Preparation and Boron-11 and Proton Nuclear Magnetic Resonance Study of the Anions $[B_9H_{14}]^-$, $[B_9H_{13}(NCS)]^-$, and $[B_9H_{13}(NC)BH_3]^-$, and a Comparison with the Neutral Derivatives $B_9H_{13}(SMe_2)$, $B_9H_{13}(SEt_2)$, and $B_9H_{13}(CH_3CN)$; Isolation of $[B_8H_{12}(NCS)]^-$

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The structure and fluxional character of derivatives of $[B_9H_{14}]^-$ containing anionic or neutral ligands has been investigated by high-field ^{11}B and ^1H n.m.r. spectroscopy. The anionic derivatives $[B_9H_{13}(NCS)]^-$ and $[B_9H_{13}(NC)BH_3]^-$ showed significant dynamic and structural differences from those of the parent ion $[B_9H_{14}]^-$ or the neutral compounds $B_9H_{13}(SMe_2)$, $B_9H_{13}(SEt_2)$, and $B_9H_{13}(CH_3CN)$. The synthesis of the anionic derivatives led to interesting side-reactions in which $[B_8H_{12}(NCS)]^-$ was produced and the dual chemical character of $[BH_3(CN)]^-$ was illustrated as both a two-electron σ-donor ligand and hydride-transfer reagent.

The tetradecahydrononaborate(1−) ion, $[B_9H_{14}]^-$,[1] has been shown to have the solid-state crystal structure of C_s symmetry, Figure 1(*a*), in which the *arachno*-boron is formally derived from the 11-atom polyhedron, with two bridging hydrogens between boron atoms 4 and 5 and 4 and 9, and BH_2 groups with *exo*- and *endo*-hydrogens at positions 6—8.[2] The neutral derivatives, $B_9H_{13}L$,[3] have been shown to have a similar boron cage, but in the case of $B_9H_{13}(CH_3CN)$, the crystal structure [Figure 1(*b*)] indicated two bridging hydrogens between boron atoms 5 and 6 and 8 and 9, with *exo*- and *endo*-hydrogens at atoms 6 and 8 and *endo*-hydrogen and *exo*-ligand at 4.[4] The only anionic derivative reported was the $[B_9H_{13}(NCS)]^-$ ion, although its structure was inadequately characterized since its crystal structure was not determined, and the n.m.r. data comprised only 19.3-MHz ^{11}B studies from which the boron shifts were not adequately obtained.[5]

In solution, ^{11}B and ^1H n.m.r. studies [2b,6] of $[B_9H_{14}]^-$ were consistent with a structure of higher symmetry (C_{3v}) than that in the solid state. Only three boron resonances were found, and also five fluxional bridge-like hydrogens were observed, arising from dynamic equilibration of the two crystallographically determined bridging hydrogens and one of the terminal hydrogens (presumably *endo*) from each of the BH_2 groups. ^{11}B N.m.r. studies [7] of neutral $B_9H_{13}L$ compounds indicated the presence of six non-equivalent boron environments, consistent with the crystallographically observed C_s symmetry of $B_9H_{13}(CH_3CN)$, but the analysis of the spectra did not yield full details of chemical shifts and coupling constants because of overlapping resonances at the maximum operating frequency (80.2 MHz), and fine structure due to bridge-hydrogen coupling was not resolved. No detailed ^1H high-field data have been reported, and no correlation between proton shifts and boron positions has previously been derived. Boron-11 and ^1H n.m.r. studies [3e] of $B_9H_{13}(CO)$ indicated that there were only two bridging hydrogens in the molecule, but suggested the presence of BH_2 groups comparable to the unusual BH_2 group in B_5H_{11}.[8]

We have therefore prepared the anionic derivatives $[B_9H_{13}(NCS)]^-$ and $[B_9H_{13}(NC)BH_3]^-$ and have investigated their ^{11}B and ^1H n.m.r. spectra together with the spectra of $[B_9H_{14}]^-$, $B_9H_{13}(SMe_2)$, $B_9H_{13}(SEt_2)$, and $B_9H_{13}(CH_3CN)$, (*a*) to elucidate the fluxional behaviour of these systems, (*b*) adequately to characterize the structure of the anionic derivatives, and (*c*) fully to derive the n.m.r. parameters and to correlate boron and proton chemical shifts in both neutral and anionic derivatives.

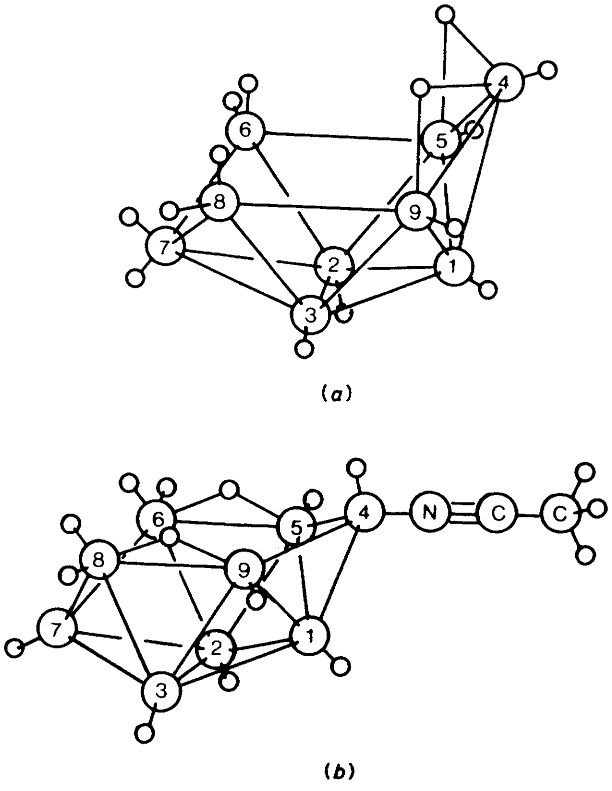

Figure 1. The structures of $[B_9H_{14}]^-$ (*a*) and $B_9H_{13}(CH_3CN)$ (*b*)

The published route to $[B_9H_{13}(NCS)]^-$ involved the degradative reaction between $B_{10}H_{14}$ and NCS^- in aqueous dioxane.[5] We found that this method could not be applied to the preparation of $[B_9H_{13}(NC)BH_3]^-$, and therefore an alternative, more general route to these anions through a ligand-displacement reaction on $B_9H_{13}(SMe_2)$ was developed.

Table 1. 115.55-MHz ^{11}B, 250-MHz ^{1}H, and 360-MHz H-{^{11}B, continuous wave} n.m.r. spectroscopic data for derivatives of $[B_9H_{14}]^-$

Compound (solvent)	Boron or hydrogen assignment (boron irradiation position)	^{11}B		250-MHz ^{1}H		360-MHz ^{1}H	
		δ/p.p.m.	J(BH)/ Hz	δ/p.p.m.*	J(BH)/ Hz	δ/p.p.m.*	Comments
$[NMe_4][B_9H_{14}]$[^{11}B, CD_3CN; ^{1}H, $(CD_3)_2CO$]	5, 7, 9	−6.8	137	2.10(3)	137		
	4, 6, 8	−19.2	136	1.60(3)	130		
	1, 2, 3	−22.4	138	1.10(3)	140		
	Bridge			−1.50(5)			
	$[NMe_4]^+$			3.40(12)			
$[N(PPh_3)_2][B_9H_{13}(NCS)]$ (^{11}B, $CDCl_3$; ^{1}H, CD_2Cl_2)	7	14.8	134	3.45(1)	136	3.68(1)	
	1	4.2	140	3.00(1)	130	2.85(1)	
	5, 9	−16.4	146	1.62(2)	138	1.53(2)	
	6, 8	−18.0	143	1.85(2)	142		
	6, 8 *exo*					1.86(2)	*exo* and *endo* only resolved below 233 K
	6,8 *endo*					−0.41(2)	
	4	−22.0					
	4 *endo*					0.60(1)	
	2,3	−38.3	146	0.32(2)	144	0.25(2)	
	Bridge			−1.40(5)		−3.30(2)	
	$[N(PPh_3)_2]^+$			7.50(30)			
$[N(PPh_3)_2][B_9H_{13}(NC)BH_3]$ (^{11}B, $CDCl_3$)	7	16.2	130				
	1	4.8	137				
	5,9	−15.5	141				
	6,8	−19.4	124				
	4	−25.5					
	2, 3	−38.6	146				
	$(NC)BH_3$	−43.0	89.5				
$B_9H_{13}(SMe_2)$ (^{11}B and ^{1}H, $CDCl_3$)	7	18.8	152	4.15(1)	150	4.04(1)	
	1	5.1	134	3.10(1)	137	3.03(1)	
	5, 9 *exo*	−15.8	144	1.85(2)	142	1.82(2)	
	Bridge		28 ± 1				
	6,8 *exo*	−20.8	150	2.00(2)	137	1.96(2)	
	endo		60	−0.50(2)	64	−0.02(2)	
	Bridge		30	−3.55(2)		−3.60(2)	
	4	−23.0	131	0.35(1)	133	0.39(1)	
	2, 3	−38.6	149				
	$S(CH_3)_2$			2.60(6)			See Table 2
$B_9H_{13}(SEt_2)$ (^{11}B and ^{1}H, $CDCl_3$)	7	18.8	148	4.10(1)	150	3.96(1)	
	1	5.2	137	3.05(1)	140	3.04(1)	
	5, 9 *exo*	−15.4	142	1.85(2)	142	1.75(2)	
	Bridge		34 ± 1				Bridge H affected
	6, 8 *exo*	−20.7	150	1.95(2)	140	1.87(2)	
	endo		60	−0.05(2)	60	−0.05(2)	
	Bridge		30	−3.55(2)		−3.46(2)	Broad, residual coupling
	4	−25.1	134	0.30(1)	130	0.31(1)	
	2, 3	−38.4	149	0.50(2)	150	0.34(2)	
	CH_2			2.95(4)			See Table 2
	CH_3			1.45(6)			See Table 2
$B_9H_{13}(CH_3CN)$ (^{11}B, CD_3CN)	7	17.7	155				
	1	5.6	137				
	5, 9 *exo*	−14.0	145				
	Bridge		27 ± 1				
	6, 8 *exo*	−20.2	150				*exo*-Coupling
	endo		60				*endo*-Coupling
	Bridge		30				Bridge coupling
	4	−27.0	134				
	2, 3	−38.3	149				

* Relative intensities are given in parentheses.

Results and Discussion

(*a*) *Preparations*.—It is well established that neutral derivatives of the type $B_9H_{13}L$ undergo ligand-displacement reactions with neutral ligands.[3,6] We now report that the method may conveniently be extended to include anionic ligands. Thus, the reactions between $B_9H_{13}(SMe_2)$ and salts of NCS^- and $[BH_3(CN)]^-$ led to the substituted anions $[B_9H_{13}(NCS)]^-$ and $[B_9H_{13}(NC)BH_3]^-$. In addition, interesting side-reactions occurred in each case.

The reaction between $B_9H_{13}(SMe_2)$ and $[N(PPh_3)_2][NCS]$ proceeded smoothly in refluxing 1,2-dichloroethane to give

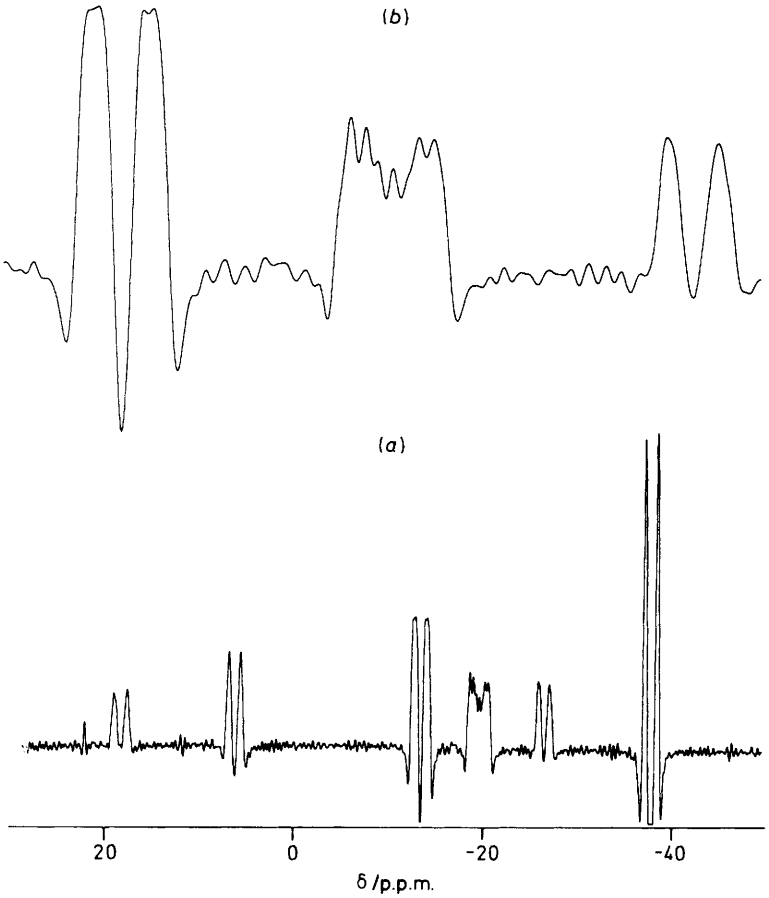

Figure 2. ^{11}B N.m.r. spectrum (115.55 MHz) of $B_9H_{13}(CH_3CN)$ (line narrowed) (*a*) and sub-spectrum (*b*) showing resonances due to B(4), B(5), and B(9), and B(6) and B(8) (line narrowed)

the $[N(PPh_3)_2]^+$ salt of $[B_9H_{13}(NCS)]^-$ in high yield [equation (1)]. Also isolated from the reaction mixture, in low yield, was

$$B_9H_{13}(SMe_2) + NCS^- \longrightarrow [B_9H_{13}(NCS)]^- + SMe_2 \quad (1)$$

a species identified as $[N(PPh_3)_2][B_8H_{12}(NCS)]$, presumably as a result of a degradation reaction. However, systematic attempts to increase the yield of this product by a rational degradative synthesis have so far been unsuccessful. The ion represents the first stable example of an anionic eight-boron cluster in which no other element is present in the cluster and it may be regarded as a derivative of the hypothetical $[B_8H_{13}]^-$ anion.[9]

The reaction between $B_9H_{13}(SMe_2)$ and $[N(PPh_3)_2][BH_3(CN)]$ in 1,2-dichloroethane at 70 °C gave the ion $[B_9H_{13}(NC)BH_3]^-$, in low yield. Other products of the reaction were the anions $[B_9H_{14}]^-$ and $[BH_3(CN)BH_2(CN)]^-$.[10] At lower temperatures, no significant reaction was noted, and at reflux (82 °C), the anions $[B_9H_{14}]^-$ and $[BH_3(CN)BH_2(CN)]^-$ were formed exclusively [equations (2) and (3)]. Reactions (2) and (3) show

$$B_9H_{13}(SMe_2) + [BH_3(CN)]^- \longrightarrow [B_9H_{13}(NC)BH_3]^- + SMe_2 \quad (2)$$

$$B_9H_{13}(SMe_2) + 2[BH_3(CN)]^- \longrightarrow [B_9H_{14}]^- + [BH_3(CN)BH_2(CN)]^- + SMe_2 \quad (3)$$

examples of the dual chemical character of the $[BH_3(CN)]^-$ anion, in which it functions either as a two-electron σ-donor ligand [reaction (2)] or as a hydride-transfer reagent [reaction (3)].

It is interesting to note that preliminary experiments showed that when $B_{10}H_{14}$ was treated with 1 molar equivalent of $Na[BH_3(CN)]$ in aqueous dioxane, no substituted B_{10} or B_9 species were isolated, but $[B_9H_{14}]^-$ was obtained instead. In acetonitrile solution, $B_{10}H_{14}$ reacted with $[BH_3(CN)]^-$ to yield an equimolar mixture of $[B_{10}H_{13}]^-$ and $[B_{10}H_{15}]^-$ along with $[BH_3(CN)BH_2(CN)]^-$ and thus the $[BH_3(CN)]^-$ ion again acted as a hydride-transfer reagent. It should also be noted that, during the course of preparing $[B_3H_7(NC)BH_3]^-$,[11] a small quantity of $[BH_3(CN)BH_2(CN)]^-$ was also formed.

(*b*) *^{11}B and ^{1}H N.M.R. Spectra of Neutral and Anionic Derivatives*, $B_9H_{13}L$, $[B_9H_{13}X]^-$, *and* $[B_9H_{14}]^-$.—We have obtained ^{11}B spectra at 80.239 and 115.55 MHz and ^{1}H spectra at 250 and 360 MHz. A number of the compounds were examined with either broad-band or specific frequency-decoupling irradiation, and at several temperatures. We have been able to analyse BH_2 and bridge H couplings as a result of line-narrowing techniques which were not employed by previous workers. Table 1 lists the relevant ^{11}B and ^{1}H parameters for $[B_9H_{14}]^-$, $[B_9H_{13}(NCS)]^-$, $[B_9H_{13}(NC)BH_3]^-$, $B_9H_{13}(SMe_2)$, $B_9H_{13}(SEt_2)$, and $B_9H_{13}(CH_3CN)$. In contrast to previously reported results,[7] we find significant differences in the spectra of the anionic compounds from those of the neutral species.

Neutral derivatives. In the ^{11}B spectrum of $B_9H_{13}(CH_3CN)$ [Figure 2(*a*)] the resonance at −20.2 p.p.m. due to atoms

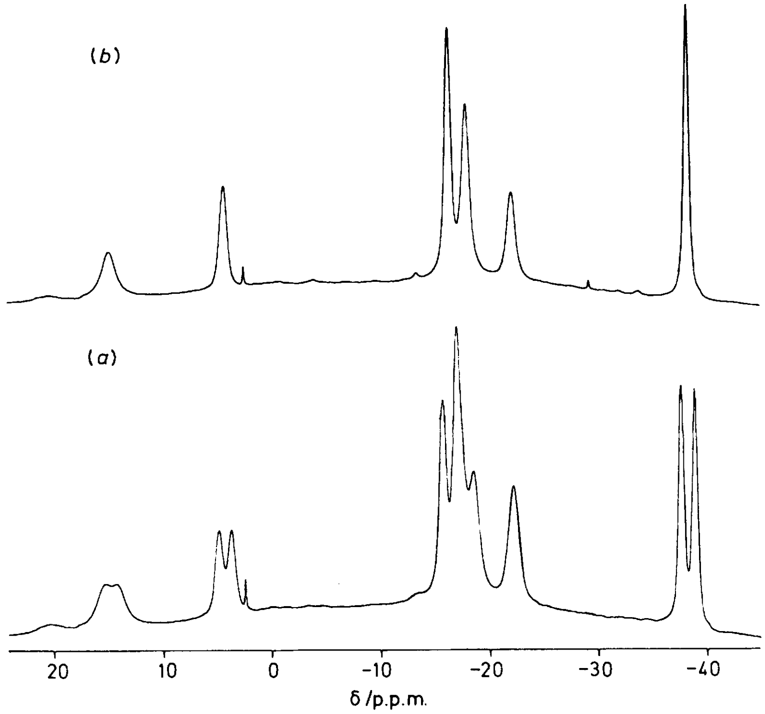

Figure 3. ^{11}B (*a*) and $^{11}B-\{^1H\}$ (*b*) n.m.r. spectra (115.55 MHz) of $[B_9H_{13}(NCS)]^-$

B(6) and B(8) appeared broad, and this was previously attributed to hydrogen exchange in the unique BH_2 groups. Through line-narrowing techniques [Figure 2(*b*)] we found that the broadening was due to poorly resolved couplings of *ca.* 60 and 30 Hz. Similar resolution was obtained for the corresponding resonance in the ^{11}B spectrum of $B_9H_{13}(SMe_2)$ and that of $B_9H_{13}(SEt_2)$. Thus, this resonance comprised a doublet of doublets of doublets, and is attributed to coupling from terminal (*exo*), terminal (*endo*), and bridging hydrogen atoms. The resonance at −14.0 p.p.m. of $B_9H_{13}(CH_3CN)$ [and corresponding resonances of $B_9H_{13}(SMe_2)$ and $B_9H_{13}(SEt_2)$] was also resolved into a doublet of doublets on line narrowing, due to coupling from terminal and bridging hydrogen atoms, and was assigned to the atoms B(5) and B(9). These assignments were further confirmed by selective irradiation at the bridging hydrogen resonance of $B_9H_{13}(CH_3CN)$, $B_9H_{13}(SMe_2)$, and $B_9H_{13}(SEt_2)$ which produced a selective sharpening of the ^{11}B resonances due to B(6), B(8), and B(5), B(9). Additionally, this irradiation also caused a small reduction in the coupling constant at B(4).

The ^1H spectra at 360 MHz of $B_9H_{13}(SMe_2)$ and $B_9H_{13}(SEt_2)$ were examined at 298 K with specific frequency $\{^{11}B\}$ decoupling. The results of these experiments enabled the assignments of ^1H shifts to the specific boron positions to which the protons are coupled (and consequently bonded). These assignments confirmed, without any ambiguity, that the structures of all these neutral derivatives are similar to that crystallographically determined for $B_9H_{13}(CH_3CN)$.[4] The results also show that in most cases the order of chemical shifts of the boron atoms followed those of the hydrogens which are bonded to them.

The ^1H spectra were examined in C_6D_6, CD_3CN, $CDCl_3$, and $CD_3C_6D_5$ at temperatures up to 363 K. Only minor changes were observed in the resonances due to hydrogens on the boron cage, primarily as a result of linewidth changes as a result of longer relaxation times at higher temperatures. No tautomerism of bridging and *endo*-terminal hydrogens was observed. However, significant changes in chemical shift of the resonances due to hydrogens on the Me_2S or Et_2S ligand were noted in different solvents (Table 2) and this presumably arises as a result of solvent association in the vicinity of the co-ordinated ligand.

Table 2. Solvent effect on ligand resonances in the ^1H spectra of $B_9H_{13}(SR_2)$ derivatives

(*a*) $B_9H_{13}(SMe_2)$

Solvent	*T*/K	ν/MHz	δ(Me)/p.p.m.
CD_3CN	294	250	2.57
$CD_3C_6D_5$	363	250	1.57
C_6D_6	333	250	1.50
C_6D_6	295	250	1.38
$CDCl_3$	298	360	2.59

(*b*) $B_9H_{13}(SEt_2)$

Solvent	*T*/K	ν/MHz	δ(CH_2)/ p.p.m.	δ(CH_3)/ p.p.m.
C_6D_6	295	250	2.01 [a]	0.70
C_6D_6	333	250	2.09 [a]	0.75
CD_3CN	298	360	1.93 [b]	1.4
$CDCl_3$	298	250	2.95 [c]	1.45

[a] Centre of ab(x_3) multiplet, δ(a–b) ≈ 40 Hz. [b] Centre of ab(x_3) multiplet, δ(a–b) < 10 Hz. [c] Centre of ab(x_3) multiplet, δ(a–b) ≈ 30 Hz.

Anionic derivatives. In the ^{11}B spectra of $[B_9H_{13}(NCS)]^-$ (Figure 3) and $[B_9H_{13}(NC)BH_3]^-$ five doublets were observed, similar to the corresponding resonances in the neutral $B_9H_{13}L$ species, but the resonance associated with the substituted atom B(4) was a singlet. In addition the spectrum of $[B_9H_{13}(NC)BH_3]^-$ exhibited a quartet due to the $BH_3(CN)$ moiety. In contrast to the neutral derivatives, the small couplings due to the *endo*-terminal hydrogens were not observed even in the line-narrowed spectra. Furthermore, selective irradiation at the ^1H resonance of the bridge hydro-

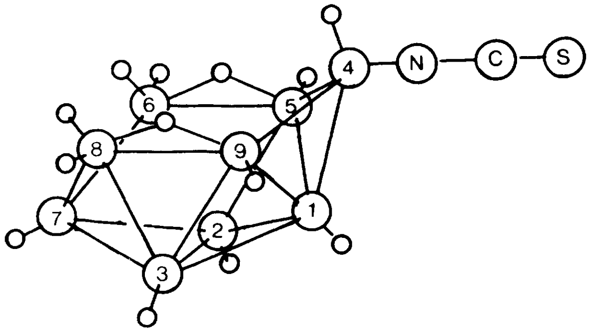

Figure 4. The structure of $[B_9H_{13}(NCS)]^-$

gens resulted in selective sharpening of the resonances due to atoms B(6) and B(8), B(5) and B(9), and B(4) in $[B_9H_{13}(NCS)]^-$. In addition, some decoupling, or reduction of the apparent magnitude of the terminal J(BH) coupling was observed in most of the resonances. The ^{11}B data suggested that these ions were fluxional, and further evidence of this was obtained from the ^1H spectrum of $[B_9H_{13}(NCS)]^-$. At room temperature the presence of five bridging hydrogens at $\delta = -1.4$ p.p.m. ($CDCl_3$ solution) was found. Thus, rapid intramolecular exchange occurred on the n.m.r. time-scale, and involved the two bridging hydrogens of the structure in Figure 4 with two *endo*-terminal hydrogens from B(6) and B(8) and the single terminal hydrogen from B(4). Proton n.m.r. spectra were also obtained at several temperatures down to 203 K, and at selected temperatures specific frequency $\{^{11}B\}$-decoupled spectra were recorded. At temperatures below 233 K the bridging hydrogen resonance, now observed near -3.3 p.p.m., showed the presence of only two bridging hydrogens. In addition a new resonance appeared at -0.41 p.p.m. indicating two hydrogens in an *endo*-terminal environment. When the temperature was reduced to 203 K difference spectra indicated a further new terminal hydrogen near 0.6 p.p.m. Thus, the intramolecular exchange between the bridging hydrogens, the two *endo*-terminal hydrogens, and the terminal hydrogen at B(4) was sufficiently slowed to indicate a coalescence temperature near 243 K, but the static structure was not fully achieved above 203 K.

$[B_9H_{14}]^-$. In agreement with previous work the ^{11}B spectrum of $[B_9H_{14}]^-$ consisted of three doublets, suggesting three-fold symmetry. However, selective $\{^1H\}$ irradiation at the bridging hydrogen resonance resulted in decoupling at all three boron resonances at high decoupling power, whereas at low power only B(1)—B(3) were affected. The ^1H spectrum showed five fluxional bridging hydrogens at -1.5 p.p.m. at all temperatures down to 203 K.

From these results we can conclude that the substitution of an anionic ligand for a neutral ligand on the $B_9H_{13}L$ cage substantially lowers the energy barrier to intramolecular hydrogen exchange, although the static structures of the neutral and anionic derivatives are similar. {Preliminary crystallographic data [12] on $[N(PPh_3)_2][B_9H_{13}(NCS)]$ indicate that its heavy-atom structure is similar to that of $B_9H_{13}(CH_3CN)$, although exact positions of the *endo*-terminal hydrogens have not yet been located.} The substituted anionic derivatives are therefore intermediate in their behaviour between the neutral compounds and the unsubstituted $[B_9H_{14}]^-$ anion.

It is pertinent to note that the differences in the hydrogen arrangements of the $[B_9H_{14}]^-$ ion and the derivatives $B_9H_{13}X$ or $B_9H_{13}L$ are smaller than is at first sight apparent. An alternative description of the substituted derivatives is one in which the substituent is placed in the *exo*-position of B(6) [or B(8)] in the numbering scheme of $[B_9H_{14}]^-$, with the minor transpositions of the *endo*-hydrogen at B(7) to a bridging position and of a bridging hydrogen to an *endo*-terminal site of B(4).

(*c*) *^{11}B and ^1H N.M.R. Spectra and Structure of* $[B_8H_{12}(NCS)]^-$.—The ^{11}B n.m.r. spectrum of $[B_8H_{12}(NCS)]^-$, shown in Figure 5, comprised five doublets of relative area 1, one doublet of relative area 2, and a triplet of relative area 1. The detailed parameters and their assignments are presented in Table 3. The ^1H spectrum showed a complex pattern of overlapping 1 : 1 : 1 : 1 quartets due to terminal hydrogens on boron, and in addition, two resonances of relative area 2 : 1 at -2.1 and -3.0 p.p.m. which may be assigned to bridging hydrogens. Proton n.m.r. spectra with specific frequency boron decoupling were also obtained (Table 3) and confirm the assignments derived from the ^{11}B spectrum. The proximity of the ^{11}B signals of B(1) and B(6), B(7) resulted in the ^1H-$\{^{11}B\}$ experiments not being completely selective. The n.m.r. data are consistent with a structure (Figure 6) with no plane of symmetry. It is presented to show the relationship with the structure of $[B_9H_{13}(NCS)]^-$ (Figure 4), whose numbering system has been retained to avoid confusion. Formal removal of B(8) from $[B_9H_{13}(NCS)]^-$ and rearrangement of hydrogens around the resulting open face yields $[B_8H_{12}(NCS)]^-$.

The proposed structure is in accord with that predicted for compounds of the type $B_8H_{12}L$,[13] and is structurally related to the known derivative $[(EtHN)B_8H_{11}(NH_2Et)]$.[14] It is likely that the compound is also structurally similar to the neutral derivatives $B_8H_{12}(NMe_3)$ and $B_8H_{12}(CH_3CN)$, whose ^{11}B n.m.r. spectra have been recorded only at 19.3 MHz.[15]

Experimental

I.r. Spectroscopy.—The i.r. spectra were obtained as mulls in Nujol or hexachloro-1,4-butadiene or as thin films between KBr plates. They were recorded on a Perkin-Elmer 457 grating i.r. spectrometer.

N.M.R.—250-MHz ^1H and 80.24-MHz ^{11}B n.m.r. spectra were recorded on a Bruker WH-250 spectrometer, 115.55-MHz ^{11}B and 360.13-MHz ^1H and ^1H-$\{^{11}B\}$ spectra on a Bruker WH 360 spectrometer. Boron-11 frequencies used in ^1H-$\{^{11}B\}$ spectra were obtained by running boron spectra on the decoupler coils of the proton probe, immediately prior to obtaining the proton spectra. The ^1H-$\{^{1}B\}$ specific frequency-decoupling experiments were obtained using decoupler powers typically of the order of 0.5 W, which allowed for boron resonances 0.5 p.p.m. apart to be decoupled individually. Lock was achieved in these cases by the use of a deuteriated solvent. Chemical shifts, δ, are quoted as being negative to high field of the reference standards which were tetramethylsilane for ^1H n.m.r. and $BF_3{\cdot}OEt_2$ for ^{11}B n.m.r. All spectra were recorded at ambient temperatures (25—30 °C) unless otherwise stated.

Intermediates and Reagents.—*nido*-Decaborane was purchased from Callery Chemical Company and was purified by sublimation before use. The salt $[NMe_4][B_9H_{14}]$ was prepared by the method of Greenwood and co-workers; [1b] $[N(PPh_3)_2][BH_3(CN)]$ and $[N(PPh_3)_2][NCS]$ were prepared from $[N(PPh_3)_2]Cl$ and $Na[BH_3(CN)]$ and KNCS, respectively, in water. All other reagents were used as received.

Preparations.—$B_{10}H_{12}(SMe_2)_2$. This was prepared by a slight modification of the method of Greenwood and co-workers.[16] *nido*-Decaborane (3.66 g, 30 mmol) was dissolved in an excess of Me_2S and set aside for 60 h at room temperature

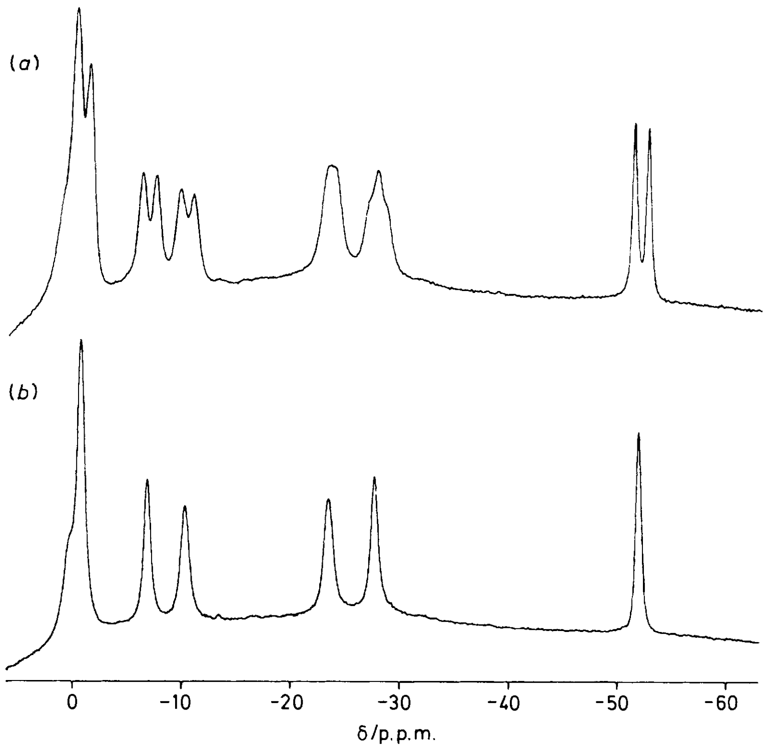

Figure 5. ^{11}B (*a*) and $^{11}B\text{-}\{^{1}H\}$ (*b*) n.m.r. spectra (115.55 MHz) of $[B_8H_{12}(NCS)]^-$

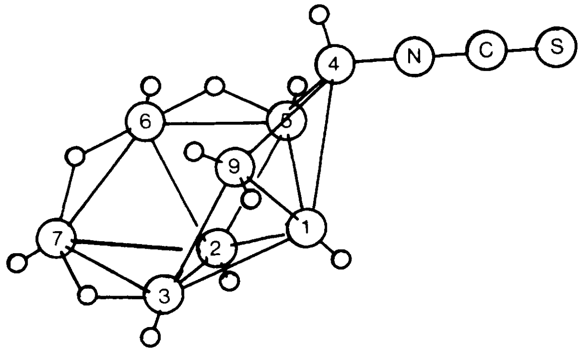

Figure 6. Proposed structure of $[B_8H_{12}(NCS)]^-$

(*ca.* 20 °C) in a flask equipped with a reflux condenser and a drying tube. The white crystals which formed were washed with diethyl ether and dried under vacuum (6.59 g, 90%). The product was identified by comparison of its ^{11}B n.m.r. spectrum with that in the literature.[17]

$B_9H_{13}(SMe_2)$. This was prepared by a slight modification of the method of Hawthorne and co-workers.[3a] The compound $B_{10}H_{12}(SMe_2)_2$ (6.59 g, 27 mmol) was refluxed in dry CH_3OH (30 cm^3) for 0.5 h. The reaction mixture was cooled to *ca.* 20 °C and the solvent removed under reduced pressure. The residue was extracted into diethyl ether (150 cm^3) and the ether extract evaporated to dryness to yield a white solid which was identified as $B_9H_{13}(SMe_2)$ (3.30 g, 71%) by comparison of its ^{11}B n.m.r. spectrum with that in the literature.[7]

$B_9H_{13}(CH_3CN)$. This was prepared by the electrochemical oxidation, at a platinum electrode, of an acetonitrile solution of $[NMe_4][B_9H_{14}]$. The salt $[NMe_4][B_9H_{14}]$ (0.185 g, 1 mmol) was dissolved in acetonitrile (20 cm^3) and introduced into the anode compartment of the electrochemical cell. The cathode compartment contained a solution of $[NBu^n_4][BF_4]$ (0.1 mol dm^{-3}) in acetonitrile (20 cm^3). Both working and secondary electrodes were constructed from platinum foil. A potential of +0.75 V was applied to the working electrode and 900 C were passed (93% of theoretical for a one-electron oxidation). Gas evolution was observed in the anode compartment. T.l.c. analysis of the anolyte solution, using 90% CH_2Cl_2–10% CH_3CN as eluant, showed the presence of a major component (R_f = 0.85) and a number of very minor components of lower R_f values. The solvent was removed from the anolyte and the residue was chromatographed on silica gel using the above solvent system as eluant. Fractions containing the major product were collected and the solvent removed to yield a white solid which was identified as $B_9H_{13}(CH_3CN)$ by comparison of its ^{11}B n.m.r. spectrum with that in the literature.[7]

$[B_9H_{13}(NCS)]^-$ *and* $[B_8H_{12}(NCS)]^-$. The compounds $B_9H_{13}(SMe_2)$ (1.72 g, 10 mmol) and $[N(PPh_3)_2][NCS]$ (6.69 g, 11 mmol) were dissolved in 1,2-dichloroethane (50 cm^3) and the solution was held at the reflux temperature (82 °C) for 1.5 h. After cooling to *ca.* 20 °C, t.l.c. analysis of the solution using CH_2Cl_2 as eluant showed the presence of a major product (R_f = 0.70) and a minor product (R_f = 0.30). All the $B_9H_{13}(SMe_2)$ was consumed. The solvent was removed under vacuum and the residue dissolved in the minimum of CH_2Cl_2 and chromatographed on silica gel using CH_2Cl_2 as eluant. Fractions containing the major product were eluted first. The solvent was removed from these fractions, under reduced pressure, and the residue recrystallized from CH_2Cl_2–n-hexane to yield a white solid (3.50 g, 49%) which was identified as $[N(PPh_3)_2][B_9H_{13}(NCS)]$ as described in the Results and Discussion section. The minor component was eluted next and the fractions containing this product were evaporated to dryness. The residue was recrystallized from CH_2Cl_2–n-hexane to yield a *white solid* (0.19 g, 3%) which

Table 3. ^{11}B and ^{1}H-{^{11}B, continuous wave} n.m.r. spectroscopic data for $[B_8H_{12}(NCS)]^-$ in $CDCl_3$

	^{11}B		^{1}H	
Position	δ/p.p.m.*	J(BH)/Hz	δ/p.p.m.	Comments
1	0.3	155	3.0	Some enhancement of bridging H signals due to proximity of B(1) and B(6), B(7) resonances
6, 7	−0.8	140	2.93 2.27	Sharpening of bridging H resonances at δ = −2.1 and −3.0
3	−6.9	152	2.35	Sharpening of bridging H resonance at δ = −2.1
5	−10.4	140	2.11	As for B(3)
4	−23.6	93	1.42	
9	−27.8(t)	90	0.79 0.23	BH_2 group with non-equivalent H atoms
2	−52.0	146	−0.56	

* All unlabelled signals were doublets; t = triplet.

was identified as $[N(PPh_3)_2][B_8H_{12}(NCS)]$ as described in the Results and Discussion section.

$[B_9H_{13}(NC)BH_3]^-$. The compounds $B_9H_{13}(SMe_2)$ (1.72 g, 10 mmol) and $[N(PPh_3)_2][BH_3(CN)]$ (6.38 g, 11 mmol) were dissolved in 1,2-dichloroethane (50 cm^3) and the solution was held at 70 °C for 2 h. On cooling to *ca.* 20 °C, t.l.c. analysis of the solution, using CH_2Cl_2 as eluant, showed the presence of three major products (R_f = 0.70, 0.55, and 0.30). The solvent was removed under vacuum and the residue dissolved in the minimum of CH_2Cl_2 (20 cm^3). An excess of diethyl ether (150 cm^3) was added, resulting in the precipitation of a white solid (I). The filtrate was reduced to dryness under vacuum to yield a second white solid (II). T.l.c. analysis of (I), using CH_2Cl_2 as eluant, showed it to contain two major species (R_f = 0.55 and 0.30). Solid (I) was dissolved in the minimum of CH_2Cl_2 and chromatographed on silica gel using CH_2Cl_2 as eluant. The solvent was removed from fractions containing the first component eluted to yield a white solid (2.28 g, 35%) which was identified as $[N(PPh_3)_2][B_9H_{14}]$ by comparison of its ^{11}B n.m.r. spectrum with that of an authentic sample. The second component eluted was identified as $[N(PPh_3)_2][BH_3(CN)BH_2(CN)]$ (0.98 g, 16%) by comparison of its ^{11}B n.m.r. and i.r. spectra with those of an authentic sample.

T.l.c. analysis of solid (II) showed the presence of a single major component (R_f = 0.70). The solid was dissolved in the minimum of CH_2Cl_2 and chromatographed on silica gel using CH_2Cl_2 as eluant. Fractions containing the first product eluted were evaporated to dryness and the residue was recrystallized from CH_2Cl_2–n-hexane to yield a white solid (1.04 g, 15%) which was identified as $[N(PPh_3)_2][B_9H_{13}(NC)BH_3]$ as described in the Results and Discussion section.

Reaction between $B_{10}H_{14}$ *and* $[BH_3(CN)]^-$.—(*a*) *In aqueous dioxane*. The compounds $B_{10}H_{14}$ (0.61 g, 5 mmol) and $Na[BH_3(CN)]$ (0.31 g, 5 mmol) were suspended in water (40 cm^3). Dioxane (40 cm^3) was added and the mixture stirred for 18 h. The $B_{10}H_{14}$ dissolved with some gas evolution and the solution turned yellow. The mixture was filtered and a solution of $[NMe_4]Br$ (1.54 g, 10 mmol) in water (10 cm^3) was added to the filtrate to yield a white precipitate. This was filtered off, dried under vacuum, and shown to be $[NMe_4][B_9H_{14}]$ by comparison of its ^{11}B n.m.r. spectrum with that of an authentic sample.

(*b*) *In acetonitrile*. The compounds $B_{10}H_{14}$ (0.122 g, 1 mmol) and $[NBu^n_4][BH_3(CN)]$ (0.564 g, 2 mmol) were dissolved in CH_3CN (10 cm^3). The solution was heated to *ca.* 50 °C for 1 h and examined by ^{11}B n.m.r. spectroscopy. This showed the presence of an equimolar mixture of the anions $[B_{10}H_{13}]^-$ and $[B_{10}H_{15}]^-$, along with $[BH_3(CN)BH_2(CN)]^-$.

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