Borane Anions with Bridging Cyanide Ligands; Preparation and Properties of Derivatives of $[B_3H_8]^-$ and $[B_9H_{14}]^-$

Dominic G. Meina and John H. Morris *
Department of Pure and Applied Chemistry, University of Strathclyde, 295 Cathedral Street, Glasgow G1 1XL

A series of cyanide-bridged derivatives of the *arachno*-octahydrotriborate(1 −) and *arachno*-tetradecahydrononaborate(1 −) ions, $[B_3H_8]^-$ and $[B_9H_{14}]^-$ respectively, have been prepared using chemical and electrochemical methods. Compounds prepared include the triborate species $[B_3H_7(NC)B_3H_7]^-$ and its substituted derivatives, $[B_3H_6Cl(NC)B_3H_7]^-$ and $[B_3H_6Cl(NC)B_3H_6Cl]^-$ together with the ions $[B_3H_7(NC)BH_2(NC)BH_3]^-$ and $[B_3H_7(NC)BPh_3]^-$. The ions $[B_3H_7(NC)BH_2(CN)]^-$ and $[B_3H_7(NC)BH_2(CN)B_3H_7]^-$ have also been obtained. The nonaborate derivatives include $[B_9H_{13}(NC)BPh_3]^-$, $[B_9H_{13}(NC)BH_2(NC)BH_3]^-$, $[B_9H_{13}(NC)BH_2(CN)]^-$, and $[B_9H_{13}(NC)BH_2(CN)B_9H_{13}]^-$.

Previously, the ability of the cyanide group to bridge between two borane species has been restricted to derivatives of $[BH_3(CN)]^-$ in which co-ordination of this ion occurred to another borane acceptor. Species of this type included those of monoborane acceptors, *e.g.* $[BH_3(CN)BH_3]^-$, $[BH_3(CN)BH_2(CN)]^-$ and the polymeric $[BH_2(CN)]_x$.[1–4] We have also described recently the species $[BH_3(CN)B_3H_7]^-$ and $[BH_3(CN)B_9H_{13}]^-$ [5,6] and have also reported the complex ion, $[Ag\{(CN)B_3H_7\}_2]^-$.[7]

Earlier work[1] on the reaction of B_4H_{10} with Na(CN) was reported to result in its symmetric cleavage to yield $Na[B_3H_7(CN)]$ as one product, although this must be questioned since our previous studies had failed to synthesise this ion by more direct methods.[3a,7] We have therefore investigated the behaviour of the cyanide group towards polyborane systems more thoroughly. Some of our previous unpublished work[8] indicated that the cyanide group may bridge between two polyborane moieties, since we had some evidence for $[B_9H_{13}(NC)B_9H_{13}]^-$.

We now wish to report the synthesis of a number of new cyanide-bridged derivatives from the polyborane acceptors B_3H_7 and B_9H_{13}, including several in which two polyborane acceptors are involved. We report their characterisation primarily through ^{11}B and ^1H n.m.r. spectroscopy and describe some of their chemical behaviour.

Experimental

Starting Materials and Reagents.—The solvents CH_2Cl_2 and MeCN were of high-performance liquid chromatography grade and were dried over CaH_2. The supporting electrolyte $[NBu^n{}_4][BF_4]$ and $Na[BPh_3(CN)]$ were used as supplied (Fluka A.G.). The reagent $Na[BH_3(CN)BH_2(CN)]$ was prepared as previously described.[3a] The $[N(PPh_3)_2]^+$ salts of $[BH_3(CN)BH_2(CN)]^-$ and $[BPh_3(CN)]^-$ were prepared by mixing $[N(PPh_3)_2]Cl$ and the sodium salt of the anion in water, and extracting the product by phase transfer into dichloromethane. After the solvent was removed, the products were recrystallised from CH_2Cl_2–Et_2O to give colourless needle-like crystals.

$Na[BH_2(CN)_2]$ was obtained by the published method.[9] $[N(PPh_3)_2][BH_2(CN)_2]$ was prepared by adding a solution of $Na[BH_2(CN)_2]$ in water to an excess of $[N(PPh_3)_2]Cl$ in MeOH. The white precipitate which immediately formed was filtered off, extracted into CH_2Cl_2, and recrystallised by dropwise addition of Et_2O.

Electrochemical Method.—Cyclic and a.c. voltammetry were carried out using a model 363 E.G. and G. Princeton Applied Research potentiostat, a Hi-Tek Instruments Ltd. waveform generator (model PPR1), and a home-built a.c. generator, phase-sensitive detector, and amplifier system. Voltammograms were recorded on a Bryans 25000 *X–Y* recorder. Coulometry was carried out using a Hi-Tek Instruments Ltd. DT2101 potentiostat and gated digital integrator. Undivided cells were used for voltammetry, but two-compartment cells separated by Nafion 427 ion-exchange membrane were used for coulometry. Working and secondary electrodes were made from platinum wire or mesh. The reference electrodes were Ag–$AgNO_3$ (0.1 mol dm^{-3}) in MeCN or Ag–$[N(PPh_3)_2]Cl$ (0.1 mol dm^{-3}) in CH_2Cl_2, and the reference solution was separated from the anode by a porous ceramic sinter.

N.M.R. Spectra.—These were recorded on Bruker WH250 and WH360 spectrometers (^1H, 250 and 360 MHz; ^{11}B, 80.2 and 115.5 MHz) as solutions in $CDCl_3$ or CD_3CN. Chemical shifts are quoted as being positive to high frequency (low field) of the reference standards $SiMe_4$ or $BF_3{\cdot}OEt_2$.

Synthesis of $[N(PPh_3)_2][B_3H_7(NC)BPh_3]$, (**1**).—$[N(PPh_3)_2][B_3H_7Cl]$ (0.61 g, 1 mmol) and $[N(PPh_3)_2][BPh_3(CN)]$ (0.806 g, 1 mmol) were placed in a 250-cm^3 round-bottomed flask fitted with a stopcock adapter. Dried, degassed CH_2Cl_2 (40 cm^3) was condensed in under vacuum and the resulting clear solution stirred for 4 h at room temperature. Thin-layer chromatographic (t.l.c.) analysis of the solution on silica using 100% CH_2Cl_2 as eluant (conditions under which $[N(PPh_3)_2]Cl$ has $R_f = 0$) showed a single major product ($R_f = 0.69$). Purification by column chromatography on silica gel using 100% CH_2Cl_2 as eluant gave $[N(PPh_3)_2][B_3H_7(NC)BPh_3]$ (**1**) as a white solid (0.67 g, 0.8 mmol, 80% yield). Recrystallisation from CH_2Cl_2–Et_2O produced colourless needles (analytical data in Table 1).

Synthesis of $[N(PPh_3)_2][B_3H_7(NC)BH_2(NC)BH_3]$, (**2**).—This was prepared in a manner similar to (**1**) and was obtained as a colourless oil, crystalline at low temperatures, in 78% yield ($R_f = 0.8$).

Synthesis of $[N(PPh_3)_2][B_3H_7(NC)B_3H_7]$, (**3**).—Cyanogen bromide, BrCN (0.617 g, 5.83 mmol), was placed in a round-bottomed flask fitted with a stopcock adapter. Dried, degassed CH_2Cl_2 was condensed in under vacuum, the mixture allowed

Table 1. Analytical data for bridging cyanide derivatives (**1**)—(**10**)

	Analysis (%)							
	C		H		N		P	
Compound	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.
(**1**)	77.80	78.05	6.20	6.20	3.00	3.30	7.70	7.30
(**3**)	68.90	69.00	6.95	6.90	4.30	4.35	9.65	9.65
(**4**)	72.15	72.00	6.35	6.35	2.55	3.05	6.60	6.75
(**7**)	59.60	63.90	6.05	6.35	5.30	5.90	8.30	8.65
(**9**)	70.45	70.95	6.10	6.10	5.20	6.55	9.70	9.65
(**10**)	65.50	65.50	6.50	6.40	3.95	4.15	9.00	9.15

to warm to room temperature and stirred until the BrCN had dissolved. The clear solution was cooled to −196 °C and $[N(PPh_3)_2][B_3H_8]$ (6.74 g, 11.65 mmol) introduced. After the mixture had been re-evacuated and warmed to room temperature, there was vigorous gas evolution and the reaction was continued until gas evolution had ceased. T.l.c. analysis of the solution indicated a major component ($R_f = 0.61$) and a minor component ($R_f = 0.4$). Separation by column chromatography on silica gel using 100% CH_2Cl_2 as eluant yielded the first fraction, identified as $[N(PPh_3)_2][B_3H_7(NC)B_3H_7]$ (**3**) (analytical data in Table 1) (1.425 g). Recrystallisation from CH_2Cl_2–n-C_6H_{14} gave colourless cubic crystals in 38% yield. The second fraction eluted was shown to be $[N(PPh_3)_2][B_3H_7(NC)BH_3]$ by comparison with authentic material.

Synthesis of $[N(PPh_3)_2][B_9H_{13}(NC)BPh_3]$, (**4**).—$B_9H_{13}(SMe_2)$ (0.34 g, 2 mmol) and $[N(PPh_3)_2][BPh_3(CN)]$ (1.6 g, 2.1 mmol) were placed in a 250-cm^3 three-necked flask fitted with a condenser and thermometer, and flushed with dry nitrogen. Dry 1,2-$C_2H_4Cl_2$ was added and the clear solution refluxed under nitrogen for 1.5 h, during which time a white precipitate formed. This was filtered off and identified as $B(OH)_3$. T.l.c. analysis of the solution indicated a major component ($R_f = 0.67$) and several minor components. Purification by column chromatography on silica gel yielded the major product as a white solid, (**4**), which was recrystallised from CH_2Cl_2–Et_2O in 77% yield (analytical data in Table 1).

Synthesis of $[N(PPh_3)_2][B_9H_{13}(NC)BH_2(NC)BH_3]$, (**5**).—This was prepared by a procedure similar to that for (**4**). T.l.c. analysis using 100% CH_2Cl_2 as eluant showed a single major product ($R_f = 0.70$), which was purified by column chromatography. It was obtained as a colourless oil in 82% yield.

Synthesis of $[N(PPh_3)_2][B_9H_{13}(NC)BH_2(CN)B_9H_{13}]$, (**6**), *and* $[N(PPh_3)_2][B_9H_{13}(NC)BH_2(CN)]$, (**7**).—$B_9H_{13}(SMe_2)$ (0.86 g, 5 mmol) and $[N(PPh_3)_2][BH_2(CN)_2]$ (3.70 g, 6.1 mmol) were placed in a three-necked round-bottomed flask fitted with a condenser and thermometer, and flushed with dry nitrogen. 1,2-$C_2H_4Cl_2$ (*ca.* 50 cm^3) was added and the clear solution refluxed for 3 h. A white precipitate, identified as $B(OH)_3$, was filtered off and the filtrate reduced to a white solid under vacuum. T.l.c. analysis on silica using 100% CH_2Cl_2 as eluant indicated a major fraction ($R_f = 0.42$) and a minor fraction ($R_f = 0.67$). Purification by column chromatography on silica gel using 100% CH_2Cl_2 as eluant gave the first fraction as an oil in low yield (0.48 g, 23%). This was identified as $[N(PPh_3)_2][B_9H_{13}(NC)BH_2(CN)B_9H_{13}]$ (**6**) by its ^{11}B n.m.r. spectrum.

The second fraction was collected and reduced under vacuum to a clear, crystalline solid, which was recrystallised from CH_2Cl_2–n-C_6H_{14} (2.2 g, 62%) and identified as $[N(PPh_3)_2][B_9H_{13}(NC)BH_2(CN)]$ (**7**) by its ^{11}B n.m.r. spectrum.

It was found that if the reaction was carried out using a $B_9H_{13}(SMe_2)$ to $[N(PPh_3)_2][BH_2(CN)_2]$ mol ratio of 2:1, the major product was $[N(PPh_3)_2][B_9H_{13}(NC)BH_2(CN)B_9H_{13}]$ (**6**) (yield 54%).

Synthesis of $[N(PPh_3)_2][B_3H_7(NC)BH_2(CN)B_3H_7]$, (**8**), *and* $[N(PPh_3)_2][B_3H_7(NC)BH_2(CN)]$, (**9**).—$[N(PPh_3)_2][B_3H_7Cl]$ (3.68 g, 6 mmol) and $[N(PPh_3)_2][BH_2(CN)_2]$ (4.10 g, 6.8 mmol) were placed in a 250-cm^3 flask fitted with a stopcock adapter. Dried, degassed CH_2Cl_2 (*ca.* 50 cm^3) was condensed in under vacuum. The solution was allowed to warm to room temperature and stirred for 4 h, after which time the solvent was removed under reduced pressure. T.l.c. analysis of the white solid on silica using 100% CH_2Cl_2 as eluant indicated a minor component ($R_f = 0.65$) and a major component ($R_f = 0.32$). Purification by column chromatography on silica gel using 100% CH_2Cl_2 as eluant gave the first fraction containing (**8**) as a crystalline white solid in low yield (0.68 g, 16.6%). The second fraction, recrystallised from CH_2Cl_2–n-C_6H_{14}, gave colourless needle-like crystals of (**9**) (2.2 g, 57% yield) (analytical data in Table 1).

Substitution Reactions of $[B_3H_7(NC)B_3H_7]^-$.—$[N(PPh_3)_2][B_3H_7(NC)B_3H_7]$ (0.706 g, 1.09 mmol) was placed in a 250-cm^3 flask fitted with a stopcock adapter. Dried, degassed CH_2Cl_2 (30 cm^3) was condensed in under vacuum. Gaseous HCl (6 mmol) was introduced and the mixture stirred for 3 h. Dichloromethane was removed under vacuum to yield a white solid. T.l.c. analysis showed a single major fraction ($R_f = 0.67$) and recrystallisation from CH_2Cl_2–n-C_6H_{14} gave colourless crystals in 82% yield. The analytical data for the product, $[N(PPh_3)_2][B_3H_6Cl(NC)B_3H_7]$, (**10**), are presented in Table 1.

Electrochemical Synthesis of $[N(PPh_3)_2][B_3H_6Cl(NC)B_3H_7]$, (**10**), *and* $[N(PPh_3)_2][B_3H_6Cl(NC)B_3H_6Cl]$, (**11**).—$[N(PPh_3)_2][B_3H_7(NC)B_3H_7]$ (0.42 g, 0.65 mmol) was placed in the anodic compartment of a divided cell together with 20 cm^3 of a solution of $[NBu^n{}_4][BF_4]$ (0.4 mol dm^{-3}) in CH_2Cl_2. The cathode compartment was charged with *ca.* 50 cm^3 of 40% aqueous HBF_4 to minimise the cell resistance. The anode was a large Pt mesh and the cathode was Pt foil. A reference electrode {Ag–[N(PPh$_3$)$_2$]Cl (0.1 mol dm^{-3}) in CH_2Cl_2} was inserted in the anode compartment. Initial experiments had shown that high currents of *ca.* 120 mA through the cell caused local heating at the membrane interface, resulting in the solvent boiling. Therefore, the oxidation was carried out at 0 °C in an ice-bath. Constant potential electrolysis was carried out at a potential of 1.6 V and was continued until a charge equivalent to a two-electron oxidation had passed. T.l.c. analysis on the contents of the anode compartment using 100% CH_2Cl_2 as eluant indicated a single major component ($R_f = 0.6$). Separation by column chromatography on silica using 100% CH_2Cl_2 as eluant resulted in a white solid, identified as $[N(PPh_3)_2][B_3H_6Cl(NC)B_3H_7]$ (**10**) in 60% yield.

When the electrochemical oxidation was continued until a charge equivalent to five- or six-electron equivalents had passed, the major product obtained ($R_f = 0.65$) was $[N(PPh_3)_2][B_3H_6Cl(NC)B_3H_6Cl]$ (**11**) in 45% yield as a white solid.

When $[N(PPh_3)_2]Cl$ (0.1 mol dm^{-3}) in CH_2Cl_2 was used as the supporting electrolyte solution in an undivided cell, (**11**) was obtained in low yield.

Anodic Dissolution of Copper in an Acetonitrile Solution of $[B_3H_7(NC)BPh_3]^-$.—$[N(PPh_3)_2][B_3N_7(NC)BPh_3]$ (0.845 g, 1 mmol) and PPh_3 (0.526 g, 2 mmol) were 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

Table 2. ^{11}B N.m.r. spectral data for the complexes obtained by anodic dissolution

	$\delta(^{11}B)$ in $CDCl_3$/p.p.m.		
Complex	B(1)	B(2), B(3)	Other
$[Cu(PPh_3)_2\{B_3H_7(NC)BPh_3\}]$	−17.35	−30.40	−37.00 ($BH_3{\cdot}PPh_3$) −11.65 (BPh_3)
$[Ag(PPh_3)_2\{B_3H_7(NC)B_3H_7\}]$	−34.85*	−12.42*	
	−49.69	−12.42	

* *N*-Co-ordinated cage resonance.

acetonitrile (20 cm^3). Both working and secondary electrodes were constructed of copper foil. A potential of 0.0 V was applied to the working electrode and the initially high current (32 mA) fell exponentially to 2 mA after 121 C had passed. In this case the anolyte did not change colour as the electrolysis progressed. The net weight loss of the copper anode was 0.0602 g (*cf.* the theoretical value of 0.0635 g for Cu → Cu^I). The solvent was removed under reduced pressure to give a white solid. T.l.c. analysis of the white solid on silica gel indicated the presence of a single major product (R_f = 0.62) and several minor products. Purification by chromatography on silica gel yielded the major component as a white solid. The ^{11}B n.m.r. spectrum (Table 2) of the purified product indicated the presence of $[Cu(PPh_3)_2\{B_3H_7(NC)BPh_3\}]$ and $BH_3{\cdot}PPh_3$.

Anodic Dissolution of Silver in a Dichloromethane Solution of $[B_3H_7(NC)B_3H_7]^-$.—$[N(PPh_3)_2][B_3H_7(NC)B_3H_7]$ (0.643 g, 1 mmol) and PPh_3 (0.526 g, 2 mmol) were dissolved in a solution of $[N(PPh_3)_2]Cl$ (0.1 mol dm^{-3}) in dichloromethane (20 cm^3) and introduced into the anode compartment of the electrochemical cell. The cathode compartment contained a solution of $[N(PPh_3)_2]Cl$ (0.1 mol dm^{-3}) in CH_2Cl_2 (20 cm^3). The working electrode was a silver wire and the secondary electrode was platinum foil. A potential of 1.0 V was applied to the working electrode and the initially high current (64 mA) fell exponentially to 2 mA after 103 C had passed. A crystalline white precipitate was formed during electrolysis that redissolved on heating. The white precipitate was thought to be $[N(PPh_3)_2]Cl$. The net weight loss of the silver anode was 0.1066 g (*cf.* the theoretical value of 0.1078 g for Ag → Ag^I). The solvent was removed from the anolyte under reduced pressure to give a white crystalline solid. T.l.c. analysis on silica gel using 100% CH_2Cl_2 as eluant showed a single major fraction (R_f = 0.52). The 80.2-MHz ^{11}B n.m.r. spectrum of the crude product indicated the presence of the metallaborane $[Ag(PPh_3)_2\{B_3H_7(NC)B_3H_7\}]$.

Results and Discussion

It has previously been established that the octahydrotriborate(1−) ion, $[B_3H_8]^-$, will undergo substitution reactions to form mono- and di-substituted derivatives, particularly with halides or pseudohalides such as F^-, Cl^-, Br^-, NCS^-, $NCSe^-$, or NCO^-.[5,7] However, our attempts to prepare triborane derivatives with a simple CN^- substituent have been unsuccessful, and reactions of the chloride-substituted ions $[B_3H_7Cl]^-$ or $[B_3H_6Cl_2]^-$ with Ag(CN) led instead to the silver bridged anions, $[Ag\{(CN)B_3H_7\}_2]^-$ or $[Ag\{(CN)B_3H_6Cl\}_2]^-$.[7,10] Furthermore, we had observed that the anion $[BH_3(CN)]^-$ would displace halide and produce cyanide-bridged species involving monoboron and triboron fragments, in which the carbon was associated with the BH_3 and nitrogen with B_3H_7, *e.g.* $[B_3H_7(NC)BH_3]^-$.[5,7] We have therefore examined the versatility of the cyanide group to bridge between a variety of borane acceptors and have synthesised a number of new compounds by a variety of synthetic techniques.

Synthetic Methods.—The first and simplest synthetic method involved the now established route of utilising the displacement of a labile substituent on a borane species by a cyanide on another borane group. Equations (1)—(8) summarise the species prepared by this method.

$$[B_3H_7Cl]^- + [BPh_3(CN)]^- \longrightarrow [B_3H_7(NC)BPh_3]^-\ (\mathbf{1}) + Cl^- \quad (1)$$

$$[B_3H_7Cl]^- + [BH_3(CN)BH_2(CN)]^- \longrightarrow [B_3H_7(NC)BH_2(NC)BH_3]^-\ (\mathbf{2}) + Cl^- \quad (2)$$

$$B_9H_{13}(SMe_2) + [BPh_3(CN)]^- \longrightarrow [B_9H_{13}(NC)BPh_3]^-\ (\mathbf{4}) + SMe_2 \quad (3)$$

$$B_9H_{13}(SMe_2) + [BH_3(CN)BH_2(CN)]^- \longrightarrow [B_9H_{13}(NC)BH_2(NC)BH_3]^-\ (\mathbf{5}) + SMe_2 \quad (4)$$

$$B_9H_{13}(SMe_2) + [BH_2(CN)_2]^- \longrightarrow [B_9H_{13}(NC)BH_2(CN)]^-\ (\mathbf{7}) + SMe_2 \quad (5)$$

$$2B_9H_{13}(SMe_2) + [BH_2(CN)_2]^- \longrightarrow [B_9H_{13}(NC)BH_2(CN)B_9H_{13}]^-\ (\mathbf{6}) + 2SMe_2 \quad (6)$$

$$[B_3H_7Cl]^- + [BH_2(CN)_2]^- \longrightarrow [B_3H_7(NC)BH_2(CN)]^-\ (\mathbf{9}) + Cl^- \quad (7)$$

$$2[B_3H_7Cl]^- + [BH_2(CN)_2]^- \longrightarrow [B_3H_7(NC)BH_2(CN)B_3H_7]^-\ (\mathbf{8}) + 2Cl^- \quad (8)$$

A second synthetic method, which has not been reported previously, involved the simultaneous oxidation and substitution of a borane anion by the reagent cyanogen bromide, BrCN. By this method, we have synthesised the first bridge-cyanide derivative containing *two* polyborane substituents [equation (9)].

$$2[B_3H_8]^- + BrCN \longrightarrow [B_3H_7(NC)B_3H_7]^-\ (\mathbf{3}) + Br^- + H_2 \quad (9)$$

Chemical and Electrochemical Substitution of (**3**).—$[B_3H_8]^-$ and its substituted derivatives $[B_3H_7X]^-$ (X = NCO, NCS, or $NCBH_3$) have been shown to undergo substitution on treatment with HCl, and a series of disubstituted derivatives were described.[7] In this work we have found that (**3**) underwent substitution in only one of the B_3 cages on treatment with HCl, and the ^{11}B n.m.r. data suggested that this took place on the cage bonded to nitrogen [equation (10)]. Further substitution

$$[B_3H_7(NC)B_3H_7]^- + HCl \longrightarrow [B_3H_6Cl(NC)B_3H_7]^-\ (\mathbf{10}) + H_2 \quad (10)$$

in the C-bonded cage did not occur even with an excess of HCl. Reaction of HCl with (**1**) did not yield identifiable disubstituted products, although a similar reaction with (**2**) gave a mixture whose n.m.r. spectrum indicated disubstitution.

The monochlorinated derivative $[B_3H_6Cl(NC)B_3H_7]^-$ (**10**) was also prepared by controlled potential oxidation at 1.6 V of (**3**) in CH_2Cl_2 using two-electron equivalents of charge. When the electrochemical oxidation was continued well beyond the charge required for two-electron oxidation, the disubstituted species $[B_3H_6Cl(NC)B_3H_6Cl]^-$ (**11**) was obtained. Complex

Table 3. Voltammetry and coulometry of octahydrotriborate(1−) derivatives

Anion	First oxidation peak potential (V)[a] MeCN	First oxidation peak potential (V)[a] CH_2Cl_2	Coulometry[b] E_{app}/V	Coulometry[b] *n*
$[B_3H_7(NC)BH_3]^-$	1.2	1.2	1.6	2.2[c]
$[B_3H_7(NC)BPh_3]^-$	1.7	1.6	1.6	1.8[c,d]
$[B_3H_7(NC)BH_2(NC)BH_3]^-$	1.25		1.3[e]	4.2[d]
$[B_3H_7(NC)BH_2(CN)B_3H_7]^-$	1.26		1.3[e]	2.1[d]
$[B_3H_7(NC)B_3H_7]^-$	*f*	1.6	1.6	2.0[d]

[a] Reference Ag–$AgNO_3$ (0.1 mol dm^{-3}) in MeCN; Ag–AgCl {$[N(PPh_3)_2]Cl$, 0.1 mol dm^{-3}} in CH_2Cl_2; supporting electrolyte $[N(PPh_3)_2]BF_4$ (0.1 mol dm^{-3}). [b] In CH_2Cl_2. [c] Current constantly high throughout electrolysis; experiment terminated after passage of this charge. [d] Complex mixture of products. [e] In MeCN. [f] Insoluble.

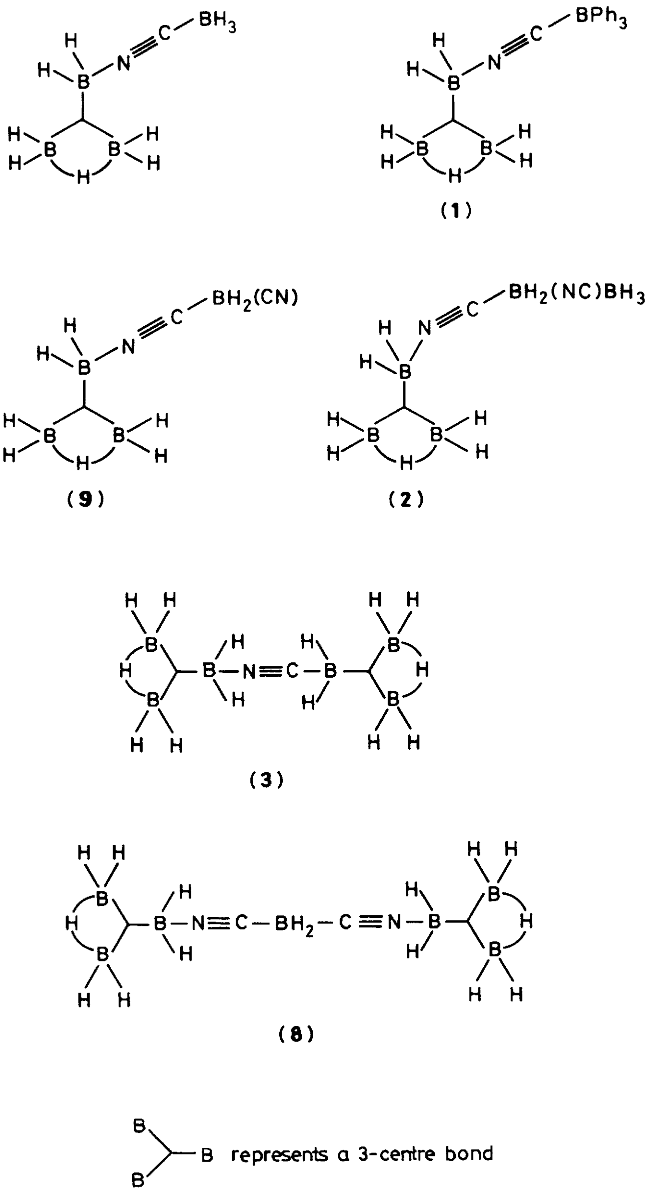


Figure 1. Structures of bridge-cyanide derivatives of monosubstituted triboranes

Table 4. 115.5-MHz ^{11}B N.m.r. data for bridge-cyanide derivatives of the $[B_3H_8]^-$ anion

Compound	$\delta(^{11}B)^a$/p.p.m. (J_{BH}/Hz) B(1)	B(2)	B(3)	Other
$[B_3H_7(NC)BH_3]^-$ [b]	−36.1		−9.9	−43.8 (q)
(1)[c]	−34.8		−9.2	−10.5
(2)[c]	−35.0		−8.1	−27.7 (t), −43.1 (q)
(3)[b]	−49.5[d] −34.9		−12.4[d] −9.5	
(8)[b]	−34.8		−8.3 (41)	−40.5 (t) (104)
(9)[b]	−34.8		−8.9 (41)	−40.8 (t) (99.4)
(10)[b]	−31.0 −49.8[d]	−0.2	−3.8 −11.9[d]	
(11)[b]	−31.3 −45.0[d]	16.1 14.6[d]	−13.3 −16.0[d]	

[a] q = Quartet, t = triplet. [b] $CDCl_3$. [c] CD_3CN. [d] C-Co-ordinated cage.

(11) was also obtained by oxidation in a single compartment cell containing $[N(PPh_3)_2]Cl$ as supporting electrolyte, suggesting the substitution proceeded *via* chlorine radicals resulting from solvent oxidation. These reactions may be summarised by equations (11)—(13). A similar preparative electrochemical

$$CH_2Cl_2 \xrightarrow{-e} [CH_2Cl_2]^{\bullet +} \longrightarrow [CH_2Cl]^+ + Cl^{\bullet} \quad (11)$$

$$[B_3H_7(NC)B_3H_7]^- + 2Cl^{\bullet} \longrightarrow [B_3H_6Cl(NC)B_3H_7]^- \ \mathbf{(10)} + HCl \quad (12)$$

$$[B_3H_6Cl(NC)B_3H_7]^- + 2Cl^{\bullet} \longrightarrow [B_3H_6Cl(NC)B_3H_6Cl]^- \ \mathbf{(11)} + HCl \quad (13)$$

reaction of $[B_3H_7(NC)BH_3]^-$ by oxidation in CH_2Cl_2 also led to chlorine substitution, and to a mixture of products similar to those obtained earlier in reactions with HCl.[7]

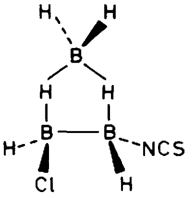
Cyclic Voltammetry and Coulometry.—Voltammetric studies on $[B_3H_7(NC)BH_3]^-$ had earlier[11] shown that this ion was substantially more stable to oxidation than the unsubstituted ion $[B_3H_8]^-$. In this work we have found that all of the bridge-substituted species derived from $[B_3H_8]^-$ were at least as stable as this, and no oxidation occurred at potentials below 1.2 V in MeCN; studies in CH_2Cl_2 revealed similar behaviour, and in several compounds oxidation of the solvent or supporting electrolyte occurred before the anion oxidation. The observed oxidation waves were all irreversible, and undoubtedly accompanied by following chemical reactions. The parameters are reported in Table 3. As a result of the voltammetry we were able to utilise the solvent oxidation as a synthetic route to substituted species in several instances.

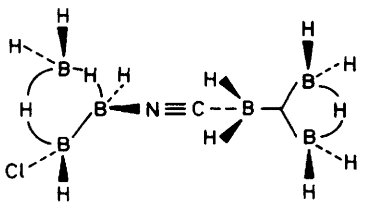
N.M.R. Spectra and Structures.—The ^{11}B n.m.r. spectra of the cyanide-bridged triborate anions **(1)** and **(2)**, derived from $[BPh_3(CN)]^-$ and $[BH_3(CN)BH_2(CN)]^-$ clearly show structures similar to that previously reported[10] for $[B_3H_7(NC)BH_3]^-$ (see Figure 1), in that the boron resonances of the triborane cage comprised a low-field signal of relative intensity 2, corresponding to the unsubstituted borons, B(2) and B(3), and a high-field signal of relative intensity 1, corresponding to the boron which carried the ligand, B(1), and the chemical shifts indicated the ligands were N-bonded to the triborate cage. Line-narrowed ^{11}B n.m.r. spectra of **(1)** and **(2)** resolved B-H

Table 5. Correlated ^{11}B (115.5 MHz) and ^{1}H (360 MHz) n.m.r. data for bridge-cyanide substituted tridecahydrononaborate(1 –) anions[a,b]

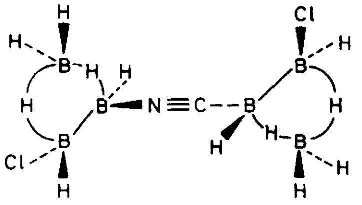
			Position[a]										
Compound	Nucleus		7	1	5,9	6,8	4	2,3	BH_2	BH_3	BPh	Bridge	$[N(PPh_3)_2]$
$[B_9H_{13}(NC)BH_3]^-$	$\delta(^{11}B)$		16.2	4.8	–15.5	–19.4	–25.5	–38.6		–43.0			
	J_{BH}		130	137	141	124	(s)	146		89.5			
	$\delta(^{1}H)^c$	*exo*	3.75	2.88	1.60	1.81		0.19		0.44		–3.52	7.50
		endo				–0.35	0.38						
(4)	$\delta(^{11}B)$		16.6	5.2	–14.9	–19.6	–25.8	–38.4			–10.8		
	J_{BH}			136.6	140.6		(s)	144.6					
	$\delta(^{1}H)$				1.83	1.91						–3.4	
(5)	$\delta(^{11}B)$		17.1	5.07	–14.7	–20.2	–27.2	–38.6	–20.2	–43.3			
	J_{BH}			139	139.5			146		92			
	$\delta(^{1}H)$	*exo*	3.9	3.03	1.79	1.88		0.37	2.09	0.57		–3.53	7.50
		endo				–0.27	0.43						
(6)	$\delta(^{11}B)$		17.3	5.2	–14.6	–20.2	–27.0	–38.6	–40.4				
	J_{BH}			138	138			144	90				
	$\delta(^{1}H)$	*exo*											
		endo											
(7)	$\delta(^{11}B)$		16.9	5.0	–14.9	–20.0	–26.4	–38.6	–40.7				
	J_{BH}			138	138			144	90				
	$\delta(^{1}H)$	*exo*				1.87			1.33			–3.51	
		endo				–0.31	0.41						

[a] Chemical shifts, δ/p.p.m., to high frequency of the references ($BF_3{\cdot}OEt_2$ for ^{11}B; $SiMe_4$ for ^{1}H); coupling constants, J_{BH}, in Hz; s = singlet. [b] *Exo*- and *endo*-hydrogens are quoted for species which are static at the operating temperature, in which cases the bridge hydrogens have relative intensities of 2. In all other cases, the species are fluxional and the bridge hydrogens have relative intensities of 5. [c] CD_2Cl_2 solution at 223 K.





(10)



(11)

Figure 2. Structures of bridge-cyanide derivatives of disubstituted triboranes

couplings and the low-field resonance in each case consisted of the six major lines of an 'octet,' with the two outermost lines being lost in the noise. This clearly indicated that each structure was fluxional, and the borons equivalently coupled to all seven hydrogen nuclei on the n.m.r. time-scale. This was consistent with earlier studies.[12] The ^{11}B n.m.r. spectra of (**8**) and (**9**), each of which is derived from $[BH_2(CN)_2]^-$ interacting with B_3H_7 species, also confirmed similar interactions with the triborate cages, with the chemical shifts being closely similar to the other compounds. Line-narrowing also confirmed the presence of seven fluxional hydrogens in the B_3 cages of each compound. Compound (**3**), in which the cyanide bridges between two triborate cages, showed four resonances, of which the two at δ –34.9 and –9.5 clearly arose from the N-co-ordinated B_3 cage and therefore the resonances at δ –49.5 and –12.4 resulted from the C-co-ordinated B_3 cage (Table 4).

The chemical shifts of the resonances in compound (**10**) clearly demonstrated that Cl substitution had occurred in the N-co-ordinated B_3 cage, while the C-co-ordinated B_3 cage remained unsubstituted. Further evidence came from line-narrowed spectra which revealed the five major lines of a 'septet' in the resonance at δ –0.2 p.p.m., resulting from fluxionality of six hydrogens in the Cl,N-substituted B_3 cage, whereas the resonance at δ –11.9 exhibited the 'octet' structure from the seven fluxional hydrogens of the C-substituted B_3 unit. The six unique boron resonances of (**11**) unambiguously demonstrate the fact that each B_3 cage was disubstituted and line-narrowing indicated 'septets' which resulted from both cages having six fluxional hydrogens. The data are consistent with structures analogous to that observed for $[B_3H_6Cl(NCS)]^-$ (see Figure 2).

In most of the compounds, ^{11}B–^{11}B coupling was not readily resolved even in the line-narrowed spectra (at ambient temperature in $CDCl_3$). Only in (**11**) did the ^{11}B-$\{^{1}H\}$ spectrum indicate boron–boron coupling, with apparent coupling constants $J(^{11}B$–$^{11}B)$ (from the separation of the two observable lines of a partly relaxed 1:1:1:1 quartet) of 69.7 and 72.8 Hz for the resonances at δ 16.1 and 14.6 p.p.m. respectively.

Proton Spectra.—The ^{1}H and ^{1}H-$\{^{11}B\}$ n.m.r. spectra of $[N(PPh_3)_2][B_3H_7(NC)BH_2(NC)BH_3]$ (**2**) at room temperature in $CDCl_3$ at 360 MHz showed resonances due to the cation centred on δ 7.5 p.p.m. (relative intensity 30), a broad resonance at δ 1.58 p.p.m. (relative intensity 7), corresponding to the seven fluxional hydrogens on the triborane cage, and two sharper resonances at δ 0.58 (relative intensity 3) and 1.99 p.p.m. (relative intensity 2) which were attributed to the BH_3 and BH_2 moieties of the substituent. The ^{1}H-$\{^{11}B\}$ spectra of $[N(PPh_3)_2][B_3H_7(NC)B_3H_7]$ (**3**) reflected the asymmetry of the ion resulting from the bridging cyanide. The anion resonances, each of relative intensity seven, were centred at δ 1.04 and 1.51 p.p.m. respectively. Successive single frequency decoupling experiments at the boron resonance frequencies corresponding to the chemical shifts of the boron environments at δ –9.5 and –34.9 p.p.m. caused a selective sharpening of the fluxional hydrogens at δ 1.51 p.p.m. Since the resonance at δ –34.9 p.p.m. is clearly due to the N-co-ordinated boron atom, these three resonances must all have arisen from the same triborane cage. Similarly, irradiation of the boron resonances at δ −12.4 and −49.5 p.p.m. resulted in sharpening of the protons at δ 1.04 p.p.m. and thus these are attributed to the nuclei of the C-co-ordinated cage.

Further confirmation of the structure of (**3**) has been obtained from the *X*-ray crystal structure which confirmed that both cages had the three-centre bonded structure.[10]

Nonaborate Derivatives.—The ^{11}B n.m.r. assignments, together with selected ^{1}H chemical shifts, correlated with boron positions, of compounds (**4**)—(**7**), together with $[B_9H_{13}(NC)BH_3]^-$ for comparison, are presented in Table 5.

Previous studies[6] on the structure of $[B_9H_{13}(NC)BH_3]^-$ had concluded from ^{11}B n.m.r. data that the ion adopted a structure similar to that found[13] crystallographically for $B_9H_{13}(NCCH_3)$ except that the resonance due to B(4) was found to be a singlet. This was interpreted in terms of a structure which was fluxional at room temperature on the n.m.r. time-scale. No ^{1}H data on the species were available at that time.

During the present study, the ^{11}B spectrum of (**5**) also showed a singlet due to B(4), but the ^{1}H-$\{^{11}B\}$ spectra clearly revealed *exo*- and *endo*-hydrogens at B(6,8), and and *endo* hydrogen at B(4), together with only two bridge hydrogens at −3.53 p.p.m. This unambiguously established a static structure. Similar observations of *exo*- and *endo*-hydrogens at B(6,8) were revealed by specific frequency decoupling experiments on (**6**) and (**7**) indicating that these also were static at ambient temperature. We have since examined the ^{1}H-$\{^{11}B\}$ spectra of $[B_9H_{13}(NC)BH_3]^-$ at several temperatures and observed that it was fully static only below 273 K. At 298 K *endo* hydrogens were not observed but it was still essentially static since the bridge hydrogens were observed near δ −3.5, and even on warming to 333 K it had not become fully fluxional. The anomaly of the ^{11}B spectra at room temperature in which B(4) appeared as an apparent singlet presumably arose as a result of slow exchange of bridge and *endo*-terminal hydrogens together with unresolved couplings and quadrupolar relaxation broadening.

In contrast, the ^{11}B and ^{1}H data of (**4**) showed that although the nonaborate clusters retained local C_s symmetry, the ion was fluxional at room temperature since there were no *endo* hydrogens at B(6,8) or B(4).

It is clear from these observations that deductions on fluxionality in derivatives of $[B_9H_{13}X]^-$ need to be made from both ^{11}B and ^{1}H-$\{^{11}B\}$ spectra over a range of temperatures. It is evident that the barrier to intramolecular hydrogen exchange on boron in derivatives of the type $[B_9H_{13}(NC)Z]^-$ depends in a subtle way on the nature of the group Z, although the structures are basically those indicated in Figure 3.

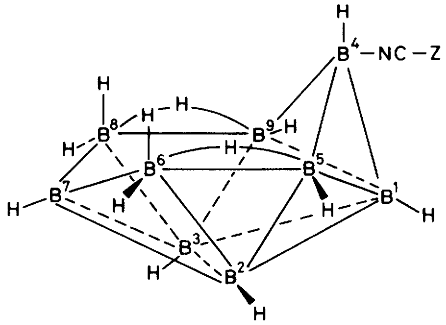


Figure 3. Structures of bridge-cyanide derivatives of tridecahydrononaborane. Z = BH_3, BPh_3 (**4**), $BH_2(NC)BH_3$ (**5**), $BH_2(CN)B_9H_{13}$ (**6**), or $BH_2(CN)$ (**7**)

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