Electrochemical and Chemical Oxidation of $[BH_3(CN)]^-$ to $[BH_3(CN)BH_2(CN)]^-$; Electrochemical Preparation of $[Fe\{BH_3(CN)\}_2(NCCH_3)_4]$ [†]

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The electrolysis of an acetonitrile solution of $Na[BH_3(CN)]$ at an iron electrode yields $[Fe\{BH_3(CN)\}_2(NCCH_3)_4]$, but at molybdenum or vanadium anodes $Na[BH_3(CN)]$ is oxidised to $Na[BH_3(CN)BH_2(CN)]$. Chemical oxidation of $Na[BH_3(CN)]$ using either Hg_2Cl_2 or $HgCl_2$ also gives $Na[BH_3(CN)BH_2(CN)]$, together with oligomeric $BH_2(CN)$ in the case of $HgCl_2$.

THE anodic dissolution of metals in solutions of borane anions is a useful method of preparing metalloborane complexes.[1,2] It has also been shown that electrolyses carried out at certain metal anodes induces oxidation of the borane species in solution.[1,3] A number of iron complexes with $[BH_3(CN)]^-$ have been reported [2,4] previously.

We have found that cyclic voltammetry studies of $Na[BH_3(CN)]$ in CH_3CN solutions, at different metal electrodes, provides useful information regarding the processes occurring in each system.

RESULTS AND DISCUSSION

The anodic dissolution of iron in an acetonitrile solution of $Na[BH_3(CN)]$ occurred readily at potentials between 0.100 and 0.600 V (all potentials quoted being relative to Ag–$Ag[NO_3]$, 0.1 mol dm^{-3} in CH_3CN). The weight loss of the iron corresponded with the overall electron-transfer process (1).

$$Fe \longrightarrow Fe^{2+} + 2e^- \qquad (1)$$

The complex *trans*-$[Fe\{BH_3(CN)\}_2(NCCH_3)_4]$ was isolated as a thermally unstable, air-sensitive, pale green solid. Attempts to dry the solid *in vacuo* resulted in partial loss of acetonitrile ligands. The i.r. spectrum of the complex showed bands due to BH stretching modes at 2 350 and 2 370 cm^{-1}, the latter appearing as a shoulder. A single sharp band at 2 210 cm^{-1} could be ascribed to CN stretching in the $[BH_3(CN)]^-$ ligands, and is at higher frequency than the corresponding band in the spectrum of $Na[BH_3(CN)]$ (2 180 cm^{-1}). That a single CN stretching band was observed indicates that the product has adopted the *trans* configuration. A single band at 2 290 cm^{-1} was ascribed to CN stretching in the acetonitrile ligands. This is in reasonable agreement with the value of 2 287 cm^{-1} quoted in the literature for $[Fe(NCCH_3)_6]^{2+}$.[5] A band at 2 318 cm^{-1} was assigned as a combination of C–C stretching (ν_3) and CH_3 deformation (ν_4) modes in acetonitrile.[5]

The system was established as high-spin octahedral Fe^{2+} by its magnetic moment, μ, and its near infrared–ultraviolet (n.i.r.–u.v.) spectrum. Due to the unstable nature of the complex in the solid state, we felt it necessary to determine μ in solution (by n.m.r.),[6,7] and a value of 4.80 B.M.[‡] was obtained in this way. This is in reasonable agreement with the value (4.90 B.M.) calculated for a high-spin d^6 iron(II) octahedral system.

The n.i.r.–u.v. spectrum in CH_3CN solution showed $\nu_{max.}$ at 11 500 cm^{-1} ($\varepsilon = 5.0$ dm^3 mol^{-1} cm^{-1}) with a shoulder at 9 700 cm^{-1}. The complex cation $[Fe(NCCH_3)_6]^{2+}$ has been shown to exhibit $\nu_{max.}$ at 11 000 cm^{-1} ($\varepsilon = 8.0$ dm^3 mol^{-1} cm^{-1}), with a shoulder at 9 100 cm^{-1}.[8] To confirm that we did not have this cation in solution, we prepared it by the anodic dissolution of iron in a solution of a non-co-ordinating electrolyte (BF_4^-). The n.i.r.–u.v. spectrum of a solution produced in this way showed $\nu_{max.}$ at 11 000 cm^{-1} ($\varepsilon = 5.1$ dm^3 mol^{-1} cm^{-1}) with an ill resolved shoulder, significantly different from $[Fe\{BH_3(CN)\}_2(NCCH_3)_4]$, but very similar to the literature values given for $[Fe(NCCH_3)_6]^{2+}$.

Both the ^1H and ^{11}B n.m.r. spectra were broadened as a result of the complex being paramagnetic. The ^{11}B n.m.r. spectrum consisted of a single broad resonance at δ −66 p.p.m. The very high-field shift for the boron-atom resonance in a $BH_3(CN)$ moiety (*cf.* the ^{11}B n.m.r. spectra of the complexes $[Fe\{BH_3(CN)\}_2\{P(OR)_3\}_4]$, in which the resonances were found at *ca.* δ −40 p.p.m.) [2] possibly arose as a result of bulk susceptibility effects or a paramagnetic shift. The ^1H n.m.r. spectrum showed a broad singlet at δ +2.00 p.p.m., the shift being consistent with that expected for acetonitrile protons.

The preparative method shows that the ratio of Fe to $[BH_3(CN)]^-$ in solution is 1 : 2. The i.r. and n.m.r. data indicate that all the $[BH_3(CN)]^-$ is present as a co-ordinating ligand, and that no free $[BH_3(CN)]^-$ is present. The u.v. and magnetic data show the iron to be present as high-spin Fe^{II} in an octahedral environment. These data are therefore completely consistent with the solution species being $[Fe\{BH_3(CN)\}_2(NCCH_3)_4]$.

The i.r. spectrum described earlier suggested that the complex was obtained as a single isomer, the *trans* isomer, and thin-layer chromatography (using CH_3CN as one of the components of the eluant mixture) showed a single compound. Furthermore, the addition of trimethyl phosphite to a solution of $[Fe\{BH_3(CN)\}_2(NCCH_3)_4]$ gave $[Fe\{BH_3(CN)\}_2\{P(OMe)_3\}_4]$ as the *trans* isomer only, as shown by its ^1H n.m.r. spectrum and t.l.c.[2]

Cyclic voltammetry studies were carried out on a

[†] Tetrakis(acetonitrile)bis(cyanotrihydroborato)iron(II).

[‡] Throughout this paper: 1 B.M. ≈ 9.27×10^{-24} A m^2.

CH_3CN solution of Na[BH_3(CN)] at an iron electrode. The potential at which metal dissolution commenced was noted (−0.30 V), and a linear increase in current with increasing potential was observed after metal dissolution commenced.

The cyclic voltammogram of an acetonitrile solution of Na[BH_3(CN)] at a molybdenum electrode was very different to those described above at iron. In this case the voltammogram showed a definite oxidation wave at +1.20 V, and an associated reduction wave at +1.06 V. Cyclic voltammetry of an acetonitrile solution of Na[BH_3(CN)] at a vanadium electrode showed some simarilities to the voltammogram obtained at iron. Here an increase in potential beyond +0.20 V produced an increase in current consistent with metal dissolution.

To study the reactions occurring at molybdenum and vanadium, preparative-scale electrolyses of acetonitrile solutions of Na[BH_3(CN)] were carried out at anodes of both metals. The electrolyses at molybdenum and vanadium proceeded readily at potentials of +0.750 and +0.900 V respectively. The weight loss of the molybdenum anode was inconsistent with the generation of any single oxidation state, however that of the vanadium anode was consistent with the overall electron-transfer process (2).

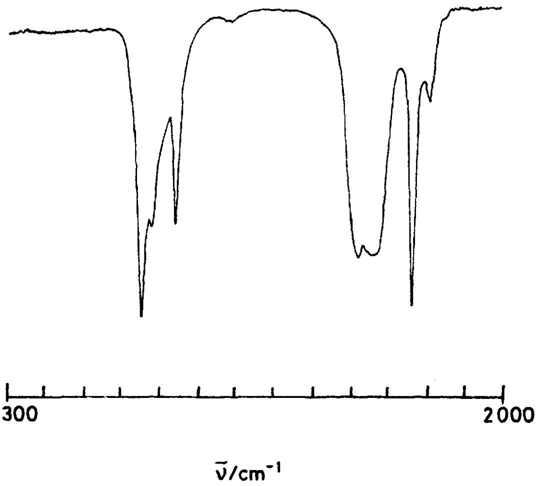
$$V \longrightarrow V^{IV} + 4e^- \qquad (2)$$

In both cases, however, the major borane-containing product was found to be the new anion [BH_3(CN)BH_2(CN)]$^-$, formed as the sodium salt. Although the compound was very hygroscopic, the anion proved to be stable to aqueous hydrolysis. Full characterisation was effected on the tetra-n-butylammonium salt, and is described below.

The ^{11}B n.m.r. spectrum of [NBu^n_4][BH_3(CN)BH_2(CN)] comprised two multiplets of equal intensity, a broad triplet at δ −28.6 p.p.m. [J(B–H) = 105 Hz] and a sharp quartet at δ −43.95 p.p.m. [J(B–H) = 95 Hz], both of which collapsed to singlets on proton decoupling. The fact that the triplet is broadened suggests that the BH_3(CN) part of the anion is *N*-bonded to the BH_2(CN) grouping. A similar effect was noted in the ^{11}B n.m.r. spectrum of the anion [BH_3(CN)BH_3]$^-$ which comprised two quartets at δ −23.7 and −44.2 p.p.m., with the low-field resonance being broadened.[9,10]

The i.r. spectrum of [NBu^n_4][BH_3(CN)BH_2(CN)] (see Figure) was consistent with the proposed structure. Carbon–hydrogen stretching modes were found at 2 965, 2 935, and 2 880 cm^{-1}, entirely consistent with bands found in a standard spectrum of a [NBu^n_4]$^+$ salt. Two broad strong bands at 2 395 and 2 355 cm^{-1} were assigned to BH terminal stretching modes. A strong sharp band at 2 255 cm^{-1} and a sharp medium-intensity band at 2 205 cm^{-1} were assigned to CN stretching. By analogy with the i.r. spectrum quoted for [BH_3(CN)BH_3]$^-$,[10] in which the CN stretching band occurred at 2 260 cm^{-1}, the band at 2 255 cm^{-1} in the spectrum of [BH_3(CN)BH_2(CN)]$^-$ can be ascribed to the bridging CN. The value of 2 205 cm^{-1} for the terminal CN in the anion is in reasonable agreement with corresponding modes in compounds of the type L·BH_2(CN).[11,12]

The processes responsible for the formation of this anion at molybdenum and vanadium anodes appear, on the basis of cyclic voltammetric data and the anode weight losses, to be different. It would seem that at the molybdenum anode two separate processes occurred simultaneously; one of these involved metal dissolution the other the production of [BH_3(CN)BH_2(CN)]$^-$. At the vanadium anode it is possible that an unstable vanadium complex was initially formed and that subsequent decomposition of this gave the ultimate product.



The i.r. spectrum (2 000—3 300 cm^{-1}) of [NBu^n_4][BH_3(CN)BH_2(CN)]

In neither case is a mechanism immediately obvious, although in both cases the overall process can be summarised as in equations (3) and (4).

$$[BH_3(CN)]^- \longrightarrow BH_2(CN) + \tfrac{1}{2}H_2 + e^- \qquad (3)$$

$$[BH_3(CN)]^- + BH_2(CN) \longrightarrow [BH_3(CN)BH_2(CN)]^- \qquad (4)$$

To study further the oxidation of [BH_3(CN)]$^-$ we looked at its reactions with mercury halides in donor solvents [CH_3CN and tetrahydrofuran (thf)]. Reactions of mercury halides with small borane anions, *e.g.* [BH_4]$^-$ and [B_3H_8]$^-$, in donor solvents have been shown to yield compounds of the type L·BH_3 and L·B_3H_7 respectively.[13]

The reaction of mercury(I) chloride, Hg_2Cl_2, with Na[BH_3(CN)] was found to produce Na[BH_3(CN)BH_2(CN)]. The reaction occurred at a much greater rate in thf than in CH_3CN. This meant that it was possible to follow the conversion of [BH_3(CN)]$^-$ into [BH_3(CN)BH_2(CN)]$^-$, in CH_3CN, by obtaining ^{11}B n.m.r. spectra of the reaction mixture at different stages of the reaction. This shows the gradual disappearance of the spectrum of [BH_3(CN)]$^-$, and the corresponding growth of the spectrum of [BH_3(CN)BH_2(CN)]$^-$.

By using the stronger oxidising agent mercury(II) chloride, $HgCl_2$, the oxidation of [BH_3(CN)]$^-$ in either

CH$_3$CN or thf proceeded in a more complex manner. The i.r. spectrum of the reaction mixture, in the range 2 000—2 500 cm^{-1}, was very complicated. A number of bands were attributable to BH and CN stretching modes in the anion [BH$_3$(CN)BH$_2$(CN)]$^-$. Subtraction of these from the spectrum left bands at 2 467, 2 442, and 2 427 cm^{-1}, due to BH stretching, and at 2 298 cm^{-1} due to CN stretching. No bands due to co-ordinated solvent were found, implying the presence of a BH$_2$(CN) oligomeric species, i.r. spectra of which have been quoted in the literature[14,15] and correspond well with the values given here.

The ^{11}B n.m.r. spectrum of the mixture was made up of two resonances, a broad triplet at δ −28.9 p.p.m. [J(B–H) = 105 Hz] and a sharp quartet at δ −44.8 p.p.m. [J(B–H) = 95 Hz], both of which collapsed to singlets in the ^{11}B-$\{^1$H$\}$ n.m.r. spectrum. The relative areas of the resonances were 21 : 6 respectively. This would be consistent with a ratio of BH$_2$(CN) units to [BH$_3$(CN)BH$_2$(CN)]$^-$ of 1.25 : 1. The addition of triphenylphosphine to a solution of the mixture described above yielded a mixture of PPh$_3$·BH$_2$(CN) and [BH$_3$(CN)BH$_2$(CN)]$^-$, as shown by the ^{11}B-$\{^1$H$\}$ n.m.r. spectrum. This contained, in addition to the spectrum of [BH$_3$(CN)BH$_2$(CN)]$^-$ which has been described earlier, a doublet resonance which appeared at δ −33.0 p.p.m. [J(B–P) = 70 Hz]. This is almost identical to the previously reported spectrum of PPh$_3$·BH$_2$(CN).[11]

EXPERIMENTAL

All operations were carried out under nitrogen or *in vacuo*, unless otherwise stated. Acetonitrile (h.p.l.c./far-u.v. grade) was supplied by Fisons Ltd. All other solvents were purified and dried according to the literature.[16] The salt Na[BH$_3$(CN)] was recrystallised from acetonitrile. Kieselgel G (Type 60) (Merck) was used for thin-layer chromatography.

Spectroscopic Techniques.—Infrared spectra were obtained on a Perkin-Elmer 457 grating spectrometer, 32.1-MHz ^{11}B n.m.r. spectra on a JEOL-PS-100-PFT-100 spectrometer, and 100-MHz ^{1}H n.m.r. spectra on a Perkin-Elmer R14 spectrometer. Chemical shifts, δ, are quoted as being negative to high field of the reference standards which were tetramethylsilane for ^{1}H n.m.r. and OEt$_2$·BF$_3$ for ^{11}B n.m.r. N.i.r./u.v. spectra were obtained on a Beckman Acta IVM spectrophotometer.

Electrochemical Equipment.—The cell design and instrumentation used in the preparation of [Fe{BH$_3$(CN)}$_2$(NCCH$_3$)$_4$] has been described in a previous paper,[2] except that the two cell compartments were, in these preparations, separated by a cation-exchange membrane (Nafion 427) in the sodium-ion form. This enabled us to use an inert electrolyte in the cathode compartment.

The electrolyses of Na[BH$_3$(CN)] solutions at molybdenum and vanadium anodes were carried out in simple two-compartment cells. The anode compartment (capacity *ca.* 200 cm^3) was separated from a smaller co-axial cathode compartment by a polytetrafluoroethylene (ptfe) membrane. The anode compartment was stirred magnetically. The cathode was a piece of platinum foil. The instrumentation used was the same for these electrolyses as for the others described here.

Cyclic voltammetry was carried out as described previously.[2]

Electrochemical Reactions.—Preparation of trans-[Fe{BH$_3$(CN)}$_2$(NCCH$_3$)$_4$]. A solution of Na[BH$_3$(CN)] (0.63 g, 10 mmol) in CH$_3$CN (120 cm^3) was loaded into the anode compartment of the electrochemical cell and a 0.1 mol dm^{-3} solution of [NBu$^n{}_4$][BF$_4$] in acetonitrile (120 cm^3) into the cathode compartment. The anode comprised a tightly coiled piece of iron wire, and the cathode was a piece of copper foil. The electrolysis was carried out at an applied potential of +0.100 V. The current rose to a maximum of 120 mA and decayed exponentially until 965 C had passed, the final current being 50 mA. A weight loss of 0.280 g was recorded for the anode. The anolyte was filtered and the volume of the solution reduced to *ca.* 5 cm^3 *in vacuo*, when a pale green precipitate was formed. This was filtered off to give trans-*tetrakis*(*acetonitrile*)*bis*(*cyanotrihydroborato*)-*iron*(II) (0.40 g, 27%).

Owing to the inherent instability of the compound in the solid state, the precision of the microanalytical data decreased rapidly with time (Found: C, 38.7; H, 6.0; N, 27.5. C$_{10}$H$_{18}$B$_2$FeN$_6$ requires C, 40.1; H, 6.1; N, 28.0%). The sample was shown to be pure by thin-layer chromatography, R_F = 0.24, in an eluant of CH$_3$CN–CH$_2$Cl$_2$ (40 : 60).

Preparation of [NBu$^n{}_4$][BH$_3$(CN)BH$_2$(CN)]. (*a*) *At a molybdenum anode.* A 0.1 mol dm^{-3} solution (150 cm^3) of Na[BH$_3$(CN)] in CH$_3$CN was loaded into the anode compartment of the electrochemical cell; 50 cm^3 of the solution were loaded into the cathode. The anode comprised a coil of molybdenum wire, and the cathode a piece of platinum foil. The electrolysis was carried out at a potential of +0.750 V. The current rose to a maximum of 203 mA and decayed exponentially to a final value of 34 mA. A weight loss of 0.135 g was recorded for the anode after the passage of 905 C. During the course of the reaction a deep green colour formed, and precipitation of a green solid occurred. On completion of the electrolysis, the anolyte was filtered and the filtrate reduced in volume to *ca.* 10 cm^3. Addition of diethyl ether resulted in the precipitation of a green, non-borane-containing, solid. This was filtered off and the very pale green solution which remained was evaporated to dryness, yielding a pale green solid, from which Na[BH$_3$(CN)BH$_2$(CN)] was extracted into diethyl ether.

The ether solution of Na[BH$_3$(CN)BH$_2$(CN)] was evaporated to dryness, and the compound dissolved in water (*ca.* 10 cm^3). Excess of [NBu$^n{}_4$][OH] in water was added, and an oil immiscible in water was formed. This oil was extracted into diethyl ether, which was removed under vacuum. Further purification was effected by column chromatography, using silica gel as stationary phase and 15% CH$_3$CN in CH$_2$Cl$_2$ as eluant, to yield [NBu$^n{}_4$][BH$_3$(CN)BH$_2$(CN)] as a clear oil (Found: C, 67.3; H, 12.9; N, 13.1. C$_{18}$H$_{41}$B$_2$N$_3$ requires C, 67.3; H, 12.9; N, 13.1%).

(*b*) *At a vanadium anode.* The procedure during electrolysis was identical to that above, and again Na[BH$_3$(CN)BH$_2$(CN)] was obtained. In this case, the weight loss of the anode was 0.124 g, and a blue non-borane-containing solid precipitated, the remaining solution being pale blue.

Chemical Oxidation of Na[BH$_3$(CN)].—(*a*) *By reaction with* Hg$_2$Cl$_2$. Either CH$_3$CN or thf (15 cm^3) was condensed onto a mixture of Hg$_2$Cl$_2$ (0.99 g, 2.1 mmol) and Na[BH$_3$(CN)] (0.264 g, 4.2 mmol). The mixture was allowed to warm to 0 °C, and stirred until the evolution of hydrogen was complete (28 h with CH_3CN as solvent, 15 min with thf). A grey, mercury-containing slurry was produced, which was then allowed to settle out, leaving a clear supernatant liquid. This clear liquid was decanted off, and shown to contain $Na[BH_3(CN)BH_2(CN)]$ by its ^{11}B n.m.r. spectrum and the i.r. spectrum of the evaporate.

(*b*) *By reaction with* $HgCl_2$. A mixture of $HgCl_2$ (0.57 g, 2.1 mmol) and $Na[BH_3(CN)]$ (0.264 g, 4.2 mmol) in CH_3CN or thf (15 cm^3) was stirred at 0 °C until hydrogen evolution was complete (12 h in CH_3CN, 2 min in thf). A grey, mercury-containing slurry and clear supernatant liquid were produced. The liquid was decanted of and shown to contain $Na[BH_3(CN)BH_2(CN)]$ and $\{BH_2(CN)\}_x$.

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