Borane Anions with Bridging Cyanide Ligands; Preparation and Properties of Derivatives of [B₃H₈]⁻ and [B₉H₁₄]⁻

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A series of cyanide-bridged derivatives of the *arachno*-octahydrotriborate(1−) and *arachno*-tetradecahydrononaborate(1−) ions, [B₃H₈]⁻ and [B₉H₁₄]⁻ respectively, have been prepared using chemical and electrochemical methods. Compounds prepared include the triborate species [B₃H₇(NC)B₃H₇]⁻ and its substituted derivatives, [B₃H₆Cl(NC)B₃H₇]⁻ and [B₃H₆Cl(NC)B₃H₆Cl]⁻ together with the ions [B₃H₇(NC)BH₂(NC)BH₃]⁻ and [B₃H₇(NC)BPh₃]⁻. The ions [B₃H₇(NC)BH₂(CN)]⁻ and [B₃H₇(NC)BH₂(CN)B₃H₇]⁻ have also been obtained. The nonaborate derivatives include [B₉H₁₃(NC)BPh₃]⁻, [B₉H₁₃(NC)BH₂(NC)BH₃]⁻, [B₉H₁₃(NC)BH₂(CN)]⁻, and [B₉H₁₃(NC)BH₂(CN)B₉H₁₃]⁻.

Previously, the ability of the cyanide group to bridge between two borane species has been restricted to derivatives of [BH₃(CN)]⁻ in which co-ordination of this ion occurred to another borane acceptor. Species of this type included those of monoborane acceptors, *e.g.* [BH₃(CN)BH₃]⁻, [BH₃(CN)BH₂(CN)]⁻ and the polymeric [BH₂(CN)]ₓ.[1-4] We have also described recently the species [BH₃(CN)B₃H₇]⁻ and [BH₃(CN)B₉H₁₃]⁻ [5,6] and have also reported the complex ion, [Ag{(CN)B₃H₇}₂]⁻.[7]

Earlier work[1] on the reaction of B₄H₁₀ with Na(CN) was reported to result in its symmetric cleavage to yield Na[B₃H₇(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 Some of our previous unpublished work[8] indicated that the cyanide group may bridge between two polyborane moieties, since we had some evidence for [B₉H₁₃(NC)B₉H₁₃]⁻.

We now wish to report the synthesis of a number of new cyanide-bridged derivatives from the polyborane acceptors B₃H₇ and B₉H₁₃, including several in which two polyborane acceptors are involved. We report their characterisation primarily through ¹¹B and ¹H n.m.r. spectroscopy and describe some of their chemical behaviour.

Experimental

Starting Materials and Reagents.—The solvents CH₂Cl₂ and MeCN were of high-performance liquid chromatography grade and were dried over CaH₂. The supporting electrolyte [NBuⁿ₄][BF₄] and Na[BPh₃(CN)] were used as supplied (Fluka A.G.). The reagent Na[BH₃(CN)BH₂(CN)] was prepared as previously described.[3a] The [N(PPh₃)₂]⁺ salts of [BH₃(CN)BH₂(CN)]⁻ and [BPh₃(CN)]⁻ were prepared by mixing [N(PPh₃)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 CH₂Cl₂–Et₂O to give colourless needle-like crystals.

Na[BH₂(CN)₂] was obtained by the published method.[9] [N(PPh₃)₂][BH₂(CN)₂] was prepared by adding a solution of Na[BH₂(CN)₂] in water to an excess of [N(PPh₃)₂]Cl in MeOH. The white precipitate which immediately formed was filtered off, extracted into CH₂Cl₂, and recrystallised by dropwise addition of Et₂O.

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–AgNO₃ (0.1 mol dm⁻³) in MeCN or Ag–[N(PPh₃)₂]Cl (0.1 mol dm⁻³) in CH₂Cl₂, 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; ¹¹B, 80.2 and 115.5 MHz) as solutions in CDCl₃ or CD₃CN. Chemical shifts are quoted as being positive to high frequency (low field) of the reference standards SiMe₄ or BF₃·OEt₂.

Synthesis of [N(PPh₃)₂][B₃H₇(NC)BPh₃], (1).—[N(PPh₃)₂][B₃H₇Cl] (0.61 g, 1 mmol) and [N(PPh₃)₂][BPh₃(CN)] (0.806 g, 1 mmol) were placed in a 250-cm³ round-bottomed flask fitted with a stopcock adapter. Dried, degassed CH₂Cl₂ (40 cm³) 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% CH₂Cl₂ as eluant (conditions under which [N(PPh₃)₂]Cl has $R_f = 0$) showed a single major product ($R_f = 0.69$). Purification by column chromatography on silica gel using 100% CH₂Cl₂ as eluant gave [N(PPh₃)₂][B₃H₇(NC)BPh₃] (1) as a white solid (0.67 g, 0.8 mmol, 80% yield). Recrystallisation from CH₂Cl₂–Et₂O produced colourless needles (analytical data in Table 1).

Synthesis of [N(PPh₃)₂][B₃H₇(NC)BH₂(NC)BH₃], (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(PPh₃)₂][B₃H₇(NC)B₃H₇], (3).—Cyanogen bromide, BrCN (0.617 g, 5.83 mmol), was placed in a round-bottomed flask fitted with a stopcock adapter. Dried, degassed CH₂Cl₂ was condensed in under vacuum, the mixture allowed

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

| | Analysis (%) | | | | | | | |
| Com- | C | | H | | N | | P | |
pound	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 $-196\ ^\circ C$ 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-cm³ 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 cm³) 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 ¹¹B 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 ¹¹B 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).—$[N(PPh_3)_2][B_3$-$H_7Cl]$ (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-cm³ flask fitted with a stopcock adapter. Dried, degassed CH_2Cl_2 (ca. 50 cm³) 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-cm³ flask fitted with a stopcock adapter. Dried, degassed CH_2Cl_2 (30 cm³) 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 cm³ 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 cm³ 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 cm³) 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

Complex	B(1)	B(2), B(3)	Other
	$\delta(^{11}B)$ in $CDCl_3$/p.p.m.		
$[Cu(PPh_3)_2\{B_3H_7(NC)BPh_3\}]$	-17.35	-30.40	-37.00 $(BH_3\cdot PPh_3)$ -11.65 (BPh_3)
$[Ag(PPh_3)_2\{B_3H_7(NC)B_3H_7\}]$	$-34.85*$ -49.69	$-12.42\bullet$ -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 e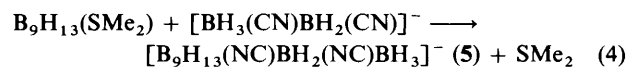lectrolysis that redissolved on heating. The white precipitate was thought to be $[N(PPh_3)_2]Cl$. The net weight loss of the silver anode was 0.1066 g (cf. the theoretical value of 0.1078 g for Ag → Ag^I). The solvent was removed from the anolyte under reduced pressure to give a white crystalline solid. 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.

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

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

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

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

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

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

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

$$2[B_3H_7Cl]^- + [BH_2(CN)_2]^- \longrightarrow$$
$$[B_3H_7(NC)BH_2(CN)B_3H_7]^- \ (8) + 2Cl^- \quad (8)$$
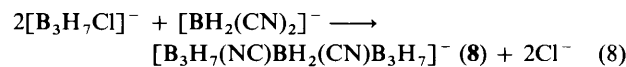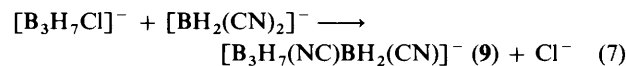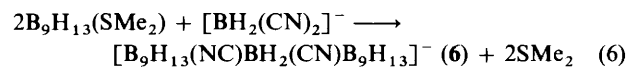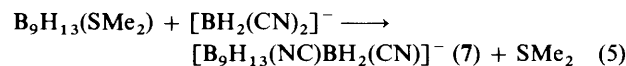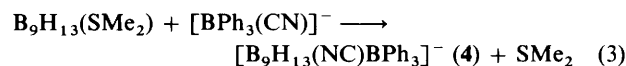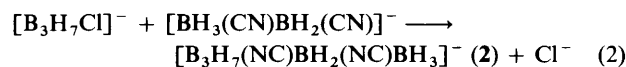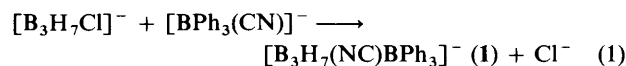
A second synthetic method, which has not been reported previously, involved the simultaneous oxidation and substitution of a borane anion by the reagent cyanogen bromide, BrCN. By this method, we have synthesised the first bridge-cyanide derivative containing *two* polyborane substituents [equation (9)].

$$2[B_3H_8]^- + BrCN \longrightarrow [B_3H_7(NC)B_3H_7]^- \ (3) +$$
$$Br^- + H_2 \quad (9)$$
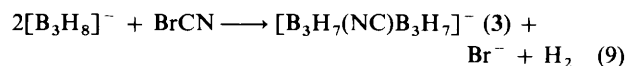
Chemical and Electrochemical Substitution of (3).—$[B_3H_8]^-$ and its substituted derivatives $[B_3H_7X]^-$ (X = NCO, NCS, or NCBH$_3$) have been shown to undergo substitution on treatment with HCl, and a series of disubstituted derivatives were described.[7] In this work we have found that (3) underwent 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

$$[B_3H_7(NC)B_3H_7]^- + HCl \longrightarrow$$
$$[B_3H_6Cl(NC)B_3H_7]^- \ (10) + H_2 \quad (10)$$
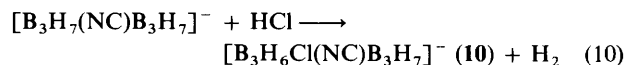
in the C-bonded cage did not occur even with an excess of HCl. Reaction of HCl with (1) did not yield identifiable disubstituted products, although a similar reaction with (2) gave a mixture whose n.m.r. spectrum indicated disubstitution.

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		Coulometry^b	
	MeCN	CH$_2$Cl$_2$	E_{app}/V	n
[B$_3$H$_7$(NC)BH$_3$]$^-$	1.2	1.2	1.6	2.2^c
[B$_3$H$_7$(NC)BPh$_3$]$^-$	1.7	1.6	1.6	1.8^{c,d}
[B$_3$H$_7$(NC)BH$_2$(NC)BH$_3$]$^-$	1.25		1.3^e	4.2^d
[B$_3$H$_7$(NC)BH$_2$(CN)B$_3$H$_7$]$^-$	1.26		1.3^e	2.1^d
[B$_3$H$_7$(NC)B$_3$H$_7$]$^-$	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$_2$Cl$_2$; supporting electrolyte [N(PPh$_3$)$_2$]BF$_4$ (0.1 mol dm^{-3}).^{b} In CH$_2$Cl$_2$. ^{c} Current constantly high throughout electrolysis; experiment terminated after passage of this charge. ^{d} Complex mixture of products. ^{e} In MeCN. ^{f} Insoluble.
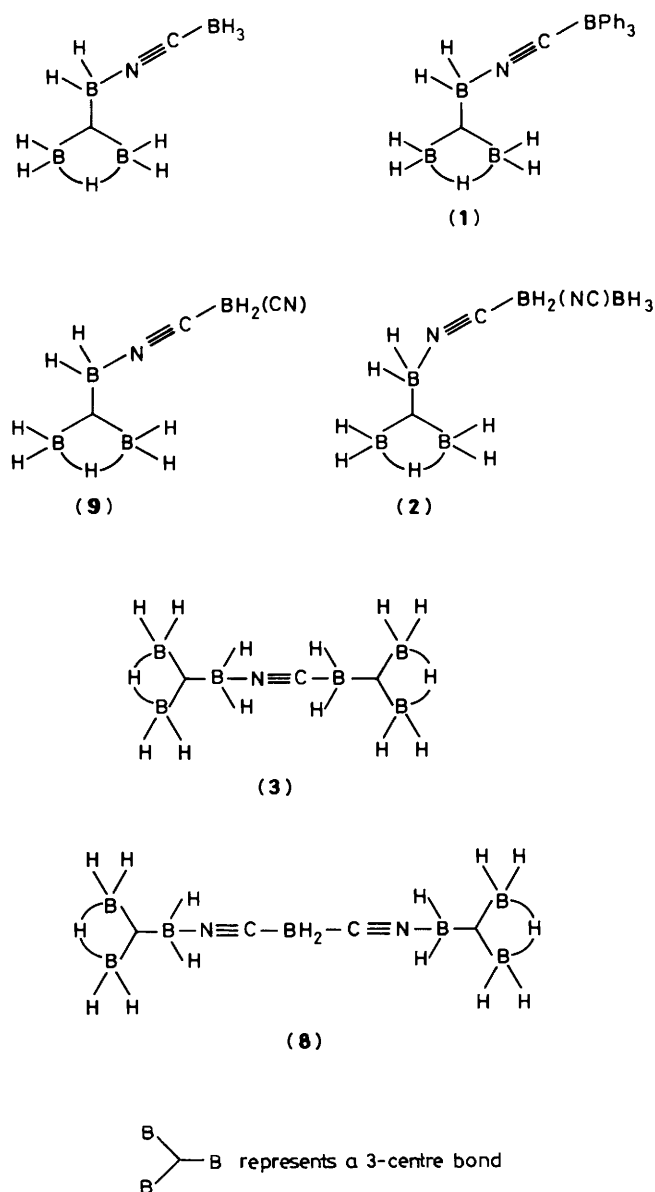
Figure 1. Structures of bridge-cyanide derivatives of monosubstituted triboranes

Table 4. 115.5-MHz ^{11}B N.m.r. data for bridge-cyanide derivatives of the [B$_3$H$_8$]$^-$ anion

Compound	$\delta(^{11}B)^a$/p.p.m. (J_{BH}/Hz)			
	B(1)	B(2)	B(3)	Other
[B$_3$H$_7$(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		−12.4^d	
	−34.9		−9.5	
(8)^b	−34.8		−8.3	−40.5 (t)
			(41)	(104)
(9)^b	−34.8		−8.9	−40.8 (t)
			(41)	(99.4)
(10)^b	−31.0	−0.2	−3.8	
	−49.8^d		−11.9^d	
(11)^b	−31.3	16.1	−13.3	
	−45.0^d	14.6^d	−16.0^d	

^{a} q = Quartet, t = triplet. ^{b} CDCl$_3$. ^{c} CD$_3$CN. ^{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

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

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

$$[B_3H_6Cl(NC)B_3H_7]^- + 2Cl^{\cdot} \longrightarrow$$
$$[B_3H_6Cl(NC)B_3H_6Cl]^- (11) + HCl \quad (13)$$
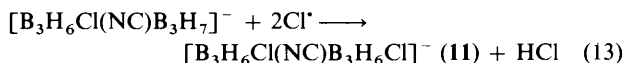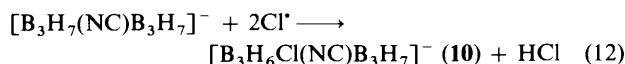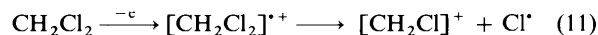
reaction of [B$_3$H$_7$(NC)BH$_3$]$^-$ by oxidation in CH$_2$Cl$_2$ also led to chlorine substitution, and to a mixture of products similar to those obtained earlier in reactions with HCl.[7]

Cyclic Voltammetry and Coulometry.—Voltammetric studies on [B$_3$H$_7$(NC)BH$_3$]$^-$ had earlier[11] shown that this ion was substantially more stable to oxidation than the unsubstituted ion [B$_3$H$_8$]$^-$. In this work we have found that all of the bridge-substituted species derived from [B$_3$H$_8$]$^-$ were at least as stable as this, and no oxidation occurred at potentials below 1.2 V in MeCN; studies in CH$_2$Cl$_2$ 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$_3$H$_7$-(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 ¹¹B (115.5 MHz) and ¹H (360 MHz) n.m.r. data for bridge-cyanide substituted tridecahydrononaborate(1 −) anions[a,b]

Compound	Nucleus		7	1	5,9	6,8	4	2,3	BH₂	BH₃	BPh	Bridge	[N(PPh₃)₂]
[B₉H₁₃(NC)BH₃]⁻	δ(¹¹B)		16.2	4.8	−15.5	−19.4	−25.5	−38.6		−43.0			
	J_BH		130	137	141	124	(s)	146		89.5			
	δ(¹H)[c] exo		3.75	2.88	1.60	1.81		0.19		0.44		−3.52	7.50
	endo					−0.35	0.38						
(4)	δ(¹¹B)		16.6	5.2	−14.9	−19.6	−25.8	−38.4			−10.8		
	J_BH			136.6	140.6		(s)	144.6					
	δ(¹H)				1.83	1.91						−3.4	
(5)	δ(¹¹B)		17.1	5.07	−14.7	−20.2	−27.2	−38.6	−20.2	−43.3			
	J_BH			139	139.5			146		92			
	δ(¹H) 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)	δ(¹¹B)		17.3	5.2	−14.6	−20.2	−27.0	−38.6	−40.4				
	J_BH			138	138			144	90				
	δ(¹H) exo												
	endo												
(7)	δ(¹¹B)		16.9	5.0	−14.9	−20.0	−26.4	−38.6	−40.7				
	J_BH			138	138			144	90				
	δ(¹H) 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 (BF₃·OEt₂ for ¹¹B; SiMe₄ for ¹H); 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] CD₂Cl₂ solution at 223 K.

(10)

(11)
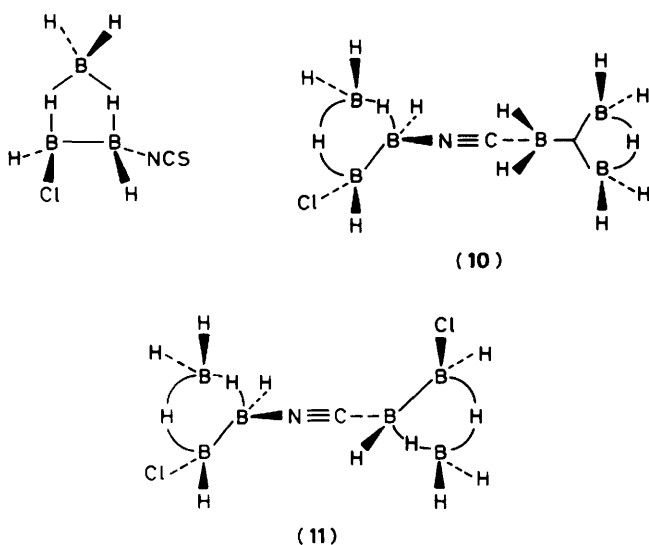
Figure 2. Structures of bridge-cyanide derivatives of disubstituted triboranes

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 ¹¹B n.m.r. spectra of (8) and (9), each of which is derived from [BH₂(CN)₂]⁻ interacting with B₃H₇ 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 B₃ 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 B₃ cage and therefore the resonances at δ −49.5 and −12.4 resulted from the C-co-ordinated B₃ cage (Table 4).

The chemical shifts of the resonances in compound (10) clearly demonstrated that Cl substitution had occurred in the N-co-ordinated B₃ cage, while the C-co-ordinated B₃ 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 B₃ cage, whereas the resonance at δ −11.9 exhibited the 'octet' structure from the seven fluxional hydrogens of the C-substituted B₃ unit. The six unique boron resonances of (11) unambiguously demonstrate the fact that each B₃ 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 [B₃H₆Cl(NCS)]⁻ (see Figure 2).

In most of the compounds, ¹¹B–¹¹B coupling was not readily resolved even in the line-narrowed spectra (at ambient temperature in CDCl₃). Only in (11) did the ¹¹B-{¹H} spectrum indicate boron–boron coupling, with apparent coupling constants J(¹¹B–¹¹B) (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 ¹H and ¹H-{¹¹B} n.m.r. spectra of [N(PPh₃)₂][B₃H₇(NC)BH₂(NC)BH₃] (2) at room temperature in CDCl₃ 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 BH₃ and BH₂ moieties of the substituent. The ¹H-{¹¹B} spectra of [N(PPh₃)₂][B₃H₇(NC)B₃H₇] (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_3-$(NCCH_3)$ 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 yet 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.
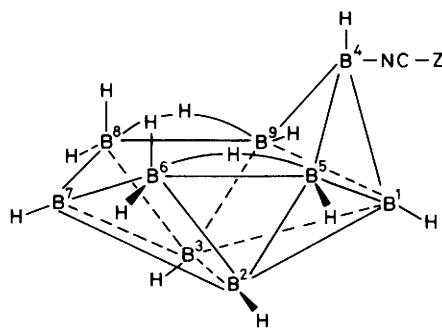
Figure 3. Structures of bridge-cyanide derivatives of tridecahydrononaborane. $Z = BH_3$, BPh_3 (4), $BH_2(NC)BH_3$ (5), $BH_2(CN)B_9H_{13}$ (6), or $BH_2(CN)$ (7)

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