide metallaborane complexes formed were stable enough to allow spectral and structural characterization. In other cases, however, removal of the solvent from the complex resulted in its rapid and complete degradation. In this paper, we describe both synthetic attempts and ^{11}B NMR spectroscopic details on the solution interactions between the paramagnetic divalent samarium ion and *nido*-pentaborane clusters.

The relationship between the bonding properties of the *nido*-octahydropentaborate ligand and other organometallic ligands, such as the ubiquitous η^5-C_5H_5 ligand which is well known to stabilize organolanthanide complexes, suggested that the pentaborate ligand might be able to stabilize organolanthanaborane species. The recognition of the isolobal relationship between the bonding properties of the large dicarbollide ligand, [*nido*-7,8-$C_2B_9H_{11}]^{2-}$, and the $[\eta^5$-$C_5H_5]^{1-}$ ligand has led to the isolation of several new lanthanide complexes of the dicarbollide ligand, such as $Ln(C_2B_9H_9D_2)(THF)_4$ (where Ln(II) = Sm, Yb).[5] Thus, it was expected that similar complexes might be formed between the smaller pentaborane cage and the samarium(II) ion.

The chemistry of the trivalent lanthanide ions has been the focus of considerable research energy for many years. In contrast, while the chemistry of the divalent lanthanides was suggested to be significantly different from the trivalent species, only recently have investigations into the chemistry of these divalent lanthanides, most notably samarium, been initiated.[8] Exploration into the chemistry of the divalent ions has gained impetus by their increased use in promoting unique organic reactions, principally acting as one-electron reducing agents, and as precursors for the formation of technologically important solid state metal boride materials.[9]

Paramagnetic transition metal ions in polyhedral borane frameworks are known to have profound effects on the ^{11}B NMR chemical shifts and line widths of the metal-bonded boron atoms.[10] While the lanthanides have $4f^n$ configurations, ^{11}B NMR measurements on the reported paramagnetic lanthanide borane and carborane complexes have been found to be readily accessible.[4-7,8a] The ^{11}B NMR spectroscopic data for these lanthanaborane and lanthanacarborane complexes, in contrast to the paramagnetic transition metal complexes reported earlier, showed only rather small changes in the both the isotropic shifts and spectral line widths of the cage resonances upon formation of a coordination compound.[4-6] The data suggest that the bonding in these paramagnetic species is predominantly ionic with charge balance and steric considerations largely determining the stability and composition of the observed complexes.[8] In this paper, in addition to our synthetic attempts, we report on the lanthanide shift reagent (LSR) features of Sm(II) on the ^{11}B NMR data observed from the solution interactions between samarium(II) and the anionic $[B_5H_8]^{-1}$ and neutral B_5H_9 clusters.

Materials and Methods

Materials. Reagent grade tetrahydrofuran (Fisher) was distilled from sodium metal/benzophenone onto sodium hydride under a dry nitrogen atmosphere, degassed by repeated freeze-thaw cycles, and finally stored *in vacuo* prior to use. Sodium hydride (80% dispersion in mineral oil, Aldrich) was washed several times with dry pentane (Fisher) and the washes decanted off to remove the mineral oil. Pentaborane(9) (B_5H_9) was taken directly from our laboratory stock.[11] Standard pentaborane(9)-THF solutions were prepared using previously reported methods.[3] The samarium(II) iodide was obtained as a 0.1 M solution in THF (Aldrich) and was freshly degassed prior to each use. The $SmI_2(THF)_x$ solutions are extremely air and moisture sensitive. All experiments and manipulations were, therefore, conducted under a dry argon atmosphere with the rigorous exclusion of both air and water.[11]

Physical Measurements. Boron (^{11}B) NMR spectra were recorded on a Cryomagnetics CM-250 spectrometer operating at 80.26 MHz. All spectra were recorded in 5 mm (o.d.) tubes in both the ^1H coupled and decoupled modes. The ^{11}B NMR chemical shifts were referenced to an external standard of boron tribromide in hexane (1.0 M) at +40.0 ppm which was sealed in a glass capillary and held coaxially with the NMR sample tube (positive chemical shifts indicate downfield resonances). Observed ^{11}B NMR isotropic shifts for the cage resonances in samarium(II) containing solutions were compared to the analogous resonances in samarium(II)-free solutions.[12,13] For each sample, an initial spectrum was acquired using a very large sweep width to check for widely shifted peaks. The sweep width was then reduced to encompass all the peaks observed in the initial spectrum (typically from +15 to -65 ppm) in order to optimize the signal to noise ratio. FT-IR spectra in the range 400 to 4000 cm^{-1} were recorded on a Mattson Galaxy 2020 spectrometer with a 4 cm^{-1} resolution and were referenced to the 1601.8 cm^{-1} band of polystyrene. Spectra were obtained in solution using anaerobic Perkin-Elmer cells with 0.1 mm Teflon spacers between either NaCl or KBr plates. The sample cells were first dried and well flushed with dry argon gas prior to charging the cell with the sample.

$SmI_2(THF)_x$-NaB_5H_8 interactions. A 100 mL THF solution of NaB_5H_8 was prepared from the reaction of 1.26 g (20.0 mmol) of B_5H_9 with 1.06 g (44.0 mmol) of hexane-washed NaH at -50° C.[2,11] The ^{11}B NMR characterization of the clear solution showed the presence of only NaB_5H_8.[13a] To this stirred solution was slowly added 100 mL (10.0 mmol) of $SmI_2(THF)_x$ while maintaining the temperature below -50° C. A ^{11}B NMR analysis of the resulting dark blue-green solution showed that the resonances of the $[B_5H_8]^{-1}$ anion had been shifted to higher field [(δ) -31.0 ppm (B(2-5)) -55.8 ppm (B(1))].[13a] The ^1H NMR spectrum in THF-d_8 showed, besides residual THF solvent signals, two broad humps for the bridging protons at δ (ppm): -1.4 and -2.2. The infrared spectrum of the cold samarium(II)/$[B_5H_8]^{-1}$ THF reaction solution displayed two quite sharp and strong B-H stretches at 2533 and 2482 cm^{-1} which were identical to those of the initial NaB_5H_8/THF solutions (2535 and 2479 cm^{-1}).[2c] Warming the reaction solution to ambient temperature resulted, however, in the rapid and complete degradation of the $[B_5H_8]^{-1}$ into $[B_3H_8]^{-1}$, $[B_9H_{14}]^{-1}$ and $[B_6H_{11}]^{-1}$.[12] Slow removal of the solvent at low temperature (<-30° C) *in vacuo* yielded a dark purple crystalline solid. This solid was again very air and moisture sensitive and quickly and completely decomposed into $[B_3H_8]^{-1}$, $[B_9H_{14}]^{-1}$ and $[B_6H_{11}]^{-1}$. No stable species were isolated under any experimental conditions employed.

<u>^{11}B NMR studies at constant temperature</u>. In a typical experiment, a THF solution of NaB_5H_8 was prepared in 26 mL of THF from the reaction of 0.32 g (5.0 mmol) of B_5H_9 with 0.29 g (12.0 mmol) of pentane-washed sodium hydride at -50° C.[2,11] The ^{11}B NMR spectral characterization of the resulting clear solution showed only the presence of NaB_5H_8.[13a] To this solution was then added slowly using a pressure equalizing addition funnel, 2 mL aliquots of a 0.1 M $SmI_2(THF)_x$ stock solution (total of 25 mL, 2.5 mmol). During these additions, the reaction temperature was maintained at -50° C. Upon the addition of each $SmI_2(THF)_x$ aliquot, the ^{11}B NMR spectra were rapidly measured at low temperature. No decomposition of the $[B_5H_8]^{-1}$ ion was observed in the ^{11}B NMR spectra throughout the various manipulations.[2] Similar experiments were performed in an analogous fashion by employing different initial NaB_5H_8 concentrations, different solvent volumes and variously sized aliquots of the standard $SmI_2(THF)_x$ solution. The NaB_5H_8 concentration was varied from 0.02 M to 0.2 M with the final concentration of the samarium(II) reagent in the solution maintained below 0.1 M.

<u>Variable temperature ^{11}B NMR study of $SmI_2(THF)_x$-NaB_5H_8 solutions</u>. A solution of NaB_5H_8 (2.9 mmol) in 20 mL of THF was prepared at -50° C from the reaction of 0.18 g of B_5H_9 (2.9 mmol) with 0.16 g of NaH (6.5 mmol).[2,11] The ^{11}B NMR characterization of the clear solution showed the presence of only NaB_5H_8.[13a] To this solution was slowly added using a pressure equalizing addition funnel, 14.3 mL (1.4 mmol) of a standardized $SmI_2(THF)_x$ solution while continuously stirring. During the addition, the temperature was maintained at -50° C. After stirring the reaction solution at -50° C for one day, the ^{11}B NMR data for the reaction solution were measured as a function of temperature from -60° C to +22° C. Only a negligible amount of the decomposition product, $[B_9H_{14}]^{-1}$, was observed at higher temperatures.[2,12] It was possible to accurately determine the ^{11}B chemical shifts and coupling constants for the $[B_5H_8]^{-1}$ species over the experimental temperature range employed. The progressive overlap of the downfield ^{11}B NMR resonance for the $[B_5H_8]^{-1}$ anion with the two upfield resonances of the minor $[B_9H_{14}]^{-1}$ decomposition impurity, however, precluded accurate spectral line width measurements for the $[B_5H_8]^{-1}$ anion at higher temperatures.

$SmI_2(THF)_x$-B_5H_9 interactions. A dry reaction flask was charged with 25 mL (2.5 mmol) of degassed $SmI_2(THF)_x$. Two equivalents of B_5H_9 (0.32 g, 5.0 mmol) were then condensed on top of the $SmI_2(THF)_x$ solution at -196° C.[11] The reaction flask was then placed in an ice bath and stirred while warming slowly to room temperature. A ^{11}B NMR analysis of the solution after ten days showed only very slight changes in the spectrum from the starting B_5H_9.[12] The reaction mixture was then refluxed for five hours. After cooling to room temperature, the ^{11}B NMR spectrum again showed only unreacted pentaborane(9). The color of the solution remained unchanged throughout the experiment.

<u>^{11}B NMR studies at constant temperature.</u> In a typical experiment, 0.32 g of B_5H_9 (5.0 mmol) were condensed onto frozen THF (15 mL) at -196°C.[2,11] After slowly warming the resulting solution to room temperature, 2 mL aliquots of a 0.1 M $SmI_2(THF)_x$ stock solution (total of 25 mL, 2.5 mmol) were added slowly with a pressure equalizing addition funnel. Upon each additional aliquot of $SmI_2(THF)_x$, the ^{11}B NMR spectrum was rapidly measured at low temperature.

Results and Discussion

The previous synthesis of reasonably stable lanthanacarborane complexes from the reactions of carborane anions with $LnI_2(THF)_2$ solutions led us to explore the synthesis of complexes using smaller borane clusters with $SmI_2(THF)_x$ solutions.[4-7] The reaction of $SmI_2(THF)_x$ with two equivalents of $[B_5H_8]^{-1}$ at low temperatures (< -50° C) was attempted and monitored by ^{11}B NMR spectroscopy. Upon addition of the two reagents, a green solution was formed from which, however, no stable lanthanaborane could be isolated. The ^{11}B resonances for the $[B_5H_8]^{-1}$ cage were significantly shifted upfield while no changes in the FTIR spectra were observed. Warming the reaction solution to room temperature resulted in the rapid and complete degradation of the $[B_5H_8]^{-1}$ cage into its known decomposition products $[B_3H_8]^{-1}$, $[B_9H_{14}]^{-1}$ and $[B_6H_{11}]^{-1}$.[2,12]

The neutral pentaborane(9) cluster, B_5H_9, was also reacted with a $SmI_2(THF)_x$ solution in an analogous fashion to that employed for the $[B_5H_8]^{-1}$ cluster. The ^{11}B NMR spectra of the reaction mixture showed only a very slight downfield shift of the pentaborane(9) cage resonances (δΔ < 2 ppm). Refluxing the reaction mixture under inert conditions did not cause a change in the observed spectrum. No changes in the FTIR spectra were again observed. One potential reaction between neutral pentaborane(9) and $SmI_2(THF)_x$ which might have been expected was the simple deprotonation of the cage to yield the corresponding $[B_5H_8]^{-1}$ anion. This expectation is based upon the precedent in which the reaction of NaI with pentaborane(9) resulted in the deprotonation of the cage by the iodide ion as shown in equation (1).[14]

$$B_5H_9 \;+\; I^- \;\underset{\text{7 days}}{\overset{\text{room temperature}}{\rightleftharpoons}}\; [B_5H_8]^- \;+\; HI \qquad (1)$$

Refluxing the pentaborane(9) and $SmI_2(THF)_x$ reaction mixture did not result in the formation of a detectable amount of the *nido*-octahydropentaborate anion. A second possible reaction, in which a metal halide is known to catalyze the cage coupling reaction of pentaborane(9) to yield the $[1,2'\text{-}(B_5H_8)_2]$ species (equation 2),[15] was similarly not observed.

$$B_5H_9 \xrightarrow{PtBr_2} [1,2'\text{-}(B_5H_8)_2] \qquad (2)$$

Since a stable samarium-pentaborate complex could not be isolated despite the large isotropic shifts which were observed in the cage's ^{11}B NMR resonances, the nature of the interactions between the paramagnetic samarium(II) ion and the pentaborane species in solution was investigated further by ^{11}B NMR spectroscopy. The most common changes in the NMR spectra of paramagnetic samples are the displacement of the signals to either higher or lower magnetic fields, depending upon the nature of the metal and the ligand.[10,16] Spectral line broadening, accompanied by the loss of nuclear coupling information, and the temperature dependence of the NMR isotropic shifts and line widths are also usually observed for paramagnetic solutions. In the $SmI_2(THF)_x$-$[B_5H_8]^{-1}$ solutions, the paramagnetically induced ^{11}B NMR chemical shifts (δB(1) and δB(2-5)), ^{11}B-^1H_t coupling constants (J_{BH}, where H_t refers to a terminal hydrogen atom), and spectral line broadening of the resonances ($\Delta\upsilon_{1/2}$) were monitored as a function of both the pentaborate(8) anion and the paramagnetic samarium(II) ion concentrations. The data clearly show the displacement of the $[B_5H_8]^{-1}$ ^{11}B NMR resonances to higher magnetic field upon increasing the $SmI_2(THF)_x$ concentration in solution. Plots of the relationships between the samarium(II) concentrations and the ^{11}B NMR chemical shifts for the cage boron atoms, the J_{BH} coupling constants and the experimental spectral line widths at half-height for the $[B_5H_8]^{-1}$ resonances are shown in Figures 1 - 3, respectively. All these plots show excellent linear correlations as a function of samarium(II) concentration.

Borane clusters typically display significant shifts in their ^{11}B NMR resonances upon formation of a metal complex.[1,10,12] From the ^{11}B NMR data for the samarium(II)-$[B_5H_8]^{-1}$ solution, it might be suggested that a discrete lanthanaborane complex was formed between the pentaborate cage and the samarium(II) center in solution since a >25 ppm upfield shift was observed for the basal boron resonances in the experiments. This complex formation in solution is not supported, however, by several observations. First, the ^{11}B NMR chemical shifts of known metallaboranes are typically not dependent upon metal cation concentration, as observed for the samarium(II)-$[B_5H_8]^{-1}$ solutions.[1,10,12] Secondly, while the ^{11}B NMR chemical shifts observed were much smaller than those reported for other paramagnetic borane complexes, they were much greater than those reported for other isolable lanthanide borane and carborane derivatives.[4-7,10] Thirdly, upon complex formation, significant changes in the frequencies of the infrared terminal B-H absorptions (usually strong and broad absorptions centered at approximately 2500 cm-1) are typically observed for metallaboranes.[1] The known lanthanaboranes also display clear changes in their infrared terminal B-H stretches, both in the frequency and the appearance of the absorptions.[4,5,17b-c] No differences in the B-H stretching absorptions were observed, however, between the metal free-$[B_5H_8]^{-1}$ cage solutions and samarium(II)- $[B_5H_8]^{-1}$ solutions. It thus appears that the Sm(II) ion is acting more like a lanthanide shift reagent (LSR) to the cage rather than in a directly bonded fashion.

Support for the existence of strong interactions between the samarium(II) metal and the $[B_5H_8]^{-1}$ ligand is gained, however, from the ^{11}B NMR behavior of the known lanthanide-boron containing complex, $[Eu(CH_3CN)_3(BF_4)_3]_2$.[18a] The ^{11}B NMR of this europium compound was reported to display a sharp resonance at 4.7 ppm and a much broader resonance at 12.0 ppm in the room temperature spectrum. Decreasing the concentration of the europium complex in solution resulted in a shift to lower applied field of the broad resonance at 12.0 ppm while the sharp signal was unaffected by metal ion concentration. These observations were shown to be due to the metal concentration dependence of the 12.0 ppm resonance assigned to the europium-complexed $[BF_4]^{-1}$ group (through Eu-F-BF_2-F-Eu interactions) while the concentration independent resonance at 4.7 ppm was due to the presence of uncomplexed $[BF_4]^{-1}$ free in solution. The concentration dependent ^{11}B and ^{19}F NMR shifts for only the europium-complexed $[BF_4]^{-1}$ group indicate that a significant interaction must exist between a boron atom and a paramagnetic metal center for such an effect to be observed. In the samarium(Il)-$[B_5H_8]^{-1}$ solutions, the concentration dependence of the ^{11}B NMR data supports the existence of at least a moderately strong interaction between the borane cage and the samarium(II) center.

A comparison of the influence of the samarium(II) ion on the ^{11}B NMR parameters for the $[B_5H_8]^{-1}$ cage, shown in Figures 1 through 3, shows that the paramagnetic influence of the metal is greatest at the basal site [basal boron atoms $\Delta\delta = -27.8$ ppm; apical boron $\Delta\delta = -6.2$ ppm] (Figure 1). Similarly, the effect of the samarium(II) concentration on the boron-hydrogen coupling constants (J_{BH}) and the spectral line widths ($\Delta\upsilon_{1/2}$) is much greater for the basal boron atoms than for the apical atom (Figures 2 and 3). Since the paramagnetic influence is stronger for the nuclei closer to the paramagnetic center, it is probable that the samarium(II) cation resides significantly closer to the basal boron atoms than to the apical boron. This would also be expected based both on steric and electrostatic considerations for the cage and the samarium(II) cation. Indeed, calculations have shown that the highest electron density is located at the base of the $[B_5H_8]^{-1}$ cluster.[19]

Paramagnetic LSR's are known to not only affect NMR chemical shifts, but also to diminish coupling constants and relaxation times. The strength of the interactions between the lanthanide center and the borane cluster determines, to a large extent, the magnitude of the changes measured in these parameters for a particular resonance. The $[B_5H_8]^{-1}$ J_{BH} coupling values[20] decrease upon increasing the samarium(II) concentration in solution (Figure 2), presumably because of a shift in electron density in the cage from the terminal B-H bonds to

Figure 1. Paramagnetically induced ^{11}B NMR chemical shift dependence for the basal [B(2-5)] and the apical [B(1)] boron atoms of the *nido*-pentaborate(8) anion, $[B_5H_8]^{-1}$, as a function of the samarium(II) concentration ([Sm(II)] < 0.1 M).

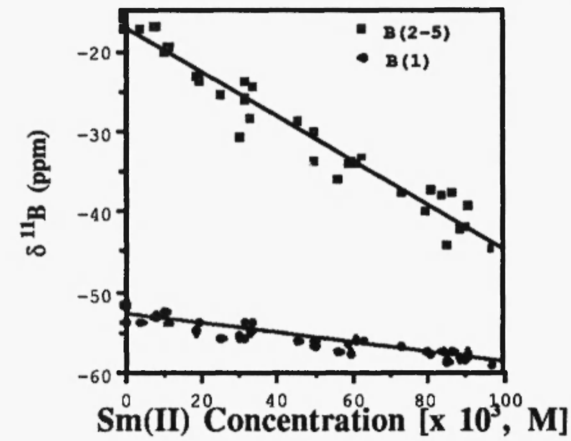


Figure 2. Variations of the ^{11}B NMR J_{BH} coupling constants for the basal (B(2-5)) and apical (B(1)) resonances of *nido*-octahydropentaborate(8) anion, $[B_5H_8]^{-1}$, as a function of the samarium(II) concentration ($[NaB_5H_8]_{initial}$ = 5.0 mmol).

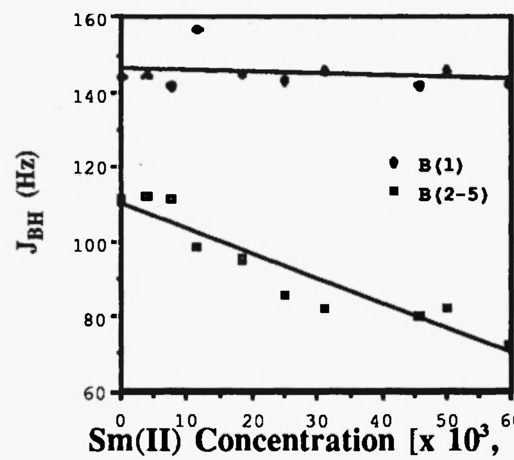
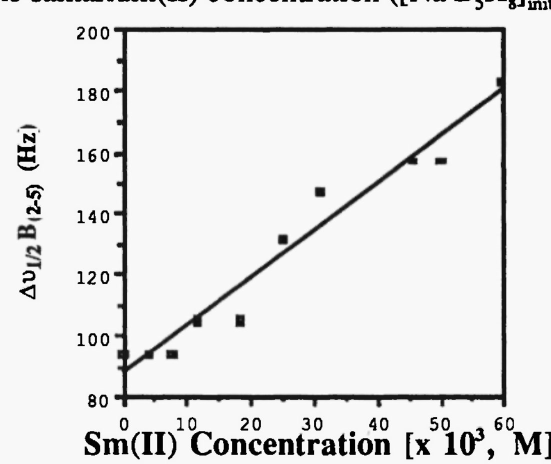


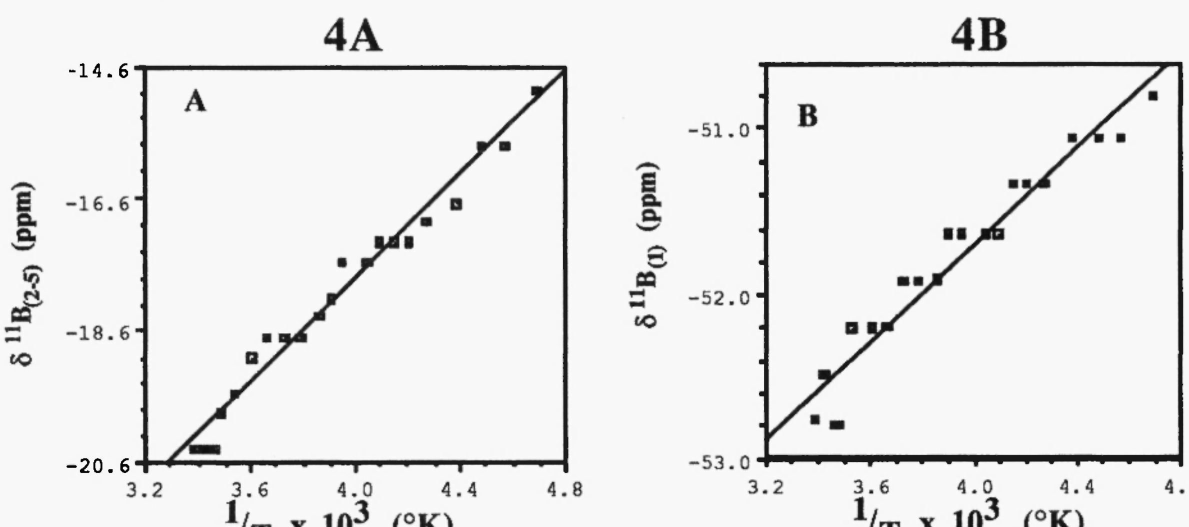
Figure 3. Variations of the ^{11}B NMR line widths at half height ($\Delta\upsilon_{1/2}$) for the basal boron atoms (B(2-5)) resonance of *nido*-octahydropentaborate(8) anion, $[B_5H_8]^{-1}$, as a function of the samarium(II) concentration ($[Na\ B_5H_8]_{initial}$ = 5.0 mmol).



the *nido*-B_4 open face, the site of the largest samarium(II)-cage electrostatic interaction. In addition, the spectral line widths at half height ($\Delta\upsilon_{1/2}$) for the basal boron atoms significantly broadens with increasing samarium(II) concentration (Figure 3). No change was observed, however, for the line width for the apical boron resonance, consistent with the primary interaction of the paramagnetic metal at the *nido*-B_4 basal face.

For LSR systems, a linear relationship should exist between the isotropic shift and the reciprocal of the absolute temperature.[16] The variable temperature ^{11}B NMR data for a samarium(II)-$[B_5H_8]^{-1}$ solution showed that both the basal and apical resonances of the $[B_5H_8]^{-1}$ moved progressively to higher field with increasing temperature (Figure 4). The magnitude of the temperature dependent shift was again much larger for the basal boron atoms ($\Delta\delta$(B(2-5)) = -5.4 ppm) than for the apical atom ($\Delta\delta$(B(1)) = -2.0 ppm), consistent with the primary metal interaction at the *nido*-B_4 open face. In the europium complex previously cited, $[Eu(CH_3CN)_3(BF_4)_3]_2$, a linear plot was also observed between the isotropic shift and $^1/_T$ in the ^{11}B NMR data for the europium-complexed $[BF_4]^{-1}$ while the uncomplexed $[BF_4]^{-1}$ resonance was unaffected by changes in temperature.[18] Again, the temperature dependent shift for only the complexed boron and fluorine resonances indicates that a significant interaction must exist between a boron atom and a paramagnetic metal center for such an effect to be observed. Therefore, in the samarium(II)-$[B_5H_8]^{-1}$ solutions, the temperature dependence of the ^{11}B NMR data again supports the existence of a moderately

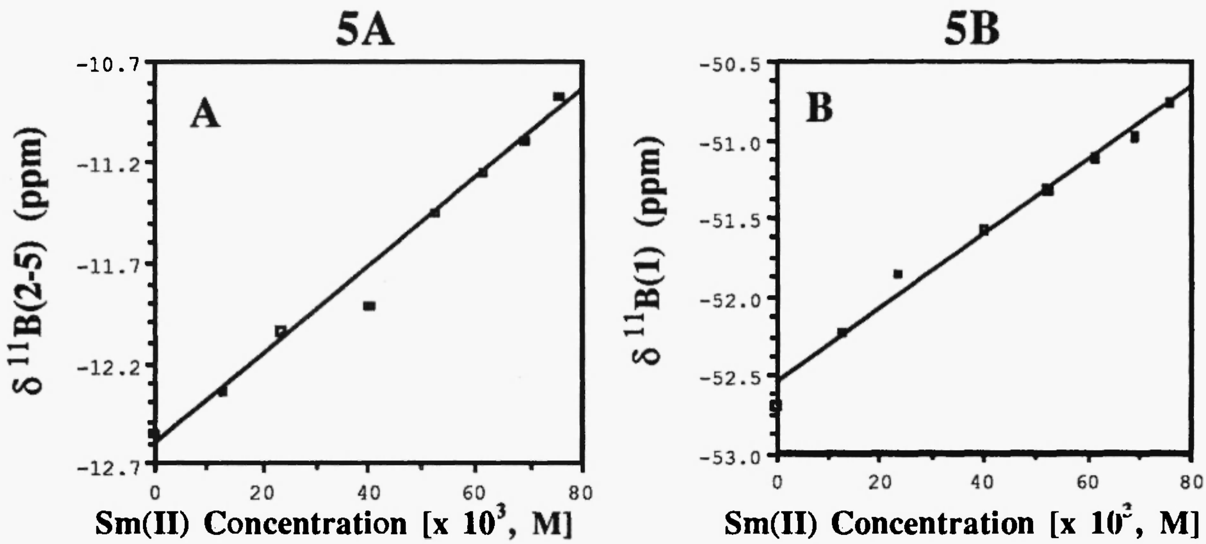
Figure 4. Variable temperature ^{11}B NMR chemical shift dependence for the (a) basal boron atoms (B(2-5)) and (b) the apical boron atom (B(1)) of *nido*-octahydropentaborate(8) anion, $[B_5H_8]^{-1}$, at constant samarium(II) concentration.



strong interaction between the base of the borane cage and the samarium(II) cation.

The effect of the paramagnetic samarium(II) cation on the neutral pentaborane(9) cluster was also investigated by ^{11}B NMR. In this system, a linear relationship was again observed between the samarium(II) solution concentration and the isotropic ^{11}B NMR chemical shifts (Figure 5). The similar magnitudes of the variations in both the basal and apical ^{11}B NMR isotropic shifts upon increasing the samarium(II) concentration (^{11}B NMR $\Delta\delta$ B(2-5) = +1.7 ppm; $\Delta\delta$ B(1) = +1.9) are, however, clearly distinct from those obtained for the samarium(II)-$[B_5H_8]^{-1}$ solutions. The magnitudes of these isotropic shifts were also more that an order of magnitude smaller and of opposite sign for the neutral pentaborane(9) solutions when compared with the corresponding $[B_5H_8]^{-1}$ solutions. Finally, the J_{BH} and J_{BB}

Figure 5. Paramagnetically induced ^{11}B NMR chemical shift dependence for the (a) basal (B(2-5)) and the (b) apical (B(1)) boron atoms of the *nido*-pentaborane(9) cluster, B_5H_9, as a function of the samarium(II) concentration ([Sm(II)] < 0.1 M) [least-squares equations for the lines: $y = -33.4 + 3.89x$, $R = 0.97$ for B(2-5) and $y = -57.6 + 1.48x$, $R = 0.94$ for B(1)].



coupling constants and the observed spectral line widths of the resonances in the neutral B_5H_9 cluster were insensitive to the samarium(II) concentration. These results indicate that the interactions of the lanthanide ion with the neutral pentaborane(9) cage were very weak and not directed toward a particular site on the borane cage.

Two types of samarium(II)-borane interactions may be proposed to account for the observed experimental data. The first type of interaction may be thought of as a weak, outer-sphere interaction. In this mechanism, the lanthanide ion and the borane cluster would not come into close contact but would rather interact through solvent and long range interactions. The magnitude of the paramagnetic effects would then be independent of the borane cluster concentration and depend only on the lanthanide ion concentration. In a second type of interaction, relatively close, although transient, coordination may occur between the paramagnetic center and the borane cluster. The transient lanthanaborane intermediate would then rapidly dissociate into free samarium(II) and the pentaborane cluster.

Several authors have noted a dependence of the magnitude of the isotropic shift on the substrate concentration in a number of lanthanide shift reagent-substrate systems.[21] For cases in which $[\text{Lanthanide}]_{\text{initial}} \leq [\text{Substrate}]_{\text{initial}}$, it has been shown that the relative induced chemical shifts for a series of protons in a given molecule vary with the substrate concentration.[21] Other authors have reported that the magnitude of the induced shifts for various nuclei is independent of the substrate concentration when $[\text{Substrate}]_{\text{initial}} >> [\text{Lanthanide}]_{\text{initial}}$.[21] Our studies, in which the $[B_5H_8]^{-1}$ cluster is always in excess relative to the lanthanide ion, fall in this latter class of experiments. The absence of a correlation between the chemical shifts of $[B_5H_8]^{-1}$ and the concentration product $([\text{Sm(II)}]_x[[B_5H_8]^{-1}]_y)$ indicates that the intermediate complex $[(L_\beta Sm^{+2})(B_5H_8)^{-1}{}_\alpha]$ does not have a sufficiently long lifetime to be observed in the NMR spectrum and thus the weighted average of the samarium(II)-complexed and free $[B_5H_8]^{-1}$ isotropic shifts is measured in the ^{11}B NMR spectra. Variable temperature NMR studies were also unsuccessful in showing the formation of the transient intermediate complex, as discussed previously. This observation is important in comparison with the reported variable temperature ^{11}B NMR study of the $[Sm(C_2B_9H_9D_2)(THF)_4]$ complex in which a discrete coordination complex was observed to exist in equilibrium with an ion paired tautomeric structure in solution.[5b] The overall NMR spectral data for the samarium(II) / $[B_5H_8]^{-1}$ system suggest that the mechanism of paramagnetic interaction with the pentaborate(8) cage is probably of the transient complex type but direct observation of the complex intermediate was not possible due to the presumed rate of the degenerate metathesis process shown in equation (5). The existence of such a

$$[Sm(B_5H_8)_x(THF)_y] + THF \rightleftharpoons [Sm(B_5H_8)_{x-1}(THF)_{y+1}][B_5H_8] \quad (5)$$

short-lived product is also strongly supported by the similar behavior reported for the $[Eu(CH_3CN)_3(BF_4)_3]_2$ complex shown in equation (6).[18a] When BF_3 was added to a

$$[Eu(CH_3CN)_n(BF_4)_2]_2^{2+} + {}^*BF_3 \rightleftharpoons [Eu(CH_3CN)_n({}^*BF_4)(BF_4)]_2^{2+} + BF_3 \quad (6)$$

solution of the $[Eu(CH_3CN)_3(BF_4)_3]_2$ complex, no new resonance for the free BF_3 was observed, while the resonance for the complexed $[BF_4]^{-1}$ was found to gain in intensity in the ^{19}F NMR spectrum.[18a] The ^{19}F atoms from the added BF_3 and the isotropically shifted complexed BF_4 atoms were, therefore, magnetically equivalent. This was shown to be due to the rapid degenerate metathesis reaction as shown in equation (6). Low temperature NMR experiments were, in this case, able to freeze out the exchange process while in our system, we were unable to sufficiently slow the exchange process for observation of the complex in the NMR spectra. In contrast to the $[B_5H_8]^{-1}$ system, it clearly appears that the weaker interactions between the neutral pentaborane(9) cluster and the samarium(II) cation can be best described as an outer-sphere interaction.

Conclusions

The solution interactions between a lanthanide ion and a small borane cluster have not been previously reported. While a stable and isolable samarium-B_5 complex was not observed, ^{11}B NMR solution data indicate that the interactions between the $[B_5H_8]^{-1}$ anion and Sm(II) ion are strong enough to induce significant ^{11}B NMR changes. The data suggest that the mechanism of interaction between the pentaborate(8) cage and the cationic samarium(II) center is of the transient complex type, but direct observation of the intermediate was not possible due to the rate of the degenerate metathesis process. In contrast, the interaction between the neutral pentaborane(9) cluster and the samarium(II) cation probably occurs through an outer sphere mechanism.

The linear relationships observed between a variety of ^{11}B NMR parameters of pentaborane clusters and the samarium(II) concentration represent the first such correlations to be observed for a lanthanide-boron hydride system. The samarium may be viewed of as an effective shift reagent towards a borane cluster.

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