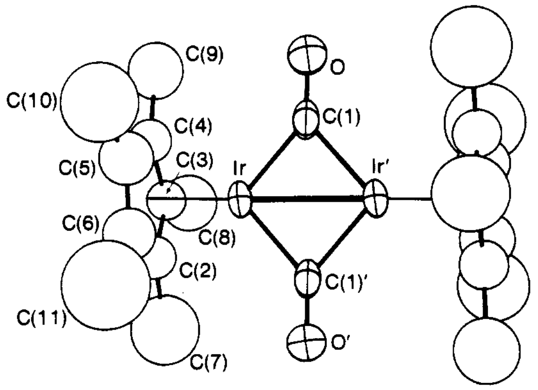

Figure 1. Molecular structure of **2**, showing the atom-numbering scheme. Primed atoms are related by a crystallographic center of symmetry.

by infrared spectroscopy[14] (eq 1). This species was reduced with zinc metal and further carbonylated in situ to afford **1** in excellent yield (eq 2). Workup of the reaction mixture was complicated by the apparent formation of the $ZnCl_2$ adduct of the product, which hinders sublimation of **1**. The product is easily freed of $ZnCl_2$ by a simple extraction of the dichloromethane solution with water. This procedure gives excellent (80%) and reproducible yields of **1**.

Synthesis of $[(\eta\text{-}C_5Me_5)Ir(CO)]_2$ (2). The iridium dimer **2** is less readily accessible from the monomer than its rhodium analogue. While $(\eta\text{-}C_5Me_5)Rh(CO)_2$ reacts readily with Me_3NO to afford $[(\eta\text{-}C_5Me_5)Rh(CO)]_2$,[15] we have found that **1** does not react with Me_3NO. The original route to the rhodium dimer[16] involved heating $(\eta\text{-}C_5Me_5)Rh(CO)_2$ at 80–85 °C, and we have found that this conversion will take place in the iridium case but only at substantially higher temperatures.[17] When a vessel containing **1** is placed in a bath at 170–180 °C, **2** is formed but much of the starting material sublimes unchanged.

We have found conditions for thermolysis of **1** that, if exactly followed, give excellent yields of **2**. A key aspect is the use of a refluxing solvent, 1-butanol (bp 117–118 °C), which returns sublimed starting material to the hot region of the thermolysis flask. Other key aspects are the bath temperature (170 °C) and the level of the bath surface, which must be higher than the solvent level in the flask (by 2.5 cm in the arrangement we describe). The product is relatively insoluble and forms as a dark crust above the solvent level. Isolation of **2** is straightforward, and a 95% yield of high-purity product is obtained after one crystallization.

The properties of **2** are similar to those of the Co and Rh analogues. The infrared spectrum exhibits a band at 1670 cm^{-1}, which is consistent with a doubly carbonyl-bridged structure. Complex **2** is highly colored, due to the intense absorption at 375 and 444 nm; large crystals appear black, while smaller crystal are deep red-orange to dark yellow-brown in color. In comparison, the dark blue Rh analogue has intense absorptions at 345 and 580 nm, while the emerald green Co analogue absorbs at 410 and 610 nm.[18] These observations are consistent with an increase in the HOMO–LUMO energy difference on descending the group. This is consistent with the results of a recent calculational and photoelectron spectroscopy study of these molecules.[19]

An interesting alternative synthesis of **2** arose from studies of the photolytic activation of methanol by $(\eta\text{-}C_5Me_5)Ir(CO)_2$. An important initial product of this reaction appears to be $(\eta\text{-}C_5Me_5)Ir(CO)(H)(CH_2OH)$,[20] and sufficiently concentrated methanol solutions on standing in the dark at room temperature afford **2** in yields of 30–60%. Useful quantities of **2** are available in this way, but the procedure at its present stage of development is inferior to the thermolysis route described above.

Structure of 2. The solid-state structure of **2** (Figure 1) reveals an Ir_2 moiety with two bridging carbonyl groups. Selected bond lengths and angles are tabulated in Table III. The crystallographic center of symmetry requires that the four-membered ring Ir–C(1)–Ir'–C(1)' is planar. The centroid of the C_5Me_5 ring (designated Cp) is 0.063 Å below the plane, while O is 0.020 Å above it; Cp' and O' would necessarily be above and below the plane, respectively. The Cp–Ir–Ir' angle is 177.9°, and the C_5Me_5 ring is tilted 4.0° with respect to the Cp–Ir vector. The *idealized* symmetry of the molecule is C_{2h}, with the pseudo-2-fold axis running through O–C(1)–C(1)'–O'. The center of inversion requires that the C_5Me_5 rings are in a mutually staggered conformation.

The rhodium dimer $[(\eta\text{-}C_5Me_5)Rh(CO)]_2$ also has the staggered arrangement and a Rh=Rh separation of 2.564 (1) Å,[21] very similar to the Ir=Ir value of 2.554 (1) Å found in this work. As expected, Co=Co in $[(\eta\text{-}C_5Me_5)Co(CO)]_2$ is much shorter, 2.338 (2)[22] and 2.327 (2) Å[23] in two determinations. In the Co analogue, the C_5Me_5 rings have an eclipsed arrangement, which was attributed[22] to a minimization of steric interactions with the bridging carbonyls. This is consistent with the staggered arrangement of **2**, where Cp–Ir is 0.20 Å longer than Cp–Co in the cobalt dimer.

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Supplementary Material Available: For **2**, lisitings of complete details of the structure determination, anisotropic thermal parameters, and bond distances and bond angles (3 pages); a table of observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

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Electrocatalytic Dehalogenation of α-Haloacetic Acids by Vitamin B_{12}

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Cob(I)alamin, the Co(I) form of vitamin B_{12}, is a powerful and versatile reductant.[1] Electrocatalytic reductions mediated by vitamin B_{12} involve reduction of the Co(II) form of the vitamin to cob(I)alamin, which then reduces a suitable substrate in solution. Cob(II)alamin (B_{12r}), regenerated in this homogeneous reaction in a thin layer of solution close to the surface of the electrode, can be continuously recycled to cob(I)alamin at the formal Co(II)/Co(I) potential.[2] Among alkyl halides, vicinal

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dichlorides and dibromides react with cob(I)alamin to yield alkenes.[2-4] Conversely, unactivated monohaloalkanes react with cob(I)alamin to form an alkylcob(III)alamin that is stable at the formal potential of the Co(II)/Co(I) redox couple.[5] The latter process is not catalytic. Herein we report electrocatalytic reductions of a series of bromo- and chloroacetic acids by vitamin B_{12}. These compounds, like vicinal dihalides, are rapidly dehalogenated by cob(I)alamin at the Co(II)/Co(I) formal potential.

Experimental Section

Chemicals. Hydroxocob(III)alamin hydrochloride (99%) was from Sigma Chemical Co. α-Chloro- and α-bromoacetic acids were from Aldrich. Spectrograde acetonitrile was from Baker Co. Distilled water was further purified with a Barnstead Nanopure system to a specific resistance >15 MΩ cm. Other chemicals were reagent grade.

Apparatus. A Bioanalytical Systems BAS-100 electrochemical analyzer was used for cyclic voltammetry (CV). A glassy-carbon working electrode, platinum-wire counter, and aqueous saturated calomel reference electrode (SCE) were used for CV. The SCE was in a salt bridge containing supporting electrolyte.

Electrolyses were done in a divided cell with 0.5 × 4 × 1.25 cm carbon-felt (WDF, Union Carbide) cathode, an SCE reference, and a spectroscopic carbon rod as counter electrode. The SCE was separated from the electrolysis solution by a salt bridge containing phosphate buffer. Potential was controlled by a McKee-Pedersen (MP-1026A) three-electrode potentiostat. Potentiometric titrations were done with a silver-wire indicator electrode, an SCE, and a Corning Model 130 pH meter.

Procedures. All experiments were done in acetonitrile/water (1:1) prepared with 0.2 M phosphate buffer, pH 3. Purified nitrogen was passed through the stirred solution prior to and during electrolyses. Halide ions were determined by potentiometric titration with 0.1005 N silver nitrate standardized against sodium chloride. Halide found in the electrolyzed solution was taken as millimoles at the equivalence point less millimoles in a blank containing 1.0 mM cob(III)alamin.

Glassy-carbon electrodes (A = 0.071 cm^2) were polished on the day of use with SiC, diamond paste, and alumina on a Buehler metallographic polishing wheel as described previously.[6] Before each scan, electrodes were polished for 2 min with 0.3-μm alumina, ultrasonicated for 2 min in pure water, polished with 0.05-μm alumina, and finally ultrasonicated in water. All solutions were purged with purified nitrogen. Ohmic drop was fully compensated in all CV experiments, which were thermostated at 25.0 ± 0.1 °C.

Kinetic Estimations. Rate constants for reactions of cob(I)alamin with haloacetic acids were estimated by using working curves for two-electron electrocatalytic reductions. These working curves[2,7] relate the value of log (k_{obs}/v) (v = scan rate) to catalytic efficiencies measured by CV in quiet solutions and expressed as $i_c/2\gamma i_d$, where i_c is the peak catalytic current of solutions containing catalyst and haloacetic acid substrate, i_d is the peak current for the catalyst alone, and γ = [substrate]/[catalyst]. The working curves used assumed semiinfinite linear diffusion and a diffusion coefficient of the substrate 10-fold that of the catalyst. This was taken from similarity of the size of the haloacetic acids to 1,2-dibromobutane, whose diffusion coefficient[2] is about 10-fold greater than that of vitamin B_{12}.

Results and Discussion

Voltammetry and Electrolyses. CV scans of vitamin B_{12} in acetonitrile/water, pH 3 buffer, show a quasireversible Co(III) reduction with formal potential close to 0 V vs SCE and a nearly reversible Co(II)/Co(I) redox couple with formal potential −0.77 V vs SCE (Figure 1a). Addition of α-haloacetic acid caused a large increase in cathodic current for reduction of Co(II) and disappearance of the anodic peak for oxidation of Co(I) (Figure 1b). Direct CV reduction of haloacetic acids gave irreversible peaks at potentials negative of −1.5 V vs SCE (Figure 1c).[8] These results are consistent with fast catalytic reduction of the haloacetic acids by cob(I)alamin, with regeneration of cob(II)alamin at the electrode.[2]

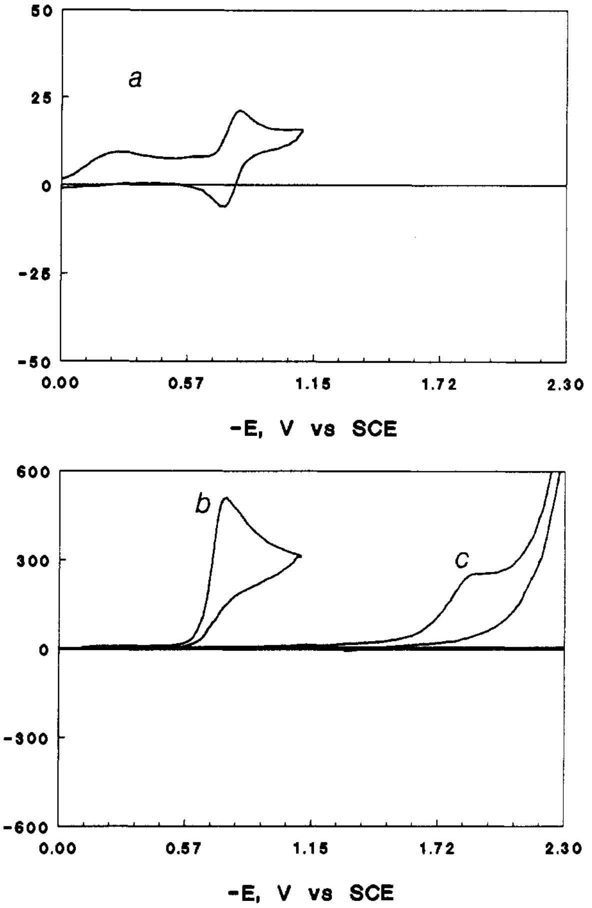

Figure 1. Cyclic voltammograms at glassy-carbon electrodes at 0.10 V s^{-1} in acetonitrile/water, pH 3 phosphate buffer: (a) 1.0 mM cob(III)-alamin; (b) 1.0 mM cob(III) alamin + 10 mM trichloroacetic acid; (c) 5 mM trichloroacetic acid. (CV scans are first scans beginning at 0 V on freshly polished electrodes.)

Table I. Catalytic Electrolysis of Haloacetic Acids[a] with Vitamin B_{12}

acid	mmol used	$-E_{app}$, V vs SCE	t, h	mmol of X^- found[b]	faradays/mol of acid reduced[c]	% total halide released
chloro	0.63	1.1	7.5	0.61	2.1	98
trichloro	0.60	1.0	5	0.86	3.2	48
	0.060[d]		3[d]	0.169		94
tribromo	0.5	0.9	5	1.05	2.4	70

[a] Using 1 mM vitamin B_{12} catalyst in 50–60 mL of acetonitrile/water (1:1), pH 3 phosphate buffer. [b] After electrolyses, by potentiometric titration. [c] Values precise to ±0.3. [d] Noncatalytic reduction: 0.36 mmol of vitamin B_{12} was electrolytically reduced to the Co(I) form in the absence of halo acid; then the circuit was disconnected, and 0.060 mmol of trichloroacetic acid was added while nitrogen was bubbled through the solution.

Previous studies of trichloro- and tribromoacetic acids demonstrated stepwise reductive dehalogenation in direct, noncatalytic electrochemical reductions.[9,10] That is, the first halogen is removed more easily than the second and so on. Electrocatalytic reductions of halo acids in the presence of vitamin B_{12} at a large carbon electrode at potentials just negative of the peak potential of cob(II)alamin confirmed that dehalogenation predominated in the catalytic reductions. For chloroacetic acid, where electrolysis was allowed to reach near completion, about 98% of the theoretical amount of chloride was measured after passage of approximately 2 faradays of electricity/mol of Cl$^-$ (Table I). Trichloroacetic

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Table II. Kinetic Data for Electrocatalytic Reductions with Vitamin B_{12}

$[B_{12}]$,[a] mM	scan rate, mV s^{-1}	E_p,[b] V vs SCE	$i_c/2\gamma i_p$	$10^{-5}k_{obs}$, M^{-1} s^{-1}
		Chloroacetic Acid		
1.03	100	0.811	0.546	0.063
	80	0.811	0.640	0.075
	50	0.818	0.628	0.043
	30	0.814	0.780	0.040
1.23	100	0.814	0.522	0.060
	80	0.811	0.655	0.065
	50	0.806	0.811	0.058
				0.058 ± 0.012 (mean)
		Trichloroacetic Acid		
1.02	200	0.727	1.86	2.5
	100	0.724	1.83	1.1
	80	0.727	2.10	1.4
	50	0.718	2.25	1.1
				1.5 ± 0.6 (mean)
		Bromoacetic Acid		
1.03	200	0.725	1.62	1.7
	100	0.716	1.70	0.91
	80	0.729	1.57	0.53
	50	0.723	1.61	0.35
1.22	200	0.737	1.52	1.1
	100	0.730	1.73	0.82
	80	0.739	1.79	0.81
				0.89 ± 0.44 (mean)

[a] Acetonitrile/water (1:1), pH 3 phosphate buffer; haloacetic acid concentrations were $10[B_{12}]$. [b] All entries are the average of three or more CV scans.

acid yielded about half of its total Cl^- in 5 h, again with about 2 faradays/mol of Cl^- passed through the cell. Electrolyses of the trihalo acids showed that more than one halide per acid molecule was removed. Less than 2 faradays/mol of Br^- was found for tribromoacetic acid, where unknown competing reactions may occur.[11] These experiments confirmed that the predominant reaction of α-haloacetic acids with cob(I)alamin is two-electron cleavage of carbon–halogen bonds.

After trichloroacetic acid was added to a pH 3 solution containing a stoichiometric amount of cob(I)alamin, titration indicated that the trichloroacetic acid released 94% of its Cl^- (Table I). The UV–vis spectrum of the vitamin B_{12} before electrolysis was nearly identical with that after electrolysis and addition of halo acid. These results suggest that dehalogenation of halo acids by cob(I)alamin is spontaneous and does not involve electroreduction of a stable organocobalt intermediate.

Kinetics. Rate constants were estimated by comparing catalytic efficiencies obtained by CV (see Experimental Section) to computer simulations based on the scheme

$$\mathrm{Co(II)} + e^- \underset{k}{\rightleftharpoons} \mathrm{Co(I)} \quad \text{(at electrode)} \qquad (1)$$

$$\mathrm{Co(I)} + \mathrm{RX} \rightarrow \mathrm{X}^- + \mathrm{Co(II)} + \mathrm{R}^\bullet \qquad (2)$$

$$\mathrm{Co(I)} + \mathrm{R}^\bullet \rightarrow \mathrm{Co(II)} + \mathrm{R}^- \quad \text{(fast)} \qquad (3)$$

The rate-determining step is assumed to be the reaction of cob(I)alamin with the halo acid (eq 2), as in other reactions of this type.[1,2] Equation 3 is kinetically invisible because of its rapid rate. It is used in the simulated reduction as the source of the second electron, a process for which alternatives exist.[2] R^- presumably undergoes protonation in the weakly acidic reaction medium.

Observed rate constants were estimated for three halo acids.[11] As expected, the more easily reduced trichloroacetic acid gave a rate constant about 25 times larger than that of chloroacetic acid (Table II). This suggests that the catalytic reduction, like direct electrolysis,[9,10] proceeds in a stepwise fashion. The rate constant for bromoacetic acid was similar to that of trichloroacetic acid but 15-fold larger than that of chloroacetic acid, consistent with the greater ease of reduction of C–Br bonds.[12]

Conclusions. Reductive dehalogenation of the α-haloacetic acids to acetic acid can be achieved by cob(I)alamin. To our knowledge, this is a new example of electrocatalytic reduction by vitamin B_{12r} in which a reduced organic product is formed directly at the formal potential of Co(II)/Co(I). Dehalogenation of halo acids by cob(I)alamin is spontaneous. If an organocobalt intermediate exists, it must be made reductively unstable by the carboxylic acid group. These reactions are similar to dehalogenation of vicinal dihalides to alkenes by cob(I)alamin.[2] Characteristic large catalytic currents for these reactions are in contrast to the behavior of monohaloalkanes with vitamin B_{12r}, for which catalytic currents are not observed at the Co(II)/Co(I) potential, and more negative potentials are needed to decompose the stable alkylcob(III)alamins formed.[5,13]

Comparison of direct reduction potentials of the halo acids[8] with potentials of the B_{12}-mediated reductions (Table II) shows that overpotentials for dehalogenation are decreased by 0.75–1.4 V by electrocatalysis. These large decreases in overpotential and the high catalytic rate constants suggest an inner-sphere mechanism. The reduction of vicinal dihalides by cob(I)alamin was inferred to be inner sphere from comparative kinetic studies with known outer-sphere reductants.[4,14]

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(11) Although catalytic current was also observed for tribromoacetic acid with vitamin B_{12}, subsequent scans showed the appearance of unexplained peaks. These new peaks suggested possible side reactions. Thus, rate constants were not estimated for this compound.

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Preparation, Solution Dynamics, and X-ray Crystal Structure of the Anilide-Bridged Diruthenium Complex $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu\text{-}NHPh)_3][BF_4]$

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There has been increasing interest in the potential use of transition-metal amide complexes to facilitate the formation of carbon–nitrogen bonds.[1] One class of compounds that is of particular interest in this regard is late-transition-metal amide complexes. A problem that limits the use of these compounds is a lack of general synthetic routes to such materials. Consequently, there are relatively few reported examples of late-transition-metal amides.[2] Typically, these compounds have been

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