Redox Behavior of Simple Vitamin B_{12} Model Complexes and Electrochemical Catalysis of Carbon-Skeleton Rearrangements†

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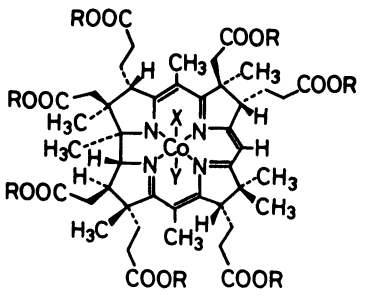
Various cobalt complexes of 4,10-dipropyl-5,9-diazatrideca-4,9-diene-3,10-dione dioxime, $(C_2C_3)(DOH)_2pn$, were prepared, and redox behavior of them was investigated by means of cyclic voltammetry; Co(II)/Co(I) redox potentials in the range of −0.69 through −0.7 V vs. Ag/AgCl. The monomethylated complex, which has a cobalt-carbon bond at one axial site of the nuclear cobalt, was disproportionated to the dimethylated complex, involving two cobalt-carbon bonds at both axial sites, and the Co^I species by one-electron reduction. The dimethylated complex was inactive for electrochemical reduction, but transformed into the monomethylated complex via cleavage of a cobalt-carbon bond upon electrochemical oxidation. The electrolyses of 1-bromo-2,2-bis(ethoxycarbonyl)propane, 1-bromo-2-cyano-2-ethoxycarbonylpropane, and 2-acetyl-1-bromo-2-ethoxycarbonylpropane in the presence of $[Co^{III}\{(C_2C_3)(DO)(DOH)pn\}Br_2]$ in *N,N*-dimethylformamide did not proceed in a divided cell at −2.0 V vs. Ag/AgCl, since the corresponding dialkylated complexes, inactive for electrochemical reduction, were formed in the course of reaction. When imidazole was added to solutions for the electrolysis, the reaction proceeded efficiently by the trans effect arising from the coordinated axial base and the corresponding carbon-skeleton rearrangement products were obtained. On the other hand, the carbon-skeleton rearrangement proceeded in an undivided cell even in the absence of imidazole; the dialkylated complex was decomposed to give the monoalkylated complex and the reduction and rearrangement products by electrochemical oxidation on the anode.

Vitamin B_{12}-dependent enzymes catalyze various isomerization reactions which result in carbon-skeleton rearrangements: methylmalonyl-SCoA⇌succinyl-SCoA, β-methylaspartate⇌glutamate, and methylitaconate ⇌α-methyleneglutarate.[1] Clarification of these reaction mechanisms is a current research target in bioinorganic chemistry.[2] In this regard, various cobalt complexes have been synthesized as model complexes,[3] and mechanistic studies of various enzyme-mimic reactions have been carried out. One of the most important aspects in designing model complexes is to pay much attention to the redox potentials of the nuclear cobalt in connection with their catalytic activities. The catalytic reactions as mediated by vitamin B_{12} and its model complexes have been carried out by electrochemical means[4,5] in the light of redox behavior of such complexes.[6–8]

We have been dealing with hydrophobic vitamin B_{12} derivatives, which have ester groups in place of the peripheral amide moieties of the naturally occurring vitamin B_{12},[9–14] and found that electrochemical carbon-skeleton rearrangements were catalyzed efficiently by these complexes.[13] In those cases, the reaction takes place with a catalytic cycle shown in Fig. 1: the Co^{II} complex is electrochemically reduced to the Co^I species, and the corresponding alkylated complex is generated by reaction of the supernucleophilic Co^I species with a substrate, a substituted alkyl bromide (RX); the alkylated complex is subsequently decomposed by photolysis or electrolysis to afford the corresponding products, and the cobalt complex acts as a mediator repeatedly. This finding prompted us to develop a simple model complex, which shows redox



Hydrophobic Vitamin B_{12}

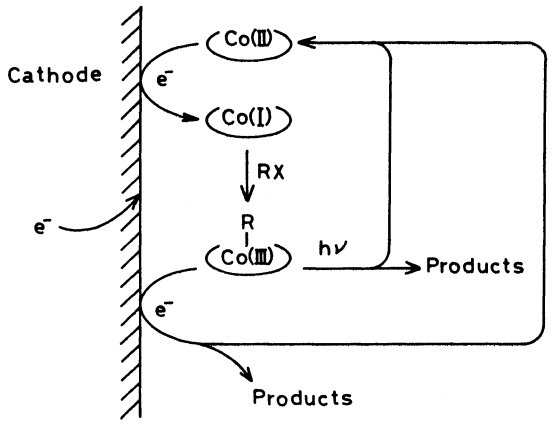


Fig. 1. Schematic representation of electrochemical catalysis.

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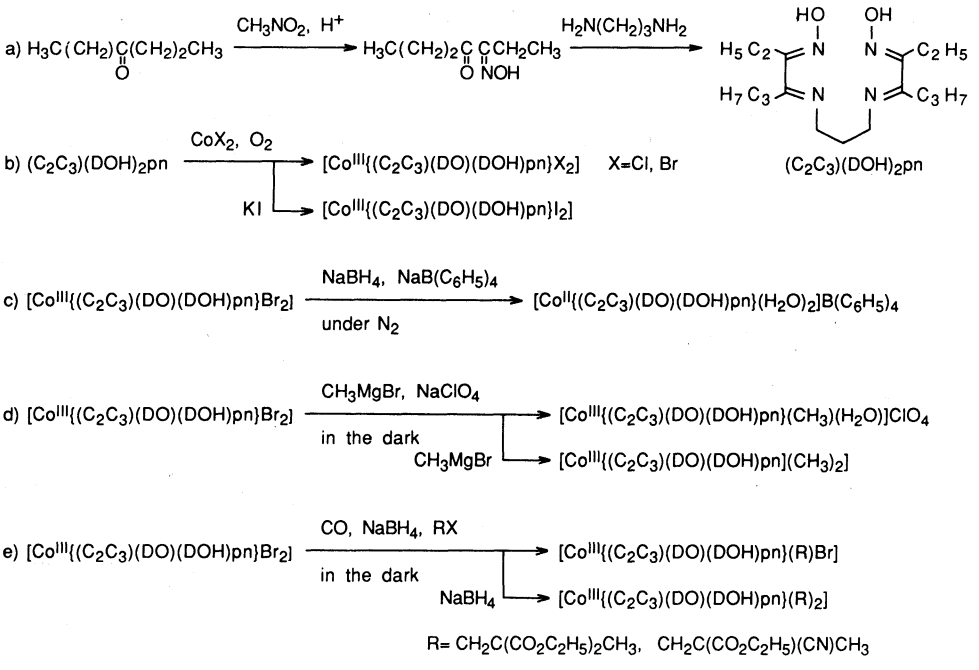
behavior analogous to that of vitamin B_{12} with respect to the nuclear cobalt and catalyzes the isomerization reaction in a similar manner. We report here on the redox behavior of model complexes which are derived from the Costa's complex[15,16] by its modification. Furthermore, the electrochemical carbon-skeleton rearrangements catalyzed by these model complexes was compared with those catalyzed by the hydrophobic vitamin B_{12}.

Experimental

General Analyses and Measurements. Elemental analyses were performed at the Microanalysis Center of Kyushu University. IR spectra were taken on a JASCO IR-810 infrared spectrophotometer, while electronic absorption spectra were recorded on a Hitachi 220A or a Hitachi 340 spectrophotometer. ESR spectra were obtained on a JEOL JES-FElG X-band spectrometer equipped with an Advantest TR-5213 microwave counter and an Echo Electronics EFM-200 NMR field meter. ^1H and ^{13}C NMR spectra were taken on a Hitachi R-24B, a JEOL JNM-EX90, or a JEOL JNM-GSX400 spectrometer installed at the Center of Advanced Instrumental Analysis of Kyushu University. Assignments of NMR signals due to the cobalt complexes were carried out by means of the 2D-NMR technique (H-H and C-H COSY). Cyclic voltammograms were obtained on an apparatus composed of a Hokuto Denko HA-501 potentiostat/galvanostat and a Hokuto Denko HB-104 function generator. An applied potential between the working and reference electrodes in the electrolysis was maintained constant with a Hokuto Denko HA-305 potentiostat/galvanostat and an electrical quantity was recorded on a Hokuto Denko HF-201 coulomb/amperehour meter. GLC analyses were carried out on a Shimadzu GC-4C or a Shimadzu GC-9A apparatus equipped with a Shimadzu C-R3A-FFC chromatopac.

Materials. *N,N*-Dimethylformamide (DMF) was dried and purified just before use according to the standard procedure.[17] Tetrabutylammonium perchlorate (TBAP) was purchased from Nakarai Chemicals and used without further purification. Tetrabutylammonium tetrafluoroborate (TBAF) was prepared after a reported procedure.[18] The substrates such as 1-bromo-2,2-bis(ethoxycarbonyl)propane (**1**), 1-bromo-2-cyano-2-ethoxycarbonylpropane (**2**), and 2-acetyl-1-bromo-2-ethoxycarbonylpropane (**3**) and authentic samples of the corresponding products such as 2,2-bis(ethoxycarbonyl)propane (**A**), 1,2-bis(ethoxycarbonyl)-propane (**B**), 2-cyano-2-ethoxycarbonylpropane (**C**), 1-cyano-2-ethoxycarbonylpropane (**D**), 2-cyano-1-ethoxycarbonyl-propane (**E**), 2-acetyl-2-ethoxycarbonylpropane (**F**), 1-acetyl-2-ethoxycarbonylpropane (**G**), and 2-acetyl-1-ethoxycarbonyl-propane (**H**) were prepared according to the methods described in literature[13] and confirmed to be sufficiently pure by ^1H NMR and GLC. The chelating ligand, 4,10-dipropyl-5,9-diazatrideca-4,9-diene-3,11-dione dioxime, and its cobalt complexes with various axial ligands were prepared by referring to reported procedures[16,19-21] along with some modifications as shown in Scheme 1.

4,10-Dipropyl-5,9-diazatrideca-4,9-diene-3,11-dione Dioxime, $(C_2C_3)(DOH)_2pn$. This ligand was synthesized by the condensation of 3-hydroxyimino-4-heptanone (62.9 g, 0.44 mol), which was prepared from 4-heptanone and methyl nitrate,[22] and 1,3-propanediamine (16.35 g, 0.22 mol): yield 51.0 g (71.4%); IR (KBr) 3200 (OH), 1625 (C=N), 970 cm^{-1} (N-O); ^1H NMR ($CDCl_3$, TMS) δ=0.93 (6H, t, $CH_2CH_2C\underline{H}_3$), 1.03 (6H, t, $CH_2C\underline{H}_3$), 1.45 (4H, m, $CH_2C\underline{H}_2CH_3$), 2.03, (2H, m, $CH_2C\underline{H}_2CH_2$), 2.52 (4H, t, $C\underline{H}_2CH_2CH_3$), 2.91 (4H, q, $C\underline{H}_2CH_3$), 3.60 (4H, t, NCH_2), 6.0 (2H, bs, OH). Found: C, 63.02; H, 9.99; N, 17.08%. Calcd for $C_{17}H_{32}N_4O_2$: C, 62.91; H, 9.96; N, 17.27%.



Scheme 1.

Dibromo(11-hydroxyimino-4,10-dipropyl-5,9-diazatrideca-4,9-dien-3-one oximato)cobalt(III), [Co^{III}\{(C_2C_3)(DO)(DOH)pn\}Br_2]. An acetone solution (10 mL) of (C_2C_3)$(DOH)_2$pn (1.6 g, 5.0×10^{-3} mol) was added dropwise to an aqueous solution (150 mL) of cobalt dibromide hexahydrate (2.0 g, 6.0×10^{-3} mol) while air was bubbled through the latter aqueous solution. After the reaction mixture was stirred for 4 h, precipitates were recovered by filtration and washed with water. The resulting cobalt complex was recrystallized from acetone-water (1:1 v/v) to afford dark green needles: yield 1.6 g (50%), mp 223—224 °C; IR (KBr) 700 cm^{-1} (Co-N); ^1H NMR ($CDCl_3$, TMS) δ=1.09 (6H, t, $CH_2CH_2C\underline{H}_3$), 1.23 (6H, t, $CH_2C\underline{H}_3$), 1.67 (4H, m, $CH_2C\underline{H}_2CH_3$), 2.61 (2H, m, $CH_2C\underline{H}_2CH_3$), 2.91 (4H, t, $C\underline{H}_2CH_2CH_3$), 2.98 (4H, q, $C\underline{H}_2CH_3$), 4.16 (4H, t, NCH_2), 19.37 (1H, s, OH); ^{13}C NMR ($CDCl_3$, TMS) δ=10.2 ($CH_2\underline{C}H_3$), 13.9 ($CH_2CH_2\underline{C}H_3$), 19.9 ($CH_2\underline{C}H_2CH_3$), 21.0 ($\underline{C}H_2CH_3$), 27.9 ($CH_2\underline{C}H_2CH_2$), 32.1 ($\underline{C}H_2CH_2CH_3$), 50.0 (NCH_2), 161.3 (ON=C), 177.7 (C-N=$\underline{C}$). Found: C, 37.72; H, 5.72; N, 10.33%. Calcd for $C_{17}H_{31}Br_2CoN_4O_2$: C, 37.66; H, 5.76; N, 10.33%.

Dichloro(11-hydroxyimino-4,10-dipropyl-5,9-diazatrideca-4,9-dien-3-one oximato)cobalt(III), [Co^{III}\{(C_2C_3)(DO)(DOH)pn\}Cl_2]. This complex was prepared from cobalt dichloride hexahydrate after the method employed for the preparation of [Co^{III}\{(C_2C_3)(DO)(DOH)pn\}Br_2], and obtained as dark green needles: yield 53%, mp 236—237 °C. Found: 44.99; H, 6.82; N, 12.32%. Calcd for $C_{17}H_{31}Cl_2CoN_4O_2$: C, 45.04; H, 6.89; N, 12.36%.

Diiodo(11-hydroxyimino-4,10-dipropyl-5,9-diazatrideca-4,9-dien-3-one oximato)cobalt(III), [Co^{III}\{(C_2C_3)(DO)(DOH)pn\}I_2]. This complex was prepared in the presence of a large excess of potassium iodide by the method employed for the preparation of [Co^{III}\{(C_2C_3)(DO)(DOH)pn\}Br_2], and obtained as dark purple prisms: yield 60%, mp 225—226 °C; λ_{max} (CH_2Cl_2) 338 (ε 1.99×10^4), 468 nm (1.02×10^4). Found: 32.12; H, 4.92; N, 8.78%. Calcd for $C_{17}H_{31}I_2CoN_4O_2$: C, 32.09; H, 4.91, N, 8.81%.

Diaqua(11-hydroxyimino-4,10-dipropyl-5,9-diazatrideca-4,9-dien-3-one oximato)cobalt(II) Tetraphenylborate, [Co^{II}\{(C_2C_3)(DO)(DOH)pn\}(H_2O)$_2$]B(C_6H_5)$_4$. This complex was prepared in Schlenk tubes under nitrogen atmosphere. [Co^{III}\{(C_2C_3)(DO)(DOH)pn\}Br_2] (0.30 g, 5.53×10^{-4} mol) in methanol-water (10:1 v/v, 50 mL) was treated with a slight excess of sodium tetrahydroborate. The solution turned blue initially, and then purple. After an aqueous solution (20 mL) of sodium tetraphenylborate (0.19 g, 5.53×10^{-4} mol) was added to it, the resulting reddish purple precipitates were recovered by filtration and washed with deaerated water. This product was recrystallized from methanol-water (10:1 v/v) to afford pale brown powder: yield 0.20 g (48%), decomp 86—87 °C. Found: C, 66.63; H, 7.51; N, 7.79%. Calcd for $C_{41}H_{55}BCoN_4O_4$: C, 66.76; H, 7.51; N, 7.60%.

Methylaqua(11-hydroxyimino-4,10-dipropyl-5,9-diazatrideca-4,9-dien-3-one oximato)cobalt(III) Perchlorate, [Co^{III}\{(C_2C_3)(DO)(DOH)pn\}(CH_3)(H_2O)]ClO_4. [Co^{III}\{(C_2C_3)(DO)(DOH)pn\}Br_2] (2.8 g, 5.2×10^{-3} mol) suspended in dry tetrahydrofuran (40 mL) was treated with methylmagnesium bromide (1.0×10^{-2} mol) at −60 °C under nitrogen atmosphere. After the resulting orange red solution was stirred for 2 h, cold water (10 mL) was added to it. The solution was neutralized with aqueous hydrochloric acid (2 mol dm^{-3}), tetrahydrofuran was removed completely in vacuo, and an excess amount of sodium perchlorate was added to the residue. After the solution was allowed to stand overnight in a refrigerator, a dark red solid was recovered and recrystallized from acetone-water (1:1 v/v) to afford fine red crystals: yield 0.73 g (31%), decomp 121—122 °C; IR (KBr) 1120, 630 cm^{-1} (ClO_4^-); ^1H NMR ($CDCl_3$, TMS) δ=0.61 (3H, s, Co-CH_3), 1.07 (6H, t, $CH_2C\underline{H}_3$), 1.18 (6H, t, $CH_2CH_2C\underline{H}_3$), 1.59 (4H, m, $CH_2C\underline{H}_2CH_3$), 2.23 (2H, m, $CH_2C\underline{H}_2CH_2$), 2.72 (8H, m, $C\underline{H}_2CH_2CH_3$ and $C\underline{H}_2CH_3$), 4.01 (4H, t, N-CH_2), 18.88 (1H, s, OH); λ_{max} (CH_2Cl_2) 468 nm (ε 3.32×10^4). Found: C, 41.96; H, 6.98; N, 10.84%. Calcd for $C_{18}H_{36}ClCoN_4O_7$: C, 41.99; H, 7.05; N, 10.88%.

Dimethyl(11-hydroxyimino-4,10-dipropyl-5,9-diazatrideca-4,9-dien-3-one oximato)cobalt(III), [Co^{III}\{(C_2C_3)(DO)(DOH)pn\}(CH_3)$_2$]. This compound was prepared in the presence of a large excess of methylmagnesium bromide after the method employed for the preparation of [Co^{III}\{(C_2C_3)(DO)(DOH)pn\}(CH_3)(H_2O)]ClO_4, and obtained as fine red crystals: yield 62%, decomp 118—119 °C; ^1H NMR ($CDCl_3$, TMS) δ=0.05 [6H, s, Co-$(CH_3)_2$], 1.00 (6H, t, $CH_2C\underline{H}_3$), 1.08 (6H, t, $CH_2CH_2C\underline{H}_3$), 1.47 (4H, m, $CH_2C\underline{H}_2CH_3$), 2.10 (2H, m, $CH_2C\underline{H}_2CH_2$), 2.55 (4H, t, $C\underline{H}_2CH_2CH_3$), 2.65 (4H, q, $C\underline{H}_2CH_3$), 3.73 (4H, t, N-CH_2), 19.59 (1H, s, OH); λ_{max} (CH_2Cl_2) 411 nm (ε 4.80×10^4). Found: C, 55.53; H, 9.10; N, 13.44%. Calcd for $C_{19}H_{37}CoN_4O_2$: C, 55.33; H, 9.04; N, 13.58%.

Bromo{2,2-bis(ethoxycarbonyl)propyl}(11-hydroxyimino-4,10-dipropyl-5,9-diazatrideca-4,9-dien-3-one oximato)cobalt(III), [Co^{III}\{(C_2C_3)(DO)(DOH)pn\}\{$CH_2C(CO_2C_2H_5)_2CH_3$\}Br]. A methanol solution (200 mL) containing [Co^{III}\{(C_2C_3)(DO)(DOH)pn\}Br_2] (500 mg, 9.2×10^{-4} mol) and 1-bromo-2,2-bis(ethoxycarbonyl)propane (1.0 g, 3.7×10^{-3} mol) was stirred while carbon monoxide was introduced into it until saturation was attained. After being stirred for 2 h, the solution turned reddish yellow, indicating formation of the Co^{II} complex. Sodium tetrahydroborate in methanol was added dropwise to the resulting solution until the solution turned deep blue under carbon monoxide atmosphere. The solution changed its color to orange after it was refluxed for 6 h in the dark. The solution was evaporated to dryness, a material insoluble in dichloromethane was removed by filtration, and then the dichloromethane solution was evaporated to dryness. The product was recrystallized from diethyl ether-tetrahydrofuran (1:20 v/v) to afford orange prisms: yield 450 mg (75%); IR (KBr) 1730 cm^{-1} (C=O); λ_{max} (CH_3OH) 474 nm. Found: C, 47.87; H, 7.00; N, 8.53%. Calcd for $C_{26}H_{46}BrCoN_4O_6$: C, 48.08; H, 7.14; N, 8.63%.

Bromo(2-cyano-2-ethoxycarbonylpropyl)(11-hydroxyimino-4,10-dipropyl-5,9-diazatrideca-4,9-dien-3-one oximato)cobalt(III), [Co^{III}\{(C_2C_3)(DO)(DOH)pn\}\{$CH_2C(CO_2C_2H_5)(CN)CH_3$\}Br]. This compound was prepared in the presence of 1-bromo-2-cyano-2-ethoxycarbonylpropane after the method for the preparation of [Co^{III}\{(C_2C_3)(DO)(DOH)pn\}\{$CH_2C(CO_2C_2H_5)_2CH_3$\}Br], and obtained as orange prisms: yield 63%; λ_{max} (CH_3OH) 465 nm. Found: C, 47.55; H, 6.80; N, 11.83%. Calcd for $C_{24}H_{41}BrCoN_5O_4$: C, 47.85; H, 6.86; N, 11.62%.

Bis{2,2-bis(ethoxycarbonyl)propyl}(11-hydroxyimino-4,10-dipropyl-5,9-diazatrideca-4,9-dien-3-one oximato)cobalt(III), [Co^{III}\{(C_2C_3)(DO)(DOH)pn\}\{$CH_2C(CO_2C_2H_5)_2CH_3$\}$_2$]. A methanol solution (200 mL) containing [Co^{III}\{(C_2C_3)(DO)(DOH)pn\}Br_2] (100 mg, 1.8×10^{-4} mol) and 1-bromo-2,2-bis(ethoxycarbonyl)propane (1.0 g, 3.7×10^{-3} mol), and sodium hydroxide (10 mg, 2.5×10^{-4} mol) was saturated with carbon monoxide by bubbling for 2 h. Sodium tetrahydroborate in

methanol was added dropwise to the resulting solution until the solution turned deep blue. The reaction mixture was then refluxed for 6 h in the dark and turned orange gradually. The mixture was evaporated to dryness, and a material insoluble in dichloromethane was removed by filtration. The dichloromethane solution was evaporated to afford an orange red solid. The product was purified by gel-filtration chromatography on columns of Sephadex LH-20 with methanol and silica gel (Wakogel C-100) with hexane–chloroform (1 : 1 v/v) in this sequence. The solution was evaporated to dryness to afford red powder: yield 74 mg (53%); IR (KBr) 1730 cm^{-1} (C=O); λ_{max} (CH_3OH) 405 nm. Found: C, 55.38; H, 7.96; N, 7.17%. Calcd for $C_{35}H_{61}CoN_4O_{10}$: C, 55.55; H, 8.12; N, 7.40%.

Bis(2-cyano-2-ethoxycarbonylpropyl)(11-hydroxyimino-4,10-dipropyl-5,9-diazatrideca-4,9-dien-3-one oximato)cobalt(III), [Co^{III}{(C_2C_3)(DO)(DOH)pn}{$CH_2C(CO_2C_2H_5)(CN)CH_3$}$_2$]. This compound was prepared in the presence of 1-bromo-2-cyano-2-ethoxycarbonylpropane after the method for the preparation of [Co^{III}{(C_2C_3)(DO)(DOH)pn}{$CH_2C(CO_2C_2H_5)_2$-CH_3}$_2$], and obtained as red powder: yield 59%; λ_{max} (CH_3OH) 402 nm. Found: C, 56.07; H, 7.75; N, 12.61%. Calcd for $C_{31}H_{51}CoN_6O_6$: C, 56.18; H, 7.76; N, 12.68%.

Cyclic Voltammetry. An electrochemical cell similar to that reported in literature[23] was used and equipped with platinum wire of 0.5-mm diameter as working and auxiliary electrodes. A saturated calomel electrode (SCE) cr an Ag/AgCl electrode was served as reference which was separated from a bulk electrolyte solution by a salt bridge prepared with 1,2:4,5-*O*-dibenzylidene-D-glucitol[24] and a DMF solution of TBAP (5.0×10^{-2} mol dm^{-3}); potentials vs. SCE are more cathodic by 30 mV relative to those vs. Ag/AgCl. DMF solutions containing the cobalt complex and TBAP were deaerated prior to each measurement, and the inside of the cell was maintained under argon atmosphere throughout each measurement. All the measurements were carried out at 20±2 °C, and the scan rate was varied in a range from 10 through 200 mV s^{-1}. Half-wave potentials ($E_{1/2}$) and anodic and cathodic currents were evaluated according to the method described previously.[25]

In order to identify the species formed at respective potentials, controlled-potential electrolyses were carried out under various conditions in a three-electrode cell modified for electronic and ESR spectral measurements, as described previously.[25] An applied potential between the working and reference electrodes was maintained constant with a potentiostat.

Catalytic Reactions. The electrolyses of various substrates were carried out upon addition of the cobalt complex in a cylindrical three-electrode cell which was divided into two internal compartments with a single sheet of microporous polypropylene membrane and equipped with platinum meshes as working and auxiliary electrodes.[13] On the other hand, an undivided cell was utilized to perform effective catalytic reactions without additives. A DMF solution of the cobalt complex, a substrate, an additive (if necessary), and TBAF was subjected to electrolysis at an appropriate controlled-potential under argon atmosphere. Then, the reaction mixture was distilled in vacuo and analyzed for products by means of GLC. Identification of the reaction products was performed by coinjection of the distilled sample and the corresponding authentic samples into columns of Silicone DC-550 and Silicone SE-30. A capillary column of Polyethylene Glycol-20M was used for identification of isomers having similar structures. Each product separated by preparative GLC on Silicone DC-550 was identified by means of ^1H NMR spectroscopy.

Results and Discussion

ESR spectra of [Co^{II}{(C_2C_3)(DO)(DOH)pn}$(H_2O)_2$]-$B(C_6H_5)_4$ in base-off and base-on forms are shown in Fig. 2 at 77 K. A typical ESR spectrum of low spin cobalt(II) was observed for the complex in chloroform without a base (A in Fig. 2). When pyridine was added in a two- to ten-fold molar excess over a quantity of the cobalt complex, only one pyridine molecule underwent coordination to the central cobalt at its axial site (B in Fig. 2): a superhyperfine structure due to the interaction between the nitrogen nucleus (I=1) and the cobalt nucleus (I=7/2) was observed in the $g_{\parallel}$ region. In the presence of a large excess of pyridine (ca. 600-fold),

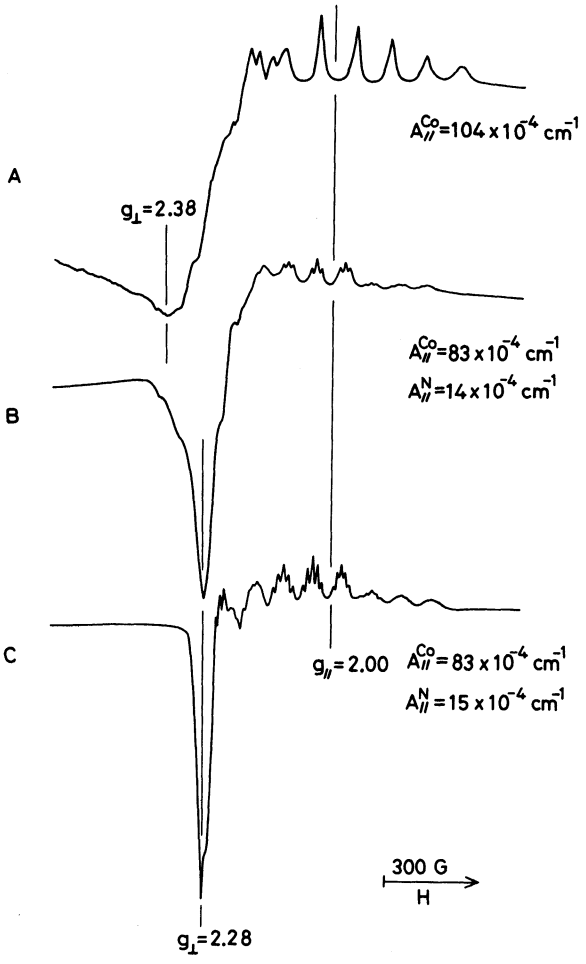
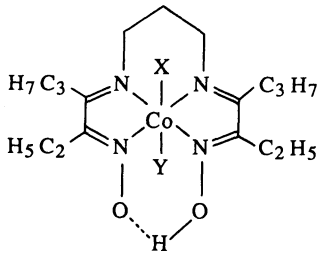


Fig. 2. ESR spectra of divalent cobalt complexes in chloroform at 77 K: A, [Co^{II}{(C_2C_3)(DO)(DOH)pn}-$(H_2O)_2$]$B(C_6H_5)_4$ (1.5×10^{-3} mol dm^{-3}); B, [Co^{II}{(C_2C_3)-(DO)(DOH)pn}$(H_2O)_2$]$B(C_6H_5)_4$ (1.7×10^{-2} mol dm^{-3}) and pyridine (1.8×10^{-1} mol dm^{-3}); C, [Co^{II}-{(C_2C_3)(DO)(DOH)pn}$(H_2O)_2$]$B(C_6H_5)_4$ (1.7×10^{-2} mol dm^{-3}) and pyridine (10 mol dm^{-3}).



$[Co^{III}\{(C_2C_3)(DO)(DOH)pn\}Cl_2]$: X=Y=Cl

$[Co^{III}\{(C_2C_3)(DO)(DOH)pn\}Br_2]$: X=Y=Br

$[Co^{III}\{(C_2C_3)(DO)(DOH)pn\}I_2]$: X=Y=I

$[Co^{III}\{(C_2C_3)(DO)(DOH)pn\}(H_2O)_2]B(C_6H_5)_4$: X=Y=$H_2O$

$[Co^{III}\{(C_2C_3)(DO)(DOH)pn\}(CH_3)(H_2O)]ClO_4$: X=$CH_3$, Y=$H_2O$

$[Co^{III}\{(C_2C_3)(DO)(DOH)pn\}(CH_3)_2]$: X=Y=$CH_3$

$[Co^{III}\{(C_2C_3)(DO)(DOH)pn\}\{CH_2C(CO_2C_2H_5)_2CH_3\}Br]$:
X=$CH_2C(CO_2C_2H_5)_2CH_3$, Y=Br

$[Co^{III}\{(C_2C_3)(DO)(DOH)pn\}\{CH_2C(CO_2C_2H_5)(CN)CH_3\}Br]$:
X=$CH_2C(CO_2C_2H_5)(CN)CH_3$, Y=Br

$[Co^{III}\{(C_2C_3)(DO)(DOH)pn\}\{CH_2C(CO_2C_2H_5)_2CH_3\}_2]$:
X=Y=$CH_2C(CO_2C_2H_5)_2CH_3$

$[Co^{III}\{(C_2C_3)(DO)(DOH)pn\}\{CH_2C(CO_2C_2H_5)(CN)CH_3\}_2]$:
X=Y=$CH_2C(CO_2C_2H_5)(CN)CH_3$

both axial sites of the central cobalt were occupied by pyridine molecules as confirmed by ESR spectroscopy (C in Fig. 2). The present ESR behavior and the corresponding spin Hamiltonian parameters are comparable to those observed for the hydrophobic vitamin B_{12r} bearing a corrinoid ligand.[9]

Redox Behavior of Simple Vitamin B_{12} Model and Alkylated Derivatives. The redox behavior of the present complexes was investigated in DMF by means of cyclic voltammetry. A cyclic voltammogram of $[Co^{III}\{(C_2C_3)(DO)(DOH)pn\}I_2]$ is shown in Fig. 3. Three redox pairs were observed at −0.13, −0.70, and −1.45 V vs. Ag/AgCl in the range of 0 through −2.0 V vs. Ag/AgCl. The complex species responsible for these redox potentials were indentified by spectroscopic methods under controlled-potential electrolysis conditions as follows. The species present at +0.3 V vs. Ag/AgCl was ESR-silent, while ESR signals characteristic of Co(II) species were observed at −0.5 V vs. Ag/AgCl. Therefore, the redox potential at −0.13 V vs. Ag/AgCl is assigned to the Co(III)/Co(II) redox couple. The electrochemical reduction at −1.0 vs. Ag/AgCl was followed by electronic spectroscopy. An absorption maximum characteristic of the monomethylated complex was observed at 465 nm in the presence of methyl iodide; formation of the Co(I) species became evident at this potential. Consequently, the potential at −0.70 V vs. Ag/AgCl is assigned to the Co(II)/Co(I) redox couple. The potential at −1.45 V vs. Ag/AgCl is presumably concerned with the redox

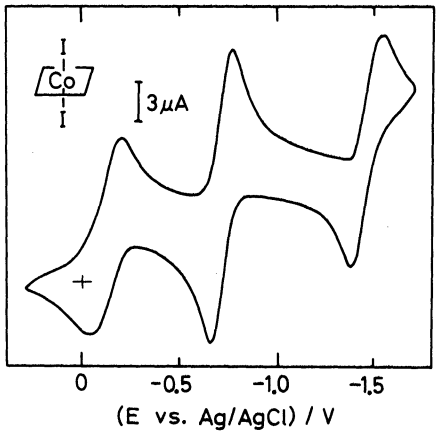


Fig. 3. Cyclic voltammogram of $[Co^{III}\{(C_2C_3)(DO)(DOH)pn\}I_2]$ (4.5×10^{-3} mol dm^{-3}) containing 0.10 mol dm^{-3} TBAP in DMF at 20±2 °C; scan rate, 100 mV s^{-1}.

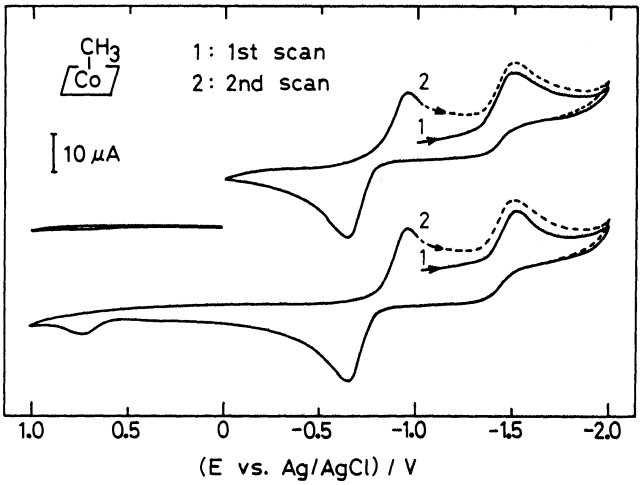


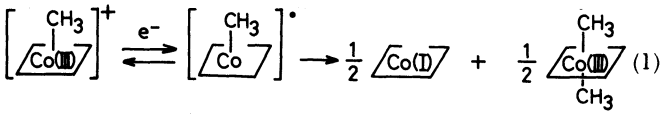
Fig. 4. Cyclic voltammogram of $[Co^{III}\{(C_2C_3)(DO)(DOH)pn\}(CH_3)(H_2O)]ClO_4$ (4.5×10^{-3} mol dm^{-3}) containing 0.10 mol dm^{-3} TBAP in DMF at 20±2 °C in the dark; scan rate, 100 mV s^{-1}.

reaction of the equatorial ligand. The complexes with the other halogen ligands, comparable redox potentials were observed: −0.16, −0.70, and −1.43 V vs. Ag/AgCl for $[Co^{III}\{(C_2C_3)(DO)(DOH)pn\}Br_2]$; −0.27, −0.69, and −1.46 V vs. Ag/AgCl for $[Co^{III}\{(C_2C_3)(DO)(DOH)pn\}Cl_2]$. As for $[Co^{II}\{(C_2C_3)(DO)(DOH)pn\}(H_2O)_2]B(C_6H_5)_4$, the reversible Co(II)/Co(I) redox couple was also observed at −0.69 V vs. Ag/AgCl. The above redox behavior is identical with that for the Costa's complex.[26,27] These Co(II)/Co(I) redox potentials are close to that observed for the hydrophobic vitamin B_{12};[10] −0.61 V vs. SCE in DMF. The Co(II)/Co(I) redox potential for cobaloxime, a vitamin B_{12} model frequently used, is observed by far in a more cathodic range relative to these values; −1.11 V vs. SCE in acetonitrile.[16]

The redox behavior of the mono- and dimethylated

cobalt complexes, $[Co^{III}\{(C_2C_3)(DO)(DOH)pn\}(CH_3)(H_2O)]ClO_4$ and $[Co^{III}\{(C_2C_3)(DO)(DOH)pn\}(CH_3)_2]$, respectively, was investigated in DMF.[28] The redox behavior of the Costa's complexes with the cobalt–carbon bond was studied in acetonitrile rather extensively.[16,29] As shown in Fig. 4 for $[Co^{III}\{(C_2C_3)(DO)(DOH)pn\}(CH_3)(H_2O)]ClO_4$, a single and irreversible one-electron reduction peak was observed at −1.50 V vs. Ag/AgCl during scanning for the potential range from −1.0 through −2.0 V vs. Ag/AgCl. In the course of scanning for the potential range from −1.0 V vs. Ag/AgCl toward the anodic side, there were observed two oxidation peaks; a reversible Co(I)/Co(II) oxidation peak at −0.65 V vs. Ag/AgCl and another irreversible and small oxidation peak at +0.73 V vs. Ag/AgCl, the latter originating from the one-electron oxidation of the dimethylated complex, $[Co^{III}\{(C_2C_3)(DO)(DOH)pn\}(CH_3)_2]$. The latter oxidation peak was not observed when the potential was scanned for the range from 0 through +1.0 V vs. Ag/AgCl.

After the controlled-potential electrolysis of $[Co^{III}\{(C_2C_3)(DO)(DOH)pn\}(CH_3)(H_2O)]ClO_4$ was completed at −2.0 V vs. Ag/AgCl under anaerobic conditions, the absorption maximum originally observed for $[Co^{III}\{(C_2C_3)(DO)(DOH)pn\}(CH_3)(H_2O)]ClO_4$ at 465 nm was shifted to 410 nm when the sample was exposed to air for elimination of the Co^{I} species; the latter band being due to $[Co^{III}\{(C_2C_3)(DO)(DOH)pn\}(CH_3)_2]$. This apparently indicates that the monomethylated complex is disproportionated to the dimethylated complex and the Co^{I} species by the electrochemical reduction (Eq. 1). When a large excess of imidazole was added, the



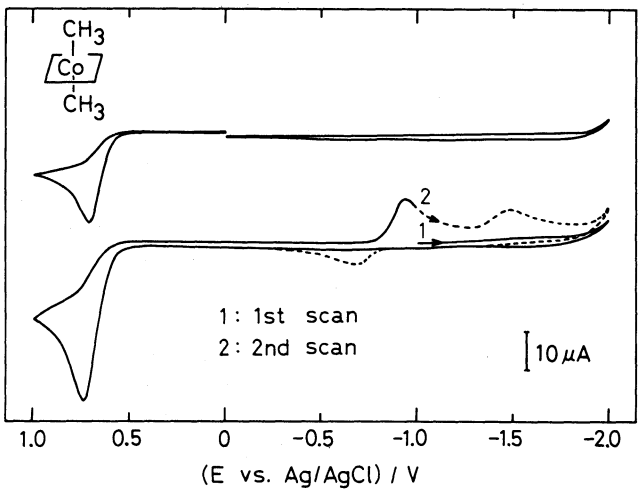
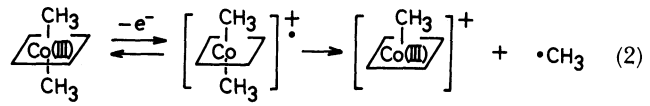


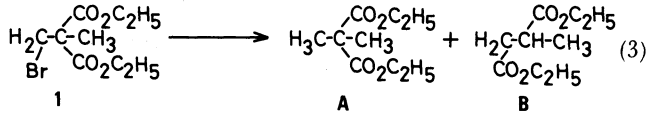
Fig. 5. Cyclic voltammogram of $[Co^{III}\{(C_2C_3)(DO)(DOH)pn\}(CH_3)_2]$ (4.5×10^{-3} mol dm^{-3}) containing 0.10 mol dm^{-3} TBAP in DMF at 20±2 °C in the dark; scan rate, 100 mV s^{-1}.

disproportionation reaction did not take place. This behavior is quite different from that observed for the corresponding hydrophobic vitamin B_{12}.[30] The one-electron reduction potential for the present monomethylated complex is close to those for the methylated hydrophobic vitamin B_{12} and methylcobinamide; −1.32 V vs. SCE in DMF[30] and −1.46 V vs. SCE in DMF–1-propanol (1:1 v/v),[31] respectively. On the other hand, the corresponding potential for methylcobaloxime is −2.2 V vs. SCE in acetonitrile at −26 °C,[16] which is by far in a more cathodic range relative to the value for vitamin B_{12} and must arise from the difference in ligand nature; the present and corrinoid ligands are monoanionic, while the cobaloxime ligand is dianionic.

The dimethylated complex is inactive for electrochemical reduction; no peak was observed in the potential range from 0 through −2.0 V vs. Ag/AgCl as shown in Fig. 5. An irreversible oxidation peak was observed at +0.73 V vs. Ag/AgCl. When the potential was sweeped repeatedly in the range of +1.0 through −2.0 V vs. Ag/AgCl, the redox behavior became similar to that of $[Co^{III}\{(C_2C_3)(DO)(DOH)pn\}(CH_3)(H_2O)]ClO_4$. These facts indicate that the dimethylated complex is cleaved to afford the monomethylated complex and the methyl radical by the electrochemical oxidation (Eq. 2).[29]



Catalytic Reactions under Electrochemical Conditions. On the basis of the above redox behavior, the catalytic function of $[Co^{III}\{(C_2C_3)(DO)(DOH)pn\}Br_2]$ was investigated by using 1-bromo-2,2-bis(ethoxycarbonyl)propane (**1**) as a substrate under electrochemical conditions (refer to Eq. 3).[32] The electrolysis was carried out in a



three-electrode cell, which was divided into two internal compartments with a diaphragm. The following findings were obtained on the basis of the product analyses under various conditions indicated in Table 1. (i) Products **A** and **B** were scarcely detected without imidazole at every potential in the range of −1.0 through −2.0 V vs. Ag/AgCl. (ii) The rearrangement product (**B**) was largely obtained at −1.5, −1.8, and −2.0 V vs. Ag/AgCl in the presence of imidazole. (iii) The rearrangement reaction proceeded more favorably under stronger reduction conditions. When other complexes, such as $[Co^{III}\{(C_2C_3)(DO)(DOH)pn\}Cl_2]$, $[Co^{III}\{(C_2C_3)(DO)(DOH)pn\}I_2]$, and

Table 1. Product Analyses for Controlled-Potential Electrolysis of **1** as Catalyzed by a Simple Vitamin B_{12} Model in the Divided Cell[a]

Entry	Electrolysis conditions					Yield/%[e]	
	Potential	Irradiation[b]	Additive[c]	Charge[d]	Period	A	B
	V vs. Ag/AgCl			F mol^{-1}	h		
1	−1.0	Irradiation	Imidazole	0.6	26	ca. 2	Trace
2	−1.5	In the dark	None	0.5	24	Trace	Trace
3	−1.5	In the dark	Imidazole	2.0	14	16—20	18—26
4	−1.8	In the dark	None	0.5	24	1—2	Trace
5	−1.8	In the dark	Imidazole	2.0	10	35—40	40—47
6	−2.0	In the dark	None	2.0	7	7—11	1—2
7	−2.0	In the dark	Imidazole	2.0	6	20—25	55—61

a) Electrolysis was carried out in a two-compartment cell equipped with Pt electrodes at 20±2 °C under argon atmosphere. Starting solutions composed of: [Co^{III}\{(C_2C_3)(DO)(DOH)pn\}Br_2], 30 mg (5.5×10^{-5} mol); **1**, 1.0 g (3.8×10^{-3} mol); 30 mL of DMF containing 0.5 mol dm^{-3} TBAF. b) Irradiation with a 300-W tungsten lamp at a distance of 50 cm. c) Imidazole, 100 mg (1.5×10^{-3} mol). d) Electrical charge passed per mol of the substrate. e) Based on an initial amount of the substrate; the rest was the unreacted substrate; analyzed by GLC; refer to Eq. 3.

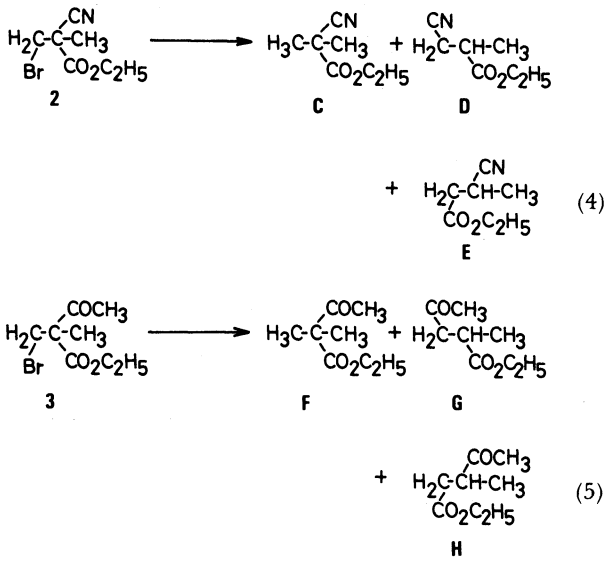
Table 2. Product Analyses for Controlled-Potential Electrolysis Catalyzed by a Simple Vitamin B_{12} Model in the Divided Cell[a]

Substrate[b]	Electrolysis conditions			Yield/%[d]	
	Potential	Charge[c]	Period	Unrearranged Product[e]	Rearranged Product[f]
	V vs. Ag/AgCl	F mol^{-1}	h		
2	−1.5	1.0	14	8—10	20—22
2	−2.0	2.1	8	12—14	74—76
3	−1.5	2.0	21	14—15	60—61
3	−2.0	2.0	6	3—4	85—90

a) Electrolysis was carried out in a two-compartment cell equipped with Pt electrodes at 20±2 °C under argon atmosphere. Starting solutions composed of: [Co^{III}\{(C_2C_3)(DO)(DOH)pn\}Br_2], 30 mg (5.5×10^{-5} mol); **2**, 1.0 g (4.5×10^{-3} mol) or **3**, 1.0 g (4.2×10^{-3} mol); imidazole, 100 mg (1.5×10^{-3} mol); 30 mL of DMF containing 0.5 mol dm^{-3} TBAF. b) Refer to Eqs. 4 and 5. c) Electrical charge passed per mol of the substrate. d) Based on an initial amount of the substrate; the rest was the unreacted substrate; analyzed by GLC; refer to Eqs. 4 and 5. e) Unrearranged products were **C** and **F** for substrates **2** and **3**, respectively. f) Rearrangement products were **D** and **E** for **2**, and **G** and **H** for **3**, respectively.

$[Co^{II}\{(C_2C_3)(DO)(DOH)pn\}(H_2O)_2]B(C_6H_5)_4$, were used as the catalysts, similar results were obtained.

In order to make further qualification of the simple vitamin B_{12} model as the isomerization catalyst, other substrates, such as 1-bromo-2-cyano-2-ethoxycarbonylpropane (**2**) and 2-acetyl-1-bromo-2-ethoxycarbonylpropane (**3**), were also used here. These substrates and the corresponding products are shown in Eqs. 4 and 5, and the product analysis data are shown in Table 2. The 1,2-migration of carboxylic ester, acetyl, and cyano groups proceeds efficiently under these experimental conditions.



On careful comparison between the electrochemical carbon-skeleton rearrangement reactions catalyzed by the present simple vitamin B_{12} model and the hydrophobic vitamin B_{12},[33] some differences are noted between these complexes in their catalytic performance. (i) The hydrophobic vitamin B_{12} does not require an organic base for the catalytic reaction, while a base such as imidazole is essential to the reaction catalyzed by the present complex. Imidazole must be bound to the nuclear cobalt of the alkylated vitamin B_{12} model, so that the cobalt–carbon bond is effectively activated by the trans effect arising from the coordinated axial base. The axial ligation constant (K) of imidazole to the monomethylated cobalt complex is fairly large; $\log K=2.67$ in DMF by means of the spectroscopic

method.[9] When imidazole is not present, the corresponding dialkylated complex, that is inactive for electrochemical reduction, is formed in the course of reaction, and consequently the catalytic reaction does not take place to a detectable extent. (ii) The hydrophobic vitamin B_{12} requires a proton source for the formation of product **B** during the electolysis at −1.5 V vs. Ag/AgCl, while the present model complex affords the products in a significant yield without such an additive under the comparable conditions. The reaction scheme in the divided cell is schematically illustrated in Fig. 6.

In the light of the redox behavior of the dimethylated complex, $[Co^{III}\{(C_2C_3)(DO)(DOH)pn\}(CH_3)_2]$, the dialkylated complex is expected to give products, plausibly involving the corresponding isomerization product, by electrochemical oxidation. Therefore, we removed the diaphragm from the divided cell and the electrolysis was carried out in a single-compartment cell under argon atmosphere. Substrates **1**, **2**, and **3** were subjected to electrolysis at −2.0 V vs. Ag/AgCl of the cathode in presence of the cobalt complex in the dark. The products were analyzed by means of GLC, as summarized in Table 3. These results indicate that the rearrangement reactions proceed efficiently in the undivided cell. Under such reaction conditions, the monoalkylated complex and the corresponding dialkylated complexes were formed in a stepwise manner as the intermediates. Reduction of the former complex and oxidation of the latter species must proceed at the cathode and the anode, respectively. In order to clarify the reaction process, the electrolyses of the monoalkylated and dialkylated complexes were carried out at −2.0 V and +1.0 V vs. Ag/AgCl, respectively, in the divided cell.

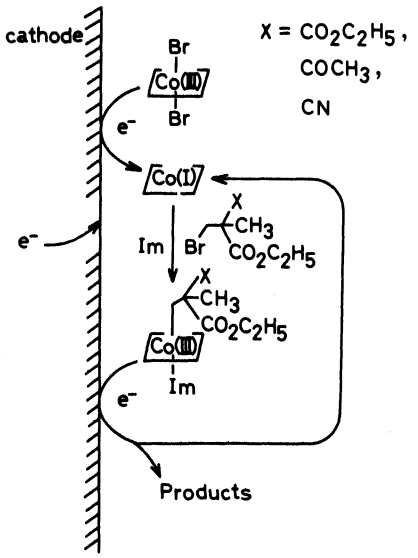
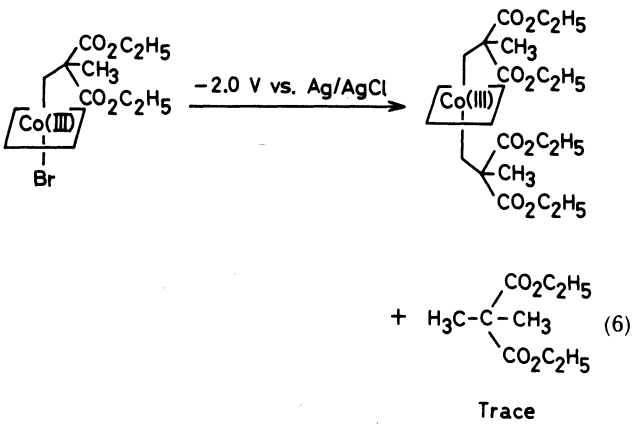


Fig. 6. Schematic representation of electrochemical catalysis in the divided cell.

A DMF solution (15 mL) of $[Co^{III}\{(C_2C_3)(DO)(DOH)pn\}\{CH_2C(CO_2C_2H_5)_2CH_3\}Br]$ (200 mg, 3.1×10^{-4} mol) and TBAF (2.0 g) was subjected to electrolysis at −2.0 V vs. SCE in the dark for 8 h. The monoalkylated complex was largely converted into the corresponding dialkylated complex as identified by electronic spectroscopy (Eq. 6), even though trace



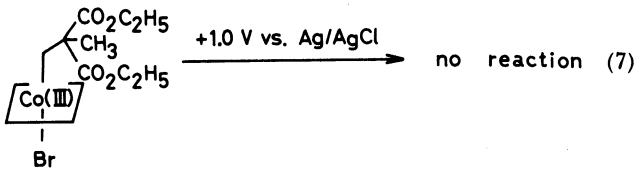
amounts of the reduction and rearrangement products were detected by GLC. When $[Co^{III}\{(C_2C_3)(DO)(DOH)pn\}\{CH_2C(CO_2C_2H_5)_2CH_3\}Br]$ was electrolyzed at +1.0 V vs. SCE, the reaction did not proceed to a

Table 3. Product Analyses for Controlled-Potential Electrolysis at −2.0 V vs. Ag/AgCl Catalyzed by a Simple Vitamin B_{12} Model in the Undivided Cell[a]

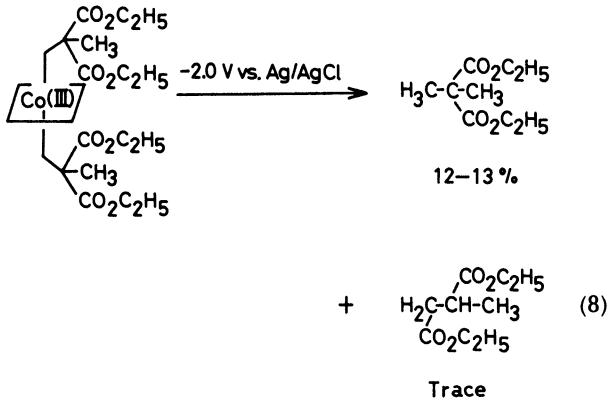
Substrate[b]	Electrolysis conditions		Yield/%[d]	
	Charge[c]	Period	Unrearranged product[e]	Rearranged product(s)[f]
	F mol^{-1}	h		
1	1.7	10	18—20	53—55
2	1.9	8	10—12	58—60
3	1.9	7	3—4	83—85

a) Electrolysis was carried out in the undivided cell equipped with Pt electrodes at 20±2 °C under argon atmosphere. Starting solutions composed of: $[Co^{III}\{(C_2C_3)(DO)(DOH)pn\}Br_2]$, 14 mg ($2.6\times10^{-5}$ mol); **1**, 1.0 g (3.8×10^{-3} mol), **2**, 1.0 g (4.5×10^{-3} mol), or **3**, 1.0 g (4.2×10^{-3} mol); 30 mL of DMF containing 0.5 mol dm^{-3} TBAF. b) Refer to Eqs. 3, 4, and 5. c) Electrical charge passed per mol of the substrate. d) Based on an initial amount of the substrate; the rest was the unreacted substrate; analyzed by GLC; refer to Eqs. 3, 4, and 5. e) Unrearranged products were **A**, **C**, and **F** for substrates **1**, **2**, and **3**, respectively. f) Rearrangement products: **B** for **1**, **D** and **E** for **2**, and **G** and **H** for **3**.

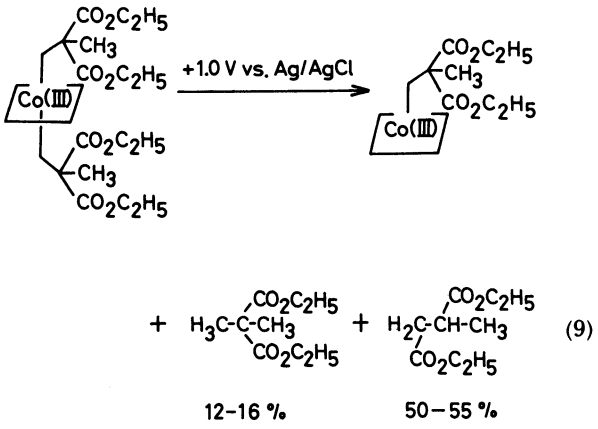
detectable extent as confirmed by electronic spectroscopy and GLC (Eq. 7). A small amount of the product



derived from the cleavage of the cobalt–carbon bond was detected in the electrolysis of [Co^{III}{(C_2C_3)(DO)(DOH)pn}{$CH_2C(CO_2C_2H_5)_2CH_3$}$_2$] (200 mg, 2.6×10^{-4} mol) at −2.0 V vs. Ag/AgCl under the identical conditions. However, the rearrangement product was little obtained under such conditions (Eq. 8). On the



other hand, when the electrolysis was carried out at +1.0 V vs. Ag/AgCl for 6 h, the dialkylated complex was transformed into the monoalkylated one, and the rearrangement product was detected as the major one (Eq. 9).



In the light of the above results, the electrolysis in the undivided cell plausibly proceeds via the reaction cycle shown in Fig. 7. The tervalent cobalt complex is first converted into the univalent cobalt complex by the electrochemical reduction, and the resulting species is subjected to the electrophilic attack by an alkyl bromide to afford the corresponding monoalkylated complex as the intermediate. This species is subsequently reduced to the one-electron reduction intermediate, which is then disproportionated to the dialkylated complex and the univalent cobalt species. The dialkylated complex is decomposed to give the monoalkylated complex and the products by the electrochemical oxidation on the anode.

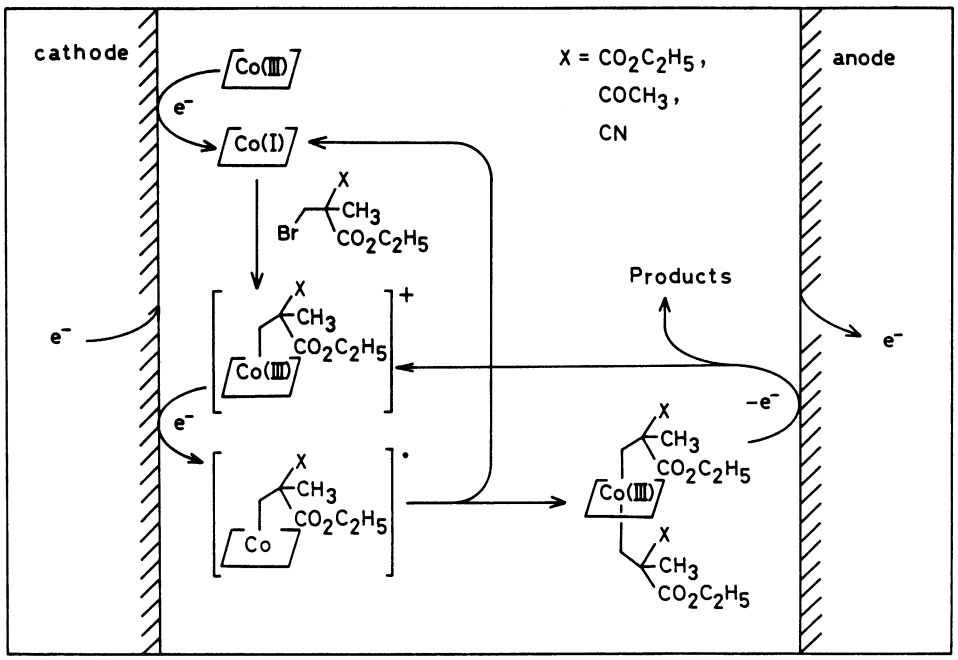


Fig. 7. Schematic representation of electrochemical catalysis in the undivided cell.

Conclusion

We clarified in the present work redox behavior of the simple vitamin B_{12} model as well as that of its alkylated derivatives in connection with the catalytic reactions of the vitamin B_{12} model under electrochemical conditions. A major difference between the simple vitamin B_{12} model complex and the hydrophobic vitamin B_{12} is in alkylation behavior; a dialkylated complex is obtained with the former species. The hydrophobic vitamin B_{12} does not form its dialkylated complex, since the steric hindrance is exercised by the methyl moiety at C(19) position of the corrin ring when an alkyl moiety attacks the nuclear cobalt from the α-face. The simple vitamin B_{12} model does not form its dialkylated complex when an axial base such as imidazole is added to the reaction media, and the electrochemical catalysis proceeds via a mechanism similar to that for the hydrophobic vitamin B_{12}. It became apparent that the coupled electrochemical redox processes facilitate the carbon-skeleton rearrangement via formation of the dialkylated complex as the oxidizable intermediate in the absence of an axial base.

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