Electrochemical and Metathetical Preparations of Isomers of Bis-(cyanotrihydroborato)tetrakis(trialkyl phosphite)iron(II) Complexes, $[Fe\{BH_3(CN)\}_2\{P(OR)_3\}_4]$

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Iron(II) complexes of the general formula $[Fe\{BH_3(CN)\}_2\{P(OR)_3\}_4]$ (R = Me or Et) have been prepared both metathetically, by the reaction of $FeCl_2.2H_2O$ with $Na[BH_3(CN)]$ and the appropriate phosphite, in either methanol or acetonitrile, or electrochemically by the anodic dissolution of iron in acetonitrile solutions of the phosphite and $Na[BH_3(CN)]$. The metathetical reactions carried out in methanol give the *trans* isomers only, as shown by the ^1H n.m.r., $^{31}P-\{^1H\}$ n.m.r., and i.r. spectra of the products. In acetonitrile, the metathetical reactions yield mixtures of isomers in the *cis* : *trans* ratio of *ca.* 30 : 70, as shown by ^1H n.m.r. and i.r. spectra, supported by thin-layer chromatographic analysis. For R = Me, the electrochemical reaction in acetonitrile yields a mixture containing *ca.* 65% of the *cis* isomer. Where R = Et however, the *cis* content is *ca.* 30%. These observations are discussed.

PHOSPHITEIRON complexes have been of interest recently because of (*a*) stabilisation of low-spin iron(II) complexes by the phosphite ligands, and (*b*) as precursors for iron(0) species.[1-7] Iron(II) complexes have been described with two to six phosphite ligands, and the geometry, magnetic properties, and stability are functions of the size and nature of the phosphite ligand and the nature of any anionic ligand incorporated in the complex. Iron(0) species have been prepared by reduction of iron(II) complexes in the presence of excess of phosphite.[1,2] Co-condensation of iron atoms and cyclo-octa-1,5-diene with subsequent addition of triphenyl phosphite led to oxidative insertion into an aromatic C–H bond of one of the ligands.[5] Apart from the metal-atom reaction described above, most of the preparations of iron phosphite complexes have involved metathetical reactions.

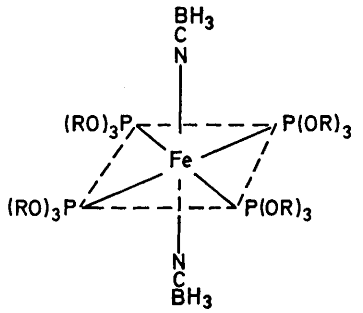
The only cyanotrihydroborate derivative of Fe^{II} previously reported is the complex bis(cyanotrihydroborato)bis(1,10-phenanthroline)iron(II), in which a *cis* arrangement of ligands was suggested.[8,9]

The anodic dissolution of metals in non-aqueous solvents has recently been shown to be a versatile method for the preparation of metal derivatives of borane anions.[10] We now report that this method can be extended to include the preparation of complex iron phosphite derivatives of the cyanotrihydroborate(1–) anion. Similar complexes were also obtained using metathetical reactions, but the products obtained from the two techniques indicate stereochemical differences.

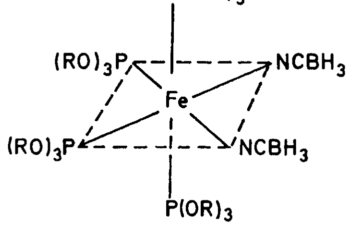
RESULTS AND DISCUSSION

The reactions of $FeCl_2{\cdot}2H_2O$ with excess of $Na[BH_3(CN)]$ and $P(OR)_3$ (R = Me or Et) in methanol were found to give complexes *trans*-$[Fe\{BH_3(CN)\}_2\{P(OR)_3\}_4]$, structure (I). In the case of R = Me, the product was readily purified by recrystallisation from CH_2Cl_2–Et_2O, and for R = Et the product could be recrystallised from CH_2Cl_2–n-hexane. The complexes were shown to be *trans* on the basis of their ^1H n.m.r., $^{31}P-\{^1H\}$ n.m.r., and i.r. spectra.

The ^1H n.m.r. spectrum of *trans*-$[Fe\{BH_3(CN)\}_2\{P(OMe)_3\}_4]$ consisted of a quintet pattern [Figure 1(a)], typical of a square-planar phosphite arrangement,[11] centred at δ 3.76 p.p.m. The $^{31}P-\{^1H\}$ n.m.r. spectrum is also consistent with this arrangement of phosphite ligands, comprising a singlet at δ 154.4 p.p.m. Two small satellite peaks, due to ^{57}Fe–^{31}P coupling, were also observed, *J*(Fe–P) = 59.6 Hz. The i.r. spectrum of the product showed a single sharp CN stretch at 2 202 cm^{-1}, the increase in frequency of the CN mode from that in $Na[BH_3(CN)]$ (2 180 cm^{-1}) being consistent with the isomer containing Fe–*N*-bonded $BH_3(CN)^-$ ligands.[12]



(I)



(II)

The BH stretching modes, at 2 323 and 2 368 cm^{-1}, were also characteristic of *N*-bonded $BH_3(CN)^-$ ligands.[12] The presence of only a single CN stretching mode is also indicative (although not definitive) of the complex being the *trans* isomer. The ^{11}B n.m.r. spectrum showed a 1 : 3 : 3 : 1 quartet at δ = –40 p.p.m. [*J*(B–H) = 91 Hz], consistent with a $BH_3(CN)^-$ ligand.

The ^1H n.m.r. spectrum of *trans*-[Fe{$BH_3(CN)$}$_2$-{$P(OEt)_3$}$_4$] was made up of two areas of resonance (Figure 2) at δ 1.32 and 4.12 p.p.m., of relative area 3 : 2 respectively. The resonance at δ 1.32 p.p.m. was found to be a triplet which can be ascribed to the CH_3 protons in the phosphite ligands. The lower-field resonance was made up of a quartet structure, with much underlying fine structure due to second-order effects, ascribable to the CH_2 protons in the phosphite ligands. This also implies a square-planar arrangement of the phosphite ligands about the metal centre, and this is supported by the ^{31}P-{^1H} n.m.r. spectrum, which consisted of a singlet at δ 151.3 p.p.m. Again, ^{57}Fe–^{31}P coupling was observed, J(Fe–P) = 59.2 Hz. The i.r. spectrum is identical, in the $BH_3(CN)$ stretching region, with that obtained for the trimethyl phosphite complex. Similarly, the ^{11}B n.m.r. spectrum consisted of a poorly resolved 1 : 3 : 3 : 1 quartet at δ −39.1 p.p.m., J(B–H) = 91 Hz.

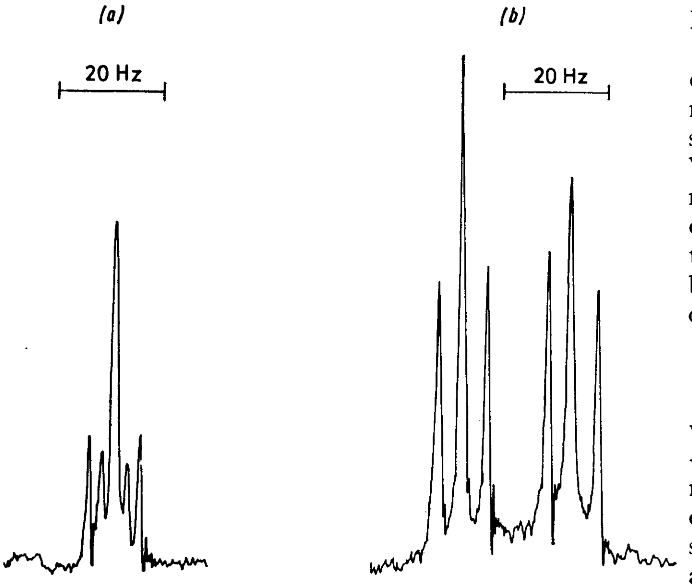


FIGURE 1 The ^1H n.m.r. spectra of (*a*) *trans*-[Fe{$BH_3(CN)$}$_2${$P(OMe)_3$}$_4$] and (*b*) *cis*-[Fe{$BH_3(CN)$}$_2${$P(OMe)_3$}$_4$]

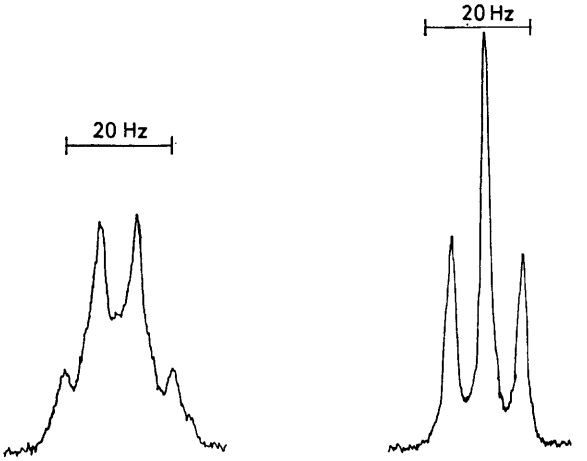


FIGURE 2 The ^1H n.m.r. spectrum of *trans*-[Fe{$BH_3(CN)$}$_2${$P(OEt)_3$}$_4$]

It is worth noting at this point that an analogous reaction to those described above, using $P(OPh)_3$ as the ligand, proved unsuccessful, the product being too unstable to isolate. The i.r. spectrum of the crude product, prior to decomposition, did show similar features to those described for the $P(OMe)_3$ and $P(OEt)_3$ analogues in the BH and CN stretching regions.

The production of [Fe{$BH_3(CN)$}$_2${$P(OR)_3$}$_4$] (R = Me or Et) as the *trans* isomers only, from the metathesis reactions described above, caused us to examine the possibility of preparing these complexes electrochemically. We found that the dissolution of an iron anode occurred readily at 0.500 V {relative to Ag–Ag[NO_3] (0.1 mol dm^{-3})} * in acetonitrile solutions of Na[$BH_3(CN)$] and the appropriate phosphite. The weight loss of iron, in both the $P(OMe)_3$ and the $P(OEt)_3$ runs, was found to correspond to the overall electron-transfer process (1).

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

In both cases, the complexes isolated from the reactions were found to correspond to the general formula [Fe{$BH_3(CN)$}$_2${$P(OR)_3$}$_4$]. The products were found to be mixtures of *cis* and *trans* isomers [structures (I) and (II)] on the basis of their ^1H n.m.r., ^{31}P-{^1H} n.m.r., and i.r. spectra, and their thin-layer chromatographic (t.l.c.) analyses. On integration of the ^1H n.m.r. spectrum of the *cis–trans* mixture of [Fe{$BH_3(CN)$}$_2${$P(OMe)_3$}$_4$], a *cis* : *trans* ratio of 65 : 35 was obtained. T.l.c. results supported this figure. For R = Et, the ^1H n.m.r. spectrum of the mixture was too complicated for such an analysis; however, t.l.c. results suggest a *cis* : *trans* ratio of 1 : 2, *i.e.* a *cis* concentration of *ca.* 30%.

The *cis* and *trans* isomers of both the trimethyl and triethyl phosphite complexes proved readily separable. For R = Me, the *trans* isomer was found to be preferentially soluble in benzene, and repeated extraction from the mixture left the *cis* isomer. For R = Et, both isomers proved to be soluble in benzene; however, addition of excess of hexane induced precipitation of the *cis* form preferentially.

For neither R = Me nor Et did the ^{11}B n.m.r. spectrum of the *cis* isomer differ significantly from that of the *trans* isomers. The ^1H n.m.r., ^{31}P-{^1H} n.m.r., and i.r. spectra of the *cis* isomers proved very characteristic, however. (The ^{31}P-{^1H} n.m.r. spectrum was obtained by subtracting the resonance given by the *trans* isomer from the spectrum of a *cis–trans* mixture.)

The ^1H n.m.r. spectrum of *cis*-[Fe{$BH_3(CN)$}$_2$-{$P(OMe)_3$}$_4$] [Figure 1 (*b*)] consisted of two triplets, centred at δ 3.84 and 3.63 p.p.m. This pattern of triplets is known to derive from the *cis* arrangement of the phosphite ligands about the metal atom (*cf. cis*-[Fe(NCS)$_2${$P(OMe)_3$}$_4$]).[7]

The ^1H n.m.r. spectrum of *cis*-[Fe{$BH_3(CN)$}$_2$-{$P(OEt)_3$}$_4$] (Figure 3) consisted of two main areas of

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* The potential of this electrode was found to be 0.335 V relative to the standard calomel electrode (s.c.e.).[13]

resonance, centred at δ 1.32 and 4.12 p.p.m. The upfield resonance, of relative area 3, showed two substantially overlapping triplets, due to the CH_3 protons of the *cis* phosphite ligands. The resonance to lower field, of relative area 2, is very complicated, and can only be said to contain two broad, overlapping, poorly resolved multiplets, caused by the CH_2 protons of the phosphite ligands.

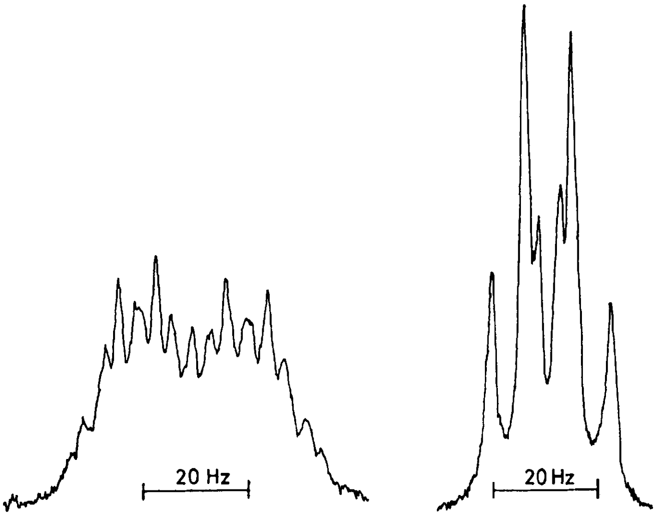

FIGURE 3 The ^1H n.m.r. spectrum of *cis*-$[Fe\{BH_3(CN)\}_2\{P(OEt)_3\}_4]$

The ^{31}P-$\{^1H\}$ n.m.r. spectra of *cis*-$[Fe\{BH_3(CN)\}_2\{P(OMe)_3\}_4]$ and the $P(OEt)_3$ analogue both consisted of two areas of resonance in an A_2B_2 pattern. The resonances in the $P(OMe)_3$ complex (Figure 4) occurred at δ 163.3 and 150.2 p.p.m., with $J(A\text{–}B) = 131.2$ Hz. For the $P(OEt)_3$ complex, the resonances occurred at δ 158.8 and 145.9 p.p.m., with $J(A\text{–}B) = 129.4$ Hz. In both cases this is consistent with a six-co-ordinate complex with a *cis* arrangement of phosphite ligands.

The i.r. spectra of the *cis* isomers in both cases showed significant differences from the *trans* isomers. For the *cis* isomers, one would expect two CN stretches, and for *cis*-$[Fe\{BH_3(CN)\}_2\{P(OMe)_3\}_4]$ two were found, at 2 208 and 2 212 cm^{-1} (*cf.* 2 202 cm^{-1} for the *trans* isomer). For the $P(OEt)_3$ complex, only one absorption, at 2 208 cm^{-1}, was found, probably due to incomplete resolution in the spectrum.

To attempt to ascertain the degree by which isomer

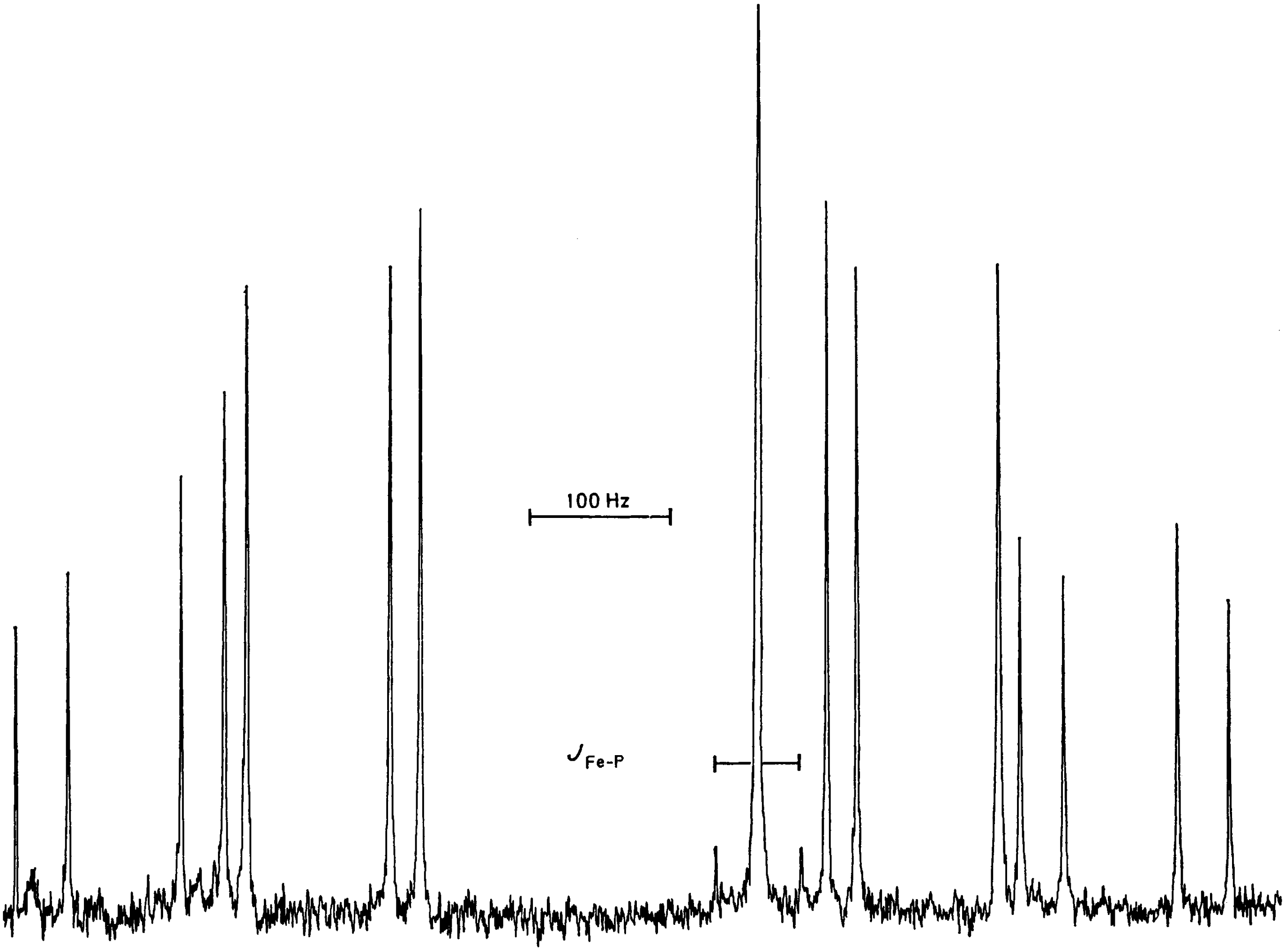

FIGURE 4 The ^{31}P-$\{^1H\}$ n.m.r. spectrum of a mixture of *cis*- and *trans*-$[Fe\{BH_3(CN)\}_2\{P(OMe)_3\}_4]$

formation was governed by either solvent or preparative technique, we now carried out the metathesis reactions in acetonitrile, under the same conditions as the reactions carried out in methanol. The following results were obtained: (*a*) a *cis–trans* isomeric mixture of [Fe$\{BH_3(CN)\}_2\{P(OMe)_3\}_4$] was obtained with a *cis* : *trans* ratio of 30 : 70; (*b*) a *cis–trans* isomeric mixture of the $P(OEt)_3$ analogue was obtained containing *ca.* 30% *cis*, comparable with the yield of *cis* obtained electrochemically.

To complete the series of reactions the electrochemical preparation of the complex [Fe$\{BH_3(CN)\}_2\{P(OMe)_3\}_4$] was attempted in methanol. It was found that an unstable dark green solution was produced, even at a potential of 0.200 V (relative to s.c.e.) (the electrochemical preparations in acetonitrile were carried out at a potential of 0.835 V relative to s.c.e.) and the solution decomposed readily upon exposure to even very small concentrations of air. A very small (9%) yield of *trans*-[Fe$\{BH_3(CN)\}_2\{P(OMe)_3\}_4$] was obtained, but no real comparison with the other reactions could be drawn from this. It is worth noting, however, that the anodic weight loss corresponded with the overall electron-transfer process (1).

The reason why the electrochemical preparation in acetonitrile appears to favour the formation of *cis*-[Fe$\{BH_3(CN)\}_2\{P(OMe)_3\}_4$], whereas the analogous electrochemical reaction using $P(OEt)_3$ yielded mainly *trans*-[Fe$\{BH_3(CN)\}_2\{P(OEt)_3\}_4$] is not obvious. It is likely that the processes occurring at the iron electrode surface involve initial adsorption of one or more of the species $BH_3(CN)^-$, $P(OR)_3$, and CH_3CN. The species that subsequently desorbs from the electrode surface then acquires further ligands to form the observed complex; the intermediates must be different from those involved in the ligand substitutions of the metathetical processes.

The complexes were found to be soluble in a number of different solvents, particularly CH_3CN, C_6H_6, CH_2Cl_2, and $CHCl_3$. If solutions of either *cis* or *trans* forms of the complexes were allowed to stand *in vacuo*, then no detectable isomerisation was found in any of the solutions even after 1 week. If, however, even a trace of air was present, then changes in the isomer ratio were observed after only 24 h. In CH_3CN solutions the *cis* isomers were preferred, whereas in C_6H_6 solutions, isomerism to the *trans* isomer was completed rapidly. In CH_2Cl_2 or $CHCl_3$, both pure *cis* and *trans* isomers were eventually converted into mixtures of *cis* and *trans* isomers. On allowing the different solutions to stand for 48—72 h some decomposition to iron(III) species became apparent.

The fact that trace amounts of air are needed to promote this interconversion of isomers suggests that the process may be proceeding *via* the formation of catalytic amounts of Fe^{III}. The preferential conversion into different isomers appears to be related to, and may be influenced by, the relative dipole moments, or dielectric constants, of the solvents, which decrease in the order:[14,15] $CH_3CN > CH_2Cl_2 > CHCl_3 > C_6H_6$.

Cyclic voltammetric studies were carried out on both of the *trans*-[Fe$\{BH_3(CN)\}_2\{P(OR)_3\}_4$] complexes (R = Me or Et). In both cases, reversible oxidation-reduction waves were not observed. However for the $P(OMe)_3$ complex, oxidation and reduction waves were observed at 0.998 and 0.300 V relative to Ag–Ag[NO_3] (0.1 mol dm^{-3}), and for the $P(OEt)_3$ complex, non-reversible oxidation and reduction waves were observed at 0.976 and 0.476 V.

EXPERIMENTAL

All operations were carried out under nitrogen or *in vacuo*, unless otherwise specified. All solvents were purified and dried according to the literature.[15] The salt Na[$BH_3(CN)$] was recrystallized from acetonitrile, recrystallised $FeCl_2·4H_2O$ was converted into the dihydrate by heating to 100 °C under vacuum for 2—3 h, and the trialkyl phosphites were distilled prior to use. Kieselgel G (type 60) (Merck) was used for thin-layer chromatography.

Spectroscopic Techniques.—Infrared spectra were obtained as mulls in Nujol on a Perkin-Elmer 457 grating spectrometer. 32.1-MHz ^{11}B n.m.r. spectra were recorded on a JEOL-PS-100-PFT-100 spectrometer, 100-MHz ^1H n.m.r. spectra on a Perkin-Elmer R14 spectrometer, and 40.5-MHz ^{31}P n.m.r. spectra on a Varian XL-100 spectrometer. Chemical shifts, δ, are quoted as being negative to high field of the reference standards which were tetramethylsilane, $SiMe_4$, for ^1H n.m.r., 85% H_3PO_4 for ^{31}P n.m.r., and $OEt_2·BF_3$ for ^{11}B n.m.r. All spectra were recorded at ambient temperature.

Electrochemical Equipment.—Electrochemical reactions were carried out in a two-compartment cell, the anode and cathode sides being separated by a two-layer Celgard 4510 membrane system. The reactions were carried out under conditons of controlled potential, which could be set using a Hi-Tek Instruments DT2101 potentiostat, and was measured relative to a Ag–Ag [NO_3] (0.1 mol dm^{-3}) reference electrode where CH_3CN was the solvent used, or to a standard calomel electrode (s.c.e.) where MeOH was the solvent used. The total current passed was recorded on a Hi-Tek Instruments gated digital integrator and digital voltmeter. The current was monitored on a Servoscribe chart recorder measuring the voltage drop across a Decade resistance box in series with the cell. The potentiostat described above, together with a Hi-Tek Instruments PPR1 waveform generator, was used for cyclic voltammetry, and the cyclic voltammograms recorded on an Advance Electronics model HR-96 X-Y recorder.

Metathesis Reactions.—*Preparation of trans*-[Fe$\{BH_3(CN)\}_2\{P(OMe)_3\}_4$]. To a suspension of $FeCl_2·2H_2O$ (1.39 g, 8.5 mmol) and Na[$BH_3(CN)$] (1.73 g, 27.5 mmol) in MeOH (50 cm^3) was added dropwise $P(OMe)_3$ (5.0 cm^3, 5.25 g, *ca.* 42 mmol) over 0.2 h. The solution immediately turned golden-orange, and a yellow precipitate formed. After stirring for another 0.3 h, the mixture was filtered. Repeated extraction of the precipitate with CH_2Cl_2 and reprecipitation with Et_2O yielded trans-*bis*(*cyanotrihydroborato*)*tetrakis*(*trimethyl phosphite*)*iron*(II) as a yellow solid (3.11 g, 58%) (Found: C, 26.55; H, 6.60; B, 3.65; N, 4.40; P, 18.95. $C_{14}H_{42}B_2FeN_2O_{12}P_4$ requires C, 26.6; H, 6.70; B, 3.40; N, 4.45; P, 19.6%). T.l.c. showed one component, R_F 0.38 (eluting solvent 99% CH_2Cl_2–1% EtOH). Relevant spectral data are presented and discussed in the text in all cases.

Reaction in CH_3CN. The reaction conditions were identical to those described above, except that the solvent used was CH_3CN. The product was obtained by filtering the solution, removal of the CH_3CN *in vacuo*, and extraction of the solid as described above, to give a yellow powder (4.29 g, 80%). T.l.c. showed two components, R_F 0.38 and 0.22 (eluant 99% CH_2Cl_2–1% EtOH) in the ratio 70% *trans* : 30% *cis*.

Preparation of trans-$[Fe\{BH_3(CN)\}_2\{P(OEt)_3\}_4]$. The scale was identical to that adopted in the analogous $P(OMe)_3$ reaction, using $P(OEt)_3$ (7.8 cm^3, 7.5 g, *ca.* 45 mmol). In this case the reaction mixture was stirred for 0.3 h after addition of the $P(OEt)_3$. The orange-red solution was then filtered and the solvent removed under vacuum. Repeated extraction of the residue with CH_2Cl_2 and precipitation with n-hexane gave trans-*bis(cyanotrihydroborato)tetrakis(triethyl phosphite)iron*(II) (5.07 g, 74.5%) as a yellow solid (Found: C, 37.65; H, 8.10; B, 4.20; N, 3.30; P, 15.45. $C_{26}H_{66}B_2FeN_2O_{12}P_4$ requires C, 39.05; H, 8.30; B, 2.70; N, 3.50; P, 15.5%). T.l.c. showed one component, R_F 0.57 (eluant 99.5% CH_2Cl_2–0.5% EtOH).

Reaction in CH_3CN. The reaction conditions were identical to those adopted for the reaction carried out in MeOH. The product was obtained as a mixture of the *cis* and *trans* isomers of $[Fe\{BH_3(CN)\}_2\{P(OEt)_3\}_4]$ (5.84 g, 86%). T.l.c. showed two components, R_F 0.60 and 0.29 (eluant 99.5% CH_2Cl_2–0.5% EtOH).

Electrochemical Reactions.—Preparation of $[Fe\{BH_3(CN)\}_2\{P(OMe)_3\}_4]$. A solution of $Na[BH_3(CN)]$ (0.63 g, 10 mmol) in CH_3CN (300 cm^3) was loaded into the cell described earlier. Trimethyl phosphite (2.5 cm^3, 2.6 g, *ca.* 21 mmol) was added to the anode compartment, and the system flushed with nitrogen. The anode was a tightly coiled piece of iron wire (1.774 g), and the cathode was made of copper foil. The electrolysis was carried out at an applied voltage of 0.500 V. The current rose to a maximum of 220 mA, and decayed exponentially until 965 coulombs had passed, the final current being 30 mA. The anode was reweighed (1.521 g, weight loss 0.253 g). The product was isolated in the same way as in the metathesis reactions, and obtained as a bright yellow solid (1.93 g, 68%). T.l.c. and ^1H n.m.r. spectroscopy showed the product to be 65% *cis* and 35% *trans*.

Preparation of $[Fe\{BH_3(CN)\}_2\{P(OEt)_3\}_4]$. The scale was identical to that of the reaction using $P(OMe)_3$. The reaction did not proceed as rapidly as that using $P(OMe)_3$, the current in this case reaching a peak value of 70 mA. The product was isolated in the same manner as in the metathesis reaction. T.l.c. implied a *cis–trans* mixture containing *ca.* 30% *cis* and 70% *trans* isomers.

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