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A High-Resolution ^{11}B NMR Study of the $[(B_{10}H_{12})_2Ni]^{2-}$ Ion

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The 70.6-MHz ^{11}B NMR spectrum of $[(B_{10}H_{12})_2Ni]^{2-}$ has been assigned: $\delta_{^{11}B}$, 10.1 [B(5,7,8,10)]; ~8 [B(1 or 3)]; 0.4 [B(3 or 1)]; −4.1 [B(6,9)]; −21.7 [B(2,4)].

INTRODUCTION

The icosahedral fragment $B_{10}H_{12}$ occurs in a large number of boron hydrides, which encompass a great diversity of structure and bonding. These include the one-carbon carboranes $B_{10}H_{12}CNH_2R$ (*1*) and $B_{10}H_{12}CH^-$ (*1, 2*), heteratom boranes of types 7-$B_{10}H_{12}As^-$ and 7-$B_{10}H_{12}AsCH_6$ (*3*), and d^{10} metalloboranes containing tin, germanium (*4*), zinc, cadmium, mercury, indium, and gallium (*5–7*). Bidentate $B_{10}H_{12}{}^{2-}$ forms a novel class of metalloboranes which include group VIII metals (*8*), whose members display a distinctive chemistry owing to the presence of low-energy metal *d* orbitals which can participate in metal–boron bonding. Thus, for example, $[(B_{10}H_{12})Ir(CO)(PPh_3)_2]^-$ has been found to activate carbon monoxide and dihydrogen (*9, 10*).

As a continuation of interest in high-resolution ^{11}B NMR spectroscopy of complex boron hydride derivatives, we have assigned the spectrum of the $[(B_{10}H_{12})_2Ni]^{2-}$ ion. This work represents the first detailed ^{11}B NMR study of a large *nido*-metalloborane (*11*).

RESULTS AND DISCUSSION

The 70.6-MHz ^{11}B NMR spectra of $[(CH_3)_4]_2[(B_{10}H_{12})_2Ni]$ is shown in Fig. 1A. The spectrum consists of five doublets of relative area 4:1:1:2:2 and may be interpreted in terms of the solid-state structure of this material found by X-ray crystallography (*12*). The numbering convention is the same as that used in decaborane (Fig. 2).

In the spectrum of $[(1,2,3,4\text{-}B_{10}D_4H_8)_2Ni]^{2-}$ (Fig. 1B), collapse of the doublets at 8, 0.4, and −21.7 ppm occurs. This allows assignment of the −21.7-ppm resonance to

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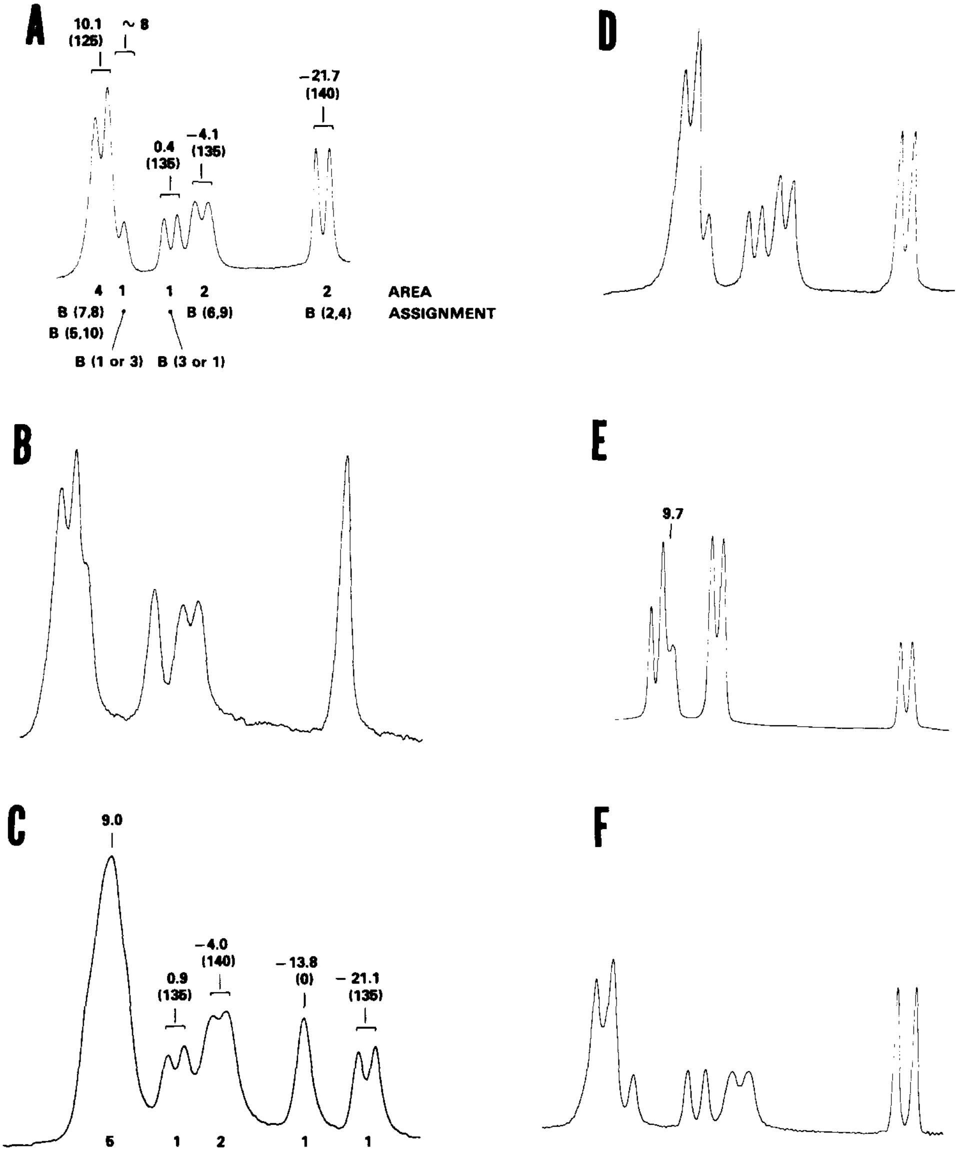

FIG. 1. ^{11}B NMR spectra (70.6 MHz) of (A) $[(CH_3)_4N]_2[(B_{10}H_{12})_2$ (acetone), (B) $[(CH_3)_4N]_2[(1,2,3,4\text{-}B_{10}D_4H_8)_2Ni]$ (acetone), (C) $[(CH_3)_4N]_2[(2\text{-}BrB_{10}H_{11})_2Ni]$ (acetone), (D) $[(CH_3)_4N]_2[(B_{10}H_{12})_2Ni]$ (acetone), bridge protons decoupled, (E) $6\text{-}B_{10}H_{13}D$ (CS_2), (F) $[(CH_3)_4N]_2[(6\text{-}B_{10}DH_{11})_2$ (acetone). Chemical shifts are in parts per million from external $BF_3 \cdot (C_2H_5)_2O$ and coupling constants are in hertz. Areas and assignments are shown beneath the spectra.

B(2,4), in accord with the observation that high-coordination-number borons are usually found at high field. This assignment is confirmed by the observation that, in the spectrum of $[(2\text{-}BrB_{10}H_{11})_2Ni]^{2-}$ (Fig. 1C), the intensity of the highest-field doublet is reduced by half. A new singlet appears downfield at −13.8 ppm due to B(2)–Br. The doublets of unit area at −8 and 0.4 ppm are then due to B(1) and B(3). Further distinction between these two positions cannot be made using labeled derivatives because, in the absence of strong, long-distance directive effects, introduction of nickel into the B_{10} framework is equally likely to occur across the B(7,8) and B(5,10) edges. A quite analogous situation occurs in $B_{10}H_{13}^-(B_{10}H_{12}^{2-}\text{-}H^+)$ (*13*), where proton addition can take place at either of these edges.

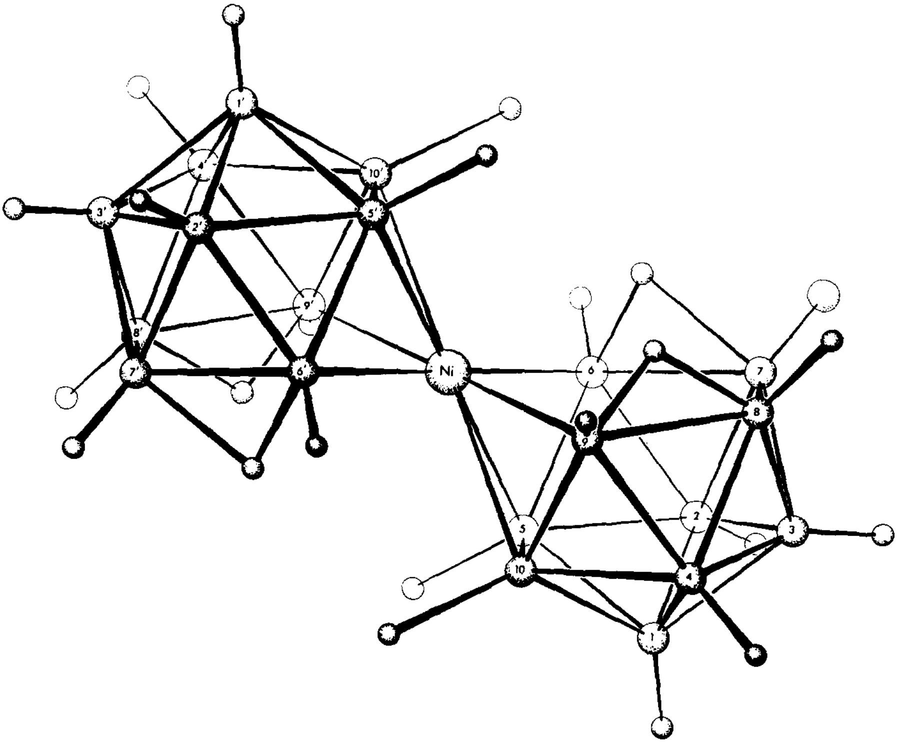

FIG. 2. Structure and numbering system in $[(B_{10}H_{12})_2Ni]^{2-}$. Reprinted, with permission of the publishers, from Ref. (*12*). © by the American Chemical Society.

The doublet at −4.1 ppm is broad, suggesting the presence of unresolved fine structure. Irradiation of the bridge protons ($\delta_{\text{acetone}} = -2.6$ ppm) results in a decrease in linewidth and an increase in intensity (Fig. 1D). This doublet must thus be due to either B(6,9) or B(7,8) since borons at these positions should spin couple to the bridge hydrogens.

A further distinction can be made through $[(6\text{-}B_{10}H_{11}D)_2Ni]^{2-}$. This labeled derivative was prepared from decaborane which was deuterated by a catalyzed exchange with dideuterium; its ^{11}B NMR spectrum (Fig. 1E) reveals collapse of the 9.7-ppm doublet, owing to selective exchange at the 6(9) positions. The line-narrowed spectrum of the deuterated nickel-decaborane (Fig. 1F) displays substantial collapse of the doublet at −4.1 ppm, indicating that this resonance is due to B(6,9). The chemical shifts of B(7,8) and B(5,10) are, then, very nearly the same, notwithstanding that only the B(5,10) borons are bonded to nickel, and they account for the doublet of area 4 at 10.1 ppm.

EXPERIMENTAL

Fourier transform ^{11}B NMR spectra were recorded at 70.6 MHz and are referenced to external $BF_3 \cdot O(C_2H_5)_2$; positive shifts are downfield of the reference.

$[(CH_3)_4N]_2[B_{10}H_{12})_2Ni]$ was prepared from $Cs_2B_{10}H_{14}$ and nickel chloride in aqueous acetone (*14*). In an analogous manner, 1,2,3,4-$B_{10}D_4H_{10}$ (*15*) and 2-$BrB_{10}H_{13}$ (*16*) were converted to $[(CH_3)_4N]_2[(B_{10}D_4H_8)_2Ni]$ and $[(CH_3)_4N]_2[(2\text{-}BrB_{10}H_{11})_2Ni]$. *Anal.* Calcd for $C_8H_{46}B_{20}Br_2NiN_2$: C, 15.87; H, 7.60; N, 4.63. Found: C, 16.03; H, 7.33; N, 4.85. A small-scale preparation of $[(CH_3)_4N]_2[(B_{10}H_{12})_2Ni]$ was carried out in D_2O–acetone; infrared analysis revealed that no deuterium had been incorporated into the product.

$[(CH_3)_4N]_2[(B_{10}H_{11}D)_2Ni]$: Dideuterium was passed through a stirred, refluxing solution of 0.45-g $(Ph_3P)_3RuHCl \cdot C_7H_8$ (*17*) and 0.96-g decaborane in 60 ml of deoxygenated toluene for 14 hr. The cooled reaction mixture was filtered and the toluene was removed under reduced pressure. The deuterated decaborane, 0.90 g, was isolated by sublimation of the residue and converted to $[(CH_3)_4N]_2[(B_{10}H_{11}D)_2Ni]$ as described above. Infrared analysis indicated that the product contained 1.4 terminal deuteriums per mole. Longer exchange times introduce deuterium into B(6,9) as well as other positions.

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