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Electrochemical and Metathetical Preparations of Cyanotrihydroborato Complexes of Cobalt

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In a series of recent papers, it was shown that anodic dissolution of transition-metals in solutions of borane anions can lead directly to interesting transition-metal complexes [1–4]. It was also shown [1] that the complexes $[Fe(BH_3CN)_2\{P(OR)_3\}_4]$ (R = Me, Et) could be prepared either by anodic dissolution of iron in solutions of the appropriate ligands or metathetically by the reaction:

$$FeCl_2 + 2NaBH_3CN + 4P(OR)_3 \longrightarrow Fe(BH_3CN)_2\{P(OR)_3\}_4] + 2NaCl.$$

The two preparative techniques were shown to give different *cis:trans* isomer ratios.

The present work describes the synthesis characterisation and reactivity of some BH_3CN^- complexes of cobalt.

Experimental

All manipulations were carried out under nitrogen or *in vacuo*, unless otherwise stated.

$[CoCl_2(py)_2]$ (py = pyridine) was prepared from $CoCl_2$ and py as described in the literature [5].

Spectroscopic Techniques. IR spectra were obtained on a Perkin-Elmer 457 grating spectrometer and 32.1 MHz ^{11}B NMR spectra on a JEOL-PS-100-PFT-100 spectrometer. Chemical shifts, δ, are quoted as being negative to high field of the reference standard, OEt_2BF_3. UV-visible spectra were recorded on a Pye-Unicam SP1800.

Electrochemical equipment. Electrolyses were carried out in a simple two-compartment cell, comprising an anode compartment (capacity *ca.* 200 cm^3) and a smaller, co-axial cathode compartment. These were separated by either a polytetrafluoroethylene (PTFE) membrane or a cation exchange (Nafion 427) membrane in the sodium ion form.

Kieselgel G (Type 60) (Merck) was used for thin layer chromatography, and Silica Gel M.F.C. (100–200 mesh) (Hopkin and Williams) was used for column chromatography.

Metathesis Reactions

Preparation of $[Co(BH_3CN)_2(CH_3CN)_2(py)_2]$

$[CoCl_2(py)_2]$ (1.00 g, 3.5 mmol) and $NaBH_3CN$ (0.45 g, 7.1 mmol) were stirred together in CH_3CN (60 cm^3) for 90 min, after which the resultant mixture was filtered, giving a white precipitate (NaCl) and a blue solution. The solution was reduced in volume to *ca.* 15 cm^3 and Et_2O (*ca.* 45 cm^3) added to yield the crude product as a pale pink powder. Purification was effected by dissolving the solid in CH_2Cl_2 (*ca.* 15 cm^3), filtering the resultant solution and adding CH_3CN (*ca.* 10 cm^3) to the filtrate. The volume of the solution thus obtained was reduced to *ca.* 10 cm^3, and Et_2O added to precipitate Bis(acetonitrile)bis(cyanotrihydroborato)bis(pyridine)cobalt (II) (0.58 g, 44%).

Preparation of $[Co(BH_3CN)_2(py)_4]$

$[Co(BH_3CN)_2(CH_3CN)_2(py)_2]$ (0.23 g, 0.61 mmol) and pyridine (0.10 g, 1.26 mmol) were stirred together in CH_3CN (*ca.* 30 cm^3) for 45 min, after which the volume of the solution was reduced to *ca.* 10 cm^3. Et_2O (40 cm^3) was added and the resultant pink precipitate collected (0.15 g, 54%). *Anal.* Found: C, 56.9; H, 5.46; N, 18.6%. Calcd. for $[Co(BH_3CN)_2py_4]$: C, 58.1; H, 5.75; N, 18.5%.

Preparation of $[Co(BH_3CN)_2(H_2O)_2(py)_2]$

A sample of $[Co(BH_3CN)_2(CH_3CN)_2(py)_2]$ was exposed to the open air for 48 hr, with the gradual replacement of co-ordinated CH_3CN by H_2O. This process was monitored by observing the relative decrease in the acetonitrile C–N stretching band (at 2280 cm^{-1}) and the acetonitrile ($\nu_3 + \nu_4$) (2310 cm^{-1}) combination band intensities, and the growth of O–H stretching bands at 3530 and 3450 cm^{-1} in the infrared spectrum of the sample.

Anal. Found: C, 43.9; H, 6.01; N, 16.2%. Calcd. for $[Co(BH_3CN)_2(H_2O)_2(py)_2]$: C, 43.3; H, 6.06; N, 16.8%.

If the sample was left in the open atmosphere for periods exceeding 3 days, the infrared spectrum showed broadening in the O–H stretching region (*ca.* 3500 cm^{-1}), and the appearance of a number of other previously undetected bands.

Electrochemical Reactions

Preparation of $[Co(BH_3CN)_2(CH_3CN)_2(py)_2]$

A solution of $NaBH_3CN$ (0.63 g, 10 mmol) in CH_3CN (200 cm^3) was loaded into the electrochemical cell, 150 cm^3 into the anode, 50 cm^3 into the cathode, these being separated by a PTFE membrane. Pyridine (0.79 g, 10 mmol) was added to the anode compartment. The anode itself was a coil of cobalt wire, the cathode a piece of platinum foil. The electrolysis was carried out at a potential of 0.00 V with respect to Ag/0.1 *M* $AgNO_3$ and the current reached a maximum of 200 mA, with a final current of 40 mA after the passage of 965 C. The weight loss of cobalt was 0.2955 g. The volume of the resulting red-mauve anolyte was reduced to *ca.* 20 cm^3, and Et_2O (*ca.* 50 ml) added, precipitating the crude product. Purification was effected as described earlier, yielding a pale pink solid (0.79 g, 42%). The compound was shown to be identical to the product obtained metathetically by its IR spectrum.

Preparation of [Co(BH₃CN)₂(py)₄]

A solution of $NaBH_3CN$ (0.64 g, 10.15 mmol) and pyridine (1.59 g, 20.12 mmol) in CH_3CN (170 cm^3) were loaded into the anode compartment of the cell. The catholyte comprised an 0.1 *M* solution of Bu_4NBF_4, separated from the anolyte by a cation exchange membrane (Nafion 427) in the Na^+ form. The anode comprised a coil of cobalt wire, the cathode a piece of platinum foil. The electrolysis was carried out at –0.350 V, with a maximum current of 250 mA, with a final current of 90 mA at 970 C. The weight loss of cobalt was 0.2961 g. The anolyte was reduced in volume to 30 cm^3, with precipitation of the product (1.42 g, 63%). The product could be obtained as pink crystals by slow evaporation of a $CH_2Cl_2–CH_3CN$ solution (*Anal.* Found C, 57.9; H, 5.90; N, 18.3%. Calcd. for $[Co(BH_3CN)_2(py)_4]$: C, 58.1; H, 5.75; N, 18.5%).

Results and Discussion

The complex $[Co(BH_3CN)_2(CH_3CN)_2(py)_2]$ could be obtained in either of two ways. It could be produced metathetically, as shown:

$$[CoCl_2(py)_2] + 2NaBH_3CN \xrightarrow{CH_3CN} [Co(BH_3CN)_2(CH_3CN)_2(py)_2] + 2NaCl$$

or by the anodic dissolution of cobalt in an acetonitrile solution containing equimolar quantities of $NaBH_3CN$ and pyridine. It was an air/moisture-sensitive pale pink solid. The IR spectrum (see Table I for details) shows bands at 2310 and 2280 cm^{-1} indicative of co-ordinated CH_3CN [2], and a strong sharp band at 2200 cm^{-1}, indicative of co-ordinated BH_3CN^- [1, 2]. Several bands ascribable to co-ordinated pyridine were present, *e.g.*, ring C–H stretching mode at 3080 cm^{-1}.

In the solid state, in air, the complex exchanged its acetonitrile ligands for water, and this could be readily observed by IR spectroscopy (Table I). In particular, the bands at 2310 and 2280 cm^{-1} disappeared, whilst simultaneously two strong O–H stretching bands appeared at 3530 and 3450 cm^{-1}. The C–N stretching frequency of the BH_3CN ligand shifted from 2200 cm^{-1} in the bis acetonitrile complex, to 2218 cm^{-1} in the bis aquo derivative. Also very noticeable were the changes observed in the ring C–H and ring deformation bands. In the bis acetonitrile complex, two bands were observed for ring C–H deformation, at 765 and 755 cm^{-1}, and two bands were obtained for ring deformation, at 698 and 705 cm^{-1}. After aquation, only single bands were left for ring C–H deformation and ring deformation, at 755 cm^{-1} and 698 cm^{-1} respectively. This data illustrates the lability of the acetonitrile ligands in $[Co(BH_3CN)_2(CH_3CN)_2(py)_2]$ in the solid state.

It is interesting to examine the lability of the acetonitrile ligands of the complex in solution, since it is readily soluble in both CH_3CN and CH_2Cl_2. In CH_3CN it gave a red-pink solution with a weak absorption maximum at 490 nm. typical of an octa-

TABLE I. IR Data of the Complexes.

Compound	IR Bands (cm^{-1})
$[Co(BH_3CN)_2(CH_3CN)_2(py)_2]$	3080(w), 2370(s, sh), 2345(s), 2310(M), 2280(s), 2230(w), 2200(VS), 600(w, br), 1900(vw, br), 1608(s), 1579(w), 1490(M), 1449(s), 1242(w), 1219(s), 1158(M), 1127(s), 1069(M), 1042(M), 1014(M), 950(w v), 930(w), 865(w), 790(w), 765(s), 755(s), 705(s), 698(s), 630(M), 432(M).
$[Co(BH_3CN)_2(H_2O)_2(py)_2]$	3530(s), 3450(s), 3200(w), 3080(w), 2340(s, sh), 2320(s), 2240(w), 2218(s), 2000(w, br), 1930(w, br), 1611(s), 1580(w), 1492(w), 1450(s), 1240(w), 1220(M), 1170(M), 1157(M), 1135(M), 1070(M), 1042(M), 1012(M), 785(w, br), 755(s), 695(s), 652(w), 630(M), 600(w, br), 430(M, br).
$[Co(BH_3CN)_2(py)_4]$	3110(w), 3090(w), 3070(w), 3050(w), 2475(w), 2370(M, sh), 2335(s), 2270(M), 2220(w), 2185(s), 2000(w, br), 1950(w, br), 1880(w), 1700(w, br), 1635(w), 1603(s), 1570(w), 1490(s), 1443(vs), 1239(w), 1220(s), 1215(s), 1160(m, sh), 1155(M), 1130(M, sh), 1120(s), 1070(M), 1060(M, sh), 1040(s), 1008(s), 980(w), 955(w), 860(w), 765(s), 745(s, sh), 742(s), 705(s), 695(vs), 625(s), 245(s), 420(M, 420(M, sh).

hedral complex. In contrast, its solution in CH_2Cl_2 was deep blue with a strong absorption at 580 nm. typical of a tetrahedral species, and the likely process is:

$$[Co(BH_3CN)_2(CH_3CN)_2(py)_2] \xrightarrow{CH_2Cl_2} [Co(BH_3CN)_2(py)_2] + 2CH_3CN$$

The ^{11}B NMR spectra of the complex, obtained in both solvents, also reflects the variable co-ordination behaviour. In CH_3CN solution, the spectrum comprised a definite, though poorly defined, quartet at $\delta + 55$ ppm; in CH_2Cl_2 the resonance showed as a broad ill-defined peak at $\delta + 71$ ppm. The low field chemical shifts arise as a result of paramagnetic Co(II) present in the molecule.

The evidence described above shows that in suitable conditions the acetonitrile ligands in $[Co(BH_3CN)_2(CH_3CN)_2(py)_2]$ are labile. However, in CH_3CN solution the complex remains predominantly octahedral. It was, therefore, of interest to examine the reactivity of the complex in CH_3CN solution. It was found that the bis acetonitrile complex was recovered intact if the solution was exposed to air or even if water was added to the solution. Although neither 2-methyl nor 2-chloro-pyridine reacted with it, the addition of 2 mole equivalents of pyridine itself to an acetonitrile solution of the complex gave $[Co(BH_3CN)_2(py)_4]$.

The complex was also prepared directly by the anodic dissolution of cobalt in an acetonitrile solution of $NaBH_3CN$ and pyridine (mole ratios 1:2).

The tetrakis pyridine complex was isolated as an air-stable crystalline pink solid, soluble in methylene chloride, but only sparingly so in CH_3CN. IR bands are listed in Table I, and indicate only BH_3CN^- and pyridine ligands in the molecule.

The complex gave a pale mauve solution in CH_2Cl_2, the UV-visible spectrum showing a mixture of octahedral and tetrahedral species present, with the octahedral form predominatly.

The ^{11}B NMR spectrum of $[Co(BH_3CN)_2(py)_4]$, in CH_2Cl_2 solution, comprised an ill-defined quartet at $\delta = +23$ ppm, again the result of a paramagnetic shift.

When the complex $[Co(BH_3CN)_2(py)_4]$ was chromatographed, using CH_2Cl_2 with 5–10% CH_3CN as eluent, a purple band was eluted, from which $[Co(BH_3CN)_2(CH_3CN)_2(py)_2]$ was isolated. This could be explained by the equilibria:

$$[Co(BH_3CN)_2(py)_4] \rightleftharpoons [Co(BH_3CN)_2(py)_2] + 2py$$

and

$$[Co(BH_3CN)_2(py)_2] + 2CH_3CN \rightleftharpoons [Co(BH_3CN)_2(CH_3CN)_2(py)_2]$$

On a retentive medium such as silica gel, the first equilibrium would be displaced to the right, as a result of the different retention times of the complex and the pyridine.

On evaporation of the resultant eluent, comprising $[Co(BH_3CN)_2(py)_2]$, to low volume, the CH_3CN concentration increase causing a bias in favour of the right hand side of the second equilibrium, and the bis-acetonitrile complex precipitated on addition of Et_2O.

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