Electrochemical Behaviour of Five-co-ordinate Nitrosyl Cobalt Complexes in an Aprotic Medium

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The cathodic and anodic behaviour of some five-co-ordinated nitrosyl cobalt complexes of the type $[CoXL_3(NO)][BPh_4]$ [X = Cl or I, L = $P(OEt)_3$ or $P(OMe)_3$] has been investigated at platinum electrodes in acetonitrile solvent. Four-co-ordinated mononitrosyl cobalt compounds of formula $[CoL_3(NO)]$ are formed *via* an e.c.e. type reduction mechanism (electron transfer followed by a chemical reaction followed by electron transfer). The anodic oxidation of these $[CoL_3(NO)]$ compounds has also been studied. The $[CoXL_3(NO)][BPh_4]$ complexes with L = $P(OEt)_3$ undergo a complicated oxidation process leading to the dinitrosyl $[CoL_2(NO)_2][BPh_4]$ and $[CoXL(NO)_2]$ compounds and to species containing no nitrosyl ligand. The chemical reactions associated with the charge-transfer steps involve traces of water.

NITROSYL cobalt complexes have been thoroughly investigated with the aim of setting up new syntheses, of elucidating their structures and reactivities,[1-10] and of examining their potential as catalysts.

However, no electrochemical study on nitrosyl cobalt compounds has been published until now, despite the powerful tools which electroanalytical techniques provide for preparing derivatives in unusual oxidation states, for revealing the formation of short-lived intermediates, and for shedding light on the oxidation and reduction mechanisms.

Thus, we have undertaken a study of the redox behaviour exhibited at a platinum electrode in an aprotic medium by five-co-ordinated nitrosyl cobalt compounds containing phosphine groups with strong π-acceptor properties. The compounds examined were of general formula $[CoXL_3(NO)][BPh_4]$, with X = Cl or I and L = $P(OEt)_3$ or $P(OMe)_3$.

RESULTS AND DISCUSSION

The cyclic-voltammetric curve recorded at a platinum electrode on a 0.1 mol dm^{-3} tetraethylammonium perchlorate acetonitrile solution of $[CoCl\{P(OEt)_3\}_3(NO)][BPh_4]$, by scanning the potential initially in the cathodic direction, is shown in Figure 1. Only one reduction peak (a) was observed, associated with an anodic response (b). For the iodo-compounds a very similar result was obtained, but peak b appeared to be split into two neighbouring peaks.

In neither case could any anodic response be detected if the solution surrounding the electrode surface was renewed by stirring after traversing peak a.

The current values of the anodic response relative to the one-electron oxidation of bis(cyclopentadienyl)iron(II) were used to evaluate the number of electrons involved in the electrode processes of the nitrosyl cobalt compounds, both on a voltammetric and a amperometric time scale. By taking into account the results of these comparisons and by analysing the data reported in Table 1 it can be deduced that for all the compounds studied the first step of the cathodic process (the only one occurring on the voltammetric and amperometric time scale) is an irreversible one-electron charge transfer. The extent of the cathodic shift of the peak potential as a function of the sweep rate, the difference between the potentials at half-peak and at the peak, together with the absence of any directly associated anodic peak, and, finally, the constancy of the $i_p/v^{\frac{1}{2}}$ parameter (v = potential scan rate) allow us to deduce the irreversible nature of the electrode process.[11] The values of the charge-transfer coefficient,

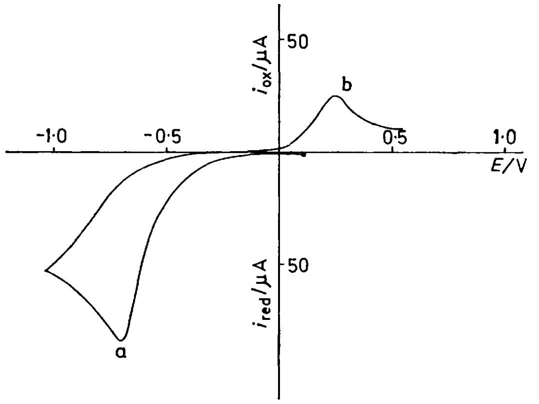


FIGURE 1 Cyclic-voltammetric curve recorded on a MeCN solution containing 3.42 × 10^{-3} mol dm^{-3} $[CoCl\{P(OEt)_3\}_3(NO)][BPh_4]$ and 0.1 mol dm^{-3} $[NEt_4][ClO_4]$ with a platinum working microelectrode, scan rate 0.2 V s^{-1}. Initial scan in cathodic direction

TABLE 1

Linear-sweep voltammetric data relative to the reduction processes

Compound	$(E_p)_c$/V [a]	$(E_{p/2} - E_p)_c$/mV	$\left[\frac{\partial (E_p)_c}{\partial \log v}\right]$/mV [b]	α [c]
$[CoI\{P(OEt)_3\}_3(NO)][BPh_4]$	−0.52	120 ± 5	75 ± 5	0.40
$[CoI\{P(OMe)_3\}_3(NO)][BPh_4]$	−0.30	135 ± 10	85 ± 10	0.35
$[CoCl\{P(OEt)_3\}_3(NO)][BPh_4]$	−0.69	170 ± 10	105 ± 10	0.28

[a] Measured at potential scan rate of 0.2 V s^{-1}. [b] Calculated by varying the potential scan rate in the range 0.05—100 V s^{-1}. [c] Mean values.

α, for the cathodic reduction of the complexes, calculated either from $(E_{p/2} - E_p)_c$ or from $\partial(E_p)_c/\partial\log v$, are also reported in Table 1. A good agreement (within 10%) was found between the α values calculated by the two different methods.

Controlled-potential coulometric tests carried out at potentials corresponding to peak a allowed us to ascertain that for all the complexes investigated two electrons per cobalt complex unit were spent in the overall reduction process. It is, therefore, evident that a slow chemical reaction, which does not occur on the voltammetric and amperometric time scale, follows the first charge-transfer step and gives rise to a species which is itself reducible, *via* a further one-electron step, at the same, or less negative, potentials as those of peak a.

The slowness of this chemical reaction is indicated by the constancy of $i_p/v^{\frac{1}{2}}$ obtained by linear-sweep voltammetric tests and of the product $it^{\frac{1}{2}}$ by chronoamperometry. These quantities showed no increase either at the lowest voltammetric scan rates or at the longest chronoamperometric times.

TABLE 2

Infrared and ^1H n.m.r. data for the reduction products

Electrolysed compound	Recovered reduction compound	$\nu(NO)/cm^{-1}$	Chemical shift [a] CH$_2$	Chemical shift [a] CH$_3$
$[CoI\{P(OEt)_3\}_3(NO)][BPh_4]$	$[Co\{P(OEt)_3\}_3(NO)]$	1 679 [b] 1 680 [c]	6.03 (q)	8.77 (t)
$[CoI\{P(OMe)_3\}_3(NO)][BPh_4]$	$[Co\{P(OMe)_3\}_3(NO)]$	1 688 [b] 1 690 [c]		6.41 (d)
$[CoCl\{P(OEt)_3\}_3(NO)][BPh_4]$	$[Co\{P(OEt)_3\}_3(NO)]$	1 679 [b] 1 680 [c]	6.03 (q)	8.77 (t)

[a] Values quoted in τ relative to $SiMe_4$ (τ 10); d = doublet, t = triplet, q = quintet. [b] As KBr pellet. [c] In dichloromethane solution.

Controlled-potential electrolyses were performed with the aim of identifying the nature of the final reduction products. The nature of the supporting electrolyte seemed to have no effect, since the same electrolysis products were recovered using either $Na[ClO_4]$ or $[NEt_4][ClO_4]$. By reducing $[CoI\{P(OEt)_3\}_3(NO)][BPh_4]$ and $[CoCl\{P(OEt)_3\}_3(NO)][BPh_4]$ the same cobalt complex, *i.e.* $[Co\{P(OEt)_3\}_3(NO)]$, could be isolated after the completion of the electrolysis. The $[Co\{P(OMe)_3\}_3(NO)]$ complex was isolated from the electrolysed solutions of $[CoI\{P(OMe)_3\}_3(NO)][BPh_4]$.

The identification of the reduction products was confirmed by elemental analysis and spectroscopic data from i.r. and ^1H n.m.r. measurements. The spectroscopic results are summarized in Table 2.

In agreement with the proposed nature of the electrolysis products, the recovered compounds were diamagnetic, both in the solid state and in solution; moreover, solutions of the cobalt species obtained by electrolysis were non-conducting. The ^1H n.m.r. data suggest equivalence of the three phosphite ligands, thus indicating a tetrahedral (or pseudo-tetrahedral) geometry for the species obtained.

It is noteworthy that neither the species $[Co\{P(OEt)_3\}_3(NO)]$ nor $[Co\{P(OMe)_3\}_3(NO)]$ has been obtained in the crystalline form by means of chemical preparative methods, since in both cases intractable oils formed.[12]

Argentometric titrations performed on the electrolysed solutions (see Experimental section) confirmed that 1 mol of halide ions was released per mol of electrolysed compound.

On the basis of the above reported data the reduction mechanism can be outlined as equations (1)—(3) with

$$[CoXL_3(NO)][BPh_4] + e^- \longrightarrow [CoXL_3(NO)] + [BPh_4]^- \quad \text{electron transfer} \quad (1)$$

$$[CoXL_3(NO)] \xrightarrow{\text{slow}} [CoL_3(NO)]^+ + X^- \quad \text{chemical} \quad (2)$$

$$[CoL_3(NO)]^+ + e^- \longrightarrow [CoL_3(NO)] \quad \text{electron transfer} \quad (3)$$

X = I and L = $P(OEt)_3$ or $P(OMe)_3$ and with X = Cl and L = $P(OEt)_3$.

A cyclic-voltammetric curve recorded at a platinum electrode on an electrolysed solution of $[CoCl\{P(OEt)_3\}_3(NO)][BPh_4]$ is shown in Figure 2. Oxidation of free iodide ions resulting from the reduction of the iodo-compounds prevented us from recording any reliable response at potentials greater than *ca.* +0.2 V *vs.* s.c.e. in these cases (s.c.e. = saturated calomel electrode). The less anodic of the two partially overlapping peaks which correspond to b in Figure 1 for the case of the iodo-compounds can be ascribed to the oxidation of iodide ions released in the reduction process. Peak c in Figure 2 and peak b in Figure 1 are located at the same potential and are attributable to the oxidation of the species $[Co\{P(OEt)_3\}_3(NO)]$. It will be shown later that peak d

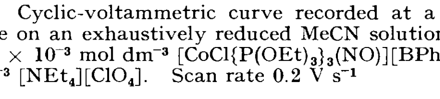
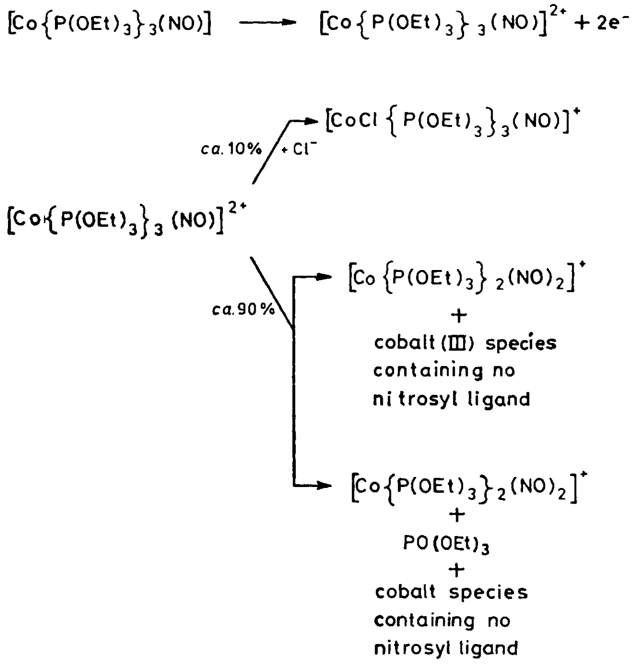


FIGURE 2 Cyclic-voltammetric curve recorded at a platinum electrode on an exhaustively reduced MeCN solution containing 7.03×10^{-3} mol dm^{-3} $[CoCl\{P(OEt)_3\}_3(NO)][BPh_4]$ and 0.1 mol dm^{-3} $[NEt_4][ClO_4]$. Scan rate 0.2 V s^{-1}

cannot be ascribed to the oxidation of the starting compound $[Co\{P(OEt)_3\}_3(NO)][BPh_4]$, which should be formed at peak c, although its position along the potential axis could suggest a similar hypothesis (see below).



SCHEME

Controlled-potential coulometric tests carried out at potentials corresponding to peak c led to a consumption of two electrons per molecule of electrolysed compound. The analysis of the product revealed that $[CoCl\{P(OEt)_3\}_3(NO)][BPh_4]$ was formed only to a minor extent (*ca.* 10%). The major product was shown to be the dinitrosyl cobalt species $[Co\{P(OEt)_3\}_2(NO)_2][BPh_4]$.

The identification of the latter compound was made on the basis of i.r. data [ν(NO) in CH_2Cl_2 at 1 811 and 1 869 cm^{-1}] [12] and of ^1H n.m.r. measurements (a triplet attributable to the methyl protons of the phosphite groups at τ 8.74 and a multiplet due to the methylenic protons of the phosphite groups at τ 6.06).[12] The presence of phosphite oxide in solution was also checked (strong i.r. band at 1 260 cm^{-1}). The dinitrosyl cobalt complex was also identified by cyclic-voltammetric tests carried out on the anodically electrolysed solutions, by comparison with those obtained on solutions of authentic samples; these voltammograms showed a reversible reduction process with a peak potential of -0.43 V and an anodic one with a peak potential at $+0.88$ V.[13] The location of the latter peak at potentials very similar to those at which the oxidation of the starting complex $[CoCl\{P(OEt)_3\}_3(NO)][BPh_4]$ occurred justifies the mistake arising from the cyclic-voltammetric curve reported in Figure 2.

As regards the reaction pathway leading to the dinitrosyl complex, we have verified that $[Co\{P(OEt)_3\}_3(NO)]$ is stable in MeCN solution; furthermore the species $[Co\{P(OEt)_3\}_3(NO)]^+$, which is formed during the reduction of the initial five-co-ordinated mononitrosyl compound, does not lead to dinitrosyl species.

On this basis it seems sensible to suggest that the $[Co\{P(OEt)_3\}_3(NO)]^{2+}$ species is formed directly at the electrode; the formation of the dinitrosyl $[Co\{P(OEt)_3\}_2(NO)_2]^+$ species can be explained by considering the occurrence of a disproportionation reaction and/or a chemical reduction *via* phosphine molecules, which are oxidized to phosphite oxide. The nitrosyl content in the recovered dinitrosyl compound corresponds to *ca.* 90% of that present in the starting cobalt complex. Moreover, the reaction between the electrogenerated species and the chloride ions released in the previous reduction accounts for the formation of a small amount of the initial compound $[CoCl\{P(OEt)_3\}_3(NO)][BPh_4]$ which can be separated from the electrolysed solution. This oxidation pathway is summarized in the Scheme.

The formation of small amounts of triethyl phosphite involves traces of water and accounts for the slight acidic character of the final solution.

The study of the anodic oxidation of the $[CoXL_3(NO)][BPh_4]$ complexes was rather difficult and more complicated than the cathodic reduction. Consequently the results obtained were less satisfactory and the oxidation steps have not been completely elucidated.

The anodic portion of a cyclic voltammogram recorded on an acetonitrile solution containing 0.1 mol dm^{-3} $[NEt_4][ClO_4]$ and $[CoCl\{P(OEt)_3\}_3(NO)][BPh_4]$ is shown in Figure 3. A well formed anodic peak was recorded, but no associated cathodic process was evident in the potential range up to the direct reduction of the initial compound. Similar voltammetric pictures were exhibited by all the other complexes studied.

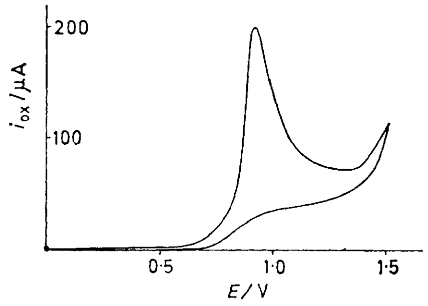


FIGURE 3 Anodic portion of a cyclic-voltammetric curve recorded at a platinum microelectrode on a MeCN solution containing 3.70×10^{-3} mol dm^{-3} $[CoCl\{P(OEt)_3\}_3(NO)][BPh_4]$ and 0.1 mol dm^{-3} $[NEt_4][ClO_4]$. Scan rate 0.1 V s^{-1}

At a potential scan rate of 0.2 V s^{-1} the E_p values for the studied compounds were as follows: $[CoI\{P(OEt)_3\}_3(NO)][BPh_4]$ $(E_p)_a = +0.86$; $[CoI\{P(OMe)_3\}_3(NO)][BPh_4]$ $(E_p)_a = +0.88$; $[CoCl\{P(OEt)_3\}_3(NO)][BPh_4]$ $(E_p)_a = +0.92$ V.

At potentials more anodic with respect to the switching potential of Figure 3, poorly defined anodic responses were observed for all the complexes. The electrode processes occurring in this potential region appeared complicated by adsorption phenomena poisoning the electrode surface; the latter must be mechanically cleaned in order to record further reproducible voltammograms. The occurrence of these poisoning effects prevented any reliable study of these processes.

Cyclic-voltammetric tests carried out at potential scan rates in the range 0.05—100 V s^{-1} revealed that the [CoI{P(OEt)$_3$}$_3$(NO)][BPh$_4$] complex exhibits a voltammetric behaviour typical for a reversible one-electron charge transfer followed by an irreversible fast chemical reaction of first order with respect to depolarizer concentration [11] up to potential scan rates of *ca.* 2 V s^{-1}. In fact the $E_p - E_{p/2}$ value was equal to 50 mV, the peak potential shifted anodically to an extent of 30 mV per ten-fold increase in sweep rate, and $i_p/v^{\frac{1}{2}}$ showed a slight decrease at increasing scan rate. Beyond 2 V s^{-1} the responses showed a departure from that typical for a reversible charge transfer; in fact both $E_p - E_{p/2}$ and $\partial E_p/\partial \log v$ values progressively increased. No associated cathodic response could be observed even at the highest potential sweep rates.

Similar e.c. type mechanisms were also found for [CoI{P(OMe)$_3$}$_3$(NO)][BPh$_4$] and for [CoCl{P(OEt)$_3$}$_3$(NO)][BPh$_4$]. However these compounds exhibit a lesser degree of reversibility for the electrode charge transfer: [CoI{P(OMe)$_3$}$_3$(NO)][BPh$_4$] showed responses typical for reversible electron transfer only up to 0.2 V s^{-1} and [CoCl{P(OEt)$_3$}$_3$(NO)][BPh$_4$] up to 0.5 V s^{-1}. In all cases, chronoamperometric tests carried out at potentials of *ca.* 250 mV beyond the peak potential showed that one electron per molecule of depolarizer is involved in the electrode processes, since the values of the $it^{\frac{1}{2}}$ product were coincident with those relative to the one-electron anodic oxidation of bis(cyclopentadienyl)iron(II) at the same concentration and remained unchanged in the range 2×10^{-3}—5 s.

However, controlled-potential coulometric tests revealed that two electrons are involved in the overall electrode processes. This result indicates that very slow chemical reactions leading to species more easily oxidizable follow the fast chemical reaction evidenced by voltammetric tests. Hence, the overall oxidation process should be an e.c.e. type mechanism, where the chemical process consists of at least two steps.

Cyclic voltammograms recorded on solutions of [CoI{P(OEt)$_3$}$_3$(NO)][BPh$_4$] and of [CoI{P(OMe)$_3$}$_3$(NO)][BPh$_4$] exhaustively electrolysed at *ca.* +1.00 V again revealed the occurrence of the anodic electrode processes complicated by adsorption phenomena similar to those observed with the starting solutions; by scanning the potential in the cathodic direction two poorly defined reduction peaks were recorded, with E_p values of −0.55 and −0.90 V, respectively. Qualitatively similar voltammetric pictures were obtained on anodically oxidized solutions of [CoCl{P(OEt)$_3$}$_3$(NO)][BPh$_4$]; the peak potentials of the process evident in the cathodic scan occurred in this case at −0.70 and −0.90 V.

Rather surprisingly, the analysis of the nitrosyl cobalt complexes present in the solutions led to the identification of two dinitrosyl species, [CoXL(NO)$_2$] and [CoL$_2$(NO)$_2$]$^+$ for X = Cl or I and L = P(OEt)$_3$. These species are in equilibrium according to equation (4).[12] The total

$$[\mathrm{CoXL(NO)_2}] + \mathrm{L} \rightleftharpoons [\mathrm{CoL_2(NO)_2}]^+ + \mathrm{X}^- \quad (4)$$

amount of these dinitrosyl species was equal to *ca.* 50% of the electrolysed [CoXL$_3$(NO)][BPh$_4$] complexes.

The absence of any paramagnetic character in the electrolysis products allowed us to exclude the formation of cobalt species with the metal in an oxidation state of two.

The electrolysed solutions showed a marked acidic character; acid–base titrations revealed the presence of a weak acid in a similar quantity to that of the starting material. However it was not possible to ascertain the nature of this acid.

The recovery of acidic protic species in the solutions suggests the occurrence of redox reactions between a cobalt species in a high oxidation state and water, always present in the nominally anhydrous solvent; this reaction may account for the low oxidation state of the cobalt species in the solutions. Moreover, a strong i.r. absorption band at 1 260 cm^{-1} suggests the presence of phosphite oxide in the solutions, although triethyl phosphite undergoes electrode oxidation, irreversible in character, only at *ca.* +1.9 V, as proved with an authentic sample. Hence, this species could also arise from a redox reaction between a cobalt species and triethyl phosphite.

As a further complication, it must be noted that [Co{P(OEt)$_3$}$_2$(NO)$_2$][BPh$_4$] is oxidizable at potential values at which the electrolyses were carried out; [13] we are therefore forced to conclude that its formation takes place during the recovery of the oxidation products.

It must also be noted that by oxidizing [CoI{P(OMe)$_3$}$_3$(NO)][BPh$_4$] no nitrosyl cobalt compound was identified in the electrolysed solution.

EXPERIMENTAL

Materials.—The acetonitrile solvent was purified by repeatedly distilling reagent grade acetonitrile (Carlo Erba) from phosphorus pentaoxide; [14] it was stored on 3 Å molecular sieves (Union Carbide). The supporting electrolyte Na[ClO$_4$] was prepared by neutralizing Na$_2$[CO$_3$] with HClO$_4$(Carlo Erba), twice recrystallized from water, and dried in a vacuum oven. Tetraethylammonium perchlorate was a Carlo Erba product; it was dried in a vacuum oven and used without further purification.

Bis(cyclopentadienyl)iron(II) (Alfa Products) was used as internal standard to evaluate the number of electrons involved in the electrode processes occurring in a voltammetric scan and in a chronoamperometric test.

The synthesis of the five-co-ordinated nitrosyl cobalt complexes of the type [CoXL$_3$(NO)][BPh$_4$] [X = Cl or I; L = P(OEt)$_3$ or P(OMe)$_3$] was performed as reported elsewhere.[13]

Apparatus and Procedure.—Both in the voltammetric and in the chronoamperometric tests the polarizing unit was a P.A.R. (Princeton Applied Research) model 170 Electrochemistry System; the recording devices were either an Amel model 862/A XY recorder, or, at potential sweep rates higher than 0.5 V s^{-1}, a Hewlett–Packard model 1123A storage oscilloscope. The working microelectrode was a platinum sphere (*ca.* 1 mm diameter); it was surrounded by a platinum-spiral counter electrode and its potential value was probed by a Luggin capillary reference electrode.

In the controlled-potential electrolyses an Amel model 551 potentiostat with an Amel model 558 integrator coulometer were used. These tests were carried out in a H-shaped cell with anodic and cathodic compartments separated by a sintered glass disk; the working electrode was a platinum gauze with an apparent area of *ca.* 10 cm^2 and the counter electrode was a mercury pool.

In all electroanalytical tests an aqueous saturated calomel electrode (s.c.e.) was used as reference electrode. All experiments were carried out at 20 ± 0.1 °C.

In the potentiometric acid–base titration a Metrohm E 630 digital pH-meter, equipped with a Metrohm EA 147 combined electrode assembly, was used; a standard solution of morpholine in acetonitrile [15] was added to the electrolysed solution by means of a Metrohm E 402 microburette. The same microburette was employed for addition of a standard $Ag[NO_3]$ aqueous solution in the argentometric titration of the halide ions; in these tests the potential of a silver electrode was monitored by a Philips model PM 2522 digital voltmeter.

Infrared spectra of KBr pellets or dichloromethane solutions were recorded with a Perkin-Elmer model 457 or 508 spectrometer. Solution spectra were obtained with NaCl cells of 0.1 or 1.0 mm thickness.

Hydrogen-1 n.m.r. spectra were recorded by using a Varian EM 390 spectrometer with tetramethylsilane as internal standard. Evans' method [16] was used to check the diamagnetism in solution.

In order to recover the electrolyses products, MeCN solvent was removed from the electrolysed solution by evaporating it *in vacuo*. The residual solid was shaken with chloroform, dichloromethane, or diethyl ether, in order to separate the sparingly soluble supporting electrolyte $Na[ClO_4]$ from the soluble electrolyses products; when $[NEt_4][ClO_4]$ was used, the product was dissolved by using benzene as solvent. The solution was evaporated *in vacuo* until an oil was obtained; the latter was crystallized from anhydrous ethanol.

At every stage of the process great care was taken to avoid contact between air and the reduction products, owing to possible oxidation of the electrolysis products. However, some tests allowed us to exclude the occurrence of a fast oxidation of the reduced species by oxygen.

The elemental analysis data of the reduction products are as follows (Found: C, 36.65; H. 7.80; N, 2.50. Calc. for $C_{18}H_{45}CoNO_{10}P_3$: C, 36.8; H, 7.70; N, 2.40. Found: C, 23.5; H, 5.75; N, 3.15. Calc. for $C_9H_{27}CoNO_{10}P_3$: C, 23.45; H, 5.90; N, 3.05%).

The quantitative determination of halide ions released in the cathodic process was made by means of argentometric titrations. Owing to the slight solubility of $Ag[BPh_4]$ (the tetraphenylborate anions arise from the starting cobalt compounds) these titrations were performed according to the following procedure. The electrolysed solutions were evaporated *in vacuo*, the residual solid was shaken with diethyl ether, in which the cobalt compounds were soluble, while both NaI and NaCl are almost insoluble. After filtration, the solid was dissolved in water and the $[BPh_4]^-$ anions were removed from the solution by adding $K[NO_3]$ to form the sparingly soluble $K[BPh_4]$ salt. The resulting solutions contained the halide ions, which were titrated by means of a standard $Ag[NO_3]$ aqueous solution, and monitoring the potential of a silver electrode dipped in solution.

Anhydrous $HClO_4$ was prepared by anodic oxidation on a platinum electrode of hydrogen gas bubbled through an acetonitrile solution of 0.1 mol dm^{-3} $[NEt_4][ClO_4]$.

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