from the monosubstituted cyclohexadiene Fe^0 complexes **3** to $[Ph_3C]^+$ has been developed. The intermediacy of the 17e Fe^I cation $\mathbf{3}^+$ has been shown by ESR, and its stability between −50 and −40 °C allows further slow H atom abstraction in the case of **3b** and **3b**. Decomposition of $\mathbf{3}^+$ is faster than H atom transfer above −40 °C for **3b** and **3c** and above −50 °C for **3d**. Note that addition of hydride to [Fe(arene)(cyclohexadienyl)]$^+$ cations often also proceeds via ET.[24]

The limits of the present strategy are (i) electrophilic reactivity of $[Ph_3C]^+$ toward some functions such as cyano in **3e**, (ii) the decomposition of the radical to **2** and R$^\bullet$ in some cases as shown here for **3d** at −50 °C. A further investigation of oxidizing **3** more rapidly and selectively with a better oxidant such as $[FeCp_2]^+$ at −80 °C is needed in order to overcome these limits.

Contrary to the rules announced by Davies et al.[25] (based on charge control), the nucleophiles always attack the odd cyclohexadienyl ligand rather than the even benzene ligand in the mixed cation $[Fe(C_6H_6)(\eta^5\text{-}C_6H_6R)]^+$ (**2**). This was previously demonstrated in the case of the parent complex **2a**, where orbital control is predominant.[10] Remarkably, it is now also true even when the cyclohexadienyl ligand is substituted in the exo position by bulky substituents in **2**. In the present work, we have never found traces of bicyclohexadienyl-type complexes even in ^1H NMR and ^{13}C NMR spectra of crude reaction products. Extension and applications of the present strategy are thus awaited.[27]

Acknowledgment. We are grateful to Drs. P. Guênot and S. Sinbandhit (CMPO, Rennes), and F. Le Floch (Brest) for helpful experimental assistance and to Dr. L. Toupet (University of Rennes) for his collaboration concerning the X-ray crystal structure of **4a**. We also thank Dr. J.-R. Hamon (University of Rennes) for stimulating discussions and the CNRS for a thesis grant to D.M.

Registry No. **2a**, 65296-91-5; **2b**, 100681-69-4; **2c**, 100681-71-8; **3a**, 71265-76-4; **3b**, 90064-38-3; **3c**, 90064-39-4; **4b**, 100681-72-9; **4c**, 122382-87-0.

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(24) Michaud, P.; Astruc, D.; Ammeter, J. H. *J. Am. Chem. Soc.* **1982**, *104*, 3755.

(25) (a) Davies, S. G.; Green, M. L. H.; Mingos, D. M. P. Tetrahedron Report 57. *Tetrahedron* **1978**, *34*, 3047. (b) These authors justified their theory by referring to the reactions of carbanions with $[Fe(mesitylene)_2]^{2+}$ which indeed give $[Fe(cyclohexadienyl)_2]$ derivatives. The bulk of the methyl groups inhibits the nucleophilic attack at the substituted arene carbon. Thus, in the second nucleophilic reaction, Helling[26] has shown that the carbanions attack the arene ligand rather than the cyclohexadienyl one. Our work[9,10] has indicated that this preference is only due to the presence of the methyl substituents in 1-, 3-, and 5-positions, not to charge control.

(26) (a) Helling, J. F.; Braitsch, D. M. *J. Am. Chem. Soc.* **1970**, *92*, 7207 and 7209. (b) Helling, J. F.; Cash, C. G. *J. Organomet. Chem.* **1974**, *73*, C10.

(27) (a) Organometallic Electron Reservoirs. 39. For part 38, see: Hamon, J. R.; Astruc, D. *Organometallics* **1989**, *8*, 000. (b) This paper overlaps with the State Thesis of D.M. (Rennes, 1985).

Electrochemical Synthesis of "Costa-Type" Cobalt Complexes

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Due to the difficulty encountered in chemical preparations, [LCo((DO)(DOH)pn)R]X species [where L = neutral ligand, R = alkyl group, (DO)(DOH)pn = $N^2,N^{2'}$-propanediylbis(2,3-butanedione 2-imine 3-oxime)] have been prepared previously with only a limited range of alkyl ligands in comparison to other model systems. In this connection, the feasibility of electrochemical methods in the synthesis of these organocobalt Costa-type B_{12} model complexes was examined. The Co(I) species produced from cathodic reduction of $Co((DO)(DOH)pn)Br_2$ at ca. −0.8 to −0.9 V (versus SCE) in acetonitrile at 25 °C reacted quickly with methyl iodide and more slowly with 2,2-bis(ethoxycarbonyl)propyl bromide ($C_2H_5O_2CC(CH_3)(CH_2Br)CO_2C_2H_5$, diester bromide). Although the product of the reaction with the diester bromide could be reduced at only slightly more negative potentials, we were able to prepare $[H_2OCo((DO)(DOH)pn)\text{-}diester]ClO_4$, a useful synthon, by controlled potential electrolysis of $Co((DO)(DOH)pn)Br_2$ at −0.8 V. This aqua complex, which we could not prepare by $NaBH_4$ reduction, was isolated and characterized. The electrochemical results are consistent with the view that both reduction of the organocobalt product and the slowness of the alkylation of the Co(I) species are responsible for previously observed difficulties in standard chemical preparations. The 1,5,6-trimethylbenzimidazole (Me_3Bzm) and pyridine (py) adducts were prepared by ligand substitution of the aqua complex and were characterized by NMR spectroscopy and elemental analysis. Rates of ligand dissociation of these adducts were found to be ~10 times faster than for the corresponding Me_3Bzm and py complexes in which R = methyl. In contrast, the γ-^{13}C py shifts of the two py derivatives were similar. These results can be rationalized if the alkyl ligands are electronically similar but sterically different, with the more bulky diester group favoring L dissociation.

Introduction

Preparation of organocorrinoid compounds, particularly 5′-deoxyadenosylcobalamin (coenzyme B_{12}) and other alkylcobalamins as well as of organocobalt B_{12} models is most conveniently carried out in aqueous or in aqueous alcoholic basic $NaBH_4$ solutions via the well-known reduction of Co(III) to Co(I), which is readily alkylated by alkylating agents such as alkyl halides.[1] However, poor yields are

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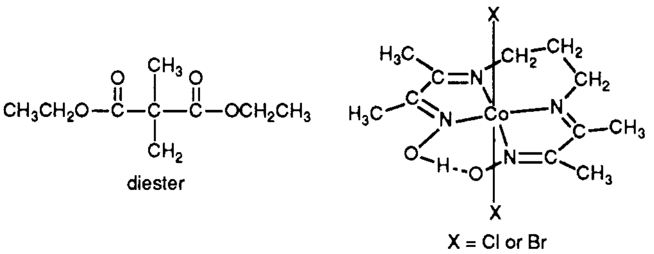
[†] Present address: Eniricerche S.p.A., 20097 S. Donato Milanese, Italy.

(1) Toscano, P. J.; Marzilli, L. G. *Prog. Inorg. Chem.* **1984**, *31*, 105 and references therein.

Chart I



often encountered and this drawback can be overcome in model systems using less convenient, but nevertheless effective, procedures involving Co(I)CO complexes.[2] This latter approach appears particularly successful in Costa-type organocobalt compounds, a class of B_{12} models which generally has the formulation [LCo((DO)(DOH)pn)R]X [where L = neutral ligand, R = alkyl group, (DO)(DOH)pn = $N^2,N^{2'}$-propanediylbis(2,3-butanedione 2-imine 3-oxime)]. See Chart I for the (DO)(DOH)pn ligand.

We recently established improved conditions under which Costa-type compounds could be prepared conveniently and in good yields by using the well-known $NaBH_4$ basic protic solvent method for generating Co(I).[3] However, in our hands, this approach works poorly for the preparation of complexes with R groups bearing electron-withdrawing substituents not only for Costa models but also for cobalamins. Therefore we have examined the preparation of Costa-type compounds in the aprotic solvent, acetonitrile, by cathodic reduction of stable Co^{III}-(DO)(DOH)pn complexes. Two alkyl halides, very different from each other with respect to their steric hindrance, were used in our study: (i) methyl iodide, to establish the appropriate reaction conditions with a nonbulky reagent and to synthesize a well-characterized compound; (ii) 2,2-bis(ethoxycarbonyl)propyl bromide ($C_2H_5O_2CC(CH_3)(CH_2Br)CO_2C_2H_5$, diester bromide), to test the method with a reagent containing electron-withdrawing substituents and to synthesize compounds we were unable to prepare by convenient standard routes[3] or by using minimal amounts of $NaBH_4$. Furthermore, the diester group is a bulky ligand (see Chart I), but unlike most other similar ligands, e.g. neo-C_5H_{11}, it is a relatively poor electron donor (see below). The electrochemical preparation yields aqua derivatives that can be readily converted to other derivatives such as those with pyridine (py) and 1,5,6-trimethylbenzimidazole (Me_3Bzm).

Experimental Section

Materials, Methods, and Instrumentation. Acetonitrile solvent (CH_3CN, anhydrous, 99+%, GOLD LABEL, water < 0.005%, packaged under nitrogen) was from Aldrich. Tetraethylammonium perchlorate (TEAP) (C. Erba) was dried for 1 week at 50 °C in a vacuum oven before use as a supporting electrolyte. [*Caution: Perchlorate salts are explosive and should be handled with care!*]

All solvents employed in isolating and characterizing the electrolysis product were from Fisher; methyl iodide was from C. Erba, and all other reagents were from Aldrich. Me_3Bzm[4] and diester bromide[5] were prepared as described.

Elemental analyses (C, H, N) were performed by Atlantic Microlab, Inc., Atlanta, GA.

An AMEL Model 471 multipolarograph and a BAS (Bioanalytical System) CV-1B cyclic voltammograph, coupled with a digital voltmeter, were used in the voltammetric tests. The recording device in the latter case was an AMEL Model 863 XY digital recorder. An AMEL Model 552 potentiostat was used in conjunction with an AMEL Model 721 digital integrator in the controlled potential electrolyses. The cells used in the voltammetric tests, as well as those in the controlled potential coulometries, have been described elsewhere.[6] An aqueous saturated calomel electrode (SCE) was used as the reference electrode. All electrochemical experiments were carried out at 25 °C, unless specified otherwise, and under prepurified N_2.

^{1}H NMR spectra were collected on a Nicolet NB-360 spectrometer operating at 361.08 MHz, and all chemical shifts are relative to internal Me_4Si. The proton-decoupled ^{13}C NMR spectrum (~30000 transients) was obtained at 22 °C on a Varian CFT-20 spectrometer (20 MHz). Concentrations of the cobalt complexes were ~50 mM.

Syntheses. [$H_2OCo((DO)(DOH)pn)diester]ClO_4$. The solvent used in the electrochemical syntheses was removed by evaporation under reduced pressure at room temperature. The resulting orange solid was suspended in a small volume of $CHCl_3$, and most of the TEAP supporting electrolyte (1.6 g for a typical preparation using 700 mg of $Co^{III}((DO)(DOH)pn)Br_2$ starting compound) was removed by filtration. The filtrate was evaporated to dryness by rotoevaporation, and the resulting residue was partly dissolved in a small volume of H_2O, to which a few drops of acetone were added to complete dissolution. The solution was filtered through paper after removal of immiscible diester bromide by pipette. After 2 days, long orange crystals formed from the filtrate left in a small flask at 23 °C. The final yield was 40%. Anal. Calcd for $C_{20}H_{36}ClCoN_4O_{11}$: C, 39.84; H, 6.02; N, 9.30. Found: C, 39.58; H, 6.05; N, 9.28; MW 602.93. ^{1}H NMR shifts (ppm) in DMSO-d_6: OH···O (s), 19.17; CO_2CH_2 (m), 3.96; NCH_2CCH_2N (two m), 3.95 and 3.55; $CN{=}CCH_3$ (s), 2.45; $ON{=}CCH_3$ (s), 2.29; $NCCH_2CN$ (two m), 2.15 and 1.75; $CoCH_2$ (s), 1.65; CO_2CCH_3 (t), 1.09; $CoCCCH_3$ (s), 1.04.

[$pyCo((DO)(DOH)pn)diester]ClO_4$. Pyridine (40 mL, 0.50 mmol) was added to a stirred solution of [$H_2OCo((DO)(DOH)pn)diester]ClO_4$ (200 mg, 0.33 mmol in 5.0 mL of methanol). After the solution was stirred a few minutes, H_2O (3.0 mL) was added, and the solution was filtered. An orange crystalline precipitate formed from the filtrate left in a small unstoppered flask at 23 °C for 2 days. Yield: 130 mg (58%). Anal. Calcd for $C_{25}H_{38}ClCoN_5O_{10}\cdot H_2O$: C, 44.09; H, 5.92; N, 10.28. Found: C, 44.10; H, 5.97; N, 10.27; MW 687.01. ^{1}H NMR shifts (ppm) in $CDCl_3$: OH···O (s), 18.80; α-H (d), 7.83; γ-H (t), 7.76; β-H (t), 7.52; NCH_2CCH_2N (two m), 4.16 and 3.70; CO_2CH_2 (m), 4.07; $CN{=}CCH_3$ (s), 2.49; $ON{=}CCH_3$ (s), 2.33; $NCCH_2CN$, obscured; $CoCH_2$ (s), 1.96; CO_2CCH_3 (t), 1.21; $CoCCCH_3$ (s), 1.23. In the spectrum, free pyridine is evident along with signals for an equivalent amount (~30%) of a second (DO)(DOH)pn species. (We believe this is the perchlorate complex formed by substitution of pyridine. In studies with other complexes, pyridine is displaced in solutions of perchlorate salts but not hexafluorophosphate salts.) ^{13}C NMR shifts (ppm) in $CDCl_3$: $CN{=}C^*$, 175.05; $ON{=}C$, 156.02; α-C py, 148.10; γ-C py, 138.79; β-C py, 126.84; $NC^*H_2CH_2C^*H_2N$, 48.66; $NCH_2C^*H_2CH_2N$, 26.93; $CN{=}CC^*H_3$, 17.93; $ON{=}CC^*H_3$, 13.16 relative to TMS. Shifts of the diester alkyl ligand are 170.95, 61.49, 56.86, 20.59, and 13.92 ppm.

[$Me_3BzmCo((DO)(DOH)pn)diester]ClO_4$. Me_3Bzm (16 mg, 0.10 mmol in 10.0 mL of methanol) was added to [$H_2OCo((DO)(DOH)pn)diester]ClO_4$ (50 mg, 0.08 mmol) in a 25-mL Erlenmeyer flask. The solution was stirred a few minutes, H_2O (5.0 mL) was added, and the solution was filtered. The filtrate was left to evaporate at 23 °C, and 5 days later an orange precipitate was collected; this was washed with H_2O (20 mL) and then with diethyl ether (5 mL). Yield: 60 mg (95%). Anal. Calcd for $C_{30}H_{46}ClCoN_6O_{10}\cdot H_2O$: C, 47.22; H, 6.34; N, 11.01. Found: C, 47.08; H, 6.25; N, 11.03; MW 763.12. ^{1}H NMR shifts (ppm) in $CDCl_3$: OH···O (s), 19.22; H2 (s), 7.50; H7 (s), 7.12; H4 (s), 7.10;

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[2] Finke, R. G.; Smith, B. L.; McKenna, W. A.; Christian, P. A. *Inorg. Chem.* **1981**, *20*, 687.

[3] Parker, W. O., Jr.; Bresciani-Pahor, N.; Zangrando, E.; Randaccio, L.; Marzilli, L. G. *Inorg. Chem.* **1985**, *24*, 3908.

[4] Simonov, A. M.; Pozharskii, A. E.; Marianovskii, V. M. *Indian J. Chem.* **1967**, *5*, 81.

[5] Randaccio, L.; Bresciani-Pahor, N.; Orbell, J. D.; Calligaris, M.; Summers, M. F.; Snyder, B.; Toscano, P. J.; Marzilli, L. G. *Organometallics* **1985**, *3*, 469.

[6] Seeber, R.; Mazzocchin, G. A.; Refosco, F.; Mazzi, U.; Tisato, F. *Polyhedron* **1987**, *6*, 1647.

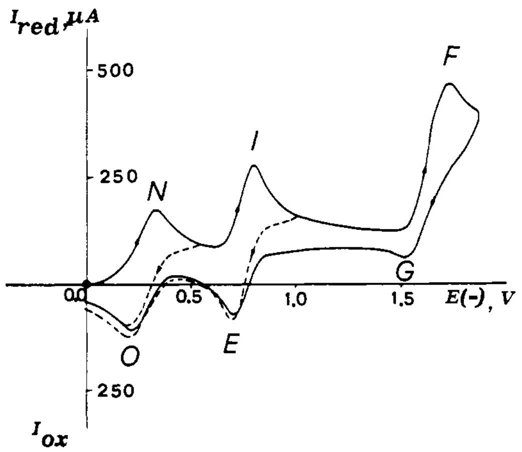

Figure 1. Cyclic voltammetric curves recorded on a 1.2×10^{-2} M Co((DO)(DOH)pn)Br_2, 0.1 M TEAP, CH_3CN solution, at 25 °C: platinum working electrode; SCE reference electrode; potential scan rate 0.2 V s^{-1}; ●, starting potential for the initially cathodic scan.

NCH_2CCH_2N (two m), 4.20 and 3.72; CO_2CH_2 (m), 4.10; C(12)H_3 (s), 3.89; CN=CCH_3 (s), 2.48; ON=CCH_3 (s), 2.33; C(10)H_3 (s), 2.33; C(11)H_3 (s), 2.31; NCH_2CCH_2N (two m), obscured and 2.16; $CoCH_2$, (s), 1.88; CO_2CCH_3 (t), 1.22; $CoCCCH_3$ (s), 1.25. H4 was assigned by irradiation of NC(12)H_3 in the 1D NOE experiment.[7]

Results and Discussion

The starting cobalt(III) compounds we commonly use to synthesize alkyl derivatives with (DO)(DOH)pn as the equatorial ligand are either the dibromo or the dichloro complexes;[8] see Chart I.

When such compounds are reduced to the +1 oxidation state with $NaBH_4$, they react with added alkylating agent[1] to give the corresponding alkylated cobalt complex.[3] However, this convenient procedure was not effective in preparing some compounds of particular interest for our studies on B_{12} models, namely, compounds in which R contained heteroatoms ($CNCH_2CH_2Br$, $(CH_3CO)_2O$, 5′-tosyladenosine, CH_3COCH_2Cl, CH_3OCH_2Br, $CH_3OCH_2CH_2Cl$) or in which R was bulky (adamantyl bromide). In such cases, no useful amount of product could be obtained. We reasoned that if the reduction potential of the resulting product is not negative enough, the chemical reducing agent $NaBH_4$ can reduce or otherwise attack the organocobalt product. The poor stability usually exhibited by reduced organocobalt compounds[9-11] could then account for the low yields. However, in some cases, we were still unable to isolate pure products even when minimal amounts of $NaBH_4$ were used. These preparations are typically performed in protic solvents under strongly basic conditions. Thus, we turned our attention to synthesis in aprotic solvents by electrochemical methods of synthesis, which allow precise adjustment of the power of the reducing agent, i.e. of the value of the electrode potential.

Electrochemical Study of Co^{III}((DO)(DOH)pn)Br_2. As an initial study, we evaluated the electrochemical behavior of Co^{III}((DO)(DOH)pn)Br_2, the starting compound of our electrochemical synthesis. Figure 1 contains cyclic voltammetric curves recorded on CH_3CN solutions of this compound. Three sequential reduction processes with characteristically different reversibility are indicated (peak systems N/O, I/E, and F/G). No anodic response attributable to the oxidation of free bromide ions was recorded at ~+0.75 V.[12]

During exhaustive reduction of the dibromo complex at a potential corresponding to the first cathodic process (peak N - electrolysis potential = -0.5 V versus SCE), one mole of electrons per mole of starting complex was spent and the solution turned from a pale green to a red-orange color. Cyclic voltammetric curves recorded on the electrolyzed solution showed the same cathodic–anodic peak systems as the starting solution, demonstrating the stability of the cobalt(II) species formed. Oxidation of free bromide ions was also recorded at +0.78 V.

Further reduction at a potential just beyond the second cathodic peak (peak I - electrolysis potential of -1.0 V) led to the consumption of one further mole of electrons per mole of the complex, and the solution became deep blue in color. Cyclic voltammograms on the electrolyzed solution once more showed the same cathodic–anodic peak systems, again with the additional peaks due to the oxidation of free bromide ions. From this cobalt(I) solution, the cobalt(II) (as well as the starting cobalt(III) species) could be regenerated in almost quantitative yield by oxidation at -0.5 V and at 0.0 V (peaks E and O), respectively. On the other hand, reduction at -2.0 V, a potential more cathodic than the last cathodic peak (F), involved the consumption of a nonreproducible number of coulombs; ill-defined voltammetric peaks were then recorded, and the current/potential curves were different from any of those described above.

On the basis of these findings and of the values of the parameters characterizing the voltammetric peaks (E_p, $E_p - E_{p/2}$, $i_{p,a}/i_{p,c}$), evaluated with electronic *iR* drop compensation in a cell of proper geometry, it can be concluded that a first quasi-reversible one-electron charge transfer leads to a cobalt(II) species, with loss of bromide ions. This complex can be further reduced through a reversible one-electron reduction to the corresponding stable cobalt(I) species. The formally cobalt(0) species produced by further reduction seems to undergo irreversible chemical decomposition, and ligand reduction could be occurring.

A voltammetric comparison of the dibromo and diaqua[13] complexes of Co^{III}((DO)(DOH)pn reveals that the Co(III)/Co(II) peak system of the former ($E_{1/2}$ = -0.23 V, ΔE_p = 110 mV at 0.2 V/s, 25 °C) is ~0.5 V more negative than that of the latter compound. In contrast, for both systems the Co(II)/Co(I) species appears at exactly the same potentials ($E_{1/2}$ = -0.72 V). For both redox systems, $i_{p,a}/i_{p,c}$ is approximately one. Bromide must partly or completely dissociate from the cobalt(II) and the cobalt(I) compounds in fast equilibrium reactions. In the case of the cobalt(III) complex, the association/dissociation equilibria must lie toward the dibromo derivative, as evidenced by the absence of the peaks attributable to bromide ion during oxidations on the starting solution. These findings on the Co(II)/Co(I) couple are consistent with previous studies on closely related Costa-type compounds with a slightly different ligand.[9,11] However, in one case, a cobalt(III) diiodo complex was used[9] and one iodide is displaced by acetonitrile.

Electrochemistry in the Presence of Alkyl Halides. The cyclic voltammetric curves reported in Figure 2 show

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[7] Parker, W. O., Jr.; Zangrando, E.; Bresciani-Pahor, N.; Randaccio, L.; Marzilli, L. G. *Inorg. Chem.* **1986**, *25*, 3489.

[8] Costa, G.; Mestroni, G.; de Savorgnani, E. *Inorg. Chim. Acta* **1969**, *3*, 323.

[9] Elliott, C. M.; Hershenhart, E.; Finke, R. G.; Smith, B. L. *J. Am. Chem. Soc.* **1981**, *103*, 5558.

[10] Seeber, R.; Marassi, R.; Parker, W. O., Jr.; Marzilli, L. G. *Organometallics* **1988**, *7*, 1672.

[11] Finke, R. G.; Smith, B. L.; Droege, M. W.; Elliott, C. M.; Hershenhart, E. *J. Organomet. Chem.* **1980**, *202*, C25.

[12] Magno, F.; Mazzocchin, G. A.; Bontempelli, G. *J. Electroanal. Chem.* **1973**, *47*, 461.

[13] Seeber, R., work in progress.

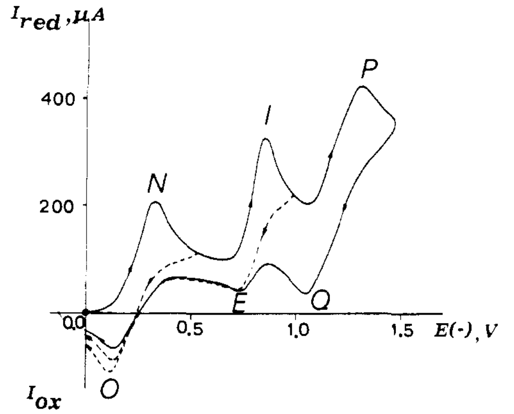

Figure 2. Cyclic voltammetric curves recorded on the same solution of Figure 1, after addition of 0.12 M CH_3I. Experimental conditions are as in Figure 1.

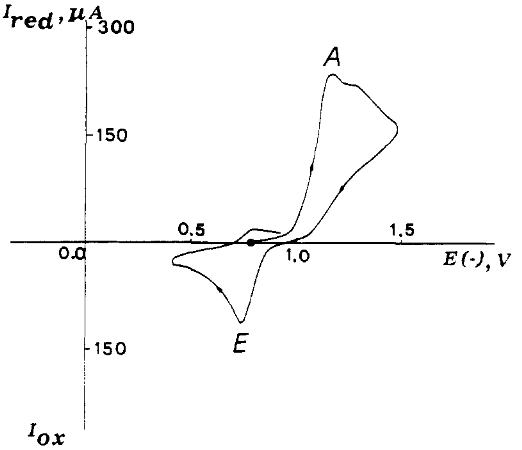

Figure 3. Cyclic voltammetric curve recorded on the solution of Figure 2, after exhaustive electrolysis at −1.0 V. Experimental conditions are as in Figure 1.

the effects of the addition of methyl iodide to a solution of $Co^{III}((DO)(DOH)pn)Br_2$ (10:1 molar ratio). The first cathodic peak (system N/O) is unaffected by the presence of the alkyl halide, while only a very small anodic peak (E) is associated with the second cathodic peak (I); these results suggest that the cobalt(I) species produced at the electrode is involved in a fast irreversible chemical reaction. The presence in Figure 2 of a new peak system, P/Q, at potentials less negative than those of peak system F/G demonstrates the formation of a new species, most probably via the same chemical reaction responsible for the disappearance of the electrogenerated cobalt(I) product. Control experiments revealed that no reduction process can be attributed to reduction of methyl iodide within these potentials.

Exhaustive electrolysis at −1.0 V of $Co^{III}((DO)(DOH)pn)Br_2$ in the presence of a 5:1 excess of methyl iodide still involved the consumption of two moles of electrons per mole of complex. However, the color turned from pale green to orange, and the voltammetric curves recorded on the reduced solution resembled that reported in Figure 3. Both the shapes and locations on the potential axis of peaks A and E were equal to those exhibited by an acetonitrile solution of $[H_2OCo^{III}((DO)(DOH)pn)CH_3]ClO_4$.[13] The alkylation mechanism does not seem to occur through a single step, since the peak system P/Q in Figure 2, arising from the primary product of reaction, is located at potentials quite different from peaks A and E recorded on the exhaustively reduced solutions. This primary intermediate is probably $[ICo^{III}((DO)(DOH)pn)CH_3]$.

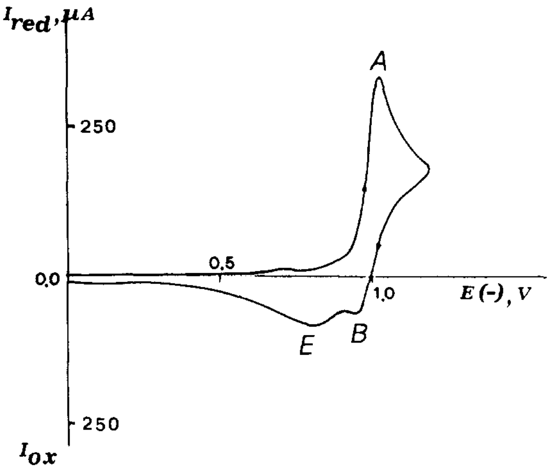

Figure 4. Cyclic voltammetric curve recorded on a 1.2 × 10^{-2} M $Co((DO)(DOH)pn)Br_2$, 0.12 M diester bromide, 0.1 M TEAP, CH_3CN solution, after exhaustive electrolysis at −0.85 V. Experimental conditions are as in Figure 1.

On the basis of the results of these tests, experiments were carried out by using diester bromide as the alkylating agent. The voltammetric behavior of $Co^{III}((DO)(DOH)pn)Br_2$ was essentially unaffected by the presence of diester bromide, *even in 10-fold excess*. In this case, the expected alkylation reaction must be much slower than for methyl iodide, a result consistent with well-established principles concerning reaction of Co(I) species with alkyl halides.[1]

In view of the difficulties in obtaining the desired product by borohydride reduction, electrolyses were performed in the presence of diester bromide at a potential that is the least negative possible, still compatible with formation of Co(I) species (∼−0.85 V). Two moles of electrons per mole of starting complex were consumed, and the color of the solution became orange. Figure 4 shows the voltammetric curve recorded for the final solution, which looks similar to those recorded for related organocobalt(III) complexes.[13] The proximity of cathodic peak A in Figure 4 to peak I in Figure 1 could account for the difficulties in preparing the alkylated cobalt(III) compound by $NaBH_4$ reduction. Similar electrochemical results were obtained with lower amounts of alkyl halide. The product from the electrochemical treatment of a 2:1 molar ratio of diester bromide to Co was isolated and chemically characterized as $[H_2OCo((DO)(DOH)pn)diester]ClO_4$ as described in the Experimental Section.

In an alternative approach, $Co^{III}((DO)(DOH)pn)Br_2$ was reduced to cobalt(I); on addition of a 2-fold excess of diester bromide to the electrolyzed solution, its blue color turned to orange. The voltammetric curve recorded was the same as that in Figure 4. The solution from this alternative electrochemical procedure was treated as described in detail in the Experimental Section for the above procedure. Both procedures gave the same product in similar yield.

The isolated $[H_2OCo^{III}((DO)(DOH)pn)diester]ClO_4$ complex was characterized by electrochemical properties essentially identical with those revealed in Figure 4. The electrochemical reduction of such organocobalt complexes is complicated and dependent on the nature of R;[9,10,13,14] we are currently investigating a series of $[H_2OCo((DO)(DOH)pn)R]ClO_4$ complexes. However, the similarity of the results with the isolated complex and those presented in Figure 4 indicates that the organocobalt complex giving

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[14] Costa, G.; Puxeddu, A.; Reisenhofer, E. *Experientia, Suppl.* **1971**, *18*, 235.

peak A lacks a coordinated bromide ligand.

Properties of [$LCo^{III}((DO)(DOH)pn)R]ClO_4$ Complexes. The γ-^{13}C py shifts of [$pyCo^{III}((DO)(DOH)pn)R]ClO_4$ are the same within experimental error (±0.05 ppm) and have values of 138.73 and 138.79 ppm for R = CH_3 and diester, respectively.[15] Good evidence exists that the γ-^{13}C shift of py complexes reflects the trans influence of the R ligand in the extensively studied complexes of the type $LCo(DH)_2R$, in which DH = monoanion of dimethylglyoxime.[16] In a recent study,[15] we showed a close parallel and a linear relationship between the ^{13}C shifts of analogous compounds with the $(DH)_2$ and (DO)(DOH)pn equatorial ligand systems. This correlation strongly implies that the γ-^{13}C py shift in (DO)(DOH)pn compounds reflects the trans influence of R. Thus, the trans influence of the diester alkyl group is similar to that of the methyl group.

By using experimental procedures and data analysis as reported in previous studies,[3,15] we determined that the first-order rate constants of L dissociation were (4.6 ± 0.1) and $(4.3 \pm 0.1) \times 10^{-1}$ s^{-1} for the py and Me_3Bzm complexes, respectively. Finding similar rates for these two ligands is consistent with previous observations that the py and Me_3Bzm ligands form complexes with very similar affinities and Co–N bond lengths in organocobalt complexes.[15,17] However, if we compare these dissociation rate constants with those reported[3,15] for the analogous methyl adducts, we find that the diester values are ~10 times larger. These faster dissociation rates for the diester species are consistent with the steric effect of the bulkier diester ligand.[18]

Summary

Although organocobalt model complexes with the diester ligand originally attracted attention since they might mimic the putative intermediate that forms during the catalytic cycle of the B_{12}-dependent enzyme, methylmalonyl Co-A mutase,[19] recent studies suggest that such Co–C bonded species probably have no significant biological role.[20,21] The Costa-type models are valuable electrochemical analogues of cobalamins,[9] and the biological relevance of our findings rests in the eventual application of electrochemical methods in the preparation of diverse organocobalamins useful in assessing the steric and electronic effects that might influence Co–C bond homolysis.[22-24] According to the nature of R, the $NaBH_4$ or the Co(I)CO preparative methods give higher yields of Costa-type products.[2,3] For diester type ligands in which a direct comparison is possible, this work demonstrates that the electrochemical preparative method described here can give yields comparable to the $Co^{I}CO$ procedure and is more convenient.

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[15] Parker, W. O., Jr.; Zangrando, E.; Bresciani-Pahor, N.; Marzilli, P. A.; Randaccio, L.; Marzilli, L. G. *Inorg. Chem.* **1988**, *27*, 2710.

[16] Bresciani-Pahor, N.; Forcolin, M.; Marzilli, L. G.; Randaccio, L.; Summers, M. F.; Toscano, P. J. *Coord. Chem. Rev.* **1985**, *63*, 1.

[17] Charland, J.-P.; Zangrando, E.; Bresciani-Pahor, N.; Randaccio, L.; Marzilli, L. G., submitted for publication.

[18] Randaccio, L.; Bresciani-Pahor, N.; Orbell, J. D.; Calligaris, M.; Toscano, P. J.; Marzilli, L. G. *Organometallics* **1985**, *3*, 469.

[19] Krebs, T.; Retey, J. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 822.

[20] Finke, R. G.; Schiraldi, D. A.; Mayer, B. *J. Coord. Chem. Rev.* **1984**, *54*, 1.

[21] Halpern, J. *Science (Washington, D.C.)* **1985**, *227*, 869.

[22] Hay, B. P.; Finke, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 4820.

[23] Kim, S.-H.; Chen, H. L.; Feilchenfeld, N.; Halpern, J. *J. Am. Chem. Soc.* **1988**, *110*, 3120.

[24] Pagano, T. G.; Yohannes, P. G.; Hay, B. P.; Scott, J.; Finke, R. G.; Marzilli, L. G. *J. Am. Chem. Soc.* **1989**, *111*, 1484.