Electrochemical Behaviour of Cobalt(I) Hydrides

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The electrochemical behaviour of hydrides $[CoHL_4]$ [L = $P(OEt)_3$, $PPh(OEt)_2$, or $PPh_2(OEt)$] in CH_2Cl_2 and MeCN was examined and the relevant oxidation mechanisms elucidated by cyclic voltammetry and coulometry. Different behaviours were observed depending on the nature both of the solvent and of the phosphite ligands. In CH_2Cl_2 the stepwise oxidation of Co^I to Co^{III} was observed, involving a first reversible one-electron oxidation step to $[CoHL_4]^+$, followed, at more positive potentials, by a second one-electron step, chemically irreversible, for all the phosphite ligands employed. In MeCN, for L = $P(OEt)_3$ or $PPh(OEt)_2$, the first reversible oxidation to cobalt(II) hydrides was followed by a second step complicated by associated chemical reactions involving the solvent to give cobalt(III) cations, $[CoH(MeCN)L_4]^{2+}$. For L = $PPh_2(OEt)$ the electrochemical behaviour was complicated by chemical reactions both of the starting cobalt(I) compound and of its oxidation products with the MeCN solvent. Preparative electrolysis allowed the synthesis of a new cobalt(II) derivative characterized as $[CoH\{P(OEt)_3\}_4]BPh_4$ by spectroscopic techniques.

A number of studies on the synthesis, structure and reactivity of cobalt(I) hydrides has been reported in recent years.[1] However, very few data are available on the electrochemical properties[2] of this class of hydrides, although these investigations can shed light on oxidation and reduction mechanisms and allow the synthesis of new cobalt complexes in unusual oxidation states.

Chemical oxidation of $[CoH\{PPh(OEt)_2\}_4]$ with triphenylmethyl salt and ferrocenium cation was studied by Sanders,[3] who discovered the unusual paramagnetic cobalt(II) and dicationic cobalt(III) hydride complexes $[CoH\{PPh(OEt)_2\}_4]^+$ and $[CoH(L)\{PPh(OEt)_2\}_4]^{2+}$ [L = MeCN, PhCN or $PPh(OEt)_2$], respectively. More recently,[4] during our studies on the reactivity of cobalt hydrides $[CoHL_4]$ [L = $P(OEt)_3$, $PPh(OEt)_2$, or $PPh_2(OEt)$], we obtained $[CoH\{PPh(OEt)_2\}_4]^+$ by chemical oxidation of the starting hydride with arenediazonium cations. However, this new reaction took place only with the $PPh(OEt)_2$ derivative, whereas no cobalt(II) complex was obtained starting from $[CoH\{P(OEt)_3\}_4]$ or $[CoH\{PPh_2(OEt)\}_4]$.

In order to compare the chemical and electrochemical properties of cobalt(I) hydrides and to determine whether the synthesis of paramagnetic cobalt(II) species using arenediazonium cations is a peculiar property of the diethoxyphenyl phosphine coligand or whether it is related to the redox properties of the cobalt(I) starting complex, an electrochemical study of cobalt(I) hydrides of the type $[CoHL_4]$ [L = $P(OEt)_3$, $PPh(OEt)_2$, or $PPh_2(OEt)$] in aprotic media, characterized by different co-ordinating properties, was undertaken.

Experimental

General Comments.—Reagent-grade solvents were dried over appropriate drying agents, degassed on a vacuum line and distilled into vacuum-tight storage flasks. Ethanol was dried over calcium hydride, tetrahydrofuran (thf) over sodium–benzophenone, acetonitrile and dichloromethane by reflux and repeated distillation over phosphorus pentaoxide. All other reagents were obtained from commercial sources in the highest available purity and used as received. The commercially available supporting electrolytes (Fluka, *puriss.*) were dried in a vacuum oven at +50 °C.

Infrared spectra were recorded on a Perkin Elmer 683 spectrophotometer, solution NMR spectra (^1H and ^{31}P) using a Bruker AC 200 spectrometer at a temperature between +30 and −90 °C, unless otherwise noted. The ^1H spectra are referred to internal tetramethylsilane; $^{31}P-\{^1H\}$ chemical shifts are reported with respect to 85% H_3PO_4, with downfield shifts considered positive. Conductivities of 10^{-3} mol dm^{-3} solutions of the complexes in nitromethane at 25 °C were measured with a Radiometer CDM 83 instrument. Magnetic susceptibility measurements in solution were performed by the Evans method[5] using a Varian EM 390 NMR spectrometer. Susceptibilities were corrected for the diamagnetism of the ligands by use of tables given by Figgis and Lewis.[6]

Electrochemical Apparatus and Procedures.—Voltammetric experiments were carried out in a three-electrode cell. The working electrode was a glassy-carbon (diameter 5 mm) or platinum disc (diameter 3 mm) mirror-polished with graded alumina powder. It was surrounded by a platinum spiral counter electrode. The potential of the working electrode was probed by a Luggin capillary reference electrode compartment the position of which was made adjustable by mounting it on a syringe barrel. All potentials were measured and are referred to an aqueous saturated calomel electrode (SCE). Tetrabutylammonium perchlorate, $LiClO_4$ or $NaClO_4$ was used as supporting electrolyte; no relevant change in the voltammograms of the compounds studied resulted upon changing the supporting electrolyte.

Macroelectrolyses were carried out in an H-shaped cell with cathodic and anodic compartments separated by a sintered-glass disc. As the compounds examined displayed comparable voltammetric behaviours on glassy-carbon and platinum electrodes, the working electrode used in macroelectrolysis was a large-area platinum gauze, while a platinum spiral served as counter electrode. Controlled-potential experiments carried out to determine the number of electrons involved in the studied processes were performed using millimolar concentrations of cobalt hydrides and 0.1 mol dm^{-3} supporting electrolyte. Preparative electrolyses in acetonitrile were carried out using more concentrated solutions, typically 10^{-2} mol dm^{-3} cobalt(I) hydride and 0.5 mol dm^{-3} $NaClO_4$. For $[CoHL_4]$ with L =

$PPh(OEt)_2$ or $PPh_2(OEt)$, such concentrations of starting compounds led to oversaturation conditions, so that yellow or orange suspensions respectively were observed. However, when L = $PPh(OEt)_2$, progressive solubilization of the solid residue was observed during electrolysis, indicating that the electrolysis products were more soluble in the electrolyte than was the starting compound. Instead, in the case of L = $PPh_2(OEt)$, a solid residue was always observed in the cell, even at the end of electrolysis.

The voltammetric equipment used was an Amel model 552 potentiostat with positive feedback correction of the uncompensated resistance (i.r. drop), in conjunction with a Amel model 568 digital logic function generator. The recording device was either a Hewlett-Packard model 7045B X-Y recorder or a Nicolet 3091 digital storage oscilloscope/waveform digitizer with analogue output for X-Y recorders, depending on the scan rate. In controlled-potential electrolyses, the Amel model 552 potentiostat was coupled to an Amel model 731 integrator. All electroanalytical measurements were carried out at room temperature under a nitrogen atmosphere.

Synthesis of Complexes.—All experiments were carried out under an inert atmosphere, using standard Schlenk techniques and/or a nitrogen-filled glove-box. Hydrides $[CoH\{PPh(OEt)_2\}_4]$ **1a** $[CoH\{P(OEt)_3\}_4]$ **1b** and $[CoH\{PPh_2(OEt)\}_4]$ **1c** were prepared following the procedures previously described.[7]

$[CoHL_4]BPh_4$ **2** [L = $PPh(OEt)_2$ **a** or $P(OEt)_3$ **b**]. These compounds were prepared by macroelectrolysis at controlled potential (−0.2 V *vs.* SCE), starting from a solution of the appropriate hydride $[CoHL_4]$ (0.5 mmol) in acetonitrile (40 cm^3) containing $NaClO_4$ (*ca.* 20 mmol). The electrolysed solution was brought to dryness under reduced pressure and the solid obtained extracted with three portions (10 cm^3) of CH_2Cl_2, in order to separate the soluble electrolysed complex from the only slightly soluble supporting electrolyte $NaClO_4$. The CH_2Cl_2 solution was evaporated under reduced pressure to give an oil which was treated with ethanol (10 cm^3). Addition of $NaBPh_4$ (0.5 mmol, 0.17 g) to the resulting solution afforded a green solid, which was filtered off and crystallized from CH_2Cl_2 (2 cm^3) and ethanol (10 cm^3); yield ≥ 90% (Found: C, 65.70; H, 6.90. Calc. for $C_{64}H_{81}BCoO_8P_4$ **2a**: C, 65.60; H, 6.95. Found: C, 55.30; H, 7.70. $C_{48}H_{81}BCoO_{12}P_4$ **2b** requires C, 55.25; H, 7.80%).

$[CoH(MeCN)\{PPh(OEt)_2\}_4][BPh_4]_2$ **3a**. The complex was prepared by macroelectrolysis at controlled potential (0.7 V *vs.* SCE) of a solution of $[CoH\{PPh(OEt)_2\}_4]$ (0.45 mmol, 0.383 g) in acetonitrile (30 cm^3) containing $NaClO_4$ (15 mmol) as supporting electrolyte. The solvent of the electrolysed solution was removed under reduced pressure to give a residual solid, which was extracted with three portions (10 cm^3) of CH_2Cl_2. The solution obtained was evaporated under reduced pressure to give an oil, which was treated with ethanol (10 cm^3). An excess of $NaBPh_4$ (1 mmol, 0.34 g) in ethanol (3 cm^3) was added to the resulting solution and the mixture stirred at room temperature. After 1 h white microcrystals separated and were filtered off and crystallized from CH_2Cl_2 (2 cm^3) and ethanol (10 cm^3); yield ≥ 90%, m.p. 117 °C (Found: C, 70.50; H, 6.90; N, 1.00. $C_{110}H_{104}B_2CoNO_8P_4$ requires C, 70.55; H, 6.85; N, 0.90%); $\delta_H[(CD_3)_2CO]$ 7.51, 6.88 (60 H, m, Ph), 3.92 (16 H, m, CH_2), and 1.26 (24 H, t, CH_3).

The related complex $[CoH(MeCN)\{P(OEt)_3\}_4][BPh]_2$ **3b** was prepared in the same way by macroelectrolysis at controlled potential of a solution of $[CoH\{P(OEt)_3\}_4]$ in acetonitrile. In this case, however, only an oily product was obtained, the IR and NMR spectra of which seemed to indicate the presence of the supposed cobalt(III) hydride.

Results

Electrochemical Behaviour in CH_2Cl_2.—Fig. 1 shows a typical cyclic voltammogram recorded for $[CoH\{PPh(OEt)_2\}_4]$ **1a**, displaying two oxidation processes in the forward scan and one cathodic process on the return. Return peak C is directly associated to A, as demonstrated on reversal of the sweep soon after peak A (see broken line in Fig. 1). A plot of $i_p(A)v^{-\frac{1}{2}}$ *vs.* v was linear and the $i_p(C)$: $i_p(A)$ ratio was always equal to 1 : 1 in the range 0.02–2 V s^{-1}. The $E_p(C) - E_p(A)$ value was about 60 mV at low scan rates (up to 0.05 V s^{-1}) but increased slightly at higher scan rates. This effect was probably due to the uncompensated i.r. drop affecting the measurements in this medium, which is of low relative permittivity. A similar increase in peak-to-peak separation with scan rate was observed even for the highly reversible couple ferrocenium–ferrocene[8] under the same experimental conditions. These results indicated the occurrence of a reversible one-electron process for the A–C pattern, confirmed by coulometric measurements at control potential.

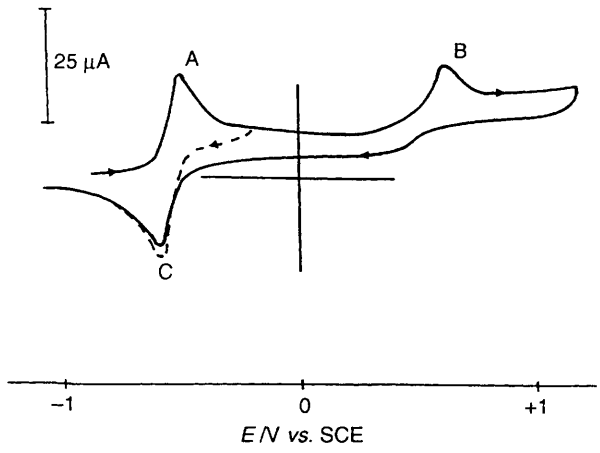


Fig. 1 Cyclic voltammogram of 2.3 mmol dm^{-3} $[CoH\{PPh(OEt)_2\}_4]$ in dichloromethane + 0.1 mol dm^{-3} NBu_4ClO_4 recorded on a glassy-carbon electrode at 0.05 V s^{-1}

The second anodic peak B, irreversible in character, displays about the same peak current as peak A, thus also indicating the occurrence of a one-electron oxidation process. The number of electrons involved was confirmed coulometrically.

Voltammograms recorded on a solution of $[CoH\{PPh(OEt)_2\}_4]^+$ **2a** displayed either a reduction process at peak C of Fig. 1 in the direct cathodic scan or an oxidation process at peak B in the direct anodic scan. The voltammetric analysis of peak B in this solution indicated that the peak potential shifts anodically by about 100 mV for a ten-fold increase in scan rate, while the current function $i_p(B)v^{-\frac{1}{2}}$ decreases by about 10% for the same variation in this parameter. The $E_p - E_{p/2}$ value was about 80 mV. This evidence, together with the circumstance that no reduction peak associated to B was observed over the whole potential window accessible in this solvent, suggested the occurrence of a rapid chemical reaction coupled with a quasi-reversible charge transfer,[9] leading to non-electroactive products.

The behaviour of $[CoH\{P(OEt)_3\}_4]$ **1b** and $[CoH\{PPh_2(OEt)\}]$ **1c** was similar to that of **1a**, apart from the relevant peak potential values, shown in Table 1. It is worth noting that preparative macroelectrolysis in this solvent did not allow isolation of pure samples of oxidation cationic products, because their solubilities were too similar to those of the available supporting electrolytes.

The cyclic voltammetric behaviour of the arenediazonium cation in CH_2Cl_2, employed for the chemical oxidation of cobalt(I) complexes,[4] was also tested. A broad irreversible reduction process, having a peak potential of about −0.02 V (*vs.* SCE) at 100 mV s^{-1}, was observed. Its irreversible character was maintained in the range of the scan rates explored (20–2000 mV s^{-1}). Both the peak shape and peak potential compare with data

Table 1 Selected potentials for cobalt complexes

	$E_{\frac{1}{2}}$ [a]/V				E_p(B) [b]/V			
	MeCN		CH_2Cl_2		MeCN		CH_2Cl_2	
Compound	*vs.* SCE	*c*	*vs.* SCE	*c*	*vs.* SCE	*c*	*vs.* SCE	*c*
1a $[CoH\{PPh(OEt)_2\}_4]$	−0.460	−0.860	−0.460	−0.950	0.430	0.030	0.650	0.160
1b $[CoH\{P(OEt)_3\}_4]$	−0.420	−0.820	−0.420	−0.910	0.680	0.280	0.900	0.410
1c $[CoH\{PPh_2(OEt)\}_4]$	−0.560	−0.960	−0.590	−1.080	0.630	0.230	0.670	0.180

[a] Obtained by use of $\frac{1}{2}[E_p(A) + E_p(C)]$ recorded at 0.1 V s^{-1}. [b] Peak potentials recorded at 0.1 V s^{-1}. [c] Potential values referred to the half-wave potential of the ferrocenium–ferrocene system, measured by cyclic voltammetry after addition of 1 mmol dm^{-3} ferrocene to the electrolyte solution.

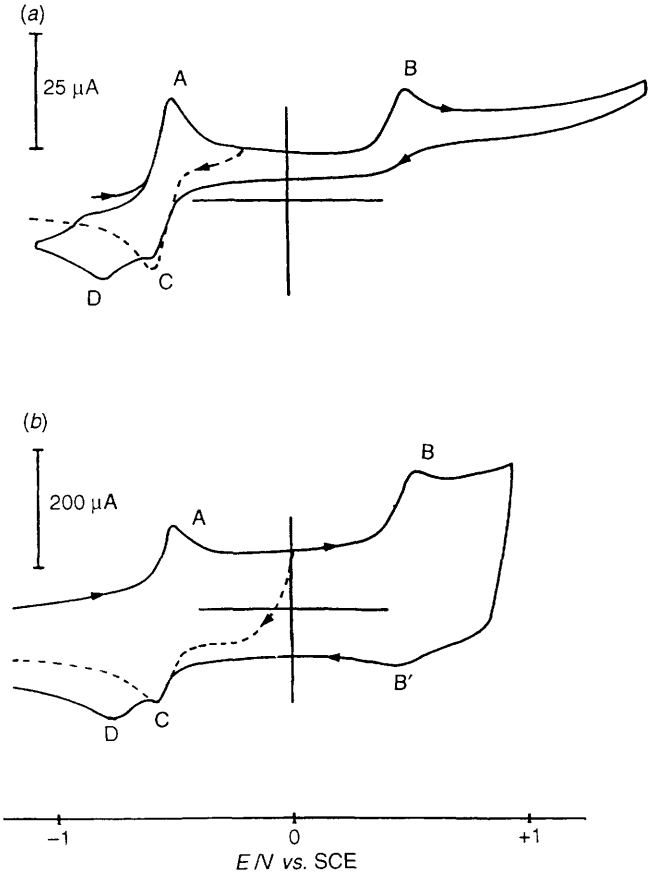


Fig. 2 Cyclic voltammograms of 1.1 mmol dm^{-3} $[CoH\{PPh(OEt)_2\}_4]$ in acetonitrile + 0.1 mol dm^{-3} NBu_4ClO_4 recorded on a glassy-carbon electrode at (*a*) 0.1, (*b*) 20 V s^{-1}

reported for similar arenediazonium salts in MeCN.[10] These values are less positive than the polarographic half-wave potential determined for the reduction of 4-$MeC_6H_4N_2^+BF_4^-$ in tetrahydrothiophene 1,1-dioxide (+0.25 V *vs.* SCE).[11]

Electrochemical Behaviour in MeCN.—The voltammogram of $[CoH\{PPh(OEt)_2\}_4]$ **1a**, in Fig. 2(*a*), differs from that of Fig. 1 mainly because of the appearance of cathodic peak D in the return scan. Also in this case, voltammetric analysis of the two associated peaks A and C showed that the experimental current function $i_p(A)v^{-\frac{1}{2}}$ and peak potential $E_p(A)$ were independent of scan rate, that the backward-to-forward peak-current ratio $i_p(C) : i_p(A)$ was always 1:1 and that the peak-potential separation $E_p(C) - E_p(A)$ was always 60 mV. These data are congruent with the occurrence of a reversible one-electron oxidation at peak A.

As far as peak B is concerned, voltammetric analysis showed that the peak potential shifted by about 30 mV towards more positive values for a ten-fold increase in scan rate, while the peak-current function was almost constant. At scan rates as high as 20 V s^{-1} a small reduction peak B′, directly associated to B, was observed in the reverse scan, with a peak-potential separation of about 100 mV [see Fig. 2(*b*)]. It is interesting that peak D shifts towards more negative potential values, while its experimental current function decreases progressively with increasing scan rate. These results indicate that a rapid chemical reaction following charge transfer takes place at peak B and that the heterogeneous electron transfer is quasi-reversible in character, as indicated by the $E_p - E_{p/2}$ value of about 90 mV.[9] The product of the chemical reaction is the species which is reduced at peak D.

Preparative macroelectrolyses carried out at −0.2 V gave $[CoH\{PPh(OEt)_2\}_4]^+$ as confirmed by comparison with the voltammetric pattern recorded on an authentic sample and by isolation and characterization of the electrolysed product. Further oxidation at 0.7 V gave rise to a charge consumption corresponding to a one-electron process. A white solid characterized as $[CoH(MeCN)\{PPh(OEt)_2\}_4][BPh_4]_2$ **3a** was isolated from this electrolysed solution.

The voltammogram recorded on electrolysis product **3a** is shown in Fig. 3. It displays one reduction peak with a potential equal to that of peak D in Fig. 2 and with a peak height almost double that of peak A in the same figure, thus indicating the occurrence of a two-electron reduction process. In the reverse scan two small peaks E and A are observed. As shown in the insert of Fig. 3, the $i_p(E) : i_p(D)$ ratio increased with scan rate; however, even at scan rates as high as 50 V s^{-1} it never reached 1:1. At the same time, peak A never disappeared, although its experimental peak-current function decreased slightly. These data indicate that the product of the reduction of $[CoH(MeCN)\{PPh(OEt)_2\}_4]^{2+}$ follows a quite complex kinetic pathway, leading to the formation of a small amount of **1a** and to unidentified non-electroactive products.

Coulometric experiments performed on $[CoH(MeCN)\{PPh(OEt)_2\}_4]^{2+}$ confirmed that its reduction at −1.2 V involved two electrons per mol. The cyclic voltammogram recorded on this electrolysed solution revealed the presence of peak A only; from its height, the amount of **1a** was estimated to be about 10% of the original cobalt(III) compound. Spectroscopic data confirmed the formation of a small amount of **1a** as the only identifiable product.

The behaviour of $[CoH\{P(OEt)_3\}_4]$ **1b** is similar to that of **1a**, apart from the relevant peak potentials which are shifted slightly towards more positive values, (Table 1). However, it is worth noting that, in this case, the analogous reduction peak of B′ associated to peak B (Fig. 2) can be observed only at scan rates higher than 50 V s^{-1}, while the relevant heterogeneous electron-transfer process displays the quasi-reversible character already observed for compound **1a**.

Fig. 4 shows that the voltammogram for $[CoH\{PPh_2(OEt)\}_4]$ **1c** displays some important differences with respect to those recorded for **1a** and **1b** at the same scan rate. In the forward scan both peaks A and B are preceded by two smaller peaks E and F. Moreover, a new peak G, located at a quite positive potential

(1.1 V), is now present. All the new peaks E–G are larger in aged solutions; for instance, they reached about 15% of the initial height of peak A 2 h after preparation of the solution. This may indicate the occurrence of a reaction with the solvent [see below, equation (1)] the product of which is responsible for peak E, while the starting hydride may be responsible for peak A.

The experimental current function of peak B increased with scan rate at the expense of peak F, thus indicating that the species which are oxidized at these two peaks are in equilibrium.[12]

In freshly prepared solution (*i.e.* peak E almost negligible in the direct scan), when the potential was switched soon after peak A by increasing the scan rate, peak C tended to prevail over D. The $i_p(C):i_p(A)$ ratio approached 1 : 1 at about 1 V s^{-1}, with the concomitant disappearance of peak D. Instead, on reversal of the sweep after peak B, $i_p(C):i_p(D)$ increased although peak D never disappeared.

Attempts to carry out preparative macroelectrolyses on this compound at both peaks A (0.0 V) and B (+0.66 V) were unsuccessful because of the evident instability of the oxidation products.

Since acetonitrile seems to play an important role, particularly in the electrochemical behaviour of compound **1c**, cyclic voltammograms on this compound were also recorded in tetrahydrofuran, *i.e.* in a solvent with co-ordinating properties between those of MeCN and CH_2Cl_2. Fig. 5(*a*) shows that in this case the electrochemical behaviour of **1c** becomes similar to that observed in acetonitrile solution for $[CoH\{PPh(OEt)_2\}_4]$ **1a** and $[CoH\{P(OEt)_3\}_4]$ **1b**. It must be emphasized that peaks E and F disappear, indicating that they come from the reaction products of Co^I and Co^{II} with acetonitrile. In fact, as shown in Fig. 5(*b*), the stepwise addition of MeCN to tetrahydrofuran solutions of $[CoH\{PPh_2(OEt)\}_4]$ causes the progressive change of the voltammetric pattern into that observed in pure acetonitrile.

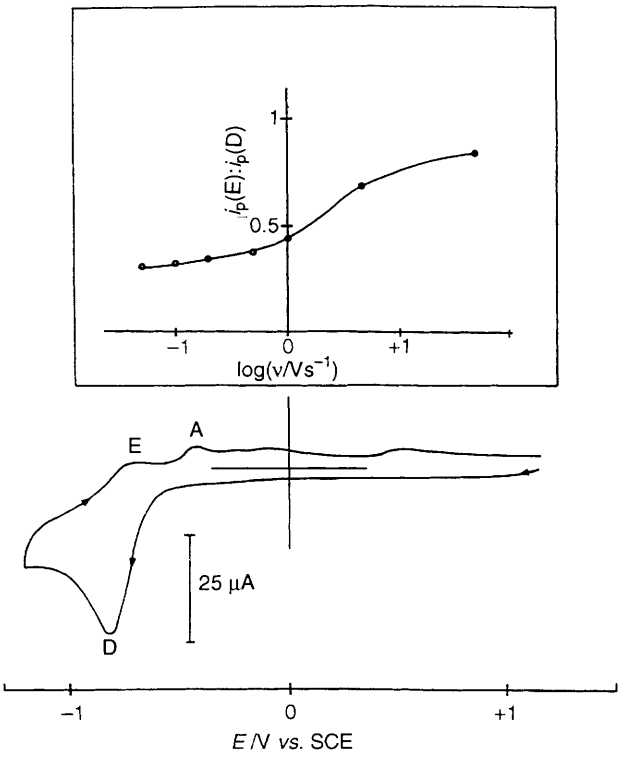


Fig. 3 Cyclic voltammogram recorded at 0.1 V s^{-1} on the solution in Fig. 2 after exhaustive macroelectrolysis at +1.1 V. Insert: dependence on scan rate of the ratio between the currents of peaks E and A recorded after macroelectrolysis

Characterization of Complexes.—The cobalt(II) hydrides $[CoH\{PPh(OEt)_2\}_4]BPh_4$ **2a** and $[CoH\{P(OEt)_3\}_4]BPh_4$ **2b** are green crystalline solids stable in an inert atmosphere and soluble in polar organic solvents, where they behave as 1 : 1 electrolytes[13] (Λ_M between 52.8 and 53.1 S cm^2 mol^{-1}). Elemental analyses, infrared spectra and magnetic data (Table 2) confirmed the proposed formulation for the compounds, which have a precedent only for the $PPh(OEt)_2$ derivative[4] [obtained by chemical oxidation of the corresponding cobalt(I) hydride], whereas $[CoH\{P(OEt)_3\}_4]BPh_4$ is new. Its infrared spectrum (KBr pellet) shows a medium-intensity band at 1935 cm^{-1} attributed to ν(CoH). In CH_2Cl_2 solution at 25 °C its magnetic moment is 2.01 μ_B, as expected for a low-spin cobalt(II) complex and in agreement with the proposed formulation.

The complex $[CoH(MeCN)\{PPh(OEt)_2\}_4][BPh_4]_2$ **3a** is a pale yellow solid, diamagnetic and stable in the solid state and

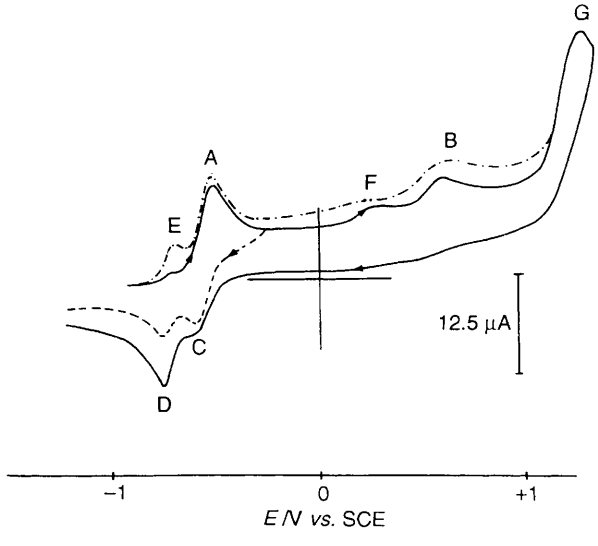


Fig. 4 Cyclic voltammograms of 1 mmol dm^{-3} $[CoH\{PPh_2(OEt)\}_4]$ in acetonitrile + 0.05 mol dm^{-3} NBu_4ClO_4. (—) In freshly prepared solution; (• – • – •) solution aged for 4 h; (– – – –) scan reversed soon after peak A. Scan rate: 0.1 V s^{-1}

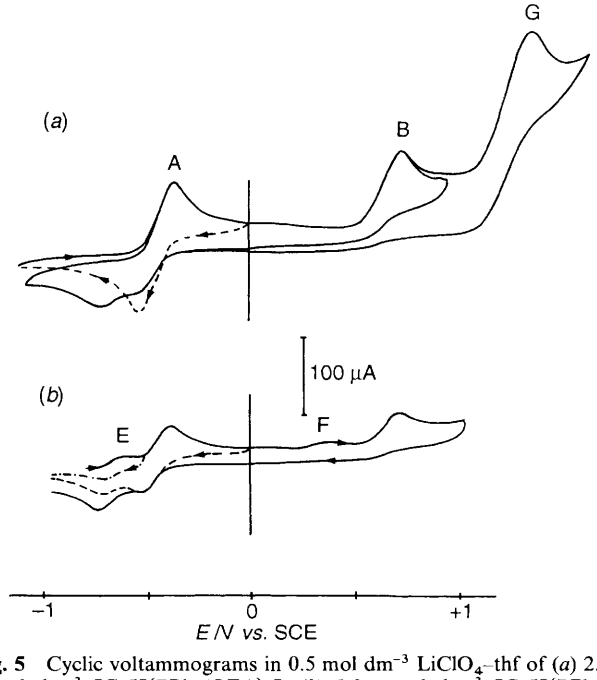
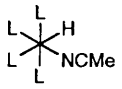


Fig. 5 Cyclic voltammograms in 0.5 mol dm^{-3} $LiClO_4$–thf of (*a*) 2.5 mmol dm^{-3} $[CoH\{PPh_2(OEt)\}_4]$, (*b*) 2.3 mmol dm^{-3} $[CoH\{PPh_2(OEt)\}_4]$ + 6.5 × 10^{-2} mol dm^{-3}MeCN. Scan rate: 0.1 V s^{-1}



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in solution of polar organic solvent, where it behaves as a 1:2 electrolyte[13] (Λ_M = 113.2 S cm^2 mol^{-1}). The infrared spectrum shows a weak band at 2280 cm^{-1} (KBr pellet) attributed to the ν(CN) of the acetonitrile ligand. Furthermore, apart from the signals due to the phosphite $PPh(OEt)_2$ ligand and the BPh_4 anion, the ^{1}H NMR spectra show a quintet at δ −19.34 (J_{PH} = 51.7 Hz) attributed to the hydride and another quintet at δ 2.73 (J_{PH} = 1.5 Hz) due to the methyl group of the acetonitrile ligand (Table 2). The multiplicity of this signal is probably due to weak coupling of the methyl protons of MeCN with the four phosphite ligands. These data, together with the elemental analyses, confirm the above formulation for the complex, which was previously prepared[3] by chemical oxidation of $[CoHL_4]^+$ with ferrocenium salt in the presence of MeCN. A mutually *trans* geometry was also assigned[3] to the complex on the basis of the quintet present in the hydride region. However, we found that the ^{31}P-{^{1}H} NMR spectrum is temperature-dependent and, while only one broad signal is present at room temperature, a multiplet appears at −80 °C. Although even at this temperature the signal is still too broad to allow any simulation, the multiplet indicates the presence of a *cis* geometry, only one singlet being expected for a *trans* structure.

The ^{1}H and ^{31}P NMR spectra (Table 2) of the starting hydride $[CoH\{PPh_2(OEt)\}_4]$ **1c** change with the nature of the solvent used. In C_6D_6, apart from the phosphite signals, the ^{1}H spectrum shows only one quintet at δ −14.83, attributed to hydride resonance; the ^{31}P-{^{1}H} spectrum shows only one signal at δ 140.2. Instead, in CD_3CN as solvent, the ^{1}H NMR spectrum displays two multiplets in the hydride region, *i.e.* a quintet at δ −15.48 and a quartet at δ −14.92, attributable to a new hydride containing three phosphite ligands. The intensity of the two multiplets changes with time, leading to an increase in the quartet and a corresponding decrease in the quintet. Moreover, three signals appear in the ^{31}P-{^{1}H} NMR spectrum, one of which, at δ 31.4, is attributable to the free $PPh_2(OEt)$ phosphite ligand. These results may reasonably be explained on the basis of a substitution reaction of one phosphite ligand by CD_3CN, giving the new hydride $[CoH(CD_3CN)L_3]$ as shown in equation (1). The occurrence of such

$$\underset{\mathbf{1c}}{[CoHL_4]} + CD_3CN \rightleftharpoons \underset{\mathbf{1c'}}{[CoH(CD_3CN)L_3]} + L \quad (1)$$

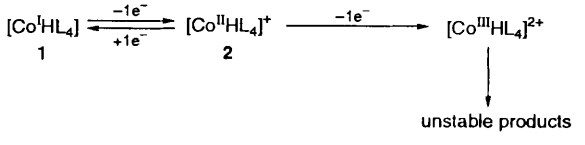
an equilibrium is supported by the observation that the addition of free $PPh_2(OEt)$ to the CD_3CN solution of $[CoHL_4]$ decreases the intensity of the quartet while increasing that of the quintet, and that the solid obtained by evaporation of the CD_3CN solution is $[CoHL_4]$ in pure form, with a ^{1}H NMR spectrum in C_6D_6 identical to that of an authentic sample.

Discussion

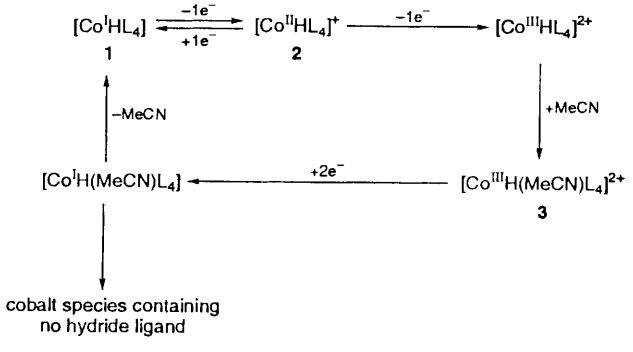
On the basis of the electrochemical and spectroscopic results, the electrochemical oxidation of $[CoHL_4]$ hydrides may be represented by different schemes depending not only on the solvent but also on the nature of the phosphite ligands employed. In CH_2Cl_2 the electrochemical results clearly indicate the occurrence of a stepwise oxidation of Co^I to Co^{III} (see Scheme 1). The first oxidation to Co^{II} is a reversible process, while the further oxidation leading to cobalt(III) is irreversible, probably because of the instability of five-co-ordinate cobalt(III) complexes. The poorly co-ordinating properties of CH_2Cl_2 prevent the formation of octahedral species, which has been observed in MeCN (see below).

The influence of the phosphite ligands is reflected by the different values of the half-wave potentials of the first process (Table 1). The facility of the first oxidation, $E_{\frac{1}{2}}$, of **1** is in accord with the lower π-acceptor character[14] of the phosphite[2] ligand, which stabilizes the higher oxidation state. However, no correlation with the peak-potential values, E_p(B), can be expected because of the coupled chemical reaction.

The electrochemical oxidation of $[CoHL_4]$ hydrides in MeCN depends on the nature of the phosphite ligand (see Schemes 2 and 3). In the case of L = $PPh(OEt)_2$ and $P(OEt)_3$ (Scheme 2) the one-electron oxidation of cobalt(I) leads to the stable cobalt(II) products, which have been isolated and identified as paramagnetic hydrides $[CoHL_4]^+$ **2a** and **2b**. The reversible character of the relevant voltammetric pattern peak system (A–C in Fig. 2) is in accord with the maintenance of the same co-ordination sphere in the oxidized product. It may be noted that the paramagnetic hydride with the triethoxyphosphine ligand, $[CoH\{P(OEt)_3\}_4]^+$, is new.



Scheme 1 L = $PPh(OEt)_2$, **a**; $P(OEt)_3$, **b**; or $PPh_2(OEt)$, **c**; in CH_2Cl_2

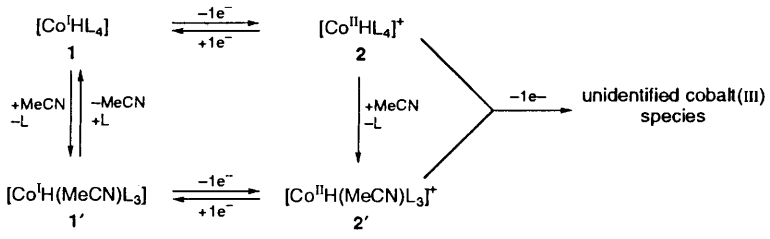


Scheme 2 L = $PPh(OEt)_2$, **a** or $P(OEt)_3$, **b**; in MeCN

Table 2 Selected IR and NMR data for cobalt complexes

Compound	IR[a]/cm^{-1}	^{1}H NMR[b] Solvent	δ (J/Hz)	Assignment	^{31}P-{^{1}H} NMR (δ)[b]
$[CoH\{P(OEt)_3\}_4]BPh_4$[c]	1935 ν(CoH)				
$[CoH(MeCN)\{PPh(OEt)_2\}_4][BPh_4]_2$	2280 ν(CN)	$(CD_3)_2CO$	2.73 (qnt) (J_{PH} = 1.5)	CH_3CN	149 (br) [151 m][d]
			−19.34 (qnt) (J_{PH} = 51.7)	Hydride	
$[CoH\{PPh_2(OEt)\}_4]$		C_6D_6	−14.83 (qnt) (J_{PH} = 30)	Hydride	140.2 (s)
		CD_3CN	−15.48 (qnt) (J_{PH} = 30)	Hydride	140.5 (br)
			−14.92 (q) (J_{PH} = 11)		110.9 (br) [31.4 (s)][e]

[a] In KBr pellets. [b] At room temperature. [c] μ_{eff} = 2.01 μ_B in CH_2Cl_2 at 25 °C. [d] At −90 °C. [e] Signal of $PPh_2(OEt)$ free ligand.



Scheme 3 L = $PPh_2(OEt)$, **c**; in MeCN

The cobalt(II) derivatives **2a** and **2b** may be further oxidized to a cobalt(III) species by an irreversible one-electron process (peak B, Fig. 2), affording the intermediate $[CoHL_4]^{2+}$. This irreversibility is caused by the quite rapid chemical reaction following the charge transfer, giving the octahedral compounds $[CoH(MeCN)L_4]^{2+}$ **3a** and **3b** as final products. Support for such a mechanism comes from the isolation in pure form and high yield ($\geqslant 90\%$) of **3a** and **3b** from the electrolysed solution. Furthermore, the addition of a molecule of MeCN to the primary oxidation product $[CoHL_4]^{2+}$ was expected on the basis of Sanders' long-standing isolation[3] of $[CoH(MeCN)\{PPh(OEt)_2\}_4]PF_6$ under similar conditions, as well as on the instability of this 16-electron intermediate species. The formation of such an intermediate is supported by the cyclic voltammograms recorded at high scan rates, in which a reduction peak B′ directly associated to B is observed.

The final product of the latter chemical reaction, *i.e.* the $[CoH(MeCN)L_4]^{2+}$ complex, was electroactive and underwent a two-electron reduction complicated by coupled chemical reactions. The primary product of the charge transfer, probably the octahedral cobalt(I) species $[CoH(MeCN)L_4]$, is unstable and its decomposition leads to small amounts of the starting cobalt(I) $[CoHL_4]$ complex and to unidentified products. Evidence for the generation of such a cobalt(I) octahedral intermediate was obtained by measurements performed at high scan rates, which showed that the backward-to-forward peak ratio increases with increasing sweep rate (see insert in Fig. 3). These octahedral species of cobalt(I) $[CoH(MeCN)L_4]$ may easily lose a ligand to reach the five-co-ordination typical of phosphite-containing cobalt(I) hydrides.[1,4] However, the expected dissociation of the MeCN ligand to give $[CoHL_4]$ is not the predominant reaction (about 10%), decomposition of the $[CoH(MeCN)L_4]$ complex probably being the main reaction.

More complicated behaviour is observed with $[CoH\{PPh_2(OEt)\}_4]$ **1c**, owing to the reaction of both the starting hydride and its oxidation products with the MeCN solvent. The starting cobalt(I) complex $[CoHL_4]$ reacts slowly with MeCN to give $[CoH(MeCN)L_3]$ **1c′**, a product revealed by the NMR spectra [Equation (1)]. The latter compound is responsible for the small voltammetric peak E observed in Fig. 4, while the starting compound **1c** is responsible for peak A. The easier oxidation of $[CoH(MeCN)L_3]$ with respect to the starting hydride is in accord with the fact that the MeCN ligand has less π-acceptor character than does the phosphite ligand. Both the cobalt(I) hydrides $[CoHL_4]$ **1c** and $[CoH(MeCN)L_3]$ **1c′** undergo a one-electron reversible oxidation, giving $[CoHL_4]^+$ **2c** and $[CoH(MeCN)L_3]^+$ **2c′** cobalt(II) hydrides which, being unstable, cannot be isolated, unlike related hydrides **2a** and **2b**. Notwithstanding, the voltammetric results clearly support the formation of the cobalt(II) derivatives. It should be noted that $[CoH(MeCN)L_3]^+$ can be formed not only by direct oxidation of the parent complex **1c′**, but also by a chemical reaction following the charge transfer between **2c** and acetonitrile. The occurrence of this reaction is suggested by the trend observed for $i_p(C):i_p(A)$ with scan rate, as well as by the fact that no reaction takes place in thf bulk solvent (see Fig. 5). The product formed is probably $[CoH(MeCN)L_3]^+$, in that an octahedral species such as $[CoH(MeCN)L_4]^+$ is not probable for a d^7 cobalt(II) species containing monodentate ligands. Such a reaction appears to proceed *via* a pseudo-first-order mechanism in which the addition of MeCN is the rate-determining step. The rate of this reaction decreases dramatically when measurements are carried out in thf, even in the presence of a 50-fold excess of MeCN over the cobalt complex.

The further oxidation of the cobalt(II) complex **2c** is complicated by coupled chemical reactions leading to mixtures of products which are difficult both to separate and identify. For this reason no further details are reported here.

Finally the voltammetric results in CH_2Cl_2 should be set against the anomalous observation that reaction (2) with

$$[CoHL_4] \xrightarrow{-1e^-} [CoHL_4]^+ \qquad (2)$$

arenediazonium salts in CH_2Cl_2 proceeds for L = $PPh(OEt)_2$ **1a**, but not for $P(OEt)_3$ **1b** or $PPh_2(OEt)$ **1c**. From a comparison of the $E_{\frac{1}{2}}$ values found for the one-electron oxidation of $[CoHL_4]$ **1** (Table 1) with the potential for the reduction of $4\text{-}MeC_6H_4N_2^+BF_4$ (see Results), it may be observed that all cobalt(I) hydrides are similarly easy to oxidize and that all $[CoHL_4]$ should be oxidized to $[CoHL_4]^+$ by the arenediazonium cation. Therefore, these electrochemical studies seem rather to increase the anomalous nature of previous chemical observations [Equation (2)] rather than explain them.

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References

1 D. A. Buckingham and C. R. Clark, in *Comprehensive Coordination Chemistry*, ed. G. Wilkinson, Pergamon, New York, 1987, vol. 4, p. 635.
2 C. Bianchini, F. Laschi, M. Peruzzini, F. M. Ottaviani, A. Vacca and P. Zanello, *Inorg. Chem.*, 1990, **29**, 3394; C. Bianchini, A. Meli and P. Zanello, *J. Chem. Soc., Chem. Commun.*, 1986, 628; G. Pilloni, G. Schiavon, G. Zotti and S. Zecchin, *J. Organomet. Chem.*, 1977, **134**, 305.
3 J. R. Sanders, *J. Chem. Soc., Dalton Trans.*, 1973, 748; *J. Chem. Soc., Dalton Trans.*, 1975, 2340.
4 G. Albertin, P. Amendola, S. Antoniutti and E. Bordignon, *J. Chem. Soc., Dalton Trans.*, 1990, 2979 and refs. therein.
5 D. F. Evans, *J. Chem. Soc.*, 1959, 2003; R. A. Bailey, *J. Chem. Educ.*, 1972, **49**, 297.
6 B. N. Figgis and J. Lewis, in *Modern Coordination Chemistry*, eds. J. Lewis and R. G. Wilkins, Interscience, New York, 1960.
7 J. J. Levinson and S. D. Robinson, *Inorg. Synth.*, 1972, **13**, 105; D. Titus, A. A. Orio and H. B. Gray, *Inorg. Synth.*, 1972, **13**, 117.
8 A. M. Bond, T. L. E. Henderson, D. R. Mann, T. F. Maxin, W. Thornmann and C. G. Zoski, *Anal. Chem.*, 1988, **60**, 1878.
9 A. J. Bard and L. R. Faulkner, *Electrochemical Methods*, Wiley, New York, 1980.

10 M. Delamar, R. Hitmi, J. Pinson and J. M. Savéant, *J. Am. Chem. Soc.*, 1992, **114**, 5883.
11 R. M. Elofson and F. F. Gadallah, *J. Org. Chem.*, 1969, **34**, 854; M. P. Doyle, J. K. Guy, K. C. Brown, S. N. Mahapatro, C. M. VanZyl and J. R. Pladziewicz, *J. Am. Chem. Soc.*, 1987, **109**, 1536.
12 R. S. Nicholson and I. Shain, *Anal. Chem.*, 1964, **36**, 706.
13 W. J. Geary, *Coord. Chem. Rev.*, 1971, **7**, 81.
14 C. A. Tolman, *Chem. Rev.*, 1977, **77**, 313.

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