Electrochemical Behavior of 'Costa-type' Organocobalt Coenzyme B_{12} Models

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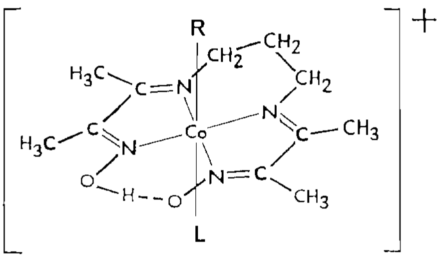
Abstract

The cathodic reduction of nine 'Costa-type' organocobalt B_{12} model compounds, [RCo(III)L]ClO_4 (where R = alkyl ligand; L = N^2,$N^{2'}$-propanediylbis-(2,3-butanedione 2-imine 3-oxime) and a neutral base), was studied in acetonitrile solvent, using cyclic voltammetry, controlled potential coulometry, and spectroelectrochemical techniques. The effect of the alkyl substituents, namely i-C_3H_7, neo-C_5H_{11}, i-C_4H_9, CH_3CH_2, $C_6H_5CH_2$, CH_3, $HO(CH_2)_2$, CH_3COOCH_2 and CF_3CH_2, on the relevant cobalt reduction mechanisms and potentials was investigated. A marked influence of axial group bulk on the reactivity of the low oxidation state cobalt derivatives formed in the reduction process has been evidentiated. The reactivity of these electrogenerated compounds is conditioned for the most part by their ability to form stable bisalkyl complexes.

Introduction

Increasing attention has been paid recently to the many-sided aspects of the biological role of coenzyme B_{12} [1, 2]. One crucial chemical aspect of this molecule and of related compounds lies in the characteristics of the cobalt–carbon bond. This has led to a great effort in searching for organocobalt model compounds with a metal binding environment as similar as possible, both electronically and sterically, to that of the corrin ring [3].

In this context, attention has been devoted to the measurement of the electrochemical properties of different model compounds, i.e. to the determination of the stability potential range of these species, as well as to the definition of the relevant cathodic reduction mechanisms [4–15]. Despite some limitations shown with respect to other chemical properties, cobalt complexes with the N^2,$N^{2'}$-propanediylbis(2,3-butanedione 2-imine 3-oxime) equatorial ligand, (DO)(DOH)pn, the so-called 'Costa-type' ligand (a), exhibit the closest electrochemical behavior to the corrin ring compounds of any B_{12} model [11].



a

Long-lived alkyl derivatives with this equatorial ligand and the metal in low oxidation state (namely Co(II) and Co(I) species) have been obtained only in the presence of N-donor heterocyclic ligands [11], or in the case of particularly bulky axial ligands such as neopentyl [15] or phenyl [5] groups.

As an alternative to the mechanism involving simply uncomplicated charge transfer(s) leading to these stable species three different pathways, summarized in Scheme 1, have been proposed to account for the cathodic behavior of the methyl derivative. In all cases the final products are Co(I)L and $(CH_3)_2$-Co(III)L[†]. Costa *et al.* [5] proposed that their formation occurs by transfer of the methyl group

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[†] We depart somewhat from the molecular formulas used in the previous literature for these organocobalt complexes, to a more abbreviated notation. In these, as well as in any other formula in the present paper L represents the tetradentate (DO)(DOH)pn ligand together with zero, one, or two axial solvent molecules, depending on the number of axial alkyl ligands present. The (DO)(DOH)pn equatorial ligand and the alkyl group both bear a −1 formal charge; the cobalt oxidation state will always be specified.

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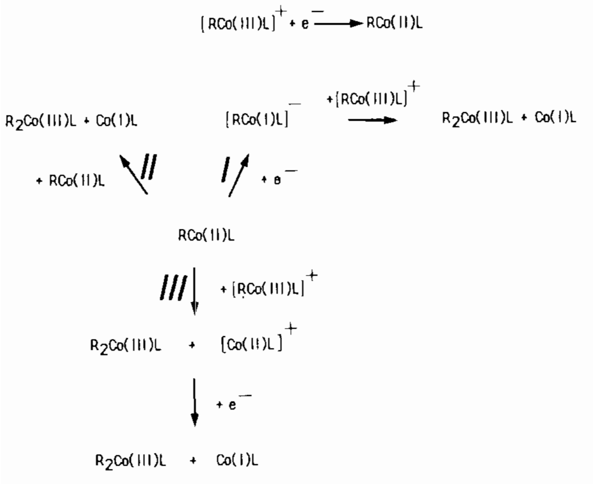

Scheme 1.

from the cobalt(I) compound formed by two electron reduction, to the cobalt(III) starting molecule (path I). Alternatively, according to the same authors, the same products might form as a consequence of an exchange of one alkyl group between two equal cobalt(II) molecules produced by one electron reduction (path II). Based on voltammetric, coulometric and *in situ* spectroscopic measurements, Elliott *et al.* [11] concluded that the transfer of the methyl group takes place between the cobalt(II) species produced by one electron reduction and the starting cobalt(III) compound (path III). Recently, Costa *et al.* [14] pointed out that all three mechanisms are possible, depending on the potential at which the reduction is carried out.

Scheme 1 ($R = CH_3$) is comprehensive for all three proposed mechanisms, one being different from the other regarding the fate of the electrogenerated cobalt(II) compound.

The overall stoichiometry for either reaction path (I, II, III) in Scheme 1 is the same

$$2[CH_3Co(III)L]^+ + 2e^- \longrightarrow (CH_3)_2Co(III)L + Co(I)L$$

Cathodic reduction of a series of complexes containing the axial groups i-C_3H_7, neo-C_5H_{11}, i-C_4H_9, CH_3CH_2, $C_6H_5CH_2$, CH_3, $HO(CH_2)_2$, CH_3COOCH_2 and CF_3CH_2, with wide ranging steric and electronic properties, allowed us to study the influence of the R group on electrode reduction. The absence of a strong base in the acetonitrile solvent provides complexes with a weaker Co–C bond [2, 11], allowing a study of Co–C reactivity. Spectroelectrochemical measurements with optically transparent thin layer electrodes (OTTLE cells) provided a deeper understanding of the electrode processes, and confirmed a marked dependence of low-valent organocobalt complexes reactivity on the nature of the alkyl group.

Experimental

Preparation of Cobalt Complexes

All reagents used in the syntheses were obtained from Aldrich and used without purification.

The syntheses of $Co(III)LX_2$ (X = Cl, Br) and of some of the $[RCo(III)L]ClO_4$ complexes studied here have been reported previously: dihalides, R = i-C_3H_7, neo-C_5H_{11}, CH_3CH_2, $C_6H_5CH_2$, CH_3COOCH_2, CF_3CH_2 [16]; $R = CH_3$ [17].

$[Co(III)L(H_2O)_2](ClO_4)_2$

A rapidly stirred suspension of $Co(III)LBr_2$ (10.9 mmol; 5.0 g) in methanol (400 ml) was treated with a $AgNO_3$ solution (24 mmol, 4.0 g in 10 ml H_2O). The resulting white suspension was stirred well for 10 min and then filtered through celite. The filtrate was treated with conc. $HClO_4$ (until pH = 0) and the volume reduced by rotary evaporation (30 °C) until precipitation began. The solution was cooled overnight (5 °C) and a brown crystalline product obtained. Yield 5 g (86%).

$[HO(CH_2)_2Co(III)LH_2O]ClO_4$

This complex was prepared as for the methyl acetate derivative reported previously [16] with the following exceptions. $Br(CH_2)_2COOCH_3$ was the alkylating agent which underwent hydrolysis during the synthesis. 1 N HCl, rather than HNO_3, was used to neutralize the solution. The oily product which formed during rotary evaporation was dissolved in water, with a small amount of acetone, and placed in a separatory funnel. CH_2Cl_2 was added and after the extraction process the aqueous layer was treated as usual to obtain a crystalline product. Yield 135 mg (14%). *Anal.* Found: C, 32.88; H, 5.78; N, 11.68; Calc. for $C_{13}H_{26}ClCoN_4O_8 \cdot H_2O$: C, 32.61; H, 5.89; N, 11.70%.

$[i\text{-}C_4H_9Co(III)LH_2O]ClO_4$

Synthesized as for the neo-C_5H_{11} derivative [16] with the following exceptions. Quantities of the dibromo complex, alkyl halide ($BrCH_2C(CH_3)_3$) and $NaBH_4$, were three times greater and the volume of methanol was 100 ml. After completion of N_2 purging a $NaClO_4$ solution (saturated, 10 ml) was added and precipitation of the product accomplished by rotary evaporation. Yield 1.34 g (65%). The product was recrystallized from methanol:H_2O and $NaClO_4$ solution (saturated). *Anal.* Found: C, 37.94; H, 6.57; N, 11.76. Calc. for $C_{15}H_{30}ClCoN_4O_7 \cdot H_2O$: C, 38.02; H, 6.59; N, 11.82%.

The prepared complexes were pure as established by ^1H NMR spectroscopy [18].

Electrochemical Measurements

Acetonitrile (AN) (Aldrich, anhydrous, 99+%, GOLD LABEL, water <0.005%, packaged under nitrogen) was used as solvent without further purification. Tetraethylammonium perchlorate (TEAP) (C. Erba) and tetraethylammonium tetrafluoroborate (Fluka) supporting electrolytes were dried for 48 h at 50 °C in a vacuum oven before use. $NaClO_4$ was obtained from $NaClO_4 \cdot H_2O$ (Fluka), by keeping the salt under vacuum at 70 °C for 48 h. Thermal gravimetric analysis technique was used to check the crystal status of the salt. All electrochemical experiments were carried out under prepurified N_2.

Voltammetric experiments were conducted with a PAR (Princeton Applied Research) Model 170 Electrochemistry System or a BAS (Bioanalytical System) CV 1B voltammograph. The potential was monitored with a home-made digital voltmeter. The resulting voltammograms were recorded either on a Linseis Model LY 1800 pen recorder or on a Hewlett Packard Model 1223A X/Y storage oscilloscope. In these experiments two different electrochemical cells with proper geometry were used. In both of them the working electrode was a platinum sphere (diameter of about 2 mm) surrounded by a platinum spiral auxiliary electrode. In some preliminary tests a gold sphere freshly covered with mercury was used as working electrode. The reference electrode of the first cell was a saturated calomel electrode (SCE), connected to the working electrode compartment through a salt bridge ending in a Luggin capillary. In the second cell, for low temperature experiments, a silver wire was used as quasi-reference electrode. In this cell all the electrodes were at the end of a single glass tube, dipped inside a simple glass airtight vessel, as shown in Fig. 1.

At the end of each voltammetric experiment bis(cyclopentadienyl)iron(II) was added to the solution. Thus, all potential values could be referred to $E_{1/2}{}^{r}$ of this redox couple (Fc^+/Fc), where $E_{1/2}{}^{r}$ is an experimental approximation of the standard potential of the redox couple involved, computed as the half-sum of anodic and cathodic peak potentials [19]. Superscript r indicates a reversible electrode reaction. The use of an internal standard makes the potential scale exactly defined both for quasi-reference and SCE; in the latter case the potential measured is unaffected by variable liquid junction potentials at the aqueous–non-aqueous solvent interface [20]. In order to allow some comparison with literature data we point out that under our experimental conditions $E_{1/2}{}^{r}$ for the couple bis(cyclopentadienyl)iron(III)/iron(II) was +0.38 ± 0.02 V versus SCE. For all the complexes studied cyclic voltammetric tests were performed at potential scan rates ranging from 0.05 to 100 V s^{-1}, at temperatures of +20, 0 and −17 °C. This last temperature was chosen with the aim of reducing as much as possible the rate of homogeneous chemical reactions coupled to charge transfer.

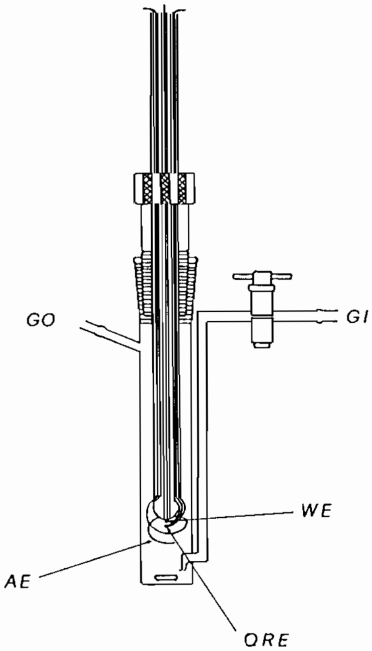

Fig. 1. Schematic drawing of one of the electrochemical cells used in the voltammetric tests. GI and GO: input and output for inert gas, respectively; WE: half-sphere platinum working electrode; QRE: silver wire quasi-reference electrode; AE: platinum wire auxiliary electrode.

An AMEL Model 552 potentiostat connected to an AMEL Model 558 integrator was used in controlled potential coulometric tests, which were performed at 0 °C in H-shaped cells with a sintered glass disk interposed between anodic and cathodic compartments. The working electrode was a platinum gauze, and only in a few cases was a mercury pool used. The auxiliary electrode was a mercury pool and the reference electrode was still a SCE.

In the spectroelectrochemical measurements (0 °C) the electrode was a 80:20 platinum:rhodium alloy mesh (80 l.p.i.) sandwiched between two microscope slides [21]. Teflon spacers were used to obtain the desired path length (0.2–0.3 mm). The electrode assembly was held together by a Teflon frame, without the use of any epoxy glue. Typical volumes were about 50 μl. The cell was similar to that described elsewhere [22]. The spectra (wavelength range 350–820 nm) were recorded using a Hewlett Packard Model 8452 diode array spectrophotometer (resolution 2 nm). The data were processed on-line by an Olivetti M28 personal computer and plotted with a Calcomp M84 digital plotter. In these experiments the spectra were recorded either in potentiostatic conditions or during a slow scan rate potential sweep (typically 0.2–0.3 mV s^{-1} – one spectrum every 10 mV) [15, 23]. In the potentiostatic tests the potential was stepped at a selected value, with spectra collected every ten seconds until there was no significant change between subsequent spectra (typically 300–500 s). The reference was either air or the starting solution. In order to minimize the uncompensated ohmic drop the concentration of supporting electrolyte was as high as 0.4 M.

Results

Serious problems were encountered upon electrochemical reduction of the organocobalt complexes studied due to poisoning of the electrode surface by adsorption phenomena. As a consequence, reproducible current–potential responses were only obtained using solid (platinum) electrodes and by following careful cleaning procedures which were different depending on the case: rest for some minutes between two subsequent runs, polarization of the electrode by flow of a small anodic current (oxidation of the starting compound), or mechanical cleaning. Adsorption effects are much more severe on mercury electrodes [24]: all our attempts to obtain reproducible responses on this material have failed. This drawback suggests some caution in the interpretation and evaluation of polarographic results reported in the literature.

Cyclic Voltammetric Experiments

Figures 2–4 show three typical examples of the voltammetric behavior of complexes with isopropyl, 2,2,2-trifluoroethyl and ethyl alkyl groups, respectively. Our main interest is in the reduction processes occurring at peaks A and C in Fig. 2, or at peak A in Figs. 3 and 4. Isopropyl (Fig. 2) and isobutyl complexes show voltammetric profiles similar to those of the neopentyl compound, described by us previously [15]. For all three of these complexes, at all temperatures and scan rates attempted, two subsequent cathodic–anodic peak systems (A/B and C/D) were recorded due to quasi-reversible (A/B), and reversible (C/D) charge transfer processes. For these three compounds, in contrast with all other derivatives studied, no further cathodic peak is recorded before the solvent discharge, and no further anodic peak is noted on the backward scan before that due to direct oxidation of the starting compound.

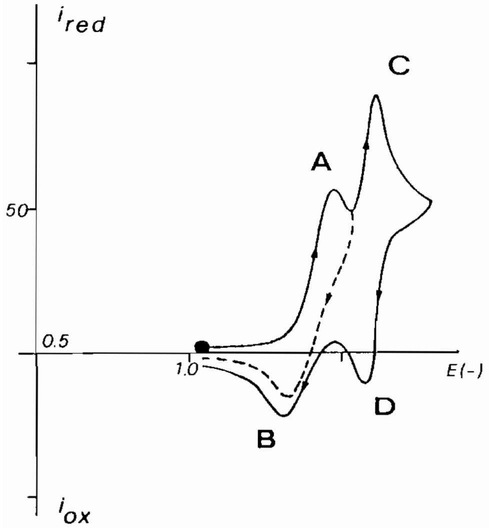

Fig. 2. Cyclic voltammetric curves recorded on a 2.3 × 10^{-3} M [i-C_3H_7CoL]ClO_4, 0.1 M TEAP, AN solution. Pt working electrode; 0.2 V s^{-1} potential scan rate; −17 °C; ●: starting potential for the initially cathodic scan. Potential (E in V) is referred to $E_{1/2}^r$ of the couple ferricinium ion/ferrocene. Current (i) in μA.

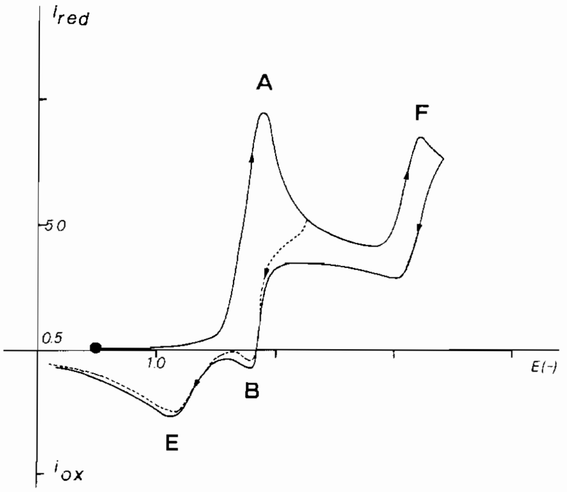

Fig. 3. Cyclic voltammetric curves recorded on a 5.2 × 10^{-3} M [CF_3CH_2CoL]ClO_4 solution. Experimental conditions as in Fig. 2.

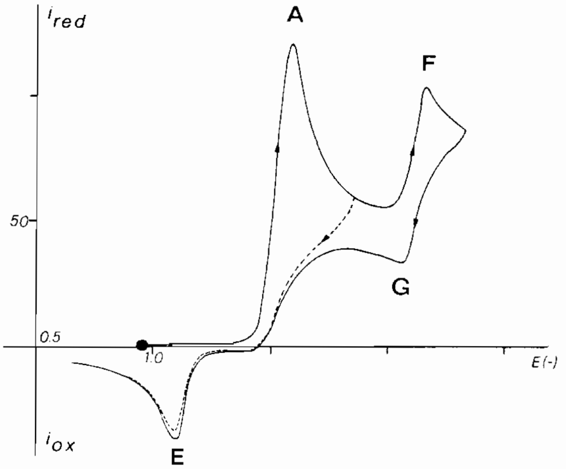

Fig. 4. Cyclic voltammetric curves recorded on a 6.3 × 10^{-3} M [CH_3CH_2CoL]ClO_4 solution. Experimental conditions as in Fig. 2.

In the case of the 2,2,2-trifluoroethyl derivative (Fig. 3), as well as for the methyl and 2-hydroxyethyl compounds, the reduction process observed corresponds to a single cathodic peak A and a directly associated backward anodic peak B is recorded only at low temperature or high potential scan rate.

By contrast, the ethyl derivative (Fig. 4) and compounds with benzyl and methyl acetate axial groups do not exhibit any backward anodic peak directly associated with peak A, even at a potential scan rate of 100 V s^{-1} and at −17 °C.

Other differences in the three typical voltammograms are the presence of an additional cathodic peak F and, on the reverse anodic scan, of an oxidation peak E for the complexes in Figs. 3 and 4. The methyl acetate derivative is reduced at significantly less cathodic potentials than the other compounds, so much so that the relevant voltammetric profile can be mistaken for a simple quasi-reversible system. On increasing the scan rate the cathodic peak A shifts cathodically, as expected for a reversible or quasi-reversible charge transfer followed by a fast irreversible chemical reaction. The position of the anodic peak, coincident with peak E in Figs. 3 and 4, remains unchanged. These changes in response on varying scan rates make the voltammetric behavior of this compound similar to that of the ethyl compound (Fig. 4).

The first two columns in Table 1 summarize the most significant features of the voltammetric curves described above. The number reported for cathodic and anodic peaks refers to A/B and C/D peak systems, not to peaks like F and E (Figs. 3 and 4), which involve dealkylated cobalt species (*vide infra*).

Controlled Potential Electrolysis Experiments

Exhaustive controlled potential coulometric tests were carried out at the potentials of peak C for those complexes whose voltammetric profiles are similar to that of Fig. 2 and at the potentials of peak A for complexes exhibiting voltammetric behaviors similar to those in Figs. 3 and 4. Besides the evaluation of the number of electrons involved in the cathodic processes, the aim of these tests was to study the nature of electrolysis products. Table 1 reports the overall number of electrons (*n*) involved in the exhaustive electrolyses.

Identification of the electrolysis products was performed by voltammetric methods, as well as through OTTLE techniques, since the high reducing power of the electrolyzed solutions precluded the isolation of sufficiently stable reduction products. In addition to the compounds having low oxidation state metal, earlier studies [11] demonstrated that isolation of $R_2Co(III)L$ compounds from these systems is also quite difficult.

Voltammetric curves were recorded on the reduced solutions, the first anodic sweep starting at the potentials where exhaustive electrolyses were performed. As Fig. 5(a) shows, two anodic peaks (E and H) are present in the voltammetric curves recorded on electrolyzed solutions of the methyl complex. Likewise, peak E and another anodic peak in the same potential region of peak H are also observed on electrolyzed solutions of the ethyl, 2-hydroxyethyl, benzyl, methyl acetate and 2,2,2-trifluoroethyl complexes. Additional anodic peaks corresponding to peaks D and B in Fig. 2 appear in the voltammograms of the isopropyl and isobutyl compounds. We recall that only peaks corresponding to D and B were recorded on neopentyl derivative solutions [15]. Furthermore, in contrast to the behavior of the neopentyl compound, all the compounds studied gave a cathodic peak F (as in Fig. 5(a)) with a directly associated anodic peak G.

Useful information about the nature of reduction products was gained from the electrochemical behavior of a solution of $[Co(III)L(H_2O)_2](ClO_4)_2$,

TABLE 1. Cathodic reduction of $[RCo(III)L]ClO_4$ complexes

R	Number of cathodic peaks	Directly associated anodic backward peak(s)	Coulometric result n	Identifiable electrolysis products
$i\text{-}C_3H_7$	2	detectable	0.81[a]	$[(i\text{-}C_3H_7)Co(I)L]^-$ + Co(I)L
$neo\text{-}C_5H_{11}$[b]	2	detectable	1.96	$[(neo\text{-}C_5H_{11})Co(I)L]^-$
$i\text{-}C_4H_9$	2	detectable	1.40	$[(i\text{-}C_4H_9)Co(I)L]^-$ + Co(I)L $\{+ (i\text{-}C_4H_9)_2Co(III)L\}$[c]
CH_3CH_2	1	undetectable	1.04	$(CH_3CH_2)_2Co(III)L$ + Co(I)L
$C_6H_5CH_2$	1	undetectable	0.94	$(C_6H_5CH_2)_2Co(III)L$ + Co(I)L
CH_3	1	detectable	0.98	$(CH_3)_2Co(III)L$ + Co(I)L
$HO(CH_2)_2$	1	detectable	0.98	Co(I)L
CH_3COOCH_2	1	undetectable	0.92	Co(I)L
CF_3CH_2	1	detectable	1.93	Co(I)L

Voltammetric tests were performed at −17 °C; coulometric tests at 0 °C.

[a] Serious poisoning of the electrode prevents exhaustive reduction. [b] Data from ref. 15. [c] Possible product.

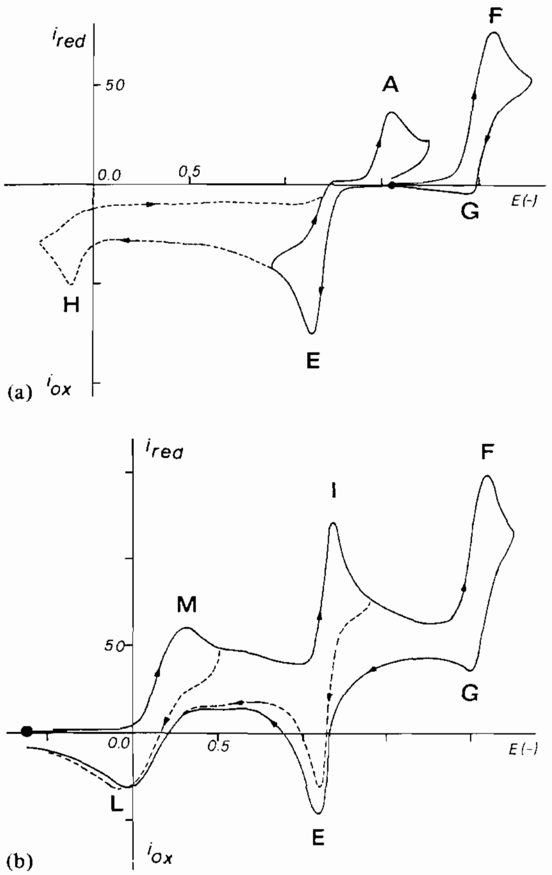

Fig. 5. (a) Cyclic voltammetric curves recorded on 4.6 × 10^{-3} M $[CH_3CoL]ClO_4$ solution, previously reduced at −1.34 V vs. SCE; 0 °C; other conditions as in Fig. 2. (b) Cyclic voltammetric curves recorded on 4.5 × 10^{-3} M $[CoL(H_2O)_2]ClO_4$ solution; 0 °C; other experimental conditions as in Fig. 2.

whose voltammetric response is reported in Fig. 5(b). The peak systems M/L and I/E can be attributed to the couples Co(III)/Co(II) and Co(II)/Co(I), respectively, while peak F corresponds to the reduction of Co(I)L [25]. Solutions of Co(I)L were obtained by two electron reduction of $[Co(III)L(H_2O)_2](ClO_4)_2$ at −1.3 V versus Fc^+/Fc, i.e. at the potentials of peak I in Fig. 5(b). On this basis the anodic peak E in Figs. 3, 4 and 5(a) can be attributed to the oxidation of Co(I)L to $[Co(II)L]^+$ and peak F in the same Figures can be ascribed to reduction of the same Co(I)L species to a complex reoxidized at peak G. This complex exhibits different reactivity depending on the solution composition, as deduced from the varying heights of peak G for the different derivatives.

Furthermore, for the methyl derivative the more anodic peak (peak H in Fig. 5(a)) can be attributed to the oxidation of the bismethylcobalt(III) complex, based on the voltammetric behavior of an authentic sample of this complex and on literature data [11]. This peak is not to be confused with peak L (Fig. 5(b)) which is due to oxidation of $[Co(II)L]^+$. The two different processes can be discriminated on the basis of reversibility, since the oxidation of the bismethyl derivative is totally irreversible*. Although bisalkyl complexes of the whole series were not available, the location on the potential axis and the irreversible characteristics of the more anodic peak observed for reduced solutions of ethyl and benzyl complexes suggest that the corresponding bisalkyl derivative also forms for these complexes. On the contrary, the quasi-reversible characteristics of the more anodic response recorded on reduced solutions of hydroxyethyl, methyl acetate and 2,2,2-trifluoroethyl compounds suggests that it has to be attributed to the oxidation of $[Co(II)L]^+$ formed at peak E in the first part of the backward scan. Hence, the bisalkyl derivative is not formed in the cases of complexes bearing these axial groups.

We found previously a situation different from those described above [15]: two electron reduction of the neopentyl cobalt(III) complex leads in fact to the $[neo\text{-}C_5H_{11}Co(I)L]^-$ species.

A peculiar intermediate situation was found for the isobutyl complex. For this compound voltammetric curves recorded after exhaustive cathodic reduction show peaks, with reference to Figs. 2 and 5, that correspond to: (i) D and B; (ii) E; (iii) F; poor reproducibility of the curves does not allow us to state if a fourth anodic peak is due to the oxidation of $R_2Co(III)L$ or $[Co(II)L]^+$ (either peak H or L). These results suggest the formation of $[RCo(I)L]^-$ in addition to Co(I)L and do not allow us to ascertain if formation of $R_2Co(III)L$ occurs. The coulometric *n* value listed in Table 1 for the isobutyl complex, intermediate between 1 and 2, and the presence of both $[RCo(I)L]^-$ and Co(I)L indicate that an overall one electron and an overall two electron reduction process occur simultaneously.

A similar sequence of anodic peaks is recorded on electrolyzed solutions of the isopropyl compound. However, in this case the fourth anodic peak is clearly attributable to the oxidation of $[Co(II)L]^+$. For this derivative strong poisoning adsorptions prevented us from carrying out exhaustive electrolyses and hence from computing a reliable datum for the number of electrons involved in the overall reduction process.

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*In Ref. 11 the authors do not record the peak due to oxidation of the $(CH_3)_2Co(III)L$ and justify this by reaction with the $[Co(II)L]^+$ species produced at less anodic potentials (peak E). In point of fact, as Fig. 5(a) shows, we do record the oxidation of the bisalkylcobalt(III) compound. A likely explanation for the presence of peak H in our voltammograms lies in the fact that in AN, the solvent used by us, the diffusion coefficient of the uncharged species is significantly higher than that of the cationic one.

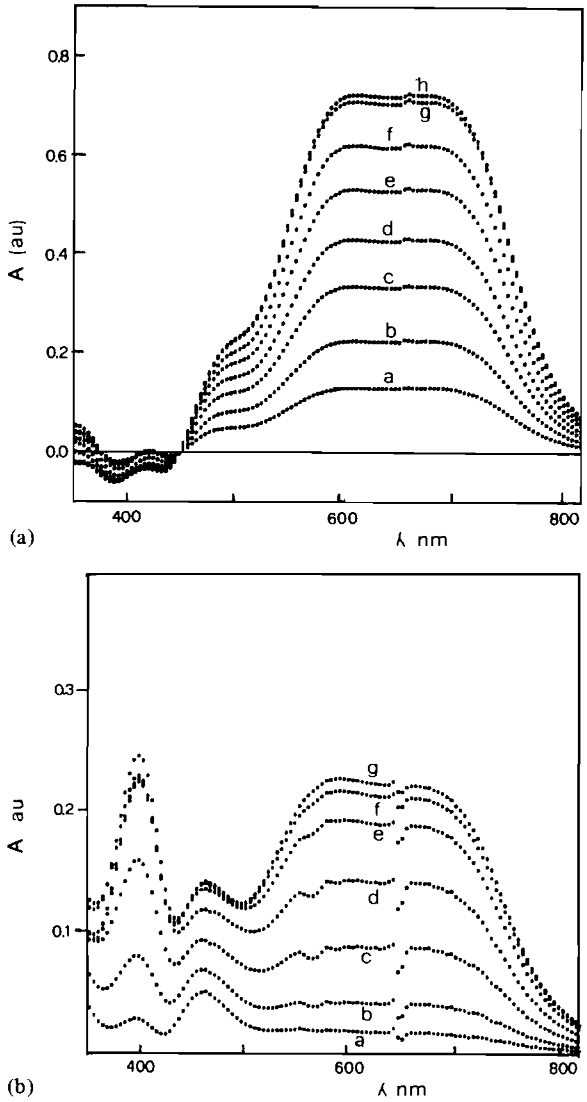

Fig. 6. Series of spectra recorded on an OTTLE cell during a cathodic potential scan on: (a) 5.0 × 10^{-3} M [$HO(CH_2)_2$-CoL]ClO_4, 0.4 M TEAP, AN solution; (b) 5.0 × 10^{-3} M [CH_3CH_2CoL]ClO_4, 0.4 M TEAP, AN solution. 0 °C; starting solution as reference. Potential values (V vs. SCE): a: −1.00; b: −1.05; c: −1.10; d: −1.15; e: −1.20; f: −1.25; g: −1.30 (in (b)); −1.35 (in (a)); h: −1.35.

Thus, controlled potential electrolysis experiments reveal $R_2Co(III)L$ complex formation for R = CH_3CH_2, $C_6H_5CH_2$ and CH_3 derivatives, no bisalkyl complex formation for R = $HO(CH_2)_2$, CH_3COOCH_2, CF_3CH_2, neo-C_5H_{11} and i-C_3H_7 derivatives, while the situation for i-C_4H_9 is unclear.

OTTLE Experiments

Spectra recorded during potential sweeps performed with an OTTLE cell on [neo-$C_5H_{11}Co(III)L$]-ClO_4 solutions have been reported and discussed in ref. 15. Figure 6(a) and (b) report analogous sequences of spectra recorded on [$HO(CH_2)_2Co(III)$-L]ClO_4 and [$CH_3CH_2Co(III)L$]ClO_4 solutions, respectively, as described in 'Experimental'. These three patterns are representative of three typical behaviors. Spectra were recorded during the reduction of the other complexes studied, see 'Supplementary Material'.

The most salient features of the spectrum of the neopentyl compound are peak-shaped absorptions with λ_{max} = 632 and 806 nm linked to each other by an isobestic point at 686 nm. Isobutyl and isopropyl complexes both show similar sharp absorptions at λ_{max} = 638 and 634 nm, respectively. The absorptions at higher wavelengths are not so well defined as for the neopentyl compound, but isobestic points are still detectable at 664 and 688 nm, respectively. The presence of an isobestic point supports the hypothesis advanced in ref. 15 that two stable species, (RCo(II)L and [RCo(I)L]$^-$, are interconverted by changing the potential.

The spectra recorded during the reduction of 2-hydroxyethyl (see Fig. 6(a)), as well of 2,2,2-trifluoroethyl and methyl acetate derivatives, show only one broad band centered at about 640 nm. By comparison with authentic samples, obtained by *in situ* two electron reduction of either the diaqua or the dibromo corresponding complexes, and with literature data [11] this broad band can be ascribed to Co(I)L. The plots in Fig. 6(b) are representative for the ethyl, methyl and benzyl derivatives. All these compounds exhibit a broad band centered at about 640 nm. By comparison with the authentic sample spectrum [11] the absorption at λ_{max} = 408 nm for the methyl compound can be attributed to the bismethylcobalt(III) complex. Corresponding bands are also present in the spectra of benzyl (416 nm) and ethyl (400 nm) (see Fig. 6(b)) complexes.

The last column in Table 1 reports the proposed reduction products for the different compounds studied, as determined from the voltammetric, coulometric and spectroelectrochemical measurements reported above.

Oxidation of the Reduction Products

We studied the anodic oxidation of exhaustively reduced solutions of isobutyl, benzyl, ethyl and methyl compounds with the aim of obtaining information about the possible reversibility of the overall reduction processes.

As regards the methyl derivative, the most extensively studied compound in the literature, we determined in advance that mixing equal amounts of $(CH_3)_2Co(III)L$ and [$Co(II)L$]$^+$ yields [CH_3Co-$(III)L$]$^+$, Co(I)L and $(CH_3)_2Co(III)L$. This was confirmed by comparison of the voltammetric curves recorded on the resulting solution (example Fig. 7) with those of authentic samples. This finding can be accounted for by the following overall reac-

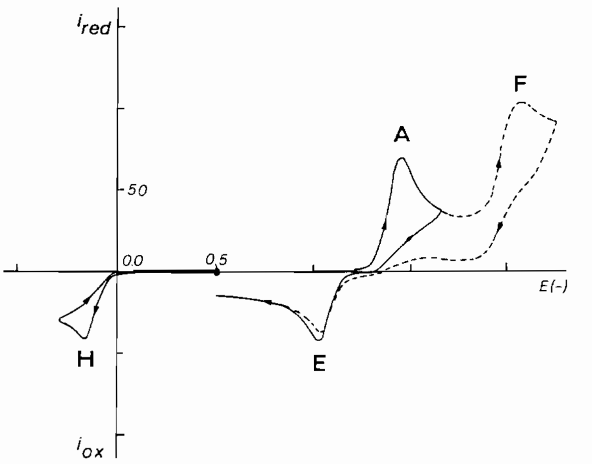

Fig. 7. Cyclic voltammetric curves recorded on a solution obtained by adding 9.6 × 10^{-3} M $(CH_3)_2CoL$ to 9.6 × 10^{-3} M $[CoL]ClO_4$, prepared by one electron reduction of $[CoL(H_2O)_2](ClO_4)_2$. ●: starting potential for both initially anodic and initially cathodic scans; 0 °C. Other experimental conditions as in Fig. 2.

TABLE 2. Oxidation of reduced solutions containing Co(I)L and $R_2Co(III)L$

R	Coulometric value[a] n	Reoxidation product
i-C_4H_9	1.05	$[i\text{-}C_4H_9Co(III)L]^+$
CH_3CH_2	0.8	$[CH_3CH_2Co(III)L]^+$
$C_6H_5CH_2$	0.7	$[C_6H_5CH_2Co(III)L]^+$
CH_3	0.7	$[CH_3Co(III)L]^+$

All tests performed at 0 °C. [a]The coulometric n values are lower than stoichiometrically expected. This is not surprising if we take into account partial decomposition of reduced species in the long time scale of these tests which often take hours. The value greater than one found for the isobutyl compound is in agreement with the formation of $[i\text{-}C_4H_9Co(I)L]^-$ as one final reduction product.

tion and is a key step in understanding the reduction mechanism (*vide infra*).

$$(CH_3)_2Co(III)L + 2[Co(II)L]^+ \longrightarrow 2[CH_3Co(III)L]^+ + Co(I)L \qquad (1)$$

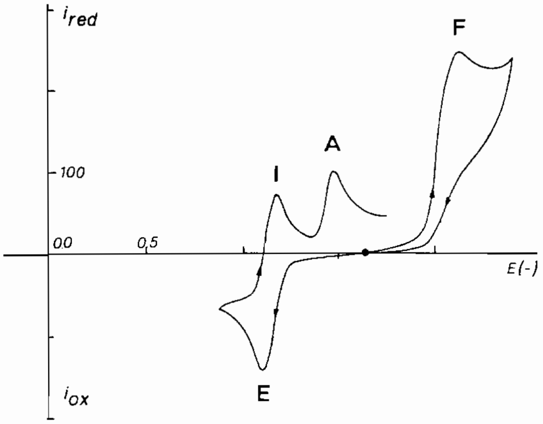

Fig. 8. Cyclic voltammetric curves recorded on a 1.2 × 10^{-3} M $[CH_3CH_2CoL]ClO_4$ solution, previously reduced exhaustively at −1.36 V vs. SCE. 0 °C; ●: starting potential for both scans. Other experimental conditions as in Fig. 2.

Hence, the absence of peak I in Fig. 5(a) is not surprising, since $[Co(II)L]^+$ electrogenerated at peak E is not long-lived in the solution and no directly associated backward cathodic peak can be detected on the reverse scan. Conversely, cathodic peak A due to the reduction of $[CH_3Co(III)L]^+$ and anodic peak H, attributed to the oxidation of $(CH_3)_2Co(III)L$, are recorded. The benzyl derivative behaves similarly. The voltammetric profile in Fig. 8 suggests that oxidation of Co(I)L to $[Co(II)L]^+$, when carried out in the presence of the bisethyl compound, induces a similar reaction which is, however, much slower, so that both $[Co(II)L]^+$ reactant (peak I) and $[RCo(III)L]^+$ product (peak A) can be detected on the reverse cathodic scan.

Table 2 summarizes the results of the coulometric electrolyses carried out at potentials corresponding to the oxidation of Co(I)L to $[Co(II)L]^+$ in the presence of the bisalkyl product. The formation of the relevant $[RCo(III)L]^+$ compound was ascertained by voltammetric and spectroelectrochemical techniques.

After OTTLE cyclic voltammetry all compounds listed in Table 2 showed spectra identical to those of the starting $[RCo(III)L]^+$ solution. This is in agreement with the conclusion that the overall electrochemical reduction processes are reversible in the sense that the starting compound is regenerated by anodic oxidation of the previously reduced solutions. Figure 9 shows the time derivative of the normalized absorbances [23] at 408 and 640 nm of the methyl complex versus the electrode potential in the forward and backward potential scans. As can be seen, the two curves overlap indicating that the two absorptions grow and decrease simultaneously. Since these two absorptions are attributed to $(CH_3)_2Co(III)L$ and Co(I)L, the trend reproted in Fig. 9 strongly supports a fast reaction between $[Co(II)L]^+$, produced by oxidation of Co(I)L, and $(CH_3)_2Co(III)L$. Development of this novel approach to interpretation of spectroelectrochemical data, for those complexes where slower homogeneous kinetics are operative, is in progress. In principle, by analyzing these responses properly it is possible to: (i) verify the presence of intermediate species; (ii) identify species which react with each other; (iii) determine the kinetic constants of the relevant reactions.

Reoxidation of reduced solutions was also performed for those compounds that led to Co(I)L

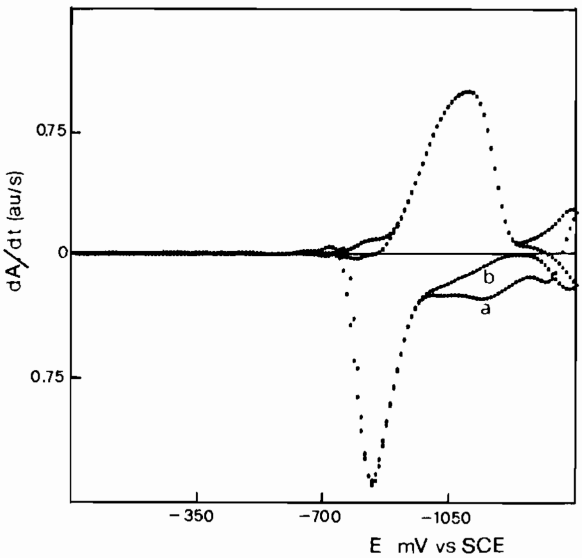

Fig. 9. dA/dt .vs. potential plot computed from a cyclic voltammetric OTTLE experiment on a 5.0 × 10^{-3} M [CH_3-CoL]ClO_4, 0.4 M TEAP, AN solution. Curve a: λ = 640 nm; curve b: λ = 408 nm. The curves are normalized to maximum value of the forward scan. 0 °C; starting solution as reference; 0.25 mV s^{-1} potential scan rate. Uncompensated ohmic drop is present.

as the only identifiable reduction product. Reoxidation was carried out at potentials of peak E. For 2-hydroxyethyl, methyl acetate and 2,2,2-trifluoroethyl compounds, 0.4, 0.4 and 0.85 mol of electrons per mol of starting $[RCo(III)L]^+$ were spent, respectively.

As a final consideration, it must be noted that all the electrochemical results obtained for these 'Costa type' complexes were independent of the supporting electrolyte used (TEAP, tetraethylammoniumtetrafluoroborate or $NaClO_4$).

Discussion

We have already emphasized the difficulties encountered in fully capitalizing on the voltammetric data collected due to poisoning adsorptions on the electrode surface. In all the cases studied in fact, to a greater or a less extent, adsorptions are coupled to heterogeneous charge transfer. This leads to voltammetric responses which deviate from purely diffusion controlled current–potential curves. These facts prevented us from exploiting the voltammetric data in order to discriminate among different mechanisms using theoretical literature data [26, 27] or computing the best fitting theoretical responses [28].

Spectroelectrochemical techniques have proved to be very effective tools since they add an additional coordinate to the simple electrochemical response (current versus time, current versus potential, or others). However, they are clearly limited by the standards necessary to assign the absorption bands. This is true especially in studies of electrode mechanisms where the chemical reactions coupled to charge transfer involve unstable intermediates.

Reduction Mechanism

Complexes with R = isopropyl, neopentyl [15] or isobutyl undergo two step cathodic reduction as evidenced by two distinct cathodic peaks (Table 1). For these complexes both $[RCo(I)L]^-$ and RCo(II)L are long-lived on the time scale of a voltammetric test. With the long periods (*c.* hours) necessary for bulk electrolysis experiments they undergo decomposition to differing extents. The neopentyl derivative exhibits the lowest reactivity and is the least reactive towards Co–C clevage (*vide infra*) of any organocobalt 'Costa-type' complexes studied to date [15]. Therefore, on a short time scale, an uncomplicated two-step charge transfer (EE mechanism) [29, 30] is operative for these compounds

$$[RCo(III)L]^+ + e^- \rightleftharpoons RCo(II)L$$

$$RCo(II)L + e^- \rightleftharpoons [RCo(I)L]^-$$

This is also supported by the spectroelectrochemical data.

The first step of the EE mechanism is affected by charge transfer overvoltage [31, 32]. The most likely hypothesis is that the charge transfer coefficient lies in the range 0.3–0.7 [32]: the relationship ${E_{1/2}}^r = (E_{p,c} + E_{p,a})/2$ can be used to evaluate ${E_{1/2}}^r$, which is our experimental approximation of the standard potential for the redox couple involved. Hence, on the basis of the relevant voltammetric curves, the 'half-wave' potential values reported in Table 3 were computed for isopropyl, neopentyl and isobutyl complexes.

On longer time scales of coulometric experiments different reactivities were revealed for the three different RCo(II)L species. The lowest reactivity is exhibited by the neopentyl complex [15] while other mechanisms, parallel to the EE process, are operative for the isopropyl and isobutyl compounds. This conclusion stems from data (coulometric n and electrolysis products) in Table 1. Unfortunately, poisoning of the working electrode prevented exhaustive electrolyses of the isopropyl compound. Therefore, the results of the OTTLE experiments are of particular importance for this complex.

The presence of a single cathodic peak, A, in the voltammetric experiments (Table 1) is *a priori* consistent with two different situations: (i) $E°(RCo(II)L, [RCo(I)L]^-)$ higher (more anodic) than $E°([RCo(III)L]^+, RCo(II)L)$; (ii) $E°([RCo(III)L]^+, RCo(II)L)$ higher than $E°(RCo(II)L, [RCo(I)L]^-)$, with the

TABLE 3. Potential values computed by cathodic reduction of $[RCo(III)L]ClO_4$ complexes

R	$E_{1/2}^r([RCo(III)L]^+/RCo(II)L)$	$E_{1/2}^r(RCo(II)L/[RCo(I)L]^-)$	$E_{p,c}$ (0.2 V/s) (V)	
i-C_3H_7	−1.34	−1.55	−1.42	−1.60
neo-C_5H_{11}[a]	−1.39	−1.51	−1.46	−1.54
i-C_4H_9	−1.4	−1.62	−1.50	−1.66
CH_3CH_2				−1.61
$C_6H_5CH_2$				−1.43
CH_3				−1.51
$HO(CH_2)_2$				−1.46
CH_3COOCH_2				−1.20
CF_3CH_2				−1.42

$E_{1/2}^r$, in V, are referred to the corresponding parameter of the redox couple bis(cyclopentadienyl)iron(III)/iron(II); −17 °C.
[a] Data from ref. 15.

charge transfer $[RCo(III)L]^+ + e^- \rightarrow RCo(II)L$ affected by an overvoltage sufficiently high so that it actually takes place at potential values more cathodic than $E^\circ(RCo(II)L,[RCo(I)L]^-)$. The former hypothesis would require the unlikely inversion of the two standard potentials involved on varying the alkyl substituent. The latter hypothesis is consistent both with the relative standard potential values of neopentyl, isopropyl and isobutyl complexes, and with the quasi-reversibility of the Co(III)/Co(II) redox couple. It must be taken into account that the latter assumption about the relative values of E° forces the homogeneous redox equilibrium

$$[RCo(III)L]^+ + [RCo(I)L]^- \rightleftharpoons 2RCo(II)L$$

to the right. This requires that $[RCo(I)L]^-$ formed at the electrode reacts with $[RCo(III)L]^+$ in the solution to give the thermodynamically stable RCo(II)L species. This conclusion rules out path I in Scheme 1. Oxidation of Co(I)L in the presence of bisalkylated compounds (see Table 2) supports path III for all complexes with a single cathodic peak, A, since the reoxidation mechanism follows this path in the opposite direction*.

Controlled potential electrolyses and spectroelectrochemical results indicate that the mechanisms discussed so far are not suitable to describe the behavior of the 2-hydroxyethyl, methyl acetate and 2,2,2-trifluoroethyl complexes for which the final reduction product is Co(I)L. The results for the 2,2,2-trifluoroethyl complex are peculiar in that they require alkyl transfer to some non-cobalt species, leading quantitatively to Co(I)L with a consumption of two mol of electrons per mol of compound (see Table 1) [13]. The identifiable reduction product of the 2-hydroxyethyl and methyl acetate complexes is the same as that of the 2,2,2-trifluoroethyl complex, but the coulometric data (see Table 1) for these derivatives must account for Co(I)L being formed in 50% yield. This is consistent with the coulometric results relative to the anodic reoxidation of the reduced solutions. Formation of unidentified side products with a higher cobalt oxidation state during the reduction of these two compounds is likely. Also, slow decomposition of the relevant bisalkylcobalt(III) compounds could take place after the same reaction sequence as for the other complexes exhibiting only one cathodic peak.

Finally, the coulometric value ($n = 1.40$) found for the isobutyl complex can be explained by the partial formation of $[RCo(I)L]^-$ in addition to $R_2Co(III)L$ and Co(I)L. As already pointed out the bisalkyl complex could undergo partial or total decomposition.

In view of the complexity of the reduction mechanism occurring at peak A, only peak potentials, which lack thermodynamic significance, can be obtained from the voltammetric curves recorded for ethyl, benzyl, methyl, 2-hydroxyethyl, methyl acetate and 2,2,2-trifluoroethyl complexes (Table 3).

To summarize, for complexes yielding $R_2Co(III)L$ + Co(I)L as final products (Table 1) path III in Scheme 1 is the most plausible reduction mechanism. For R = CH_3COOCH_2, $HOCH_2CH_2$ and CF_3CH_2 the reduction pathway remains ambiguous. Dealkyla-

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*A similar conclusion assumes that the reaction RCo(II)L + $[RCo(III)L]^+ \rightleftharpoons R_2Co(III)L + [Co(II)L]^+$ should be reversible. Equilibrium is shifted to the right during reduction owing to the further uptake of one electron by $[Co(II)L]^+$ to form Co(I)L while in the reoxidation process further oxidation of RCo(II)L to $[RCo(III)L]^+$ forces the equilibrium to the left. We suggest that reaction (1) takes place through the following steps:

$$\begin{array}{l} R_2Co(III)L + [Co(II)L]^+ \rightleftharpoons [RCo(III)L]^+ + RCo(II)L \\ [Co(II)L]^+ + RCo(II)L \longrightarrow Co(I)L + [RCo(III)L]^+ \\ \hline R_2Co(III)L + 2[Co(II)L]^+ \longrightarrow 2[RCo(III)L]^+ + Co(I)L \end{array}$$

The equilibrium of the latter (redox) step is shifted to the right due to the relative values of $E^\circ[Co(II)L]^+/Co(I)L$ [25] and $E^\circ[RCo(III)L]^+/RCo(II)L$ since this latter standard potential must be close to the potentials of peak A.

tion leads to Co(I)L as the solely identifiable product. Path III complicated by dealkylation reactions occurs for R = i-C_4H_{11} in parallel to a simple two electron charge transfer.

RCo(II)L Reactivity

Our results indicate that a key point in defining the reaction pathway of the reduction process is the reactivity of the RCo(II)L species. This reactivity is based on the relative height of the anodic peak B directly associated with the cathodic peak A.

The most reactive RCo(II)L species appear to be ethyl, benzyl and methyl acetate complexes whose voltammetric profiles never show any anodic peak B or D neither at low temperatures nor at high potential scan rates. Methyl, 2-hydroxyethyl and 2,2,2-trifluoroethyl complexes are less reactive. Their voltammetric curves show a directly associated anodic backward peak (peak system A/B in Fig. 3) but only at low temperatures and high potential sweep rates, i.e. conditions which inhibit cobalt–carbon cleavage and do not allow enough time for quantitative reaction. The appearance and increase of this backward anodic peak (B) is concomitant with a decrease of peak E due to the oxidation of Co(I)L that, according to Scheme 1, arises from Co–C cleavage. $CF_3CH_2Co(II)L$ exhibits a slightly lower reactivity than the methyl and 2-hydroxyethyl derivatives. A still lower reactivity is observed for R = i-C_3H_7 and i-C_4H_9. For R = neo-C_5H_{11} both RCo(II)L and $[RCo(I)L]^-$ are non-reactive.

For the most part the ordering of organocobalt complexes with regard to RCo(II)L reactivity, as summarized above, can be rationalized by R bulk. This is due presumably to the coupling of bisalkyl complex formation with Co–C bond cleavage. Alkyl transfer from RCo(II)L to $[RCo(III)L]^+$ is required (path III). Steric repulsion between bulky R groups and the (DO)(DOH)pn ligand is significant due to conformational distortions of (DO)(DOH)pn from planarity [1, 18]. As a consequence, only bisalkyl complexes with non-bulky alkyls have been prepared chemically [33, 34].

The role of electronic properties of R in determining RCo(II)L reactivity can be assessed only for R groups which are relatively non-bulky (and therefore more reactive). The ethyl complex is more reactive than the hydroxyethyl and 2,2,2-trifluoroethyl complexes. Thus, for alkyls of similar bulk, complexes with poorer electron donor alkyls are less reactive. The ordering of ethyl and benzyl complexes more reactive than methyl demonstrates that electronic factors outweigh those of bulk for these cases. These facts suggest that electron donating substituents on the alkyl can increase RCo(II)L reactivity by affecting the transition state of the bimolecular alkyl transfer reaction in two ways, i.e. stabilizing the migrating alkyl radical and lowering the effective charge on cobalt.

Supplementary Material

Spectra recorded during reduction of the complexes with R = i-C_3H_7, i-C_4H_9, $C_6H_5CH_2$, CH_3, CH_3COOCH_2 and CF_3CH_2 are available on request to author R.S.

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