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Reactivity of Decaborane(14) with Pyridine: Synthesis and Characterization of the First 6,6-Substituted Isomer of *nido*-$B_{10}H_{14}$, 6,6-$(C_5H_5N)_2B_{10}H_{12}$, and Application of $^{11}B-^{11}B$ Double-Quantum NMR Spectroscopy

Sophie M. Cendrowski-Guillaume, Jennifer L. O'Loughlin, István Pelczer, and James T. Spencer*

Department of Chemistry and the W. M. Keck Center for Molecular Electronics,
Center for Science and Technology, Syracuse University, Syracuse, New York 13244-4100

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In the low-temperature reaction of $B_{10}H_{14}$ with C_5H_5N, a new product, identified as *arachno*-6,6-$(C_5H_5N)_2B_{10}H_{12}$, was formed in high yield and purity. The proposed 6,6-$L_2B_{10}H_{12}$ compound represents the first known report of this decaborane substitution pattern. The formation of an asymmetric 6,6-$(C_5H_5N)_2B_{10}H_{12}$ isomer was unexpected on the basis of literature precedent describing the synthesis and structural elucidation of numerous 6,9-$L_2B_{10}H_{12}$ species (where L = Lewis base). The observed reaction sequence in the formation of the 6,6-$(C_5H_5N)_2B_{10}H_{12}$ compound proceeded through an initially observed $[H\cdot C_5H_5N]^+[B_{10}H_{13}]^-$ intermediate. In addition to the formation of the 6,6-isomer, the synthesis of the 6,9-$(C_5H_5N)_2B_{10}H_{12}$ isomer is also reported from the reflux of *nido*-$B_{10}H_{14}$ in pyridine. Refluxing the 6,6-(pyridine)$_2B_{10}H_{12}$ isomer in pyridine was also found to convert this isomer into the 6,9-isomer. Both isomers were characterized by ^{11}B NMR, FTIR, UV−vis, mass spectroscopic, and elemental analyses. The structure of the 6,6-isomer was established by 2D $^{11}B-^{11}B$ COSY NMR data and by the first application of a pure phase $^{11}B-^{11}B$ 2Q correlation NMR (double-quantum) experiment to the elucidation of a borane cluster framework. This latter NMR technique was very successful in greatly simplifying the NMR assignments of the 6,6-substituted decaborane cluster species and should be a very powerful tool in cluster structure elucidation in general.

Introduction

The reaction chemistry of *nido*-decaborane(14), $B_{10}H_{14}$, presents both a rich and varied array of reactions and products.[1] Among the numerous decaborane derivatives known, the (ligand)$_2B_{10}H_{12}$ compounds constitute a relatively large class of well-studied species.[1−5] The first example of the reaction between *nido*-$B_{10}H_{14}$ and a Lewis base ligand was reported by Schaeffer in 1957 with the synthesis of 6,9-$(CH_3CN)_2B_{10}H_{12}$ according to eq 1.[2a] Later work showed this to be a very general reaction for decaborane(14), and the reaction was extended to

$$B_{10}H_{14} + 2CH_3CN \xrightarrow{\text{reflux}} (CH_3CN)_2B_{10}H_{12} + H_2 \quad (1)$$

include ligands such as dialkylcyanamides, phosphines, phosphite and phosphinite esters, amides, dialkyl sulfides, and others.[3,4] It was also shown that the Lewis base ligands could be readily displaced from the decaborane framework by other electron pair donor ligands, as shown in eq 2. This latter route has proven to be a very useful synthetic strategy in the formation

$$6,9\text{-(ligand)}_2B_{10}H_{12} + 2\ \text{ligand}^* \xrightarrow[\text{temperature}]{\text{elevated}} 6,9\text{-(ligand}^*)_2B_{10}H_{12} + 2\ \text{ligand} \quad (2)$$

of very pure 6,9-$L_2B_{10}H_{12}$ compounds, provided that the displacing ligand is of greater nucleophilicity than the more weakly bonded, initially coordinated ligand.[4]

Single-crystal X-ray diffraction studies of the acetonitrile,[2b,c] dimethyl sulfide,[3h] and 2-bromopyridine[5i] derivatives of

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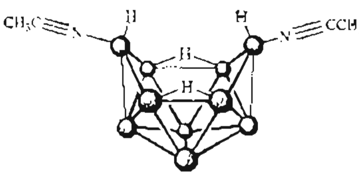

Figure 1. Structure of 6,9-$(CH_3CN)_2B_{10}H_{12}$ (terminal hydrogens of the cage boron atoms, except for B(6) and B(9), have been omitted for clarity).

(ligand)$_2B_{10}H_{12}$ compounds have shown that the structure of these species is formally derived from the parent *arachno*-$[B_{10}H_{14}]^{2-}$ ion.[6] These 6,9-$L_2B_{10}H_{12}$ compounds may be thought of as formally derived from the substitution of Lewis base ligands, which donate electron pairs to the cluster, for the 6- and 9-cage substituted hydride ions in the parent *arachno*-$[B_{10}H_{14}]^{2-}$ compound as shown in Figure 1.[1c,2b,c] The crystal structures of these 6,9-$L_2B_{10}H_{12}$ species show a bond arrangement similar to that observed in *nido*-$B_{10}H_{14}$, but with more uniform B−B bond distances.[2b,c,3i] In contrast to the bridging hydrogen arrangement in *nido*-$B_{10}H_{14}$, the 6,9-$L_2B_{10}H_{12}$ derivatives have only two bridging hydrogen atoms, which are located between the B(5,7) and B(8,10) cage pairs. To date, no substitution pattern for the (ligand)$_2B_{10}H_{12}$ compounds has been established except that of the symmetrical 6,9-isomer.

The room-temperature preparation of the disubstituted 6,9-bis(pyridine)decaborane compound 6,9-$(C_5H_5N)_2B_{10}H_{12}$ from the reaction of pyridine with decaborane(14) in a variety of solvents (pentane, hexane, and benzene) has been previously reported.[4a,5b,d,f,g] This compound was made either from the direct reaction of pyridine in a noncoordinating solvent with decaborane(14) at reflux temperatures[4a,5g] or by the initial preparation of an intermediate species, such as 6,9-$((CH_3CH_2)_2S)_2B_{10}H_{12}$, followed by a ligand displacement reaction.[5b,7]

As part of our studies on the divalent samarium derivatives of boranes and carboranes, we have examined the reactivity of (Lewis base)$_x$SmI$_2$ complexes with *nido*-$B_{10}H_{14}$ and its derivatives.[8] These investigations have disclosed a new route to 6,9-(pyridine)$_2B_{10}H_{12}$ and a novel structural isomer of this same compound. In this paper, we describe the synthesis and the previously unreported ^{11}B NMR data of 6,9-$(C_5H_5N)_2B_{10}H_{12}$, along with the synthesis and characterization of the first example of a proposed 6,6-disubstituted decaborane compound, 6,6-$(C_5H_5N)_2B_{10}H_{12}$.

In this paper, we also report the first application of a pure phase ^{11}B−^{11}B 2Q-COSY NMR (double-quantum) experiment for the elucidation of a borane cluster framework. This homonuclear ^{11}B−^{11}B double-quantum NMR experiment has significant advantages over conventional 2D ^{11}B−^{11}B COSY NMR experiments in assigning complicated or ambiguous 2D spectra. The 2Q technique provides much better peak separation and resolution with the removal of diagonal peak overlap interferences in the cross peaks than possible in the 2D ^{11}B−^{11}B COSY NMR experiment.

Experimental Section

Materials. Tetrahydrofuran (Fisher) was ACS reagent grade and was distilled under a dry nitrogen atmosphere from sodium metal/benzophenone onto sodium hydride for storage. Pyridine (Fisher) was dried over potassium hydroxide pellets, distilled from barium oxide, and freshly distilled from sodium metal immediately prior to use. Pentane (Fisher) was distilled from sodium metal under a dry nitrogen atmosphere. Acetonitrile (Fisher) was ACS reagent grade and was distilled under a dry nitrogen atmosphere from P_2O_5 prior to use. All solvents were degassed by repeated freeze−thaw cycles, and finally stored *in vacuo*. Solvent transfers were accomplished by trap-to-trap distillations at −196 °C. *nido*-Decaborane(14), $B_{10}H_{14}$ (Callery), was sublimed under vacuum prior to use. The Sm(THF)$_x$I$_2$ solutions (Aldrich) were used as received. The $[Me_4N][B_{11}H_{14}]$ and $[Me_4N][B_{10}H_{13}$(pyridine)] compounds, used for the conductivity measurements, were prepared and purified by literature methods.[9,10] All experiments and manipulations were conducted under a dry nitrogen atmosphere with the rigorous exclusion of air and moisture by using standard high-vacuum-line techniques.[11]

Physical Measurements. Proton (^{1}H) NMR spectra were obtained on a General Electric QE-300 spectrometer operating at 300.15 MHz. Spectra were recorded on samples dissolved in CDCl$_3$ in 5 mm (o.d.) tubes with chemical shifts referenced to internal tetramethylsilane (at 0 ppm) with a positive chemical shift indicating a resonance at a lower applied field than that of the standard. The ^{1}H spectra for the 6,6-$(C_5H_5N)_2B_{10}H_{12}$ isomer were obtained at 500 MHz by placing a 5 mm (o.d.) tube containing the sample dissolved in pyridine into a 10 mm (o.d.) tube filled with a H_2O/D_2O mixture for deuterium lock. ^{1}H chemical shifts in this case were referenced to the water signal at 4.71 ppm at 30 °C. Unit-resolution mass spectra were obtained on a Finnigan 4021 mass spectrometer, typically using an ionization potential of approximately 35 eV. 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. Solution spectra were obtained 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. Solid state samples were recorded as Nujol mulls sandwiched between KBr plates prepared in an inert atmosphere (drybox). UV−vis absorption spectra were taken on a Hewlett-Packard 8450-A diode array spectrophotometer from 200 to 800 nm. Solutions were placed in an airtight quartz cell either in a drybox or directly from a vacuum line. Conductivity measurements were performed using a YSI Model 32 conductance meter using a standard cell with a cell constant of 10 cm^{-1} in acetonitrile solutions. Elemental analyses were performed by the Schwarzkopf Microanalytical Laboratories, Woodside, NY.

^{11}B NMR Studies. General Procedures. Boron (^{11}B) NMR spectra were recorded on either a Cryomagnetics CM-250, equipped with a Bruker Aspect 3000 acquisition computer and pulse programmer, or a General Electric GN-500 spectrometer operating at 80.26 and 160.45 MHz, respectively. All spectra were recorded in 5 mm (o.d.) tubes in both the ^{1}H coupled and decoupled modes and were referenced to an external standard of boron tribromide in hexane (Fisher, 1.0 M, δ = +40.0 ppm with positive chemical shifts indicating downfield resonances) sealed in a glass capillary and held coaxially with the NMR sample tube. Typical ^{11}B NMR parameters employed were a relaxation delay of 1 s and a 90° pulse of 25 ms for the 160 MHz spectra (GN-500). Data processing was carried out using NMR1 and NMR2/Z software of NMRi (New Methods Research, Inc., E. Syracuse, NY) on a SUN computer system.

The 2D ^{11}B−^{11}B {^{1}H} COSY NMR spectra, both the absolute value and pure phase versions, were obtained on either the CM-250 or the GN-500 spectrometer. T_1 measurements were recorded in the ^{1}H-decoupled modes. The samples were prepared in a dry nitrogen

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atmosphere and referenced to BF$_3$·Et$_2$O from the previously determined chemical shifts of the compounds. Typically, a 90° pulse width of 15 to 25 ms was required on the CM-250, while the GN-500 required approximately twice this value. In most cases, a previously described absolute value mode COSY pulse sequence[12] was used to generate the t_1, t_2 data matrix (relaxation delay$-(^{\pi}/_2)-t_1-(^{\pi}/_2)-t_2$), in which t_1 was incremented by the inverse of the sweep width in the F_1 dimension and t_2 was the usual acquisition time in a 1D experiment. Typically, the t_1, t_2 matrix was collected as 128 × 256 data points unless otherwise indicated. Data processing involved the application of a DC offset and first-point correction, shifted sine bell apodization, zero filling (twice in t_1 and once in t_2), Fourier transformation, and a magnitude calculation to give the 512 × 512 2D ^{11}B$-^{11}$B COSY NMR spectrum.[8a] The final 512 × 512 F_1, F_2 matrix was usually not symmetrized prior to plotting the data. The T_1 measurements were made using the inversion$-$recovery method and three-parameter fit to the intensity values.[13]

Homonuclear pure phase double-quantum COSY spectra were acquired at 160.45 MHz using the pulse sequence[14,15] $(^{\pi}/_2)-\Delta-\pi-\Delta-(^{\pi}/_2)-t_1-(^{\pi}/_2)-\mathrm{acq}(t_2)$, where the delay for the 2Q excitation (2Δ) was set to 5 ms to compromise ^{11}B$-^{11}$B coupling and fast relaxation. Usual phase cycling was applied for double-quantum coherence selection.[14] Sign discrimination along the remote dimension was achieved by incrementing the phase of the first three pulses in 45° steps following the States$-$Haberkorn$-$Ruben acquisition scheme.[16] Spectra were acquired with the first point at half-dwell-time in the remote dimension[17] and multiple aliasing applied along F_1.[18] Acquisition size was 1024 × 128, with maximum acquisition times of 118.8 and 29.7 ms along t_2 and t_1, respectively. Overall, 2K scans were averaged for each FID. Data processing involved strong Lorentz-to-Gauss apodization with 50/80 Hz and 50/100 Hz Lorentzian sharpening/Gaussian broadening in t_2 and t_1, respectively, and one time of zero filling along t_1. The 2Q-COSY spectrum is presented with dispersive phasing along F_2 in order to enhance sensitivity and simplify the structure of cross peaks.[19]

Synthesis of 6,9-(Pyridine)$_2$B$_{10}$H$_{12}$. Under a dry, inert nitrogen atmosphere, 50 mL of dry, degassed pyridine (0.62 mol) and 1.94 g (15.8 mmol) of *nido*-B$_{10}$H$_{14}$ were refluxed for 4 h. During the reflux, the formation of an orange-yellow solid precipitate was observed from a dark red solution. The red reaction solution was found by ^{11}B NMR to contain a mixture of 6,9-(pyridine)$_2$B$_{10}$H$_{12}$, [Hpyridine]$_2{}^+$[B$_{10}$H$_{10}$]$^{2-}$ {^{11}B NMR (δ, ppm) = +1.4 (1B, apical, d, J_{BH} = 140 Hz); $-$26.4 (4B, equatorial, J_{BH} = 116 Hz},[20a] BH$_3$·pyridine {^{11}B NMR (δ, ppm) = $-$12.6 (q, J_{BH} = 96 Hz)}, and a very small amount of B(OH)$_3$. The solid precipitate was isolated, washed with cold pyridine, and partially redissolved in pure pyridine to give an orange solution which displayed a ^{11}B NMR spectrum identified as the pure 6,9-(pyridine)$_2$B$_{10}$H$_{12}$ isomer {^{11}B NMR (δ, ppm) = $-$5.3 (B(2, 4), d, J_{BH} = 120 Hz); $-$19.0 (B(5, 7, 8, 10), d, J_{BH} = 120 Hz); $-$27.5 (B(6, 9), d, J_{BH} = 123 Hz); $-$40.3 (B(1, 3), d, J_{BH} = 139 Hz)}. While the chemical shifts of the 6,9-(pyridine)$_2$B$_{10}$H$_{12}$ compound have not been previously reported,[21] the ^{11}B NMR spectrum of the orange precipitate was consistent with other reported 6,9-disubstituted decaborane derivatives (6,9-L$_2$B$_{10}$H$_{12}$, where L = Lewis base donor ligand).[6,13,20] Other characterization data for 6,9-(C$_5$H$_5$N)$_2$B$_{10}$H$_{12}$: IR (cm^{-1}) 2525 sh, 2509 vs, 2481 s, 2461 m;[4a,5a] UV$-$vis (λ, nm) 380 and 241 (maximum);[5b,22] MS (EI, 35 eV) parent envelope, as expected (M$^+$, centered at *m/z* 278 for ^{12}C$_{10}$H$_{11}{}^{14}$N$_2{}^{11}$B$_8{}^{10}$B$_2$), and free pyridine (*m/z* 79, C$_5$H$_5$N).[5b,22] Difficulties were encountered in the elemental analyses similar to those previously observed for 6,9-bis(pyridine)decaborane,[5b] tris(pyridine)decaborane,[5c] and related species.[5b]

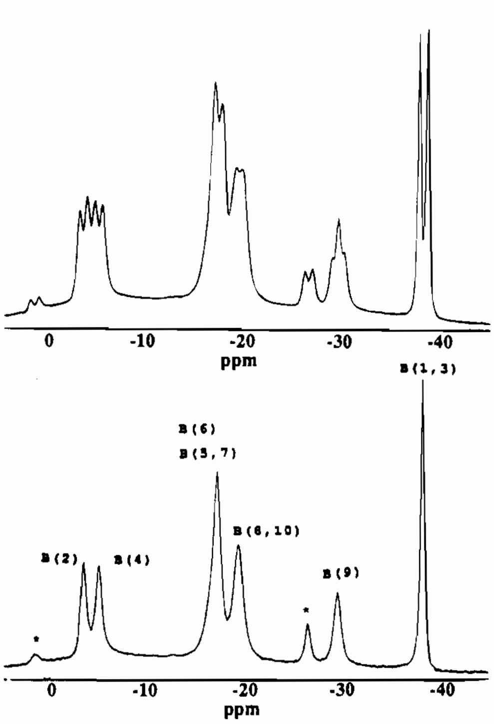

Figure 2. 1D ^{11}B{^{1}H} coupled (above) and decoupled (below) NMR spectra (160 MHz) of 6,6-(C$_5$H$_5$N)$_2$B$_{10}$H$_{12}$ in pyridine (asterisk indicates the resonances for a small amount of [HNC$_5$H$_5$]$_2$[B$_{10}$H$_{10}$] impurity in the sample).

Synthesis of 6,6-(Pyridine)$_2$B$_{10}$H$_{12}$. Under a dry nitrogen atmosphere, 0.71 g (5.8 mmol) of freshly sublimed decaborane(14) was placed in a flask and evacuated. On top of the solid decaborane(14), 15.8 mL (0.20 mmol) of dry, degassed pyridine was condensed at $-$196 °C. The flask was then allowed to slowly warm to room temperature. Upon melting of the pyridine, all the decaborane(14) was observed to dissolve to form a clear, red solution. ^{11}B NMR (80 MHz) analysis of the cold solution showed the initial presence of [Hpyridine]$^+$[B$_{10}$H$_{13}$]$^-$ (^{11}B NMR (δ, ppm) = +8.6 ppm (2B, d, J_{BH} = 120 Hz); +4.4 ppm (1B, unresolved d); $-$3.2 ppm (5B, unresolved d); $-$32.7 ppm (2B, d, J_{BH} = 140 Hz)) ($\sim$43% by ^{11}B integration), a minor amount of BH$_3$·pyridine ($\sim$14%) and a new product which was identified as 6,6-(pyridine)$_2$B$_{10}$H$_{12}$ (^{11}B NMR, Figure 2 (δ, ppm) = $-$3.3 (B(2), J_{BH} = 119 Hz, $\Delta\nu_{1/2}$ = 127 Hz); $-$4.8 (B(4), d, J_{BH} = 117 Hz, $\Delta\nu_{1/2}$ = 139 Hz); $-$17.1 (B(6 and 5,7 overlapped), s and d partially resolved, $J_{\mathrm{BH}(5,7)}$ $\approx$ 119 Hz, $\Delta\nu_{1/2}$ $\approx$ 155 Hz); $-$19.2 (B(8,10), d, J_{BH} = incompletely resolved, $\Delta\nu_{1/2}$ = 194 Hz); $-$29.4 (B(9), t, J_{BH} = 101 Hz, $\Delta\nu_{1/2}$ = 141 Hz); $-$38.1 (B(1,3), d, J_{BH} = 135 Hz, $\Delta\nu_{1/2}$ = 72 Hz)) in approximately 43% yield. The 6,6-(pyridine)$_2$B$_{10}$H$_{12}$ product was also characterized by 2D ^{11}B$-^{11}$B COSY[8a] and 2Q ^{11}B$-^{11}$B COSY 160 MHz NMR experiments; the latter spectrum is shown in Figure 3. The [Hpyridine]$^+$[B$_{10}$H$_{13}$]$^-$ was observed to rapidly disappear from the reaction mixture, on the basis of ^{11}B NMR analyses, and the pure 6,6-(pyridine)$_2$B$_{10}$H$_{12}$ product precipitated from solution in 86% yield. The 6,6-(pyridine)$_2$B$_{10}$H$_{12}$ compound was found to be slightly soluble in pyridine. The product could be extracted from the pyridine reaction mixture by pentane, benzene, or THF, with pentane providing the best extraction results. Dry air oxidation of the 6,6-(pyridine)$_2$B$_{10}$H$_{12}$ compound resulted in the formation of BH$_3$·pyridine

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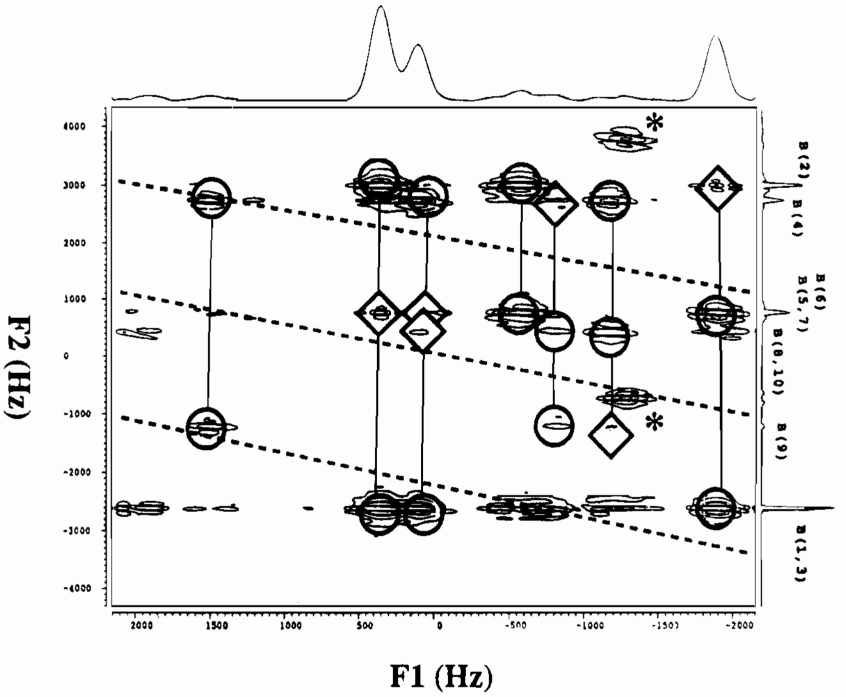


Figure 3. Double-quantum $^{11}B-^{11}B$ NMR spectrum (160 MHz) of 6,6-$(C_5H_5N)_2B_{10}H_{12}$ (asterisk indicates the resonances for a small amount of $[HNC_5H_5]_2[B_{10}H_{10}]$ impurity in the sample). The direct correlation peaks are indicated by circles on the spectrum, which are aliased along the 2Q dimension, and the pseudodiagonal is shown by a dashed line. Remote correlations are indicated by diamonds.

and $[Hpyridine]_2{}^+[B_{10}H_{10}]^{2-}$ decomposition products. The infrared spectrum of 6,6-(pyridine)$_2$B$_{10}$H$_{12}$ dissolved in pyridine displayed very strong B−H absorptions at 2530 and 2398 cm^{-1} and two medium-strong peaks at 2336 and 2295 cm^{-1}. These infrared absorptions are distinct from the infrared absorptions observed for the 6,9-(pyridine)$_2$B$_{10}$H$_{12}$ compound reported as above.[4a,5a] The UV−vis spectrum showed strong absorption bands at (λ, nm) 216, 238, 268, 302, 347 (maximum), 600, and 652 nm. A mass spectrum (EI, 35 eV) of 6,6-(pyridine)$_2$B$_{10}$H$_{12}$ showed, as the primary fragments, peaks for the parent envelope, as expected (M$^+$, centered at *m/z* 278, $^{12}C_{10}H_{11}{}^{14}N_2{}^{11}B_8{}^{10}B_2$), and free pyridine (*m/z* 79, C_5H_5N). Anal. Calcd for $C_{10}H_{22}B_{10}N_2$: C, 43.14; H, 7.97; N, 10.06. Found: C, 47.30; H, 7.57; N, 10.81.

The 6,6-(pyridine)$_2$B$_{10}$H$_{12}$ compound was also found to precipitate as an orange solid from the reaction of $B_{10}H_{14}$ and (pyridine)$_x$SmI$_2$ in pyridine (*vide infra*). Numerous attempts at single-crystal growth by the very slow removal of solvent at low temperatures (~0 °C) were not successful. Refluxing the 6,6-(pyridine)$_2$B$_{10}$H$_{12}$ isomer in dry, degassed pyridine was found to rapidly convert this isomer into the 6,9-isomer.

Reaction of (pyridine)$_x$SmI$_2$ with B$_{10}$H$_{14}$. A dry, degassed pyridine solution of (pyridine)$_x$SmI$_2$ was prepared by the complete substitution of the coordinated THF ligands in (THF)$_x$SmI$_2$ by repeated pyridine dissolution−solvent removal processes until no THF could be spectroscopically observed. To 35 mL (2.5 mmol) of the (pyridine)$_x$SmI$_2$ solution (in pyridine) was added 0.61 g (5.0 mmol) of freshly sublimed $B_{10}H_{14}$ under vacuum at room temperature. The solution spontaneously turned black-orange upon the decaborane(14) addition and was stirred for an additional 2.5 h at room temperature. This reaction solution, as monitored by ^{11}B NMR, was stable under an inert argon atmosphere for at least 8 months. A very brief air oxidation of the reaction solution, achieved by simply opening the reaction flask to dry air at room temperature, yielded pure 6,6-(pyridine)$_2$B$_{10}$H$_{12}$, as determined by ^{11}B NMR. Passing an aliquot of a solution of 6,6-(pyridine)$_2$B$_{10}$H$_{12}$ rapidly down a silica gel column (2.5 × 10 cm) at ambient temperature entirely decomposed the product to BH$_3$·pyridine and $[Hpyridine]_2{}^+[B_{10}H_{10}]^{2-}$, with the latter compound remaining on the column.

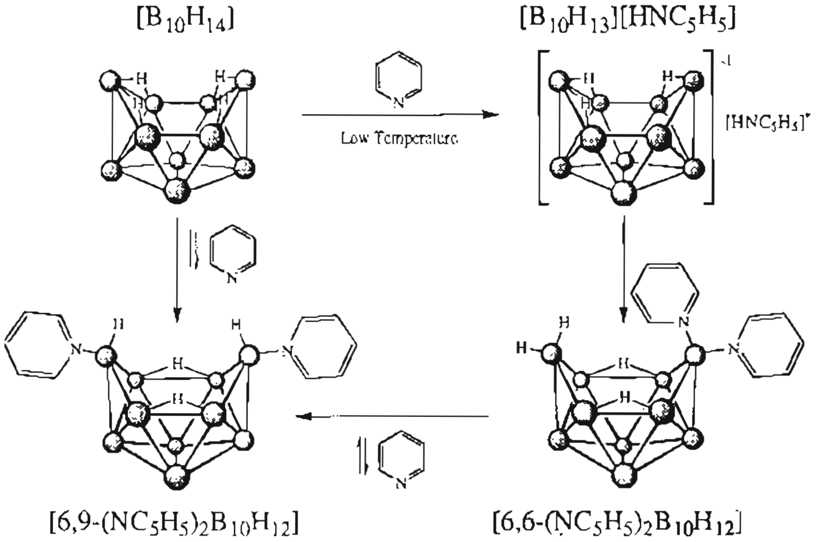
Results and Discussion

The formation of the 6,9-bis(pyridine)decaborane compound 6,9-$(C_5H_5N)_2B_{10}H_{12}$ from the reaction of pyridine with decaborane(14) has been reported previously.[5b,d,f,g] The literature spectroscopic characterization of this compound includes ultraviolet, visible, and infrared spectroscopic data.[4a,5a,b,22] The ^{11}B NMR chemical shifts and coupling data for the 6,9-(pyridine)$_2$B$_{10}$H$_{12}$ compound, however, have not been previously reported,[21] in contrast with most of the other known 6,9-(ligand)$_2$B$_{10}$H$_{12}$ compounds. Because the ^{11}B NMR data for this isomer was important for the structural assignment of another compound reported later in this paper, it was important to accurately and unambiguously determine the ^{11}B NMR data for the 6,9-bis(pyridine)decaborane compound.

The synthesis of the 6,9-$(C_5H_5N)_2B_{10}H_{12}$ isomer has previously been achieved from the reflux of either $B_{10}H_{14}$ or 6,9-$L_2B_{10}H_{12}$[5b,7] with pyridine in a noncoordinating solvent, such as benzene[4a] or pentane.[5g] In a modification of these previous methods, the 6,9-$(C_5H_5N)_2B_{10}H_{12}$ compound was prepared here directly and in higher yield from the reflux of $B_{10}H_{14}$ in neat pyridine. This compound isomer was found to precipitate from the red suspension as an orange-yellow solid. The IR, UV−vis, and mass spectral data for this compound matched those previously reported.[4a,5a,22]

The 6,9-$(C_5H_5N)_2B_{10}H_{12}$ compound was found to be sufficiently soluble in pyridine to allow the complete ^{11}B NMR characterization of the product. The ^{11}B NMR spectrum consisted of four resonances of relative intensity 1:2:1:1, all of which were observed as B−H-coupled doublets in the ^1H-coupled spectrum.[6,11,20] These resonances were observed at (δ, ppm) −5.3 (B(2,4), d, J_{BH} = 120 Hz); −19.0 (B(5,7,8,10), d, J_{BH} = 120 Hz); −27.5 (B(6,9), d, J_{BH} = 123 Hz); and −40.3 (B(1,3), d, J_{BH} = 139 Hz)). The B−H$_{(terminal)}$ couplings for all the boron resonances were resolved, including the resonance assigned to the pyridine-substituted B(6,9) atoms. The ^{11}B NMR data for this orange bis(pyridine) compound were consistent with the data reported for other 6,9-disubstituted decaborane (6,9-$L_2B_{10}H_{12}$) derivatives.[6,13,20] For comparison, the ^{11}B NMR data for 6,9-$(CH_3CN)_2B_{10}H_{12}$, 6,9-$(C_2H_5CN)_2B_{10}H_{12}$, and the parent $[B_{10}H_{14}]^{2-}$ compounds are very similar to the data for the 6,9-bis(pyridine)decaborane compound

Scheme 1. Formation of 6,6-$(C_5H_5N)_2B_{10}H_{12}$ and 6,9-$(C_5H_5N)_2B_{10}H_{12}$ from *nido*-$B_{10}H_{14}$ (Terminal B−H Hydrogens, Except for Those on B(6) and B(9), Have Been Omitted for Clarity)



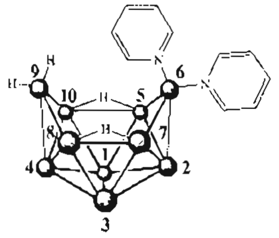


Figure 4. Proposed structure and numbering scheme for 6,6-$(C_5H_5N)_2B_{10}H_{12}$.

reported here {$(CH_3CN)_2B_{10}H_{12}$ (δ, ppm): −5.7 (B(2,4), d, J_{BH} = 137 Hz); −20.4 (B(5,7,8,10), d, J_{BH} = 135 Hz); −31.2 (B(6,9), d); −42.8 (B(1,3), d, J_{BH} = 152 Hz).[23] $(C_2H_5CN)_2B_{10}H_{12}$ (δ, ppm): −1.27 (B(2,4), d, J_{BH} = 128 Hz); −18.3 (B(5,7,8,10), d, J_{BH} = 136 Hz); −39.9 (B(6,9), d); −44.7 (B(1,3), d).[23] $[B_{10}H_{14}]^{2-}$ (δ, ppm): −8.3 (B(2,4), d, J_{BH} = 140 Hz); −23.2 (B(5,7,8,10), d, J_{BH} = 140 Hz); −36.9 (B(6,9), t, J_{BH} = 100 Hz); −42.5 (B(1,3), d, J_{BH} = 135 Hz)[6a,24]}. In contrast, the only other reported ^{11}B NMR chemical shift data for a (pyridine)$_2$B$_{10}$H$_{12}$ complex appear to be those for an asymmetrically substituted isomer with ^{11}B NMR resonances at (δ, ppm) −5.2 (d, B(4)), −5.9 (B(2)), −17.4 presumably overlapped with −20.1 (B(5,7,8,10)), −17.0 (B(6)), −19.0 (B(9)), and −40.5 (B(1,3), J_{BH} = 138 Hz).[5c] The cage substitution pattern for this species, however, was not reported and is, presumably, neither the 6,9- nor the 6,6-isomer on the basis of the ^{11}B NMR data.[5c] A 2D ^{11}B−^{11}B COSY NMR spectrum of the 6,9-bis(pyridine)decaborane product unambiguously confirmed the assignments presented above.[8a]

At low temperature, the reaction between *nido*-decaborane(14) and neat pyridine was found to form a new isomer of $(C_5H_5N)_2B_{10}H_{12}$. In this reaction, the pyridine was condensed onto *nido*-decaborane(14) at −196 °C and allowed to very slowly warm. The ^{11}B NMR analysis of a cold solution showed the presence of $[HC_5H_5N]^+[B_{10}H_{13}]^-$ (~43%)[20] and a new $(C_5H_5N)_2B_{10}H_{12}$ isomer (43 %), along with a small amount of $BH_3{\cdot}C_5H_5N$ (~14%). The $[HC_5H_5N]^+[B_{10}H_{13}]^-$ species was observed by ^{11}B NMR to disappear from the solution over a short period of time to leave only the new $(C_5H_5N)_2B_{10}H_{12}$ compound, which slowly precipitated from the cold solution. The identification of the $[B_{10}H_{13}]^-$ intermediate ion at the beginning of the reaction is consistent with the reaction sequence shown in Scheme 1. The initial formation of an $[HNR_3]^+[B_{10}H_{13}]^-$ ion pair in the reaction of decaborane(14) with amines has been previously suggested on the basis of UV−vis data and the pK_a value for decaborane(14) (3.5) and pK_b values for amines (typically 3−4).[5h] Kinetic studies on the reaction of decaborane with amines, such as *sym*-diethylthiourea, have led to mechanisms which propose the $[HC_5H_5N]^+[B_{10}H_{13}]^-$ species as an intermediate.[5h] In addition, Hawthorne has shown that the $[B_{10}H_{13}]^-$ anion reacts with diethylamine to form the $[B_{10}H_{13}NH(C_2H_5)_2][H_2N(C_2H_5)_2]$ complex.[10] Thermal pyrolysis of the $[B_{10}H_{13}NH(C_2H_5)_2][H_2N(C_2H_5)_2]$ pair was shown to produce 6,9-$(NH(C_2H_5)_2)_2B_{10}H_{12}$.[10] The direct observation of the $[HC_5H_5N]^+[B_{10}H_{13}]^-$ ion pair species, and experimental evidence for its involvement in the formation of disubstituted $L_2B_{10}H_{12}$ species has not been reported previously.

The new, low-temperature $(C_5H_5N)_2B_{10}H_{12}$ isomer was best extracted from the pyridine reaction solution by pentane, while benzene and THF also gave acceptable results. This new compound, formed in very high yield and purity, was observed to be somewhat air sensitive; upon prolonged air exposure, it decomposed to mainly $BH_3{\cdot}C_5H_5N$ and $[HC_5H_5N]_2{}^+[B_{10}H_{10}]^{2-}$. The partial solubility of the low-temperature, orange $(C_5H_5N)_2B_{10}H_{12}$ product in pyridine allowed for its complete NMR characterization (*vide infra*). The solubility of this species was much higher, however, than the 6,9-bis(pyridine)decaborane isomer. Indeed, most 6,9-$L_2B_{10}H_{12}$ species have been reported as generally insoluble in most organic solvents.[5b]

The structure of the new low-temperature isomer of $(C_5H_5N)_2B_{10}H_{12}$ is proposed to be the previously unknown 6,6-$(C_5H_5N)_2B_{10}H_{12}$ isomer on the basis of NMR spectroscopic and other characterization data. This is the first reported example of an asymmetrically disubstituted 6,6-$L_2B_{10}H_{12}$ isomer. The proposed structure and numbering scheme for 6,6-$(C_5H_5N)_2B_{10}H_{12}$ is shown in Figure 4. The ^{11}B NMR spectrum of the compound, shown in Figure 2, consists of six resonances of relative intensity 1:1:3:2:1:2 at (δ, ppm) −3.3 (B(2), J_{BH} = 119 Hz, $\Delta\nu_{1/2}$ = 127 Hz), −4.8 (B(4), d, J_{BH} = 117 Hz, $\Delta\nu_{1/2}$ = 139 Hz), −17.1 (B(6 and 5, 7 overlapped), s and d partially resolved, $J_{BH(5,7)}$ ≈ 119 Hz, $\Delta\nu_{1/2}$ ≈ 155 Hz), −19.2 (B(8, 10), d, J_{BH} =

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(23) Hyatt, D. E.; Scholer, F. R.; Todd, L. J. *Inorg. Chem.* **1967**, *6*, 630.

(24) Cation and solvents effects on the ^{11}B NMR chemical shifts for $[B_{10}H_{14}]^{2-}$ were shown to be negligible.[6a]

incompletely resolved, $\Delta\nu_{1/2}$ = 194 Hz), −29.4, B(9), t, J_{BH} = 101 Hz, $\Delta\nu_{1/2}$ = 141 Hz), and −38.1 (B(1,3), d, J_{BH} = 135 Hz, $\Delta\nu_{1/2}$ = 72 Hz). This spectral pattern is similar to that of the parent *arachno*-$[B_{10}H_{14}]^{2-}$ species [(^{11}B NMR, δ, ppm) for $Rb_2B_{10}H_{14}$: −8.3 (d, J_{BH} = 140 Hz); −23.3 (d, J_{BH} = 140 Hz); −36.9 (t, J_{BH} = 100 Hz); −42.5 (d, J_{BH} = 135 Hz)].[6,20] In the ^{1}H-coupled ^{11}B spectrum of 6,6-$(C_5H_5N)_2B_{10}H_{12}$, each resonance was observed as a proton-coupled doublet except for the peak at −29.4 ppm, which was clearly observed as a triplet. The triplet of relative intensity 1 and the observed NMR pattern indicated an asymmetrically substituted species containing a BH_2 unit at the B(9) cage position. This triplet is very similar, both in chemical shift (−29.4 and −36.9 ppm for 6,6-$(C_5H_5N)_2B_{10}H_{12}$ and $B_{10}H_{14}{}^{2-}$, respectively) and BH coupling constant magnitude (J_{BH} = 101 and 100 Hz for 6,6-$(C_5H_5N)_2B_{10}H_{12}$ and $[B_{10}H_{14}]^{2-}$, respectively) to the upfield triplet observed for the 6,9-BH_2 units in $[B_{10}H_{14}]^{2-}$.[6,20] In contrast, the ^{11}B NMR for the 6,9-bis(pyridine)-substituted species displayed a doublet for the two equivalent B(6,9) atoms. The resonance at −16.5 ppm from three boron atoms was clearly asymmetric and resulted from the coincidental overlap of two chemically inequivalent sets of boron atoms (1B + 2B). It could also be observed from the spectra that the resonance for the single boron atom was not proton coupled, while the two-boron resonance was a proton-coupled doublet. To assign the structure of this new isomer, a 2D ^{11}B−^{11}B COSY experiment was performed. Due to the complicated nature and close cross-peak interferences in the 2D spectrum, however, it was not possible to unequivocally assign all the ^{11}B resonances and cage connectivities.[8a] Thus, a double-quantum ^{11}B−^{11}B correlation NMR experiment was required to provide the detailed coupling information necessary to completely assign the structure of the new compound as the 6,6-isomer.

The use of double-quantum NMR correlation experiments to provide additional cross-peak and coupling information relative to the 2D ^{11}B−^{11}B COSY NMR experiment for boron-containing compounds is potentially a very powerful tool which has not been well explored in boron cluster chemistry.[25] In fact, only a single ^{11}B−^{11}B double-quantum correlation NMR experiment, for (μ-P$(C_6H_5)_2$)B_5H_8, has been reported previously for a boron compound.[25] This experiment has been shown to be very important in the structural assignment of unknown organic and bioorganic compounds by ^{13}C−^{13}C (INADEQUATE) NMR studies.[26] The technique provides important structural information frequently obscured in the 2D COSY NMR experiment by removing interferences caused by the overlap of intense diagonal peaks with nearby off-diagonal cross-peaks. The double-quantum technique also provides a separation of the peaks which is twice as large as that observed in the COSY spectrum, thereby providing much better resolution of the correlation information for closely separated resonances. These problems were, in fact, those specifically encountered in the 2D ^{11}B−^{11}B COSY NMR experiment for the proposed 6,6-$(C_5H_5N)_2B_{10}H_{12}$ compound.[8a]

In a typical double-quantum experiment, frequency responses are obtained only from homonuclear-coupled spins through the use of multiple-quantum coherences (MQC).[26] The resulting double-quantum spectrum displays the normal chemical shifts along the F_2 axis and the double-quantum frequencies along the F_1 axis. A correlation peak develops at a frequency of $\omega_1 + \omega_2$ in F_1 when two signals are coupled. Diagonal peaks, typically very intense in the single-quantum 2D COSY NMR experiment, are absent in the double-quantum correlation spectrum. The pairs of peaks in the F_1 domain correspond to nuclei that are spin coupled. In addition, remote and combination peaks may also be observed. The double-quantum experiment allows for the matching of directly coupled signals since the midpoints of lines connecting coupled pairs lie on the 2Q pseudodiagonal ($\omega_1 = 2\omega_2$). This latter feature, along with the removal of interferences from the diagonal peaks and additional topological information obtained, frequently allows for the straightforward interpretation of complex or poorly resolved spectra. From a known starting point in the spectrum, it may therefore be possible to determine the framework and substitution pattern of the unknown compound, otherwise inaccessible by single-quantum methods. The double-quantum spectrum of the new 6,6-$(C_5H_5N)_2B_{10}H_{12}$ compound is shown in Figure 3. The direct correlation peaks are indicated by circles on the spectrum, which are aliased along the 2Q dimension, and the pseudodiagonal is shown by a dashed line.

The assignment of the 6,6-$(C_5H_5N)_2B_{10}H_{12}$ compound by ^{11}B−^{11}B 2Q correlation NMR data may be understood by starting with the proton-coupled triplet BH_2 resonance, initially assigned to B(9) (the numbering scheme employed is shown in Figure 4). From the 2Q spectrum, two resonances are correlated with this BH_2 resonance, the peak at −4.8 ppm (relative intensity 1) and the peak at −19.2 ppm (relative intensity 2). If one considers the B_{10} framework (Figure 4), these peaks may be assigned to boron atoms B(4) and the B(8,10) pair, respectively. The resonance assigned to B(4) has correlation peaks with (besides B(9)) the B(8,10) pair and the most upfield resonance (relative intensity 2), which may be assigned to the B(1,3) pair. The B(8,10) resonance also shows a correlation peak with the B(1,3) pair, as expected. The boron atoms B(1,3) exhibit correlation peaks with the two downfield resonances, allowing the assignment of the furthest downfield signal to B(2) and supporting the assignment of the other resonance as arising from B(4). The B(2)-assigned resonance also exhibits correlation peaks to the overlapping three boron atoms at −17.1 ppm. The resonance at −17.1 ppm may, therefore, be assigned to B(6) and B(5,7). All other correlation peaks, including remote correlations (indicated by diamonds in Figure 3), fit and are self-consistent with these peak assignments. This assignment is also consistent with the preliminary assignment of the 1D spectrum on the basis of peak chemical shifts, relative intensities, and multiplicities and in comparison with the NMR data for the 6,9-$(C_5H_5N)_2B_{10}H_{12}$ isomer. All correlations for 6,6-$(C_5H_5N)_2B_{10}H_{12}$ were observed as paired signals in the 2Q spectrum, except that the 2Q correlation peaks were not observed between the B(5,7) and B(8,10) pairs. This can be attributed to the presence of BHB-bridging interactions between these pairs of atoms. The ^{11}B−^{11}B correlations between hydrogen-bridged atoms are generally very weak and are typically not observed.[12] The diminution of the correlation peak intensity is fully expected, since B−B internuclear electron density between BHB-bridged atoms is generally quite small and the development of a correlation peak depends on the presence of significant BB electron bonding density between the correlated nuclei.[27] Several examples of the absence of BHB-bridged cross peaks in 2D ^{11}B−^{11}B COSY NMR for structurally established species have been reported, including the absence of a cross peak between the hydrogen-bridged atoms B(5,7) and B(8,10) in substituted boranes such

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(25) Pelczer, I.; Goodreau, B. H.; Cendrowski-Guillaume, S. M.; Spencer, J. T., manuscript submitted.

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as Cs[*arachno*-6-Sb$_9$H$_{12}$].[28] The structural assignment of 6,6-($C_5H_5N)_2B_{10}H_{12}$ represents the first application of a double-quantum experiment for a borane cluster framework elucidation.[25]

The ^{11}B NMR data, however, do not adequately distinguish between the proposed 6,6-$(C_5H_5N)_2B_{10}H_{12}$ compound and the previously reported [$B_{10}H_{13}$·pyridine][Hpyridine] ion pair compound.[10] In order to unequivocally distinguish between these two species, solution conductivity measurements were completed for these and several other neutral and anionic borane species. The proposed 6,6-$(C_5H_5N)_2B_{10}H_{12}$ product was found to be a neutral, nonconducting compound in solution (0.113 $\mu\Omega^{-1}$, 0.02 M), while the [$B_{10}H_{13}{}^{-1}$·pyridine][NMe$_4$][10] (0.1.68 × 10^4 $\mu\Omega^{-1}$, 0.02 M) and [$B_{11}H_{14}$][NMe$_4$][9] (1.68 × 10^4 $\mu\Omega^{-1}$, 0.02 M) anions, which were independently synthesized by separate literature routes, were found to be highly conducting in solution. These data clearly show that the new complex is a neutral species, which provides further strong support for the proposed structure.

Other spectroscopic characterization of the 6,6-$(C_5H_5N)_2B_{10}H_{12}$ compound provides additional support for the assignments presented above. The ^{1}H NMR spectrum in pyridine exhibits relatively sharp singlets attributed to pyridine-substituted decaborane at (δ, ppm) 4.1 (1H), 2.3 (2H), and 1.2 (2H) [free-pyridine signals at 8.4 (2H), 7.0 (2H), and 6.3 (1H)]. The solution IR data (in pyridine) displayed, in addition to the pyridine bands, a very strong and broad B−H absorption at 2526.9 cm^{-1} with a shoulder at 2397.6 cm^{-1} and two medium-strong peaks at 2336 and 2295 cm^{-1}. These bands are clearly distinct from the absorptions observed in the 6,9-bis(pyridine)decaborane infrared spectrum.[4a,5a,22] The UV spectrum of 6,6-$(C_5H_5N)_2B_{10}H_{12}$ exhibits strong bands at 216, 238, 268, 302, 347 (maximum), 600, and 652 nm.[5b,22] Finally, the mass spectrum (EI, 35 eV) of a 6,6-$(C_5H_5N)_2B_{10}H_{12}$ sample has succeeded in showing the expected parent ion envelope (centered at *m/z* 278) as well as pyridine (*m/z* 79).

Refluxing the 6,6-(pyridine)$_2$B$_{10}$H$_{12}$ isomer in dry, degassed pyridine was found to rapidly convert this isomer into the 6,9-isomer. The proposed mechanism for the formation of the 6,6- and 6,9-(NH(C$_2$H$_5$)$_2$)$_2$B$_{10}$H$_{12}$ compounds is given in eqs 3−6. In the low-temperature reaction of pyridine with decaborane(14), the [$B_{10}H_{13}$][HNC_5H_5] ion pair is initially formed from the proton abstraction of decaborane by pyridine. As mentioned previously, the initial formation of this ion pair species, without

$$B_{10}H_{14} + NC_5H_5 \rightarrow [B_{10}H_{13}][HNC_5H_5] \qquad (3)$$

$$[B_{10}H_{13}][HNC_5H_5] + NC_5H_5 \rightarrow [6\text{-}(NC_5H_5)B_{10}H_{13}][HNC_5H_5] \qquad (4)$$

$$[6\text{-}(NC_5H_5)B_{10}H_{13}][HNC_5H_5] \rightarrow [6,6\text{-}(NC_5H_5)_2B_{10}H_{12}] \text{ (fast)} \qquad (5)$$

$$6,6\text{-}(NC_5H_5)_2B_{10}H_{12} \xrightarrow{\text{reflux}} [6,9\text{-}(NC_5H_5)_2B_{10}H_{12}] \qquad (6)$$

hydrogen evolution, is consistent with both our ^{11}B NMR spectroscopic observations and previous kinetic measurements. The observed [HC_5H_5N]$^+$[$B_{10}H_{13}$]$^-$ intermediate formed in eq 3 would be expected to react further with the pyridine solvent to form the [HC_5H_5N]$^+$[$B_{10}H_{13}NC_5H_5$]$^-$ pair in which one pyridine molecule is directly coordinated to the B(6) of the cage. The pyridine-coordinated [$B_{10}H_{13}NC_5H_5$]$^-$ cage may then rapidly react with [HC_5H_5N]$^+$ through either a three- or four-centered intermediate to eliminate hydrogen and form the observed 6,6-disubstituted product. Preferential attack by the pyridinium ion at the 6-boron site over the 9-boron site would be anticipated, primarily on the basis of electronic arguments, since B(6) would be expected to be relatively more "electron-rich" than B(9) due to the dative electron pair donation from the coordinated pyridine group to B(6). This pyridine−B(6) coordination would also facilitate the hydrogen elimination process by providing more hydridic character to the hydrogen attached to B(6). The intermediacy of the [$B_{10}H_{13}HN(C_2H_5)_2$]-[$H_2N(C_2H_5)_2$] in the thermal formation of 6,9-(($C_2H_5)_2$-NH)$_2$B$_{10}$H$_{12}$ has been previously established.[10] The final thermal conversion of the 6,6-isomer by an apparent irreversible process into the more thermodynamically stable 6,9-isomer may proceed through either intermolecular or intramolecular processes to relieve steric interactions in the bis-6,6-coordination arrangement. Experiments are currently in progress to more fully understand this final isomer interconversion process.

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